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Guidance for Environmental Background Analysis

Volume IV: Vapor Intrusion Pathway

Prepared by

Battelle Memorial Institute
CH2M Hill
NewFields Companies, LLC

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PREFACE

This guidance document supports and implements the January 2004 *Navy Policy on the Use of Background Chemical Levels*. It is part of a series devoted to background analysis that provides instructions for characterizing background conditions at sites where past property uses have resulted in actual or suspected chemical releases. Each volume in this series is devoted to a particular medium. This volume focuses on exploratory and analytical methods that can be used to identify background chemicals during the investigation of vapor intrusion emanating from known site-related subsurface releases. These methods include exploratory data, forensic and statistical analyses that can be used to evaluate whether observed indoor or outdoor concentrations can be attributed to vapor intrusion or background sources.

For the sake of completeness, each volume in the series opens with a summary of the January 2004 *Navy Policy on the Use of Background Chemical Levels* and discussions of both state and federal regulatory requirements and guidance. Each volume then describes exploratory data review and assessment procedures, explains medium-specific methods for background analysis and statistical comparisons, and presents medium-specific case studies that illustrate application of the methods. Because each volume in this series is intended to serve as a stand-alone document, some identical or similar discussions occur across the volumes. The preface of each volume identifies the sections that are unique to that volume and the medium of concern.

The background analysis methods presented in Volumes I, II, and III for soil, sediment, and groundwater, respectively, rely on analysis of the spatial characteristics of the chemical data (Exploratory Data Analysis), the geochemical processes that result in strong correlations between certain chemicals in soil and sediment (the Geochemical Method), as well as statistical comparisons of site and background data-sets (the Comparative Method). Despite certain similarities among recommended procedures, each medium has unique features that require specific modifications. For example, vapor intrusion investigations often lack the large datasets that are characteristic of other media site and background evaluations. In addition, site-specific air concentrations usually display high variation. The combination of small datasets and highly variable concentrations limits the applicability of classical statistical comparative methods, which require large, randomly collected datasets. This volume recognizes the unique features of vapor intrusion investigations and instead of relying on a single method, describes several procedures as multiple lines of evidence.

Consistent with the April 2008 *Navy/Marine Corps Policy on Vapor Intrusion* and the January 2009 *DoD Vapor Intrusion Handbook*, this document assesses multiple lines of evidence based on a “weight of evidence” approach to determine whether the detected contaminants in indoor air samples can be attributed to background sources or known site subsurface releases. The evidence is derived primarily from exploratory data analyses, which in some cases yield conclusive results concerning the origin of detected chemicals of potential concern (COPCs). In some cases, evidence can be derived from forensic and multivariate statistical methods. These latter methods are advanced procedures, which may not be applicable at many Navy sites. Forensic methods provide analytical procedures to decipher the chemical composition of collected samples to determine the source of detected contaminants. Within this context, multivariate statistical methods offer confirmatory tools and provide additional lines of evidence. The application of these advanced methods should be considered at sites involving petroleum contamination and out-of-the-ordinary vapor intrusion liabilities.

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EXECUTIVE SUMMARY

This guidance document provides instructions for evaluating background conditions in vapor intrusion investigations. As noted in the April 2008 *Navy/Marine Corps Policy on Vapor Intrusion* and the January 2009 *Department of Defense (DoD) Vapor Intrusion Handbook*, vapor intrusion is the migration of sufficiently volatile chemicals from the subsurface (soil, soil gas, or groundwater) into the indoor air of buildings located above or in close proximity to the contamination. The primary goal of the analysis is to identify sites where vapor intrusion is creating a human health risk. In order to determine if subsurface sources are responsible for indoor air contamination, it is important to distinguish between contaminants related to the subsurface release and contaminants due to background levels of indoor air contamination. In this document, background indoor air contamination refers to the level of contaminants in the air inside a building unrelated to the subsurface soil gas that migrates into a structure. Background indoor air can be impacted by a variety of indoor and outdoor sources. Indoor sources include the use and storage of consumer products (e.g., cleaners, air fresheners, aerosols, mothballs, scented candles, and insect repellants), emissions from building materials (e.g., carpets, insulation, paint, and wood finishing products), combustion processes (e.g., smoking, cooking, and home heating), and occupant activities (e.g., craft hobbies, home improvements, automotive repairs). Outdoor sources may be related to volatile releases from nearby sources (e.g. vehicles, barbeques, yard maintenance equipment, fuel storage tanks, paint, pesticides), regional sources (e.g. air emissions from regional industry, vehicle exhaust, agricultural activities, fires), or even global air pollutants. The composition of outdoor air surrounding a building is referred to as ambient air throughout this document.

The January 2004 *Navy Policy on the Use of Background Chemical Levels*, as affirmed by the April 2008 *Navy/Marine Corps Policy on Vapor Intrusion,* requires cleanup efforts at Navy sites to address only those risks associated with chemical concentrations that are elevated as a result of a site-related release. Therefore, cleanup efforts must address only chemicals that have been released at the site — not background chemicals. Because of the large number of volatile compounds that are released to indoor and outdoor air due to human activities, background levels of volatile contaminants may pose an unacceptable risk to human health when evaluated in accordance with EPA's Risk Assessment Guidance for Superfund (RAGS) Part F (USEPA 2009). These background risks are outside the scope of the Navy's Environmental Restoration Program, but Navy policy requires restoration program personnel to convey information regarding all identified risks to stakeholders. So if in the course of investigating a possible VI site, the Navy discovers unhealthful levels of contamination in indoor air, the Navy will convey this information to the stakeholders so that they can take appropriate action. The Navy background policy was developed to ensure compliance with federal and state laws and regulations, and is consistent with United States Environmental Protection Agency (U.S. EPA) technical guidance.

The background analysis techniques presented in this document are based on exploratory, forensic, and statistical methods, consistent with the January 2009 *DoD Vapor Intrusion Handbook.* The guidance recognizes the unique features of vapor intrusion investigations and treats the recommended methods as "multiple lines of evidence" that should be considered when determining whether volatile chemicals measured in indoor air should be attributed to subsurface releases, indoor air background, or possibly both. The exploratory data analysis (EDA) closely follows the procedures described in the Interstate Technology and Regulatory Council's (ITRC's) *Vapor Intrusion Pathway: A Practical Guideline*, while forensic and statistical methods are implemented in accordance with U.S. EPA's *Guidance for the Data Quality Objectives Process* and *Guidance for Data Quality Assessment: Practical Methods for Data Analysis.*

Background indoor air analysis is an integral component of any Navy vapor intrusion investigation that collects indoor air samples. A background indoor air EDA is typically initiated as soon as a decision is made to collect indoor air samples to characterize the potential for vapor intrusion or support human health risk assessments. EDA methods offer multiple approaches for examining data to gain insight into the contribution of background sources to indoor air contamination. The EDA methods are conducted in the context of the U.S. EPA decision-making and data quality objective (DQO) framework. Multiple lines of evidence are usually needed to support vapor intrusion decision making, including decisions as to whether indoor air contamination should be attributed to background sources or subsurface releases. The interpretation of multiple lines of evidence is a key theme throughout this guidance. The results of an EDA are also used to update the conceptual site model (CSM).

The background indoor air EDA methods include: (1) comparisons with site-specific or published background values, (2) examination of constituent ratios between different media, (3) comparison of the constituent compositions (i.e., ratios) of volatile organic compounds (VOCs) within and between subsurface soil-gas, indoor air, and outdoor air samples, and (4) additional methods (e.g., differential pressure monitoring, pressure cycling, tracer compound analyses, and real-time monitoring) for ascertaining the contribution of background sources to measured site-specific indoor air concentrations. Each of these techniques has varying degrees of strength for either confirming or refuting the existence of background sources, which is an important consideration during the decision-making process.

If EDA results prove to be inconclusive, in some cases, forensic evaluations may be conducted to buttress earlier findings. Environmental forensic analysis involves the use of chemical fingerprinting methods that help identify the likely origins of detected indoor air chemicals. Typical vapor intrusion investigations usually focus on a finite list of volatile chemicals. Forensic analysis broadens this focus by incorporating the entire range of source-specific assemblages of compounds. This expanded focus targets not only the few chemicals of interest, but potentially hundreds of additional compounds that are capable of defining site-specific background conditions, as well as differentiating pattern anomalies caused by vapor intrusions emanating from subsurface contamination sources. For this purpose the analysis considers a variety of information, including: (1) chemical properties of common products associated with various sources, (2) standard and forensic laboratory analytical procedures, (3) chemical variability associated with attenuation processes along the vapor intrusion pathway, and (4) forensic ratios of specific compounds which are known to be less prone to temporal or spatial variations. The application of forensic evaluations should be considered at sites impacted with petroleum contamination and out-of-the-ordinary potential vapor intrusion conditions.

Exploratory and forensic analyses may be supplemented by comparative statistical procedures. In vapor intrusion investigations, the applicable comparative procedures can be divided into two broad categories: (1) individual comparison: comparison of a measured or computed value of a given chemical to its corresponding range of background values — typically performed during EDA, and (2) multivariate comparison: comparison of chemical profiles of individual air samples — typically performed as part of a forensic analysis involving multiple chemicals measured in a variety of samples, including indoor, outdoor, soil-gas and ambient air samples to determine whether the investigated samples display similar chemical profiles. As with advanced forensic evaluations, the application of multivariate analyses should be considered at sites with petroleum contamination and out-of-the-ordinary vapor intrusion liabilities.

Practical Tips
Text Boxes

Highlighted text boxes containing practical tips are included throughout this document. These tips summarize important features of procedures discussed in the document, including how they work, how they help, the minimum number and type of samples, limitations and uncertainties, and how to improve their evaluation.

The practical tips boxes provide a map for Remedial Project Managers (RPMs) to navigate the document, understand its various sections, and quickly identify the methods that address their particular needs. RPMs can then proceed to the main text of the document for more thorough discussions.

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ACRONYMS AND ABBREVIATIONS

%D	percent detection
%R	percent recovery
amu	atomic mass units
API	American Petroleum Institute
ARAR	applicable or relevant and appropriate requirement
ASTM	American Society for Testing and Materials
avgas	aviation gasoline
BFB	bromofluorobenzene
bgs	below ground surface
BRAC	Base Realignment and Closure
BTEX	benzene, toluene, ethylbenzene, and xylenes
Cal/EPA	California Environmental Protection Agency
CCV	continuing calibration verification
CDPHE	Colorado Department of Public Health and Environment
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFC	chlorofluorocarbons
CNO	Chief of Naval Operations
COPC	chemical of potential concern
CSM	conceptual site model
DCA	dichloroethane
DCE	dichloroethene
DERP	Defense Environmental Restoration Program
DME	dimethyl ether
DoD	United States Department of Defense
DOH	Department of Health
DON	Department of the Navy
DQO	data quality objective
EDA	exploratory data analysis
ER	Environmental Restoration
ER, N	Environmental Restoration, Navy
FID	flame ionization detector
FUDS	Formerly Used Defense Sites
GC/MS	gas chromatograph/mass spectrometer
HAP	hazardous air pollutant
HAPSITE	hazardous air pollutants on site
HFA	hydrofluoroalkanes
HFO	heavy fuel oil
HVAC	heating, ventilating, and air conditioning

ICAL	initial calibration
ICV	initial calibration verification
INE/1,2,4-TMB	indene relative to 1,2,4-trimethylbenzene
ITRC	Interstate Technology and Regulatory Council
LCS	laboratory control sample
LCSD	laboratory control sample duplicate
LNAPL	light, nonaqueous-phase liquid
MADEP	Massachusetts Department of Environmental Protection
MDEQ	Michigan Department of Environmental Quality
MDL	method detection limit
MGP	manufactured gas plant
MTBE	methyl tert-butyl ether
N/B4	naphthalene relative to tetra-alkylbenzenes
NCP	National Oil and Hazardous Substances Pollution Contingency Plan
NERP	Department of the Navy Environmental Restoration Program
NESHAP	national emission standards for hazardous air pollutants
NJDEP	New Jersey Department of Environmental Protection
NYSDOH	New York State Department of Health
OSHA	Occupational Safety and Health Administration
PADEP	Pennsylvania Department of Environmental Protection
PAH	polycyclic aromatic hydrocarbon
PC	principal component
PCE	tetrachloroethene
PEL	permissible exposure limit
PIANO	paraffins, aromatics, naphthenes, and olefins
ppbv	part(s) per billion by volume
pptv	part(s) per trillion by volume
PSA	pressure sensitive adhesives
QA	quality assurance
QAPP	quality assurance project plan
QC	quality control
RBC	risk-based concentration
RCRA	Resource Conservation and Recovery Act
RPM	Remedial Project Manager
RSD	relative standard deviation
RSL	regional screening level
SAP	Sampling and Analysis Plan
SARA	Superfund Amendments and Reauthorization Act
SIM	selective ion monitoring
SPARC	SPARC Performs Automatic Reasoning in Chemistry
SPAWAR	Spare and Naval Warfare
SSC	SPAWAR Systems Center
STY/OX	styrene relative to *o*-xylene

SVOC	semi-volatile organic compound
TAGA	trace atmospheric gas analyzer
TAME	tert amyl methyl ether
TCE	trichloroethene
TEL	tetraethyl lead
TIC	tentatively identified compound
TMB	trimethylbenzene
TO	toxic organic
UFP-QAPP	Uniform Federal Policy for Quality Assurance Project Plans
UNEP	United Nations Environment Programme
U.S. EPA	United States Environmental Protection Agency
UST	underground storage tank
VOC	volatile organic compound

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GLOSSARY

Ambient or Outdoor Background Chemical Concentrations	Total concentrations of both naturally-occurring chemicals and anthropogenic chemicals in outdoor air not related to specific Navy site releases.
Anthropogenic Background	Chemicals present in the environment due to human activities that are not related to specific Navy site releases.
Aquifer	A water-bearing rock or sediment formation capable of yielding usable quantities of water, typically composed of unconsolidated materials such as sand and gravel, or consolidated bedrock such as limestone or fractured basalt.
Background Chemicals	Chemicals derived from natural or anthropogenic sources not related to specific Navy site releases.
Background Chemical Concentrations	Total concentrations of both naturally occurring and anthropogenic chemicals not related to specific Navy site releases.
Background Structures	See *Reference Structures.*
Box and Whisker Plot	A graphic summarizing a set of data measured on an interval scale. Often used in EDA, a box and whisker plot is a type of graph showing the shape of the distribution, its central value, and variability. The picture produced consists of the most extreme values in the dataset (maximum and minimum values), the lower and upper quartiles, the median, and the mean.
Comparative Method	Application of statistical tests for identifying COPCs. In this method, results collected from a nearby uncontaminated or “background” area are statistically compared to pooled or individual results from samples collected at a site of suspected contamination.
Chemical of Potential Concern (COPC)	A chemical related to a specific Navy site release, and which may be present at concentrations posing potentially unacceptable risks to human health or the environment.
Data Quality Assessment (DQA) Process	A scientific and statistical data evaluation to determine if environmental investigation data are of the right type, location, quality, and quantity to support their intended use.
Data Quality Objective (DQO) Process	A series of planning steps based on the scientific method designed to ensure that the type, location, quantity, and quality of environmental data used in decision making are appropriate for the intended application.
Dense, Nonaqueous-Phase Liquid (DNAPL)	An insoluble or low-solubility chemical with a density greater than water. DNAPLs sink to the bottom of an aquifer. Examples are chlorinated solvents such as trichloroethylene (TCE) and tetrachloroethylene (PCE or PERC).

Detection Limit	The minimum concentration of an analyte that can be measured within a given matrix and reported with a 99% confidence that the analyte concentration is greater than zero.
Distribution	The frequency (either relative or absolute) with which measurements in a dataset fall within specified classes.
Exploratory Data Analysis (EDA)	Series of statistical and graphic procedures for examining and screening available, site-specific and published data to determine evidence of vapor intrusion impact.
Facility	See *Installation.*
Geostatistics	A class of statistical techniques for the analysis of spatially correlated data. In these analyses, variograms or related techniques are used to quantify and model the spatial correlation structure. Also includes various estimation techniques, such as kriging, that use spatial correlation models.
Installation	The extent of a Navy property at which one or more activities has been or is being conducted. An installation may contain a number of sites, as well as parts, or all of the investigated sediment basin. Also referred to as a *facility.*
Inter-Quartile Range (IQR)	A measure of the spread of or dispersion within a dataset. The IQR is the difference between the 25th and 75th percentiles of the measured values of the sample. IQR is not affected by outliers.
Light, Nonaqueous-Phase Liquid (LNAPL)	An insoluble or low-solubility chemical with a density less than water. LNAPLs float on the groundwater table. Examples are petroleum products such as gasoline.
Mean	A measure of the central tendency of a distribution, which is computed by averaging a dataset (totaling the various individual results and dividing by the number of results involved).
Median	A measure of the central tendency of a distribution, which is obtained by ranking the individual results in a dataset from smallest to largest and selecting the middle value. For an even number of results, the median is computed as the arithmetic average of two middle values.
Mode	A measure of the central tendency of a distribution, which is defined as the value in the population that occurs most frequently.
Naturally Occurring Background	Concentrations of naturally occurring chemicals in environments that have not been influenced by human activity.
Nondetects	Measurements reported by the analytical laboratory as below either the detection limit or the reporting limit.
Nonparametric Test	A statistical test that does not require any specific assumptions about the exact form of the underlying probability distributions of the investigated measures. Consequently, nonparametric tests generally are valid for a fairly broad class of distributions.
Parametric Test	A test requiring specific assumptions about the exact form of the underlying probability distributions of the investigated measures. Parametric tests are not valid unless the underlying assumptions are met.

Population	The entire collection of items constituting the variable of interest.
Probability Distribution	In probability theory and statistics, a probability distribution identifies either the probability of each value of an unidentified random variable (when the variable is discrete), or the probability of the value falling within a particular interval (when the variable is continuous). For a discrete random variable, the probability distribution is described in terms of a *probability mass function*, which is a list of probabilities associated with each of the possible values of the discrete random variable. For continuous random variables, the probability distribution is described in terms of a *probability distribution function*.
Pth Percentile	The specific value of a distribution that divides the set of measurements in such a way that the P percent of the measurements fall below (or are equal to) this value, and $100 - P$ percent of the measurements exceed this value.
Pth Quantile	The specific value of a distribution that divides the set of measurements in such a way that the proportion, P, of the measurements fall below (or are equal to) this value, and the proportion $1 - P$ of the measurements exceed this value.
Random Sample	A set of items that have been drawn from a population in such a way that each time an item was selected, every item in the population had an equal opportunity to appear in the sample. In environmental field investigations, random samples imply data that are collected in an unbiased, uncorrelated, and nonclustered manner.
Range	In descriptive statistics, the difference between the highest and lowest measured value. In geostatistics, the separation distance between any pair of measured values beyond which the pair are uncorrelated.
Reference Structures	Structures not impacted by subsurface vapor intrusion with similar age, construction, occupancy, and contents to those observed in an investigated structure.
Reporting Limit	The project-specific threshold limit established for a project for which, below a numerical value, the data are reported as nondetect (U) and presented as less than (<) a numerical value. This value is typically one to five times the detection limit, depending on the analytical method and matrix. The detection limit can vary considerably from sample to sample because of matrix effects. Ideally, the reporting limit will not change, and will be set high enough to account for matrix effects, yet low enough to meet project-specific data quality objectives.
Sediment	Any material deposited at the bottom of water bodies, such as oceans, rivers, lakes, harbors, and storm drains.
Site	A zone designated for investigation because of actual, suspected, or potential chemical releases. A site usually consists of both impacted and background areas. Site-specific field data are used to evaluate the extent of each area.
Standard Deviation	A measure of dispersion of the distribution of the sample data values.
Standard Error	A measure of the variability (or precision) of a sample estimate, such as the computed arithmetic mean. Standard errors are needed to construct confidence intervals for the computed statistics.
Statistic	A measure of a statistical property of a population, computed based on sample results. An example of a statistic is the mean (i.e., average) of the measures in the sample.

Target Chemicals	Chemicals selected for background analysis. The list of target chemicals should include chemicals used at the site during its history, potential chemical breakdown products, potential site-specific background chemicals, chemicals required by regulatory criteria, and other parameters that may be useful for background analysis.
Variance	A measure of dispersion of the distribution of a set of data values. The variance is the square of the standard deviation.

1. INTRODUCTION

This guidance document supports and implements Chief of Naval Operations (CNO) background and vapor intrusion policies by providing detailed instructions for evaluating background chemicals during the investigation of a potential vapor intrusion pathway. Within the context of vapor intrusion, background indoor air contamination is *everything unrelated to the subsurface soil gas that migrates into a structure* (Interstate Technology & Regulatory Council [ITRC], 2007). Background chemicals in indoor air are derived from indoor and outdoor sources, both natural and anthropogenic, not associated with site-related subsurface chemical releases. Background analyses are essential for distinguishing between indoor air that has been impacted by a site-related chemical release and indoor air that has not been impacted by a site-related release.

The Navy is not responsible for cleanup or mitigation of either natural or anthropogenic background chemicals; therefore, at most Navy vapor intrusion investigation sites, background analysis becomes an integral component of indoor air analyses to determine whether site-related vapor intrusion contamination is occurring and contributing to site risk.

1.1 Navy Policy and Guidance

The Navy has issued policy and guidance documents that (1) address the role of background data in the Environmental Restoration Program and (2) present techniques for background analysis. Navy vapor intrusion policy describes when and how to consider vapor intrusion during a site investigation, evaluate risk for human health exposures associated with vapor intrusion, evaluate remedial alternatives, and consider previously transferred properties. Navy risk assessment policies specify requirements for the use of background data in human health and ecological risk assessments.

1.1.1 Navy Background Policy

The Navy *Policy on the Use of Background Chemical Levels* was released in January 2004 (Department of the Navy [DON], 2004a). The policy stresses the importance of eliminating background chemicals from the list of chemicals of potential concern (COPCs) carried through the risk assessment, and setting cleanup levels above the background range.

The policy specifically requires the following:

- ☐ Chemicals that may have been released at the site must be clearly identified to ensure that the Navy is focusing on remediating COPCs associated with the release.
- ☐ Chemicals detected at concentrations below background levels will not be carried through into the full baseline risk assessment. All chemicals screened out because of background considerations must be discussed and documented in the risk characterization sections of the baseline risk assessment report.
- ☐ Cleanup action levels must not be below background levels.

Care must be taken when applying the Navy's background policy within the context of a vapor intrusion investigation. The policy applies to the site as a whole, and the vapor intrusion exposure pathway may be only one of several complete human exposure pathways that must be considered in the baseline risk assessment. Site related COPCs are generally based on subsurface data (i.e., vapor sources for potential vapor intrusion), and very few volatile organic compounds (VOCs) have measurable background concentrations in the subsurface. Consequently few VOCs will be eliminated from a baseline risk assessment based on the Navy's background policy. However, indoor air potentially has many background sources of VOCs. Therefore, some of the COPCs carried forward in the risk assessment for other exposure pathways (e.g., drinking water ingestion) may be eliminated from the risk calculation for the indoor air inhalation pathway if the measured indoor air concentrations can be attributed to indoor air background sources instead of subsurface sources. Background levels of COCs in both the subsurface and indoor air may need to be considered when establishing cleanup levels for these sites. Site remediation goals for subsurface sources should be risk-based and consider all complete exposure pathways; indoor air mitigation goals associated with site releases should also be risk-based but should not be set below indoor air background levels.

Within the context of vapor intrusion, conducting a background analysis at the appropriate time in the site investigation helps ensure that the Navy's cleanup responsibilities are clearly defined. The background indoor air analysis must be supported by adequate site characterization data, including data that evaluates the subsurface sources, the physical and chemical characteristics of the vadose zone environment, building characteristics and air flow, as well as potential indoor and outdoor sources of site related COPCs. The background analysis considers indoor and outdoor sources of both natural and anthropogenic origin. The COPC selection process for the vapor intrusion assessment should be based upon subsurface detections of VOCs and should be discussed with regulators and conveyed to the community as early as possible. The indoor air background assessment should be focused on these site related COPCs.

As noted in the Navy background policy, in some cases, unacceptable risks may be associated with chemical concentrations within the background range. Because of the large number of volatile compounds that are released to indoor and outdoor air due to human activities, background levels of volatile contaminants may pose an unacceptable risk to human health when evaluated in accordance with RAGS Part F (USEPA 2009). These background risks are outside the scope of the Navy's Environmental Restoration Program, but Navy policy requires restoration program personnel to convey information regarding all identified risks to stakeholders. So if in the course of investigating a possible VI site, the Navy discovers unhealthful levels of contamination in indoor air, the Navy will convey this information to the stakeholders so that they can take appropriate action. Chemicals attributed to indoor air background sources should be evaluated against the appropriate risk-based screening criteria, and the results should be documented in the risk characterization section of the baseline risk assessment report. The Navy considers such screenings to be consistent with the United States Environmental Protection Agency guidance, *Role of Background in the CERCLA Cleanup Program* (U.S. EPA, 2002a).

Cleanup or mitigation efforts should be limited to chemicals associated with a site-related release that may pose unacceptable risks to human health or the environment.

1.1.2 Navy Vapor Intrusion Policy

In April 2008, the *Navy/Marine Corps Policy on Vapor Intrusion* (DON, 2008) was issued. This document recognizes that although no finalized guidance was available for U.S. EPA, many Navy installations had received requests for an evaluation of the vapor intrusion pathway. Thus, the CNO prepared the policy to assist with site investigations related to vapor intrusion.

Generally, the CNO recommends careful planning and compliance with existing and appropriate Department of Defense (DoD)/DON policies as they relate to individual elements of cleanup. The policy covers the following topics:

- ❑ <u>Determining whether to evaluate for a vapor intrusion pathway</u>. A site must meet the criteria of the Defense Environmental Restoration Program (DERP) and must be contaminated with sufficiently volatile compounds to have the potential to migrate into current structures.

- ❑ <u>Planning and implementing a pathway evaluation</u>. The conceptual site model (CSM) and data quality objectives (DQOs) should be used to determine sampling methodology. This includes establishing and eliminating background chemicals during the screening steps of the risk evaluation. The CSM should be developed and updated to clearly outline the contamination locations and types, the potential pathways, and applicable receptors.

- ❑ Addressing the background chemical issues. The role of background concentrations shall be consistent with *Navy Policy on the Use of Background Chemical Levels* (DON, 2004a). Environmental Restoration, Navy (ER, N) or Base Realignment and Closure (BRAC) funds shall not be used to address indoor air contamination caused by background sources. Potential background indoor air contaminants, including compounds emitted from household cleaners and solvents, paints, carpets, and pesticides, shall be identified during the site investigation.

- ❑ Evaluating risk for human health exposures associated with the vapor intrusion pathway. A variety of methodologies may be used, including site-specific exposure scenarios and Occupational Safety and Health Administration (OSHA) standards, where applicable.

- ❑ Evaluating remedial alternatives. There are a variety of alternative remedies, but the selected one must be protective of human health and the environment as well as allow for continued and future land use when necessary.

- ❑ Considering previously-transferred property. The Navy will only become re-involved in a site where the existence of a complete vapor intrusion pathway is demonstrated by the current landowner or regulatory agency, and the incremental risk must be above risk-based levels.

1.1.3 Navy Background Guidance

DON has previously generated three volumes of background analysis guidance, focused on soil, sediment, and groundwater as listed below:

- ❑ *Guidance for Environmental Background Analysis Volume I: Soil* (DON, 2002)

- ❑ *Guidance for Environmental Background Analysis Volume II: Sediment* (DON, 2003)

- ❑ *Guidance for Environmental Background Analysis Volume III: Groundwater* (DON, 2004b).

These documents provide detailed instructions for analysis of background conditions in soil, sediment, and groundwater, respectively.

1.1.4 DoD Vapor Intrusion Handbook

In January 2009, the *DoD Vapor Intrusion Handbook* (DoD, 2009) was issued to provide a general framework for conducting vapor intrusion investigations under the DERP, including both residential and occupational exposure. This handbook was developed to serve as a resource for remedial project managers (RPMs) who may need to investigate the vapor intrusion pathway at DoD facilities, both open and closed, as well as Formerly Used Defense Sites (FUDS).

The handbook advises that vapor intrusion should be evaluated when (1) volatile chemicals presently underlie existing structures or have the potential to do so in the future and (2) there may be a complete human exposure pathway. Volatile organic compounds (VOCs), including chlorinated solvents, are identified as the primary chemicals of interest for the vapor intrusion pathway. Other potential chemicals of interest include, but are not limited to, mercury, some semi-volatile organic compounds (SVOCs), e.g., polycyclic aromatic hydrocarbons (PAHs), and certain pesticides.

Various technical approaches for evaluation of the vapor intrusion pathway are discussed in the DoD handbook. It provides perspective to RPMs and associated consultants regarding the development and interpretation of vapor intrusion investigations to assist them in making an informed, site-specific, and cost-effective evaluation. Also included is guidance on how to assess the human health risks associated with vapor intrusion. Below is the handbook's summary of recommended strategic considerations:

- Undertake appropriate planning to assess vapor intrusion including assistance and input from other disciplines.
- Work with legal counsel to identify the relevant regulations that govern the conduct of response actions at the site.
- Determine whether migration of volatile subsurface contaminants to indoor air is occurring as a result of a complete exposure pathway, not just whether contaminants of concern are present in indoor air.
- Assess as many lines of evidence as appropriate to evaluate potential vapor intrusion in light of the inherent variability and uncertainty with any one line of evidence.
- To the extent practical, collect and use site-specific information and data to avoid the use of conservative default values when performing fate and transport modeling to assess risk.
- Be prepared to respond to requests to reassess the vapor intrusion pathway at sites, including closed or previously determined no further action sites.
- Carefully consider all mitigation and remedial options in light of DERP guidance.
- Prepare and plan for effective risk communication.

Appendix G of the *DoD Vapor Intrusion Handbook* discusses assessment of background levels at vapor intrusion sites. The document describes difficulties when background analysis is planned to be conducted based on statistical comparisons between indoor air quality data in potentially impacted structures versus those measured inside non-impacted structures. Difficulties include: (1) identifying "control" buildings possessing similar construction, uses, layout, and surroundings, but situated in non-impacted areas, may be infeasible if not impossible in many Navy sites, (2) high variability of indoor air quality data raising concerns about statistical adequacy of typical datasets that consist of only a few measurements within each structure, even when such control structures are identified, and (3) challenges with gaining access for indoor air sampling, especially in residential units. Appendix G does not advise indoor air sampling for background analysis purposes unless these difficulties can be adequately addressed.

In typical vapor intrusion investigations, background indoor air quality levels are established through the use of multiple lines of evidence, such as comparisons with site-specific outdoor and/or published indoor/outdoor air concentrations, comparisons of computed empirical and published attenuation factors, comparisons of constituent ratios between and/or within samples, sampling before and after source identification and removal, forensic analyses, and real-time sampling. The present document builds on these recommendations and incorporates them into a consistent weight of evidence approach.

1.1.5 Navy Risk Assessment Guidance

The Navy has issued the following policies to provide guidance on the use of background chemical concentrations in human health and ecological risk assessments:

- *Navy Policy for Conducting Human Health Risk Assessments Related to the Installation Restoration Program* (DON, 2001)
- *Navy Policy for Conducting Ecological Risk Assessments* (DON, 1999).

Background indoor air analyses are primarily driven by human risk exposures. According to Navy human health risk assessment policy (DON, 2001), background chemicals should be screened out as early in the risk assessment process as possible. In human health risk assessments, background chemicals are normally considered during the Tier 1A portion of the evaluation. This may not be possible in vapor intrusion investigations because indoor air background levels are not usually assessed until indoor air sampling is contemplated.

1.1.6 Navy Vapor Intrusion Focus Area Best Practices

In May 2009, the Space and Naval Warfare (SPAWAR) Systems Center (SSC) Pacific issued a report titled *Review of Best Practices, Knowledge and Data Gaps and Research Opportunities for the US Department of Navy Vapor Intrusion Focus Areas* (DON, 2009). The report focuses on three areas of practice:

- ❑ Subsurface sampling, focusing on those practices that best identify potential vapor intrusion pathways while minimizing sub-slab sampling
- ❑ Passive indoor air sampling methods as a means of determining the existence of indoor air exposure from a potential source
- ❑ Indoor source separation as a means of improving complete pathway verification.

The report also renders opinions concerning current knowledge gaps, the data needs for these three focus areas, and potential research directions. Ultimately, the report outlines potential research areas for the Navy to further the development of a robust and streamlined screening and assessment strategy that site managers can use at the majority of Navy sites.

1.2 Role of Background Analysis in the Environmental Restoration Program

Federal law requires the Navy to protect human health and the environment and comply with applicable or relevant and appropriate requirements (ARARs) at all Navy chemical release sites. The Navy's responsibilities for site cleanup or other response actions necessary to comply with environmental laws and regulations cannot be defined until the nature and extent of contamination associated with a chemical release have been characterized. To evaluate the nature and extent of contamination, the Navy must distinguish between contamination associated with a chemical site release and naturally-occurring or anthropogenic background conditions; therefore, background analysis is an integral part of the environmental assessment, decision-making, and cleanup process.

Figure 1-1 illustrates the roles of background analysis in environmental investigation and restoration activities conducted under the three primary regulatory frameworks (Comprehensive Environmental Response, Compensation, and Liability Act [CERCLA], Resource Conservation and Recovery Act [RCRA], and the underground storage tank [UST] program). Background analysis should be incorporated into the site identification, investigation, decision, and cleanup phases as necessary to achieve the following objectives:

- ❑ Identify chemicals associated with site-related releases (i.e., site-related COPCs) for further consideration during the quantitative risk assessment calculations.
- ❑ Eliminate naturally-occurring and anthropogenic chemicals that occur at concentrations similar to background levels from the list of Navy site-related COPCs for quantitative risk assessment calculations.
- ❑ Ensure documentation and discussion of the non-site related chemicals in the risk characterization section.
- ❑ Ensure that the cleanup level established for each COPC is not below concentrations resulting from natural or anthropogenic background sources.

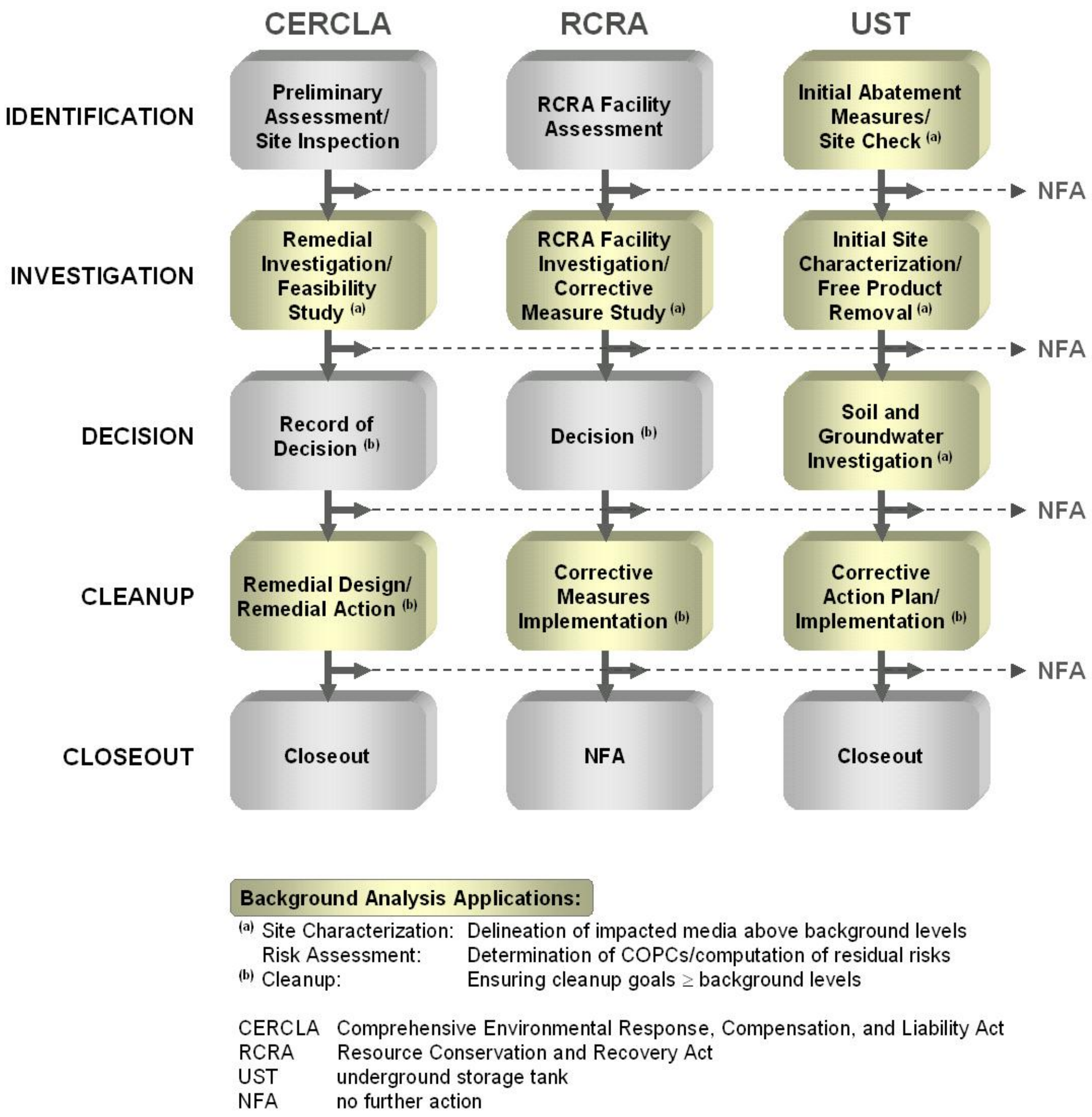

FIGURE 1-1. Roles of background analysis within regulatory cleanup frameworks

- ❑ Obtain stakeholder concurrence with site characterization and remedial conclusions.

If a chemical is retained for further consideration in the vapor intrusion evaluation or quantitative risk calculations after comparison to published or outdoor ambient levels, it does not necessarily imply that the chemical is related to vapor intrusion or requires cleanup. Decisions regarding cleanup should be made only after the baseline risk assessment and ARAR review are complete.

Evaluation of background conditions can assist in understanding uncertainties associated with qualitative or semi-quantitative information, such as commonly used published or default values. If background conditions are not explored, it may be difficult to determine whether a chemical release has occurred, to adequately define the nature and extent of contamination, or to assess the residual contribution to risk made by the release.

Background analysis can be useful for setting reasonable and attainable cleanup goals if cleanup is required. Project teams should never define cleanup goals below concentrations resulting from natural or anthropogenic background sources.

The background analysis procedures described in this guidance document will reduce the probability of decision error, and therefore can help to reassure stakeholders and regulators that the Navy has made the correct decisions regarding a vapor intrusion response action for a particular site. The project team should use the DQO process to reach agreement with stakeholders over acceptable decision error probability. Finally, when appropriate, the conclusions associated with the background evaluation should be used as scientifically defensible evidence to support a decision of no further action for a site; if cleanup or mitigation is necessary, the results from the background evaluation can aid in the selection of technically feasible and cost-effective remedial alternatives.

1.3 Statutory Requirements, Regulations, and Guidance

The *Department of the Navy Environmental Restoration Program (NERP) Manual* (DON, 2006) provides an overall synopsis of the environmental laws and regulations that define and affect the NERP, and describes the procedures developed by the Navy to ensure compliance with these laws and regulations. As specified in the *NERP Manual* (DON, 2006), all actions at Environmental Restoration (ER) sites shall comply with CERCLA, Superfund Amendments and Reauthorization Act (SARA), and the National Oil and Hazardous Substances Pollution Contingency Plan (NCP).

The *NERP Manual* (DON, 2006) also specifies that ER project teams shall reasonably interpret and apply U.S. EPA policy and guidance to make cleanup decisions and plan response actions.

1.3.1 Federal Laws and Regulations (Residential and Industrial)

Vapor intrusion, as well as general indoor air quality concerns, can occur in residential, commercial, and industrial settings. Current federal laws and regulations do not treat all of these settings in the same manner.

In industrial settings, OSHA has the authority under the Occupational Safety and Health Act, 29 U.S.C. 650, et seq., to regulate workplace safety for employees; this authority extends to air quality. OSHA publishes its Permissible Exposure Limits (PELs), which establish the maximum concentration of a chemical in air that a worker can be exposed without respiratory protection. PELs are designed for workplaces where the chemicals in question are in use, and thus are typically two or three orders of magnitude higher than U.S. EPA's more restrictive risk-based screening values. These standards would not be appropriate for homes, offices, or schools.

Outside the workplace, there are no federal standards for indoor air quality (Andersen, 2002). Federal regulations for air in more general settings concern only the emission source of the chemicals in question, not the quality of the air found in particular environments. Under the Clean Air Act, 42 U.S.C. 85, U.S. EPA is required to develop and maintain a list of hazardous air pollutants (HAPs) and to promulgate regulations setting national emission standards for hazardous air pollutants (NESHAP) for the sources of HAPs, but there are no federal standards pertaining to ambient levels of HAPs, or HAP standards for indoor air.

There are a number of reasons for the scarcity of federal regulations relating to indoor air quality: indoor air pollution is quite often the product of multiple sources and specific air quality issues can vary from building to building. Symptoms caused by poor indoor air quality can be varied and also can occur at extremely low pollutant levels, making measurement, identification, and regulation of the causal contaminant very difficult. Literally hundreds of separate chemicals can be found in most indoor air, and accurately measuring all of them pushes the limits of existing technology.

1.3.2 U.S. EPA and State Indoor Air Guidance

In lieu of set standards, U.S. EPA currently publishes voluntary guidance documents to assist building owners in preventing, identifying and correcting potential indoor air quality problems (www.epa.gov/iaq). Additionally, guidance for indoor air quality is available in a number of state publications. These guidance documents typically describe the full spectrum of potential contaminants and their respective dangers, discuss practices for avoiding and mitigating indoor air pollution, and provide methods for sampling and evaluating the quality of air.

Poor indoor air quality can be caused by a wide range of factors including second-hand smoke, biological contaminants (mold, dust mites, etc.), asbestos, carbon monoxide, nitrogen dioxide, radon, and VOCs (paints, varnishes, pesticides, cleaning products, and formaldehyde).
Some examples of indoor air quality guidance can be found below:

- **U.S. EPA Office of Air and Radiation:** *Building Air Quality: A Guide for Building Owners and Facility Managers* (1991)
- **Massachusetts Department of Environmental Protection (MADEP):** *Indoor Air Sampling and Evaluation Guide* (2002)
- **Washington State Department of Health (DOH):** *Indoor Air Quality Primer: An Overview of Residential Indoor Air Problems* (http://www.doh.wa.gov/ehp/ts/IAQ /IAQPrimer.htm).

1.3.3 U.S. EPA and State Vapor Intrusion Guidance

Vapor intrusion guidance is available from U.S. EPA and a number of state agencies. These guidance documents typically describe methods for conducting screening evaluations for the identification of complete vapor intrusion pathways, determining whether the risks posed by completed pathways are unacceptable, and determining, if necessary, proper mitigation strategies. Specific topics covered in guidance literature may include discussions of sampling and analytical requirements, site-specific screening options, remedial options, monitoring and maintenance requirements, community outreach, and methods for determining background. Additionally, U.S. EPA publishes risk-based concentration (RBC) screening levels to be used in the evaluation of a site, and the agency has identified more than 100 chemicals that have sufficient volatility and toxicity to pose a theoretical vapor intrusion hazard (U.S. EPA, 2002b).

Vapor intrusion guidance is all relatively recent, prone to change, and varies by jurisdiction; thus, investigators should make sure to check with local regulators for current guidance when undertaking any investigation.

Some examples of vapor intrusion guidance are found below:

- **U.S. EPA Office of Solid Waste and Emergency Response:** *Draft Guidance for Evaluating the Vapor Intrusion to Indoor Air Pathway from Groundwater and Soils* (2002b)
- **U.S. EPA Office of Emergency and Remedial Action:** *User's Guide for Evaluating Subsurface Vapor Intrusion into Buildings* (2004)
- **Interstate Technology and Regulatory Council (ITRC):** *Vapor Intrusion Pathway: A Practical Guideline* (2007)
- **California Environmental Protection Agency (Cal/EPA):** *Interim Final Guidance for the Evaluation and Mitigation of Subsurface Vapor Intrusion to Indoor Air* (2005)
- **Colorado Department of Public Health and Environment (CDPHE) Hazardous Materials and Waste Management Division:** *Indoor Air Guidance—Public Comment Draft* (2004)
- **New Jersey Department of Environmental Protection (NJDEP) Site Remediation and Waste Program:** *Vapor Intrusion Guidance* (2005)
- **New York State Department of Health (NYSDOH):** *Guidance for Evaluating Soil Vapor Intrusion in the State of New York, Final* (2006).

These guidance documents include discussions about indoor sources of background chemicals. Some, such as NYSDOH (2006, Appendix C), provide summaries of select existing background studies and databases, including tabulated summary statistics.

1.4 Key Definitions

Some of the keywords and concepts used in this guidance document are defined below; a more comprehensive list of terms is provided in the glossary section.

1.4.1 Ambient or Background Outdoor

Background outdoor air contamination refers to the level of contaminants in the ambient air surrounding a structure. Ambient air can contain numerous VOCs, such as benzene, tetrachloroethene (PCE), and trichloroethene (TCE), which may exceed indoor air risk-based screening levels. Depending on building air exchange rates, contaminants from outdoor ambient air may be major contributors to background indoor air conditions (ITRC, 2007).

1.4.2 Background Indoor

Background indoor air contamination refers to the level of contaminants in the air inside a building not caused by migrating vapors emanating from subsurface contamination caused by specific Navy site releases. Background indoor chemicals are attributable to ambient and indoor sources. As previously mentioned, Appendix A provides a thorough list of chemicals present in common products associated with common indoor sources.

1.4.3 Background Soil Gas

Background soil-gas contamination refers to the level of contaminants in the soil gas beneath a structure not related to specific Navy site release. A prime example of a background soil-gas chemical is naturally-occurring radon, which is often used as a tracer in vapor intrusion investigations (ITRC, 2007, page 20).

1.4.4 Vapor Intrusion

The CNO (DON, 2008) defines vapor intrusion as:

> "*The migration of vapor of sufficiently volatile chemical compounds from the subsurface environment (soil, soil gas, or groundwater) into indoor air of overlying buildings. Examples of such chemical compounds include volatile organic compounds (VOCs), e.g., trichloroethylene (TCE); semi-volatile organic compounds (SVOCs), e.g., naphthalene; and volatile metals, e.g., elemental mercury.*"

1.5 Similarities and Differences Among Background Analyses

There are a number of similarities and differences between background indoor air evaluations for vapor intrusion assessments compared with the background analyses described for soil (DON, 2002), sediment (DON, 2003), and groundwater (DON, 2004b). These similarities and differences include the following:

Similarities:

- ❑ A common goal in all media is to determine whether the concentrations measured at a site resulted from site activities or from background sources (natural or anthropogenic).
- ❑ CERCLA or RCRA decision-making framework typically demands a demonstration that chemical concentrations are not site-related. Doing so requires well-defined DQOs, which help frame the problem, ask the correct questions, and specify the quality and quantity of data.
- ❑ Performing background analyses requires input from multiple disciplines, such as the earth sciences, statistics, toxicology, and chemistry.

- Exploratory data analysis (EDA) methods are the foundation of background analyses for all media.

Differences:

- The statistical distributional comparisons, including two-sample hypothesis testing methods applied to site versus background datasets in soil, sediment, and groundwater, are rarely used in vapor intrusion background evaluations, as attested in the *DoD Vapor Intrusion Handbook* (2009, page 121). For further discussion refer to Section 5.1.3 of this document.

- Anthropogenic background impacts to soil, groundwater, and sediment are often the result of large-scale human activities (e.g., historical use of leaded gasoline). Under such circumstances, the effect of any given individual contributor is not important. In indoor air situations, however, activities of individual occupants can directly affect the background concentrations in a vapor intrusion evaluation.

- Temporal and spatial variability of contaminant concentrations are commonly much greater in air and soil gas than in soil, sediment and groundwater.

- Multiple lines of evidence are usually necessary to determine if vapor intrusion results in an indoor air risk (e.g., DoD, 2009; ITRC, 2007). Similarly, there is seldom a single line of evidence to convincingly determine the sources of volatile chemicals detected in indoor air.

- The occurrence and magnitude of vapor intrusion can depend greatly on the characteristics and operation of the building so it is important to involve mechanical engineers or others with expertise on these topics.

1.6 Unique Aspects of Vapor Intrusion and Background Indoor Air Evaluation

The unique aspects of the vapor intrusion pathway and the indoor air environment must be considered during background analysis. Due to the dynamic nature of the indoor air environment, methods and procedures for vapor intrusion investigations and response actions are different from those used for soil, sediment, or groundwater.

- **Evolving Understanding:** The scientific understanding of vapor intrusion mechanisms is growing and evolving rapidly. Earlier numerical models based solely on intruding vapors are often confounded by the fact that indoor target analytes reflect the commingling of many ongoing sources, each associated with a wide range of chemicals. Appropriate characterization of indoor air is also a major technical issue due to varying concentrations of target analytes in time and space. Another important technical question is the appropriate quantification of indoor and outdoor background sources.

- **Representative Datasets:** Background analyses in soil, sediment, and groundwater media often involve collection of large numbers of site and background samples. Vapor intrusion investigations, on the other hand, are usually performed based on a focused collection of fewer “representative” samples. For example, rather than taking numerous random indoor air samples, only a few are collected under critical conditions (e.g., negative pressure and in the immediate proximity of potential vapor pathways). The small size of datasets is mainly due to logistical or practical challenges associated with indoor and sub-slab sampling within active structures or residences. As a result, the selected procedures in background indoor air analyses must be compatible with the typically limited, yet representative, datasets. For example, certain procedures that rely on large, randomly collected datasets may not be applicable to vapor intrusion investigations.

Box 1-1 provides some practical tips for collecting a representative dataset.

Structural Aspects: Each investigated building has unique features that directly influence vapor intrusion pathways. These features cover a wide range of characteristics including the type and condition of building foundations, active and passive HVAC systems, as well as indoor activities and sources. These features must be accounted for in background analyses in any vapor intrusion investigation. As recommended by the *DoD Vapor Intrusion Handbook* (DoD 2009), prior to collecting indoor air sampling, at least one site visit and building evaluation should be performed to determine potential sources of contamination. This evaluation should aim at a better understanding of potential vapor entry points, indoor air circulation patterns, as well as indoor human activities, building materials, and furnishings that may be contributing VOCs to the indoor air. Any potential outdoor contaminant sources near the structure should also be identified during this evaluation (DoD, 2009, Appendix G).

- **Spatial Variations:** Background indoor conditions may exhibit spatial patterns. Such patterns are especially significant within a structure, where indoor air unaffected by vapor intrusion is expected to have higher concentrations near indoor sources or enclosed spaces. Ignoring such indoor patterns may lead to erroneous findings (ITRC, 2007, Section 3.7.3).

- **Temporal Variations:** Ambient background concentrations and vapor intrusion rates may have seasonal and diurnal patterns, associated with the variations of such factors as weather patterns, wind conditions, inversion layers, site activities, water table levels, temperature, soil moisture, and atmospheric pressure. Under such conditions, representative background sampling plans should account for such variations. For example, the DoD *Vapor Intrusion Handbook* (DoD, 2009, Appendix G) suggests multiple rounds of outdoor air sampling events. In cases where collection of multiple indoor air samples is feasible, then sampling should be done during critical periods, as discussed in Box 1-1.

BOX 1-1. Practical Tips: What is a Representative Dataset?

Application of standard background methods requires datasets that are adequately large relative to the variability of investigated analytes.

In typical vapor intrusion investigations, adequately large datasets are not available. This is primarily due to the fact that measured sub-slab or indoor air concentrations display wide spatial or temporal variations (e.g., up to multiple orders of magnitude).

Instead, small numbers of representative samples for a specific sampling event are collected. Samples are considered representative if they cover critical locations (e.g., basement) and periods (e.g., periods of negative pressure).

In small structures, such as a detached single family residence with a basement, representative datasets for background analysis can consist of at least: (1) one pair of collocated/concurrent indoor air and sub-slab soil gas samples collected at the center of the basement, and (2) one pair of concurrent indoor and outdoor air samples from near the living area. Such samples are often collected during negative pressure conditions, e.g., periods of low ambient temperature and/or heating, ventilating, and air conditioning (HVAC) in operation.[*]

Larger structures, as well as those subject to seasonal ambient variations, require more pairs of collocated/concurrent samples.

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[*] Colder air is heavier than warmer air, i.e., colder ambient air has a higher pressure when compared with warmer indoor air. Under such conditions, if a pathway exists, vapor intrusion will occur.

- **Regulatory and Stakeholder Acceptance:** As the issue of vapor intrusion is a relatively new regulatory concern, stakeholders generally tend towards conservative methods and practices. This tendency is further exacerbated by the fact that occupants of potentially-impacted buildings consider exposure to contaminated vapor as an urgent and real danger, as opposed to a hypothetical or avoidable risk. The RPM should bear in mind that the parties involved may not have the same comfort levels with decisions related to vapor intrusion as they would have for a medium such as soil or groundwater. Such a mindset poses additional challenges for innovative techniques or approaches. Early involvement of stakeholders in the investigation process can facilitate their acceptance of the background analysis findings.

1.7 Background Analysis Overview: A Multiple Lines of Evidence Approach

The analytical components discussed in this guidance are intended to be viewed as multiple lines of evidence and evaluated within a weight of evidence framework. The rationale for such an approach is summarized in Box 1-2.

Indoor air background analysis is an integral part of any vapor intrusion investigation that collects indoor air samples. Figure 1-2 presents a flow diagram taken from the *DoD Vapor Intrusion Handbook* (DoD, 2009, Figure 2-1) showing that a Vapor Intrusion background analysis fits into site specific evaluation phase of the overall VI process (after the screening level evaluation). Figure 1-3 presents the conceptual decision flow diagram of a typical background analysis. As displayed on this figure, whenever a conclusive result is reached, the analyses should be terminated and documented. To assist RPMs, Figure 1-3 includes a series of notes as elaborated in Table 1-1.

1.7.1 Background Indoor Air Exploratory Data Analysis or EDA

A background indoor air EDA is typically not initiated until after the risk screening step. The risk screening step involves comparing subsurface (e.g., shallow groundwater and/or soil gas) concentrations with risk-based screening concentrations to focus any subsequent EDA on constituents with a higher potential for vapor intrusion risks.

EDA methods offer multiple approaches for examining data to gain insight into the contribution of background sources to indoor air contamination. The EDA methods are placed in the context of the U.S. EPA (2006) decision-making and DQO framework. Multiple lines of evidence are usually needed to support vapor intrusion decision making including decisions as to whether indoor air contamination should be attributed to background sources or subsurface releases. The interpretation of multiple lines of evidence is a key theme throughout this guidance. The results of an EDA are also used to update the CSM.

Background indoor air EDA methods include: (1) comparisons with site-specific or published background values, (2) examination of constituent ratios between different media, (3) comparison of the constituent compositions (i.e., ratios) of VOCs within and between subsurface soil-gas, indoor air, and outdoor air samples, and (4) additional methods (e.g., differential pressure monitoring, pressure cycling, tracer compound analyses, and

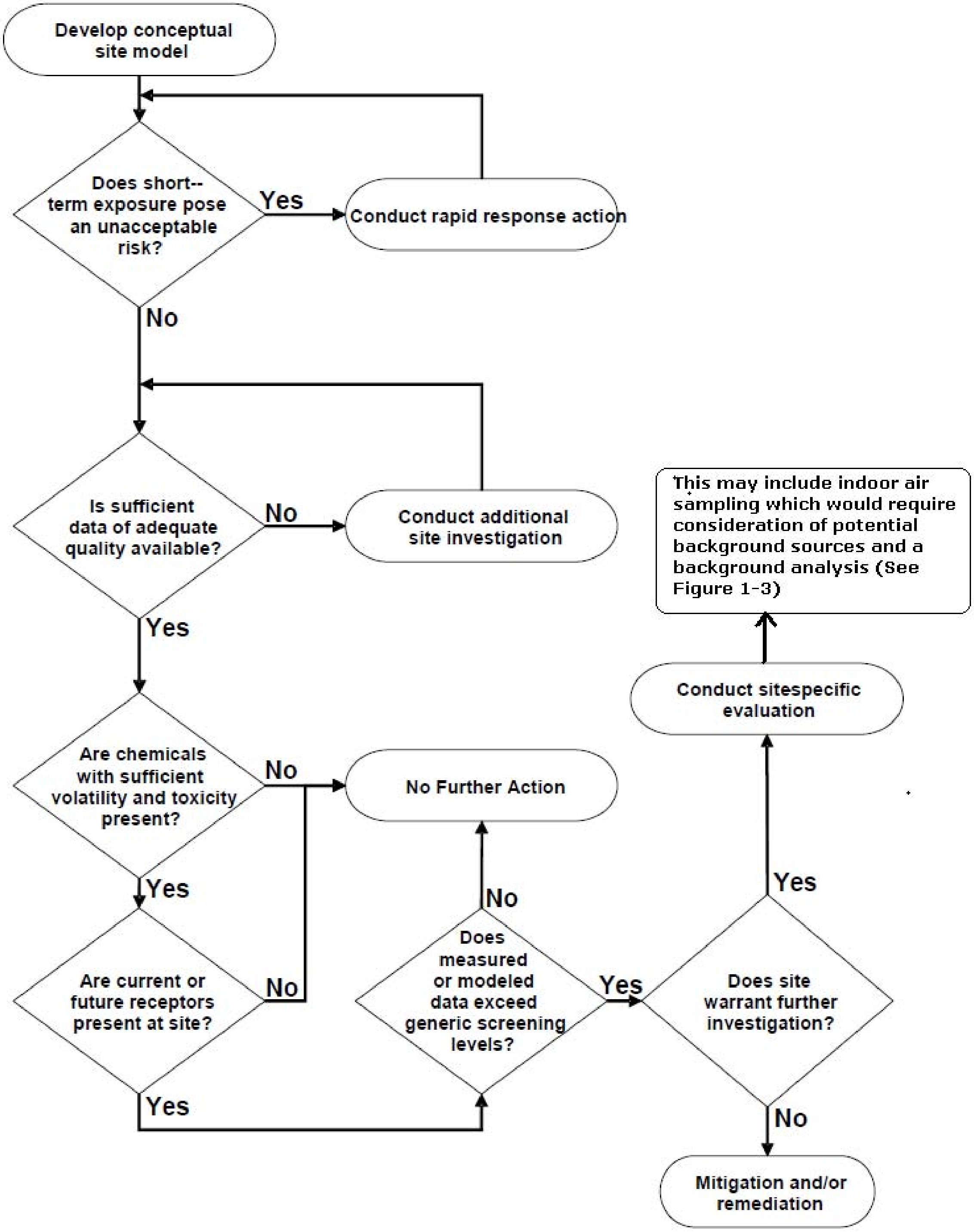

FIGURE 1-2. Flowchart showing where background analysis typically fits into a vapor intrusion study (modified from DoD VI Handbook Fig 2-1) .

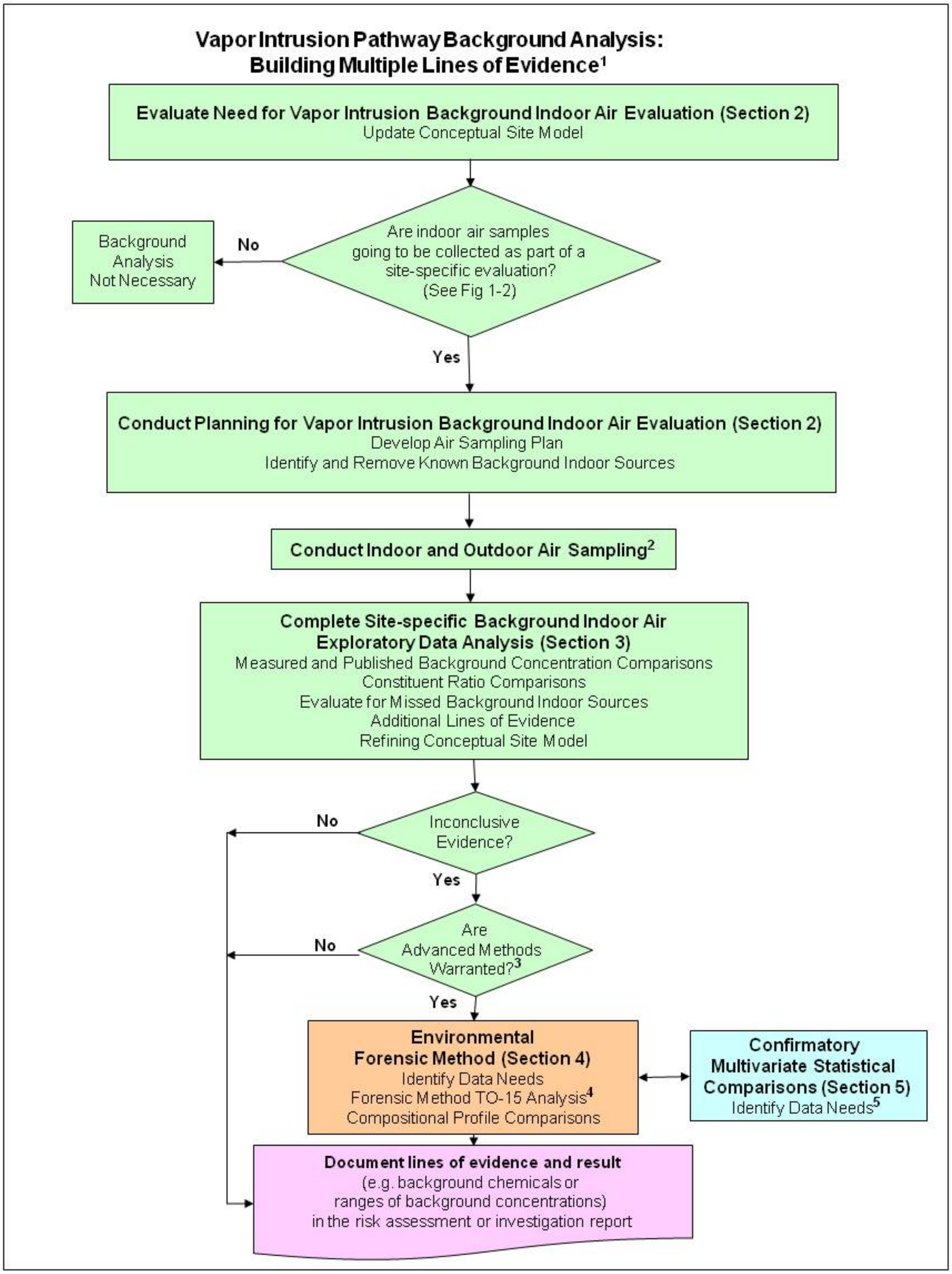

FIGURE 1-3. Typical vapor intrusion pathway background analysis decision flowchart (Footnotes listed in Table 1-1.)

TABLE 1-1. Additional notes for RPMs

1	Background analyses are based on building multiple lines of evidence. At present there is no single, simple procedure that conclusively differentiates background indoor concentrations.
2	Recommended procedures require collocated/concurrent indoor air, outdoor air, and soil-gas sampling.
3	In some cases, evidence can be derived from forensic and multivariate statistical methods. These methods are advanced procedures, which may not be applicable at many Navy sites. Forensic methods provide analytical procedures to decipher the chemical composition of collected samples in order to determine the source of detected contaminants. Within this context, multivariate statistical methods offer confirmatory tools and provide additional lines of evidence. The application of these advanced methods should be considered at sites involving petroleum contamination and out-of-the-ordinary vapor intrusion liabilities.
4	Forensic Method Toxic Organics TO-15 analysis measures more than 80 hydrocarbons capable of identifying and differentiating petroleum vapors. See Section 4 for details.
5	Confirmatory multivariate statistical techniques require a minimum of 10, ideally 20, collocated/concurrent samples representing indoor air, outdoor air, and soil gas. Collection of such datasets may not be feasible at many sites.

BOX 1-2. Practical Tips: Why Multiple Lines of Evidence?

Reasons for using multiple lines of evidence include:

Background indoor air analyses often rely on data collected during vapor intrusion investigations. These investigations usually involve small representative datasets of highly variable analyte concentrations. Such datasets are insufficient to produce conclusive results based on the application of standalone background methods.

At present, there is no single, simple procedure that can conclusively identify or quantify background indoor conditions.

Each successive method outlined in the flowchart (Figure 1-3) becomes more complex. Thus, each subsequent analysis should only be pursued if, and only if, additional clarification is expected.

If appropriate and feasible, the gathering of multiple lines of evidence shall continue until a conclusive finding regarding the source of detected indoor air concentrations has been reached.

real-time monitoring) for ascertaining the contribution of background sources to measured site-specific indoor air concentrations. Each of these techniques has varying degrees of strength for either confirming or refuting the existence of background sources, which is an important consideration during the decision-making process. Section 3 provides details on the EDA methods.

1.7.2 Chemical Forensic Methods

After completion of EDA, forensic evaluation may be conducted to support EDA background findings. Environmental forensic analysis involves the use of chemical fingerprinting methods that help constrain or identify the likely origins of detected indoor air chemicals. Such analyses usually require thorough reviews of product chemistry, subsurface data, and ambient background.

Typical vapor intrusion investigations usually focus on a finite list of volatile chemicals. Forensic analysis may broaden this focus by incorporating a wider range of source-specific assemblages of compounds. This expanded focus targets not only the few chemicals of interest, but additional compounds that are capable of defining site-specific background conditions, as well as differentiating pattern anomalies caused by vapor intrusions emanating from subsurface contamination sources.

Forensic investigators consider a variety of information, including: (1) chemical properties of common products associated with various sources, (2) standard and forensic laboratory analytical procedures, (3) chemical variability associated with attenuation processes along the vapor intrusion pathway, as well as (4) forensic ratios of specific compounds which are known to be less prone to temporal or spatial variations. Section 4 provides details on forensic methods.

1.7.3 Statistical Methods

Exploratory and forensic analyses often involve comparative procedures, which are statistical techniques for comparing chemical concentrations or compositions in various samples or datasets. A typical vapor intrusion investigation may involve a variety of comparisons involving background data. The appropriate type and scope of the statistical procedure depends on the objective of the intended comparison. In general, the comparative statistical testing during a vapor intrusion investigation can be divided into a number of broad categories:

- **Individual comparison**: Comparison of a measured or computed value associated with a given chemical to its corresponding range of background concentrations – typically performed during EDA.
- **Distributional comparison**: Comparison of the entire distribution of measured indoor or outdoor concentrations of a given chemical to the distribution of their corresponding background concentrations – typically not performed in vapor intrusion investigations because it requires a prohibitively large number of air samples.
- **Multivariate comparison**: Comparison of chemical profiles of individual air samples to determine whether the investigated samples display similar chemical profiles. This is typically performed as part of a forensic analysis involving multiple chemicals measured in a variety of samples, including indoor air, outdoor air, and soil-gas samples.

The above statistical comparisons are not intended to be used as sole proofs of presence or absence of background sources. Rather, they should be considered as complementary lines of evidence along with other physical and chemical observations. Each type of comparison entails specific and unique statistical procedures. None of the above comparisons can be applied without at least a representative set of site-specific samples from indoor and outdoor air. Section 5 identifies the appropriate statistical methods for achieving each objective, discusses their limitations, and presents guidance for implementing each method.

1.7.4 Background Analysis Documentation

Success of a background indoor air analysis is highly dependent on adequate and appropriate documentation of results and findings. The documentation should consist of at least the following components:

- Descriptions of the history and setting of the investigative site and structures.
- Technically defensible CSM, including thorough assessment of site conditions, potential pathways, background indoor and outdoor sources, site-specific fate and transport processes, as well as land use and potential receptors.
- Rationale to demonstrate that the available site-specific data adequately represent vapor intrusion conditions.
- Rationale and justification for using published and/or default values in the analysis.
- Results of exploratory, forensic, and comparative analyses and documentation of each step in the process in sufficient detail to allow a comprehensive review.

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2. STEPS LEADING TO A VAPOR INTRUSION BACKGROUND INDOOR AIR EVALUATION

A background evaluation is an important component of a site-specific vapor intrusion investigation since volatile chemicals from activities inside the building, consumer products, building materials, and outdoor air sources are commonly detected in indoor air samples (DoD, 2009; ITRC, 2007; U.S. EPA, 2002). Above-ground background (indoor or outdoor) concentrations can exceed health-based target concentrations for select volatile chemicals (e.g., benzene, PCE, TCE), highlighting the need to evaluate the contributions of background indoor and outdoor sources when evaluating the vapor intrusion pathway. The objective of this section is to summarize the steps of that lead to a site-specific vapor intrusion indoor air background evaluation.

2.1 Specific Steps Leading to the Background Evaluation

BOX 2-1. Practical Tips: When Would a Background Evaluation Start?

The planning process for vapor intrusion background assessment should begin as soon as it is determined that indoor air samples will be collected.

The purpose of this subsection is to provide an overview of the steps involved in identifying the volatile chemicals for consideration in the background EDA (Section 3). These include:

- ❑ Assembling a project team of professionals
- ❑ Developing a CSM and understanding the data needs associated with a background evaluation
- ❑ Summarizing the data-collection methods used during site-specific vapor intrusion and background evaluations
- ❑ Discussing a number of issues that should be considered when assessing data adequacy for the risk-screening step
- ❑ Conducting the risk-screening step used to identify COPCs for evaluation in Section 3.

2.1.1 Assemble Project Team

One of the first steps in the systematic planning process (U.S. EPA, 2006) for collecting and interpreting high-quality data should involve identifying and assembling a project team (Figure 2-1). Given the complexity and challenges associated with vapor intrusion and background evaluations and the need to consider multiple lines of evidence, this team should (1) be assembled early during the planning stages, (2) be multidisciplinary, and (3) include as many of the personnel identified in Figure 2-1 as necessary.

The role of the risk communicator is especially important when addressing vapor intrusion. Per the *DoD Vapor Intrusion Handbook* (DoD, 2009):

> *"An important yet often overlooked component of vapor intrusion projects is communicating potential risks with building occupants as well as with regulatory agencies. Vapor intrusion is an unfamiliar concept to most people and there is great potential for alarm, fear, and/or outrage. The success of the project may well depend on early and effective communication with all interested parties. . . . In the context of a DoD vapor intrusion study, the most common stakeholders include the service branch, U.S. EPA and local regulator authority, the building occupants and possibly offsite residents or workers, media, and environmental advocacy groups."*

Although many team members are involved in risk communication to some extent, specific organizations within the Navy (e.g., Navy and Marine Corps Public Health Center) have personnel that specialize in vapor intrusion risk communication.

Obtaining input from all of the experts shown in Figure 2-1 may not always be feasible or necessary; however, depending on the scope and extent of the investigation, as many stakeholders as possible must be involved in planning and implementing technically defensible evaluations of vapor intrusion and background indoor air.

2.1.2 Conceptual Site Model Review

A CSM is typically represented by a diagram that visually portrays the current understanding of site conditions including the nature and extent of contamination, contaminant fate and transport routes, potential receptors and contaminant exposure pathways (DoD, 2009). When evaluating the role of background indoor or outdoor air sources, it is also necessary to understand and illustrate these known or potential sources and how they might affect indoor air quality.

An understanding of the CSM is the foundation of defensible evaluations and decisions regarding vapor intrusion and the role of background sources. The importance of the CSM is demonstrated by the substantial focus it has received in vapor intrusion presentations and guidance documents (e.g., Abreu et al., 2009; DoD, 2009; ITRC, 2007; U.S. EPA, 2002).

The term *conceptual* does not necessarily denote a rough or simplistic understanding.

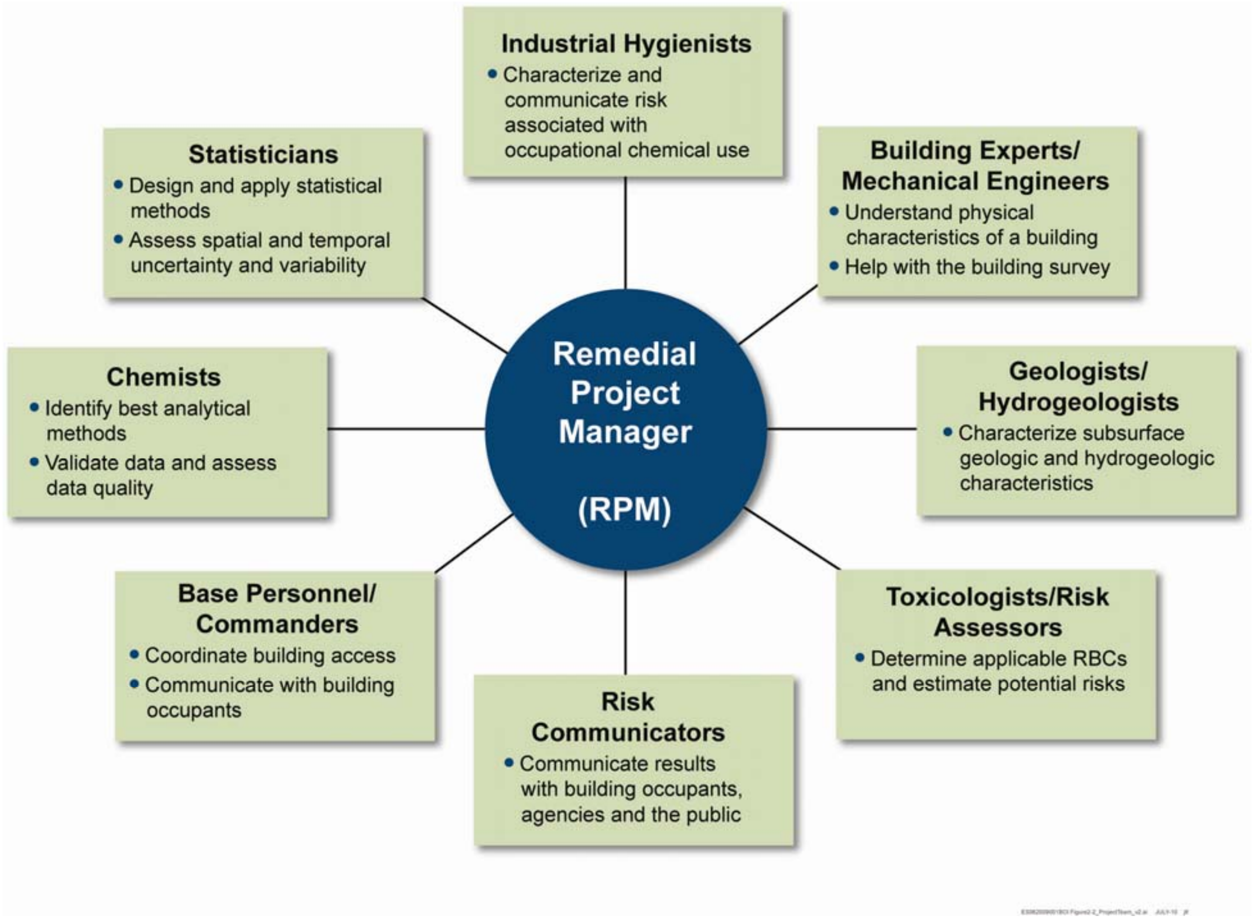

FIGURE 2-1. Project team

CSMs can be complex and comprehensive and include multiple types of data and evidence. In some circumstances, a simple CSM may be all that is necessary to support a decision. Invariably, the CSM should reflect the current knowledge of the site and evolve as new information is developed and new questions are framed and answered. The Navy recently developed a CSM checklist (Appendix B) which offers a number of recommendations regarding the types of information to include in a CSM.

A number of key elements associated with a vapor intrusion CSM are shown in Figure 2-2. A refined sample CSM will be presented in Section 3.6 to illustrate how different lines of evidence are used during the background indoor air evaluations. Some of the elements of particular interest in a background indoor air evaluation should include (1) the locations and types of known or potential indoor sources, such as consumer or industrial products, (2) information about outdoor sources, such as nearby commercial/industrial facilities and mobile sources (e.g., cars, trucks, and other equipment), (3) data on the local ambient air quality for the VOCs, (4) data on the physical properties, concentrations, and relative ratios of chemicals present in the subsurface and indoor and outdoor air, and (5) data from published studies on typical background indoor and outdoor air concentrations.

In addition to the elements shown in Figure 2-2, the number, location, and type of individuals potentially exposed to subsurface vapors volatilized into the building should be considered when developing the CSM.

2.1.3 Summary of Sampling and Analytical Methods

Various investigative and analytical methods are available during a vapor intrusion evaluation. Both sampling and analytical methods will affect the quality of the data and its use in vapor intrusion risk-screening and background evaluations. Appendix C provides (1) a brief summary of the investigative and analytical methods commonly used in vapor intrusion and background evaluations, along with references to other guidance documents that can be reviewed for more detailed discussions, (2) an overview of how the sampling methods and corresponding environmental data will be used when conducting the background evaluations described in subsequent sections, (3) a discussion of some strengths and weaknesses associated with the various sampling and analytical methods and, (4) the adequacy of different types of data for use in the risk screening step. A synopsis of this information is provided in Table 2-1. Additionally, see Appendix D for quality control (QC) procedures specific to soil-gas sampling.

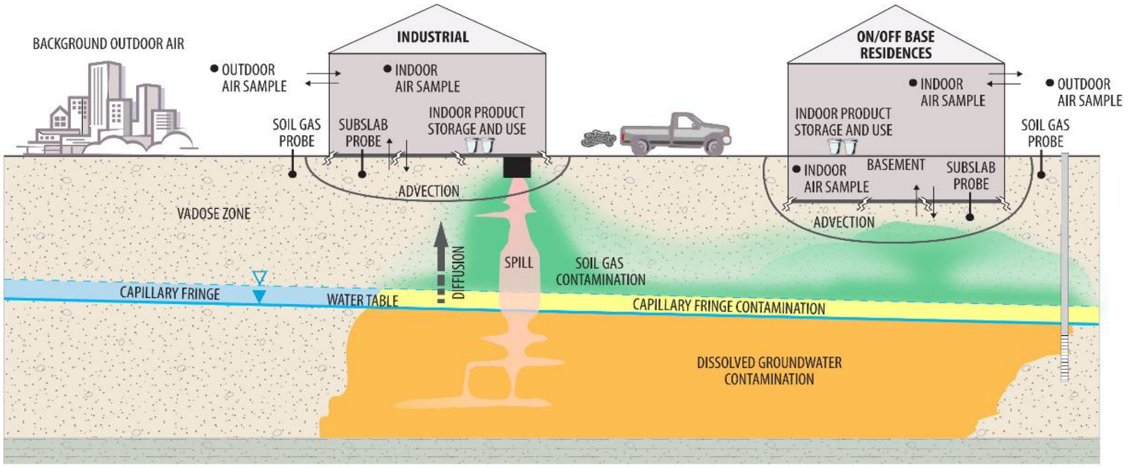

FIGURE 2-2. Sample vapor intrusion conceptual site model

TABLE 2-1. General sampling strategies for vapor intrusion evaluations

Medium	Method Used to Evaluate the Data	Issues Relevant to the Background Evaluation
Groundwater	Modeled or empirically based groundwater to indoor air ratios can be used to predict indoor air levels	o Constituent ratios between groundwater and indoor air may help distinguish groundwater, soil, and background sources of vapors. o Up to orders of magnitude uncertainty or variability in modeled or empirically based attenuation factors complicates analysis. o Some agencies prefer one type of subsurface data over another or do not allow use of data from a single subsurface medium. o Since groundwater is rarely, if ever, characterized under buildings, it is important to account for spatial variability when using groundwater to predict vapor intrusion.
Soil Gas	Modeled or empirically based soil gas to indoor air constituent ratios can be used to predict indoor air levels	o Constituent ratios within or between soil gas and other media may help differentiate between the vadose zone, groundwater, and background sources. o Up to orders of magnitude uncertainty or variability in modeled or empirically-based attenuation factors complicates analysis. o Some agencies question use of exterior soil-gas data to predict indoor air concentrations. o Historical soil-gas monitoring methods were not designed for vapor intrusion assessments. o Empirical data show the poorest correlations between soil-gas and indoor air data (U.S. EPA, 2008). o Soil-gas results are spatially or temporally variable.
Sub-slab Soil Gas	Modeled or empirically based sub-slab soil gas to indoor air constituent ratios may be used to predict indoor air levels	o Constituent ratios within or between sub-slab soil gas and other media may be used to distinguish subsurface versus background sources. o Up to orders of magnitude uncertainty or variability in modeled or empirically based attenuation factors complicates analysis. o Concurrent indoor and outdoor air data are highly recommended when implementing a background evaluation. o Up to orders of magnitude spatial or temporal variability. o Sampling may be intrusive and sometimes not feasible due to access limitations, engineering constraints, or disturbances to occupants.
Indoor (and Outdoor) Air	Generally use measured indoor air concentrations to estimate exposure	o Indoor air sampling may provide the most direct measurement for assessing inhalation exposure to occupants. o Background indoor and outdoor sources can confound interpretation and use of indoor data. o Indoor sampling is intrusive and sometimes not feasible due to access limitations or disturbances to occupants. o Spatial and temporal variability is often significantly less than variability in subsurface media data.

Thorough discussion of the sampling and analytical methods used to conduct a vapor intrusion investigation can be found in the DoD, ITRC, U.S. EPA, and various state vapor intrusion guidance documents (DoD, 2009 [Section 3]; ITRC, 2007 [Appendix D]; U.S. EPA, 2002 [Appendices A and E]; Cal/EPA, 1997, 2003, 2005; NJDEP, 2005; NYSDOH, 2006; MADEP, 2002). The Navy also recently commissioned a study to review and document best practices in subsurface and indoor air sampling methods to improve assessment of the vapor intrusion pathway (DON, 2009).

2.1.4 Summary of Risk-screening Approaches

Risk screening is performed during the initial phase of a vapor intrusion evaluation (refer to Figure 1-3). It commonly involves comparing subsurface (i.e., groundwater, exterior soil gas, or sub-slab soil gas) concentrations with conservative risk-based screening levels. Consistent with the *DoD Vapor Intrusion Handbook* (DoD, 2009) and ITRC's *Vapor Intrusion Pathway: A Practical Guideline* (2007), the objective of the risk-screening step is to ensure that those sites most likely to pose unacceptable risk from vapor intrusion are retained for the more detailed site-specific vapor intrusion evaluation.

The initial risk-screening step of a vapor intrusion evaluation also involves determining (1) which chemicals are sufficiently volatile (Box 2-6) and toxic, (2) whether the vapor intrusion and subsequent inhalation pathway is complete, and (3) whether an acute or emergency hazard resulting from vapor intrusion is suspected (DoD, 2009; ITRC, 2007). However, for the purpose of this guidance document, the risk-screening step is used to identify VOCs for consideration in the site-specific background indoor air evaluation. For detailed discussions on the broader use and methods of risk screening, readers are referred to the DoD, ITRC, U.S. EPA, and other state vapor intrusion guidance documents (DoD, 2009; ITRC, 2007; U.S. EPA, 2002; Cal/EPA, 2005; NJDEP, 2005).

The generic screening values for key VOCs are often similar to or lower than published background indoor air concentrations. Therefore, select VOCs (e.g., benzene, carbon tetrachloride, chloroform, methyl tert-butyl ether [MTBE], TCE, PCE, vinyl chloride) are commonly detected in indoor air regardless of whether vapor intrusion is occurring and systematic background evaluations are frequently needed to distinguish subsurface contributions from those associated with background sources.

BOX 2-2. Practical Tips: Risk-screening

The primary purpose of risk screening is to select VOCs for the background evaluation.

U.S. EPA and different states have developed risk-based screening. These screening levels vary considerably. Agreement between stakeholders is critical when selecting screening levels.

BOX 2-3. Defining Volatile Chemicals (ITRC, 2007)

U.S. EPA (2002) defines volatiles as chemicals with a Henry's law coefficient greater than 10^{-5} atmosphere cubic meters mol^{-1} at room temperature.

Some states (e.g., New Jersey) have slightly different definitions. The definition applicable to the state or program should be identified and applied.

U.S. EPA (2002) developed a set of generic risk-based soil-gas and groundwater screening levels for the vapor intrusion pathway. These values continue to be used by federal and state regulatory agencies. However, more than half of the state regulatory agencies in the country have developed their own policies, regulations, guidance, or screening levels for the vapor intrusion pathway. A survey conducted by ITRC in 2004 found that existing state policies, regulations, and guidance related to the vapor intrusion pathway vary widely.[1] This has resulted in screening values that vary by up to three or four orders of magnitude from state to state or compared with U.S. EPA (2002) generic screening levels.

The differences in screening values are in part due to differences in the default assumptions about the magnitude of attenuation between the subsurface (i.e., groundwater and soil gas/sub-slab) and indoor air. The importance of considering multiple lines of evidence cannot be overemphasized when conducting the screening level evaluation given the uncertainty in predicting subsurface-to-indoor air attenuation. Careful consideration should be given to the use of conservative screening values when selecting VOCs for further

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[1] See: http://www.itrcweb.org/vaporintrusionresources/ITRC_VI_Survey_8-17-05/ITRC_1_VI_Survey_Index.htm

analysis in a site-specific background evaluation to minimize the likelihood of prematurely eliminating a chemical as a COPC (i.e., committing a false negative error). Retaining a chemical for further consideration based on the screening value generally requires additional lines of evidence before a vapor intrusion conclusion can be made.

The conservative indoor air screening levels for a number of common site-related VOCs are similar to or less than the range of background indoor air concentrations reported in the literature. U.S. EPA (2008) reviews, compiles, and provides a summary statistics table for background indoor air concentrations obtained from multiple studies conducted after 1990 in North American residences. A more detailed presentation of background residential indoor air concentrations in North America is provided in the peer-reviewed report by Dawson and McAlary (2009). Table 2-2 and Figure 2-3 compare the background indoor air concentrations reported by these authors for select VOCs with (1) U.S. EPA (2009) residential air regional screening levels (RSLs) spanning U.S. EPA's target excess lifetime cancer risk range of 10^{-6} to 10^{-4}, and (2) screening levels from various states.

BOX 2-4. Practical Tips: Units of Concentration for Air

Contaminant concentrations in air are commonly reported in units of:

Mass/volume (e.g., micrograms per cubic meter [$\mu g/m^3$]) or

Volumetric (e.g., parts per billion by volume [ppbv])

The conversions between these common units are:

$$\text{ppbv} = (\mu g/m^3 \times 24)/\text{molecular weight}$$

$$\mu g/m^3 = (\text{ppbv} \times \text{molecular weight})/24$$

As discussed in numerous vapor intrusion guidance documents (e.g., DoD, 2009; ITRC, 2007), VOCs in outdoor air can also contribute significantly to measured indoor air concentrations. Conservative indoor air risk-based screening levels for select VOCs are also similar to or less than the range of available published background outdoor air concentrations. The NYSDOH (2006 [Appendix C]) compiled the results of several background outdoor air studies that have been conducted, both nationally and in the state of New York, in a variety of settings (e.g., residential or commercial buildings). Regional background outdoor air concentrations of VOCs may also be available from state ambient air toxics monitoring networks, such as the Cal/EPA Air Resource Board (www.arb.ca.gov/aaqm/toxics.htm). Site-specific outdoor air data from samples collected near the building being investigated may also be available, as discussed in Section 3. As shown in Table 2-3, risk-based residential air screening levels (i.e., U.S. EPA [2009] RSLs) for three sample VOCs (benzene, PCE, and TCE) are less than the range of outdoor air concentrations compiled in Appendix C of NYSDOH (2006).

The fact that a select number of conservative risk-based indoor air screening levels are less than (or expected to be less than) published or measured background indoor and/or outdoor concentrations is analogous to commonly reported situations where background levels for select chemicals are higher than their risk-based soil or groundwater screening levels. Additional details on the use of published background indoor and outdoor air concentrations are provided in Section 3. In summary, conservative risk screening often results in VOCs being retained. This includes many chemicals with RSLs below published background indoor or outdoor levels. Under such conditions, as discussed in Sections 1.1.1 and 1.1.2, Navy policies require ascertaining whether background sources are wholly or partially responsible for the measured or predicted indoor air concentrations of retained VOCs. It is important to note that Navy policy is to only remediate those concentrations that are above background levels.

TABLE 2-2. Example vapor intrusion screening values

	Benzene			Tetrachloroethene (PCE)		
Agency	**Groundwater (µg/L)**	**Soil Gas ($\mu g/m^3$)**	**Indoor Air ($\mu g/m^3$)**	**Groundwater (µg/L)**	**Soil Gas ($\mu g/m^3$)**	**Indoor Air ($\mu g/m^3$)**
U.S. EPA	5(a)	3.1	0.31	5(a)	4.1	0.41
California	NA	36	0.084	NA	180	0.41
New Jersey	15	16	2	1(a)	34	3
Michigan	5,600	150	2.9	25,000	2,100	42
Pennsylvania	3,500	NA	2.7	42,000	NA	36

NOTES:
µg/L = micrograms per liter
$\mu g/m^3$ = micrograms per cubic meter
(a) Maximum contaminant level or drinking water quality standard because vapor intrusion-based value would have been lower.

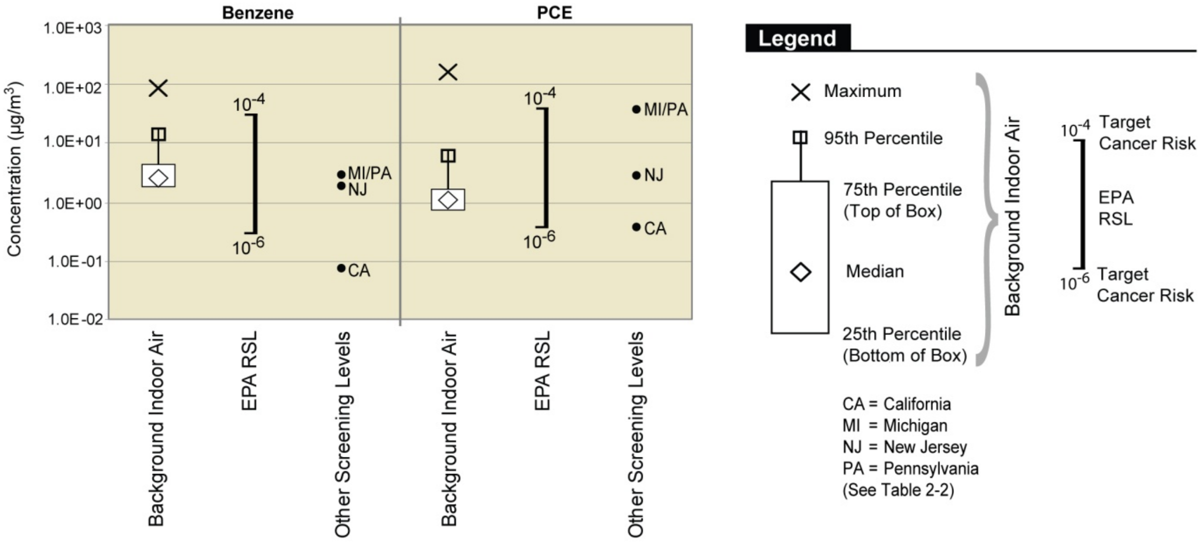

FIGURE 2-3. Sample risk-based air concentrations compared with published background indoor air concentrations (RSL at target risks of 10^{-6} and 10^{-4} [U.S. EPA, 2009].)

2.1.5 Evaluate the Data and Identify COPCs for Background Exploratory Data Analysis

The CSM should be developed or refined to the extent possible using existing data prior to conducting the risk-screening step, which is used to select VOCs for further consideration in a site-specific background evaluation. A hypothetical site example, “Alpha Naval Base,” will be used to illustrate the main steps and discuss factors that should be considered when selecting VOCs for further evaluation.

Repeated review of the CSM is highly recommended. In some instances, adequately refined CSMs may indicate that the vapor intrusion pathway is not complete or is insignificant relative to other contaminant sources; examples may include the following:

- ❑ Nature and extent of contamination: There are no contaminated media (soil, soil gas, or groundwater) near occupied structures. U.S.

TABLE 2-3. Sample risk-based air concentrations compared with published background outdoor air concentrations

Chemical	Air RSL ($\mu g/m^3$)[(a)]	Range of Outdoor Air Concentrations ($\mu g/m^3$)[(b)]
Benzene	0.31	5.2–9.6
Tetrachloroethene	0.41	1.6–10
Trichloroethene	1.2	0.5–5

NOTES:
$\mu g/m^3$ = micrograms per cubic meter
(a) RSL = U.S. EPA (2009) residential air regional screening level
(b) Source = Appendix C of NYSDOH (2006)

- EPA guidance (2002) recommends *"…that an inhabited building generally be considered 'near' subsurface contaminants if it is located within approximately 100 ft laterally or vertically of known or interpolated soil gas or groundwater contaminants … and the contamination occurs in the unsaturated zone and/or the uppermost saturated zone.*" Some states have different definitions of "near" so it is important to check with local agencies before performing this evaluation.
- Building characteristics: Existing buildings have well-designed and maintained radon mitigation systems that are required by local building codes.
- Commercial or industrial product use: Building surveys reveal widespread and frequent industrial or commercial use of site-related subsurface chemicals within the building. The occupational exposures are likely to greatly exceed potential contributions from vapor intrusion.

These are just a few examples. If the CSM is reasonably complete, it may be possible to eliminate the vapor intrusion pathway from further consideration. It may be more cost effective to circle back and review certain elements of the CSM before proceeding with further site-specific evaluations. Assuming data considered during the development of the CSM indicate the potential for vapor intrusion cannot be ruled out, the results of the risk-screening evaluation can be used to select VOCs for the background indoor air EDA.

The costs and benefits of resolving cases where COPC concentrations result in uncertain conclusions should be considered. This includes cases of (1) concentrations only slightly above or below screening levels and (2) concentrations impacted by modeling and measurement uncertainties. Such concentrations are sometimes referred to as "gray area" results. Under these conditions, if other chemicals from the same group are unquestionably going to be carried forward in the screening process, retaining similar chemicals with "gray area" concentrations may be more cost effective.

Published background indoor air results, which are discussed in more detail in Section 3, may also offer another perspective on which VOCs to include for further background evaluation (U.S. EPA, 2008). Some volatile chemicals, such as benzene and PCE, are detected quite frequently in background indoor air and are good candidates for further background evaluation. Others, such as vinyl chloride and 1,2-dichloroethene, are rarely detected in background indoor air. Thus, chemicals that are only rarely detected in background indoor air might be assumed to be site-related without further evaluation; in addition, these chemicals may be considered for use as tracer compounds (Section 3.5.3).

Example Site

Four groundwater monitoring wells were initially used at the hypothetical Alpha Naval Base to characterize a chlorinated solvent groundwater plume (Figure 2-4). Following installation and sampling of the four monitoring wells, groundwater concentrations for select chemicals (benzene, *cis*-1,2-dichloroethene [*cis*-1,2-DCE], PCE, TCE, and vinyl chloride) exceeded their screening levels (Table 2-4). Soil-gas samples were subsequently collected from four temporary probes at approximately 5 feet below ground surface (bgs) (Figure 2-4 and Table 2-4).

The Alpha Naval Base example highlights the importance of the sensitivity of quantitation limits when conducting the screening step. For example, vinyl chloride was not detected in soil

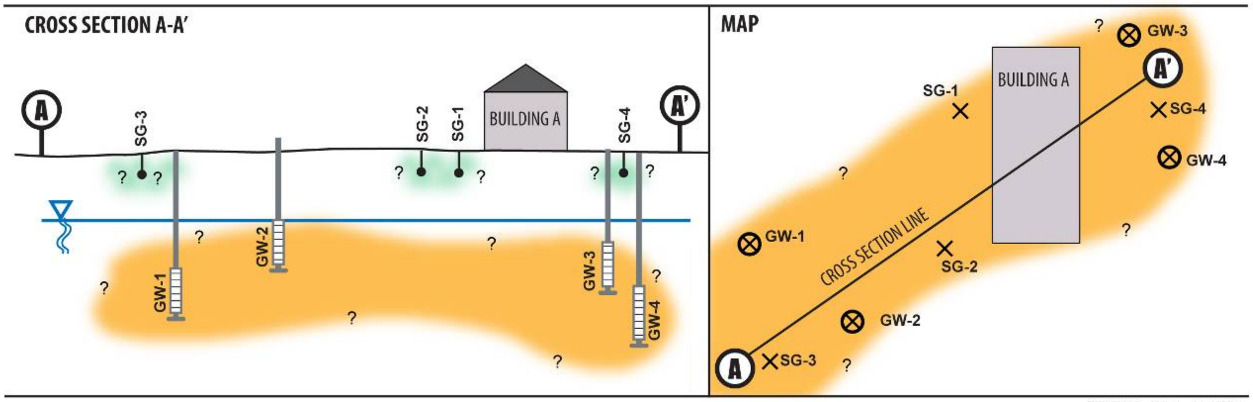

FIGURE 2-4. Risk-screening example site map and cross section

TABLE 2-4. Example comparisons of subsurface data with risk-based screening levels

	Subsurface Soil Gas (µg/m^3)					**Groundwater (µg/L)**				
Volatile Chemical	**Sample 1**	**Sample 2**	**Sample 3**	**Sample 4**	**Soil Gas Screening Level**	**Well 1**	**Well 2**	**Well 3**	**Well 4**	**Groundwater Screening Level**
Benzene	**31**	<34	<11	<24	3.1	**11**	<0.1	<0.1	4	5
Dichloroethane, 1,1-	<24	<34	<11	<24	15	<0.1	<0.1	<0.1	<0.1	2,200
Dichloroethane, 1,2-	<24	<34	<11	<24	0.94	<0.1	<0.1	<0.1	<0.1	5
Dichloroethene, 1,1-	<24	<34	<11	<24	2,100	<0.1	<0.1	<0.1	<0.1	190
Dichloroethene, *cis*-1,2-	**15,000**	**5,200**	**3,300**	**7,400**	630	3	40	22	**220**	210
Dichloroethene, *trans*-1,2-	**18,000**	**5,500**	**2,300**	**8,700**	630	30	11	23	70	180
Ethylbenzene	<120	<170	<56	<120	9.7	<0.1	<0.1	<0.1	<0.1	700
Tetrachloroethene	**33,000**	**25,000**	**11,000**	**38,000**	4.1	**98**	**40**	**14**	**43**	5
Toluene	<120	<170	<56	<120	52,000	<0.1	<0.1	<0.1	<0.1	1,500
Trichloroethane, 1,1,1-	<24	<34	<11	<24	52,000	<0.1	<0.1	<0.1	<0.1	3,100
Trichloroethene	**5,200**	**3,500**	**2,300**	**4900**	12	**39**	**15**	2	**80**	5
Vinyl Chloride	<24	<34	<11	<24	1.6	<0.1	<0.1	<0.1	**3J**	2
Xylenes, *m,p*-	310	<170	<56	<120	1,000	<0.1	<0.1	<0.1	<0.1	22,000
Xylene, *o*-	<120	<170	<56	<120	7,300	<0.1	<0.1	3	<0.1	33,000

gas, but the quantitation limits were much higher than the screening level. The quantitation limits for the two dichloroethane (DCA) isomers also exceeded the screening levels in soil gas, but these chemicals were not detected in groundwater and were not thought to be site-related.

When performing the screening steps, groundwater and soil-gas exceedances must be thoroughly considered. This is because VOCs in groundwater or adsorbed to soil in the vadose zone can be potential sources of intruding vapors. As with the groundwater, *cis*-1,2-DCE, PCE, and TCE in the example site are detected and are above their soil-gas screening levels. Although *trans*-1,2-dichloro-ethene (*trans*-1,2-

DCE) is not detected above its screening level in groundwater, it is detected above its corresponding screening level in soil gas.

Given the groundwater and soil-gas exceedances in the preceding example, the chlorinated solvents PCE, TCE, *cis*-1,2-DCE, vinyl chloride and *trans*-1,2-DCE are retained for the background evaluation.

Regarding benzene, a review of the cross section shows that the two wells with detections do not screen across the water table. In fact, the two wells screened nearest the water table are devoid of detected benzene, albeit at elevated detection limits. Supplemental information from the site hydrogeologist may indicate that benzene is consistently detected only in the deeper, finer sediment layers in the aquifer. Groundwater time series may also indicate a sporadic detection of benzene in nearby water table wells. Such information warrants a refinement of the CSM by incorporating the likely presence of a much older fuel release further upgradient of the site. This information alone is not sufficient to eliminate benzene because it needs to be weighed against the benzene detections in soil gas and the uncertainties (e.g., limited number of samples, elevated quantitation limits, using exterior data to predict sub-slab concentrations). However, it may prove useful if a further background evaluation provides one or more additional lines of evidence to support the suggestion that benzene is not a vapor intrusion concern.

Vinyl chloride is detected in only one deeper well; the result is “J” flagged (estimated) and vinyl chloride is not detected in the water table wells. Assume that the project chemist stated the “J” flag suggested a possible high bias. The project hydrogeologist indicated that traces of vinyl chloride were detected elsewhere in the deeper aquifer sediments due to localized reductive dechlorination but were not detected higher in the aquifer. Based on this assessment, there is some uncertainty about the nature and extent of vinyl chloride. Because it is a biodegradation daughter product of PCE, TCE, and DCE and the quantitation limits in groundwater exceeded the screening level, it is appropriate to retain vinyl chloride for further evaluation.

The above example illustrates a few issues that may arise when selecting COPCs for further evaluation, which leads to the following recommendations and findings:

- Involve the appropriate team members. The hydrogeologist and chemist always provide important information needed to refine the CSM.
- Quantitation limits may not be low enough, which often can be due to the dilution of samples during analysis. In some cases, this problem can be rectified by instructing laboratories to report the lowest detections (or quantitation limits) of the individual analytes within the instrument calibration range. Unless specified, laboratories may just report the highest dilution where all analytes are within the calibration range.
- The benzene example illustrates the importance of reviewing and updating the CSM. In this case, the new information may be used later when considering the possible elimination of benzene from further evaluation. It is also important to consider the uncertainties when assessing the chances of prematurely eliminating a chemical.
- *Trans*-1,2-DCE is not detected above its groundwater screening level but is detected at concentrations well above its soil-gas screening level. This can be the result of one or more factors: (1) a different underlying basis for the media-specific screening levels, (2) lower detection limits in one media versus another, or (3) spatial variability in both soil and groundwater concentrations that are not fully captured by the existing data.
- Data quality issues, such as the “J” flagged vinyl chloride, need to be considered. A second round of sampling, in addition to a consultation with the project chemist, may resolve the question of the vinyl chloride concentrations.

Site Summary

The screening step is not only important in identifying COPCs for a site-specific vapor intrusion evaluation but is used to determine which VOCs should be retained for the background evaluation. The hypothetical Alpha Naval Base example illustrates the importance of updating the CSM during the risk-screening step in order to include multiple lines of available evidence. It also exemplifies the uncertainties that are common when evaluating groundwater and soil-gas data (e.g., spatially and temporally limited datasets, data quality issues such as elevated quantitation limits). As indicated in the overall vapor intrusion evaluation flowchart (Figure 1-3), the option to collect additional data should be recognized and potentially considered during all steps of the vapor intrusion and background evaluations. Such information may help to reduce or better understand the uncertainties associated with site-specific data.

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3. SITE-SPECIFIC BACKGROUND INDOOR AIR EXPLORATORY DATA ANALYSIS

Exploratory data analysis (EDA) is a series of statistical and graphic procedures for examining and screening available, site-specific and published data to determine evidence of vapor intrusion impact. The term *exploratory data analysis* was first coined by American mathematician John W. Tukey (1962), with a goal to avoid confusion when applying complex methods to poorly defined problems. In his words:

> *"Far better an approximate answer to the right question, which is often vague, than an exact answer to the wrong question, which can always be made precise."*

BOX 3-1. Practical Tips: Exploratory Data Analysis and Vapor Intrusion

An EDA, as applied in a vapor intrusion background evaluation, consists of a series of relatively simple data comparison, calculation, and graphical procedures for examining site-specific data to determine if background sources are significantly impacting measured indoor air concentrations.

Several methods for conducting a vapor intrusion background indoor air EDA are described in this section. Some EDA procedures are based on graphical tools, such as box and whisker plots. Others include point-by-point comparisons of measured data with site-specific or published background data or a review of summary statistics (e.g., mean, median, or upper-percentiles) of concentrations measured at the site. An EDA does not refute the usefulness of more complex statistical procedures, such as those discussed in Section 5, but ensures that the problem is defined adequately so the correct questions can be asked.

A vapor intrusion background indoor air EDA is only conducted after the risk-screening step and after concurrent sub-slab, indoor, and outdoor air data have been collected. Often only limited subsurface, sub-slab, indoor, and site-specific outdoor air data are available. Rarely would there be sufficient data to go directly to more involved (and potentially expensive) forensics or statistical tests methods, such as those discussed in later sections. Even if sufficient data are available, the EDA methods should be applied first. Such analyses may determine the likely contribution of background sources to the measured indoor air concentrations and help identify the lines of evidence that might be most fruitful to investigate further.

The objectives of this section are to:

- ☐ Briefly discuss issues that should be considered when making decisions about background contributions in a vapor intrusion assessment.
- ☐ Introduce several of the lines of evidence that can be applied when conducting vapor intrusion and background evaluations.
- ☐ Identify EDA methods that may be used to assess site data for background evaluation purposes. There is no particular order or requirement when selecting the EDA methods described in this section.
- ☐ Discuss how the results of the EDA can be used to refine the CSM, in particular, to reflect the evolving understanding of the relative contributions of subsurface and background vapor sources to indoor air contamination. Frequent updating of the CSM fosters further insights and facilitates communication among the project team and other stakeholders.
- ☐ Discuss the relative strengths and weaknesses of the different lines of evidence used in the vapor intrusion background EDA.

The strengths and weaknesses of the different lines of evidence are particularly important. Different EDA methods and outcomes are not equally weighted when confirming or refuting the existence of background or subsurface sources. More often than not, individual EDA outcomes provide suggestive rather than definitive evidence of a potential source. For example, site-specific indoor air concentrations may be within the range of published background values, providing suggestive rather than definitive evidence of a potential background source. Likewise, site concentrations above published background indoor and outdoor air concentrations do not provide definitive evidence of a subsurface source. Such suggestive results yield a definitive conclusion if, and only if, the collective results of multiple lines of evidence point consistently to the same finding.

BOX 3-2. Practical Tips: Strength of the Evidence

Multiple lines of evidence are generally required when differentiating between subsurface versus background sources. The strength of the evidence depends on the outcome of the EDA method applied.

For example, if indoor air concentration are less than or equal to outdoor air concentrations, that is strongly suggestive to definitive evidence of a background outdoor source. But indoor air concentrations above outdoor concentrations are inconclusive or, at most, weakly suggestive evidence of a subsurface source because an indoor source may exist.

For some EDA methods, the outcomes may be viewed as definitive, while others are simply suggestive or inconclusive. For example, if suspected products are removed from a structure and follow-up indoor air sampling results in a drastic decrease in concentrations of the chemicals of interest, this is definitive evidence that a background indoor source existed. In contrast, if the follow-up indoor air concentrations do not decrease, the results can only be viewed as either inconclusive or, at best, suggestive because of the often limited ability to identify background indoor sources or products.

When applying the background indoor air EDA methodologies, an understanding of the strengths and weaknesses for each individual line of evidence will help users of this guidance develop investigative strategies and reasonable expectations of potential outcomes. The relative strengths of various lines of evidence are discussed throughout this section. The multiple lines of evidence and strength-of-the-evidence concepts can be illustrated by a scale (Figure 3-1), in which various evidence and their associated weights can be placed on either side of the scale.

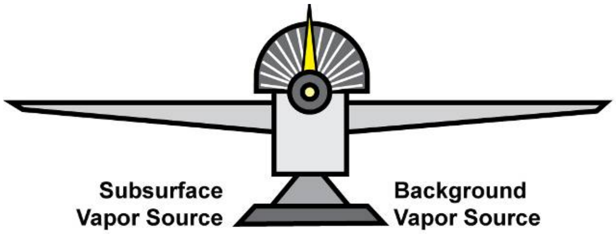


FIGURE 3-1. Weight of evidence scale

When the EDA is complete and the overall weight of the lines of evidence is considered, the scale may tip anywhere between strong evidence of a potential background source and strong evidence of a subsurface source. This “weighting” concept is not a formal scoring process, such as the one developed by U.S. EPA for evaluating the degradation of chlorinated solvents at CERCLA and RCRA sites (Wiedemeier et al., 1998). This is particularly important given the differing opinions of various stakeholders on the strength of a specific line of evidence. Furthermore, policy differences between various states and U.S. EPA regions may influence the overall conclusions when assessing multiple lines of evidence. However, consideration of the potential strengths and weaknesses associated with one or more lines of evidence during the planning stage can help focus the efforts on collecting the most useful and relevant information.

The limitations and other issues associated with each method also need to be considered. For example, the building pressurization method appears favorable because it may provide more definitive evidence that vapor intrusion is occurring or that background is the primary vapor source. However, the method is highly disruptive to building occupants and requires a separate and potentially expensive data collection effort. In addition, it may be impractical to implement on large or leaky buildings.

BOX 3-3. Practical Tips: Preferred Data Collection and Evaluation Methods

There is a general preference for select EDA methods described in this section to be applied first, such as comparisons with site-specific outdoor air concentration and constituent ratio calculations and comparisons. More disruptive, complex, or expensive methods such as building pressurization or depressurization and source removal or resampling are generally applied less frequently. The preference for applying specific EDA methods is addressed in the summary "boxes" for each method.

Application of all EDA methods described in this section is not necessary, nor do these methods need to be applied in any particular order. A discussion of compiling and determining the adequacy of existing data is included with each method; however, a number of general data quality considerations (e.g., data validation and reduction) have been discussed in Section 2. Only those data quality issues pertinent to specific lines of evidence are discussed in the following sections.

3.1 Comparisons with Measured or Published Background Air Concentrations

Background contributions to indoor air measurements may result from either indoor or outdoor sources. As discussed in Section 2, multiple studies have been conducted to characterize background indoor and outdoor concentrations at structures that have not been impacted by subsurface sources. In addition, outdoor air sampling near the building of interest is recommended to be conducted concurrent with indoor air sampling. Background indoor air concentrations from representative upgradient or non-impacted "control" buildings (i.e., buildings constructed of similar materials, with similar layouts, characteristics, and use, and in areas with similar background outdoor air conditions) are not generally available or recommended as part of vapor intrusion and background evaluations (DoD, 2009).

Comparing measured indoor air concentrations with concurrently collected site-specific background outdoor air concentrations provides a potentially strong line of evidence when determining if outdoor air concentrations are a significant source. Comparison of site indoor air concentrations with published outdoor air concentrations is not as strong of a line of evidence. Regional air quality monitoring points are unlikely to be near the building of interest; in addition, the sampling dates and durations likely differ from the site-specific sampling events. For these and other reasons, concurrent site-specific outdoor air samples should be collected (DoD, 2009 [page 90]).

Indoor air sources can vary widely within each building given the variety of products used or stored in the structure and the occupant preferences or activity patterns. There is also uncertainty in quantifying the magnitude of outdoor air contributions to the measured indoor air concentrations. Therefore, these comparisons alone do not generally provide definitive evidence of a source. However, the comparisons are helpful as individual lines of evidence in determining if additional background evaluations (e.g., constituent ratios, induced pressurizations, and tracer, forensic, or statistical evaluations) are needed, particularly when indoor air concentrations at the site are greater than published (indoor and outdoor) or measured (outdoor) background concentrations.

Refer to Box 3-4 for a succinct summary of the method, rationale, limitations and uncertainties, and considerations for improving the evaluation when comparing indoor air concentrations with measured or published background air EDA steps.

3.1.1 Compile and Determine Adequacy of Site Indoor and Outdoor Air Data

The site-specific dataset should consist of validated analytical data that are assumed to be representative of current indoor air concentrations. Both indoor and outdoor air data can exhibit short-term (hours) and long-term variability (e.g., Folkes et al., 2009; Luo et al., 2009). Thus, to the extent practical, paired indoor and outdoor samples should be collected over the

BOX 3-4. Practical Tips: Comparisons with Measured or Published Background Air Concentrations

How does it work?	Indoor air concentrations are compared with site-specific outdoor air and published indoor and outdoor air data.
How does this help?	- Indoor air levels similar to contemporaneous site-specific background outdoor measurements suggest an outdoor air source. For this comparison, it is sufficient for outdoor air concentrations to be roughly the same as or greater than indoor concentrations to strongly suggest or conclude that a significant outdoor source may exist. Datasets representative of longer time periods and having greater spatial density increase the confidence in the conclusions. - Indoor concentrations greater than contemporaneous site-specific outdoor results indicate a potential indoor or subsurface source. For example, indoor air concentrations approximately 10 times or more higher than outdoor levels are often sufficient to rule out an outdoor source. Inherent temporal and spatial variability in indoor and outdoor air concentrations will likely need to be considered when the differences in concentrations may not be significant. - Indoor air concentrations greater than published background indoor air concentrations suggest a possible subsurface source. Given the variability in published background data, site-specific indoor air concentrations would need to be significantly greater than the published values (e.g., more than 10 times) before this comparison provides even suggestive evidence that vapor intrusion may be occurring. However, it is also important to consider the possibility of building-specific indoor sources. - Consider checking with the project-specific stakeholders (e.g., regulators) to determine whether subtracting outdoor concentrations from the indoor concentrations may be acceptable for the purpose of defining exposure point concentrations.
Limitations and uncertainties	- Indoor concentrations similar to site-specific outdoor levels provide fairly conclusive evidence of background outdoor air sources. - Comparisons with published background ranges may offer suggestive (but never definitive) evidence of vapor sources. Even regionally published data are potentially problematic because of sampling dates, durations, and temporal variability. Thus, there is a strong preference for using site-specific outdoor air samples collected contemporaneously near the structure of interest. - Development of a site-specific background indoor air dataset is problematic and rarely attempted. - Small site-specific datasets may not adequately characterize variability.
How to improve the evaluation	- Collect a sufficient number of representative samples. - Evaluate VOCs separately or as groups (e.g., fuel-related or chlorinated VOCs) to gain insight on potential sources.
Minimum Data Requirements	The minimum is one indoor air sample and one outdoor air sample or published outdoor air data result. However, a minimum of three samples is needed to begin assessing data variability and its potential impact on the evaluation.
How often will this method be used?	- Site-specific indoor/outdoor comparisons will be applied frequently since the data will likely be available by the time a background vapor intrusion evaluation takes place. - Comparison with published outdoor data will be less common.

same period. The response of indoor air to outdoor air is buffered by the construction and operation of the building and its resultant air-exchange rate. As a result, instantaneous samples in the two media are less useful than time-weighted samples. In fact, 8- or 24-hour samples are recommended in vapor intrusion guidance documents (e.g., DoD, 2009; ITRC, 2007; U.S. EPA, 2002; NYSDOH, 2006).

Collecting additional indoor samples for the sole purpose of comparison to published background concentrations would rarely be warranted given the inherent uncertainties associated with the published data. As recommended by ITRC's *Vapor Intrusion Pathway: A Practical Guideline*, multiple rounds of sampling should be performed to characterize temporal and/or spatial variability of investigated media (ITRC, 2007).

3.1.2 Identify Relevant Published Background Datasets

In addition to comparisons with site-specific background outdoor air results, measured indoor air concentrations can be compared with published background data. A brief review of the most common published background datasets is provided in this section, along with a discussion of factors that should be considered when identifying the relevant background datasets.

Published Background Indoor Air Studies

Summaries of the published background indoor air concentrations have been provided in the *DoD Vapor Intrusion Handbook* (DoD, 2009), U.S. EPA (2008), and NJDEP (2005) vapor intrusion guidance documents. Dawson and McAlary (2009) also recently published a peer-reviewed article titled, "A Compilation of Statistics for VOCs from Post-1990 Indoor Air Concentration Studies in North American Residences Unaffected by Subsurface Vapor Intrusion." Dawson and McAlary (2009) provide a new compilation of background indoor air studies for the following reasons: (1) previous compilations were generated over a decade ago, (2) background indoor air concentrations vary widely, and the quality of indoor air has been generally improving with time, and (3) old compilations only reported central tendency and maximum values (i.e., limited information was provided on frequency distributions).

Eighteen background indoor air studies conducted in urban, suburban, and some rural settings were evaluated by Dawson and McAlary (2009). The studies contain indoor air concentrations for more than 40 VOCs collected from 1970 to 2005 using either absorbent media or canisters and a variety of analytical methods. Sampling durations were generally between 12 and 24 hours, and reporting limits varied by at least an order of magnitude among the studies. Summary statistics were generated using 13 of the studies with data collected after 1990. Summary statistics (25, 50, 75, 90, and 95 percentiles; maximum; number of samples; percent detect; and reporting limit ranges) are provided in Table 2 of Dawson and McAlary (2009) for 20 of the most common site-related VOCs.

As discussed previously in this guidance document, performing rigorous statistical tests is usually not feasible due to the limited number of site-specific indoor air samples (typically three or fewer samples per structure). Comparing one to three indoor air concentrations to published background levels is not sufficient by itself to conclusively determine the source of detected concentrations. Limitations or uncertainties that should be considered when using these (and other) published background indoor datasets include the following: (1) background samples are often collected from residential and not commercial or industrial structures, (2) published datasets may combine results from a variety of urban, suburban, and rural settings, (3) the construction materials, activities, and products associated with the investigated structures cover a wide range of conditions, and (4) different sampling and analysis procedures are used in background datasets resulting in orders of magnitude of variation in reporting limits.

Despite these limitations and as stated by Dawson and McAlary (2009), a comparison with published background statistics can be instructive, particularly if more than one VOC is detected in subsurface and indoor air samples and the indoor air concentrations are above typical background indoor air concentrations.

Published Background Outdoor Air Studies

Although comparisons with site-specific outdoor air sampling results are almost always recommended, comparisons with published background outdoor air concentrations are also informative. This is especially true if regional background outdoor air data are available from the state agency air toxics monitoring network, which can help assess whether localized outdoor air sources exist. Comparisons with published outdoor air concentrations can also provide an opportunity to evaluate results from the often relatively small number of site-specific background outdoor samples against much larger published datasets.

As discussed in Appendix C, NYSDOH (2006 [Appendix C]) summarizes a number of background outdoor air datasets. Regional background outdoor air concentrations of VOCs may also be available from state ambient air toxics monitoring networks (e.g., Cal/EPA Air Resource Board [www.arb.ca.gov/aaqm/toxics.htm]).

The *DoD Vapor Intrusion Handbook* discusses limitations and uncertainties associated with the use of published background outdoor air data including mixed data from both urban and rural areas; outdated samples; variable sampling conditions; seasonal differences; differing sample sizes; and inconsistent sampling and analytical methods (DoD, 2009).

3.1.3 Evaluate Data

Indoor air concentrations are most commonly compared with concurrent site-specific background outdoor air or published indoor and outdoor concentrations using tables or graphs (e.g., box and whisker or dot plots). Examples of tabular (Table 3-1) and graphical (Figure 3-2) formats are provided using data from the hypothetical "Alpha Naval Base" introduced in Section 2.

As shown in Table 3-1, many of the results were non-detect. Helsel (2005) provides a comprehensive summary of options for handling datasets with values below single or multiple reporting limits. The simplest option when there is only one reporting limit in the dataset is to truncate the Box and whisker plot at the reporting limit. This truncation is justified by the fact that

TABLE 3-1. Comparison of indoor air data with background indoor and outdoor air concentrations

	Indoor Air (µg/m³)			Published Background Indoor Air (µg/m³)(a)			Site-specific Outdoor Air (µg/m³)		Published Background Outdoor Air (µg/m³)(b)		
Volatile Chemical	**IA 1**	**IA 2**	**IA 3**	**25th%**	**50th%**	**95th%**	**OA 1**	**OA 2**	**25th%**	**50th%**	**95th%**
Benzene	**0.65**	**0.71**	**0.69**	1.9	2.5	17	0.75	0.67	0.6	1.3	5.8
Dichloroethane, 1,1-	<0.04	<0.04	<0.04	<2.0	<2.0	<2.0	<0.04	<0.04	<0.25	<0.25	<0.25
Dichloroethane, 1,2-	**0.18**	**0.23**	**0.33**	<0.25	<0.25	0.2	0.08	0.08	<0.25	<0.25	<0.25
Dichloroethene, 1,1-	<0.04	<0.04	<0.04	<2.0	<2.0	<2.0	<0.04	<0.04	<0.25	<0.25	<0.25
Dichloroethene, *cis*-1,2-	**1.1**	**1.2**	**1.5**	<2.0	<2.0	<2.0	<0.04	<0.04	<0.25	<0.25	<0.25
Dichloroethene, *trans*-1,2-	<0.04	<0.04	<0.04	<2.0	<2.0	<2.0	<0.04	<0.04	<0.25	<0.25	<0.25
Ethylbenzene	**0.89**	**1.4**	**1.7**	0.8	2	14	0.33	0.32	<0.25	<0.25	1.9
Tetrachloroethene	**1.7**	**2.3**	**2.0**	<3.4	0.9	7.4	0.18	0.17	<0.25	<0.25	1.6
Toluene	**3.2**	**3.7**	**4.5**	9	13	106	2.5	1.8	0.6	1.3	21
Trichloroethane, 1,1,1-	**0.083**	**0.083**	**0.10**	0.5	1.9	10.2	0.06	0.06	<0.25	<0.25	0.7
Trichloroethene	**0.35**	**0.54**	**0.48**	<2.7	0.3	1.6	0.14	<0.04	<0.25	<0.25	0.5
Vinyl Chloride	<0.04	<0.04	<0.04	<1.3	<1.3	0.05	<0.04	<0.04	<0.25	<0.25	<0.25
Xylenes, *m,p*-	**1.3**	**1.7**	**1.8**	2.9	5.5	41	0.88	0.89	<0.25	<0.25	3.1
Xylene, *o*-	**0.56**	**0.64**	**0.70**	1.4	2.2	16	0.35	0.32	<0.25	<0.25	2.5

µg/m³ = micrograms per cubic meter

(a) Non-detect (e.g., <2.0) values are the maximum reporting limits from the range listed in Dawson and McAlary (2009).

(b) NYSDOH (2006) Appendix C, Table C1.

Bolded values are indoor air concentrations greater than the site-specific outdoor air levels.

nothing is known about the distribution of the data below the reporting limits. The Kaplan-Meier method used by U.S. EPA (2008) may also be applied to calculate percentiles for larger data-sets with multiple detection limits.

A number of outcomes are commonly encountered when comparing indoor air with site-specific or published background concentrations and include (but are not limited to) the following:

Outcome 1: Indoor air concentrations are similar to or less than concurrent site- specific outdoor air results. This outcome is considered by many to be a relatively strong line of evidence in support of the conclusion that the measured concentrations are due to a background outdoor air source, particularly since the entire volume of building air is exchanged with outdoor air at rates of more than 0.25 exchanges per hour (U.S. EPA, 2004).

Benzene is one example from Table 3-1 (see also Figure 3-2) with detectable indoor air concentrations similar to or less than the site-specific background outdoor air levels. As discussed in Appendix C, the evidence considered during screening suggested that benzene may not be a vapor intrusion concern; however, this chemical was retained for the background evaluation since (1) the initial groundwater concentration in one well exceeded its vapor intrusion screening level, (2) benzene was not detected in the subsurface soil-gas samples, but the reporting limits were elevated above the risk-based screening level, and (3) there was conflicting, albeit relatively weak, evidence pointing to a potential subsurface source. A comparison of indoor air benzene concentrations with site-specific background outdoor air levels provides an additional strong line of evidence in support of the preliminary conclusion of a background benzene source. Further background evaluations (e.g., constituent ratios, forensic, statistical analyses) may still be pursued to confirm the source of the VOCs, even when indoor air concentrations are similar to or less than site-specific background outdoor air levels, particularly given the variability in building or product uses and occupant activities.

Outcome 2: A chemical retained in the screening process based on subsurface results is not detected in the site-specific indoor and outdoor air samples. As seen with *trans*-1,2-DCE, which was retained based on screening subsurface data (Table 2-4), its site-specific indoor and outdoor concentrations, as well as its published background results, are all nondetects (Table 3-1). As long as reporting limits are below risk-based screening values, such results can be used as conclusive evidence that *trans*-1,2-DCE is not a vapor intrusion concern. Given the significance of reporting limits, conducting a quantitation limit sensitivity analysis during the planning stages of the vapor intrusion investigations is recommended. Resampling or additional lines of evidence (e.g., review of building history/survey and subsurface [soil gas or groundwater] results) may be necessary if the quantitation limits exceed risk-based screening levels.

Outcome 3: Indoor air concentrations are higher than site-specific outdoor levels but are within the range of published background indoor concentrations. An example chemical is PCE, as listed in Table 3-1 and shown on Figure 3-2. Such results suggest there may be a background indoor source for PCE. However, due to the limitations of published background concentrations, this finding cannot be viewed as conclusive evidence by itself and warrants additional background evaluation (e.g., constituent ratios, tracer, forensic, or statistical analyses).

Outcome 4: Indoor air concentrations are greater than site-specific outdoor and published indoor air concentrations. An example chemical is *cis*-1,2-DCE, as listed in Table 3-1. Such results suggest the possible presence of background indoor or subsurface sources. Indoor concentrations well above the range of published indoor concentrations could also suggest a subsurface source; however, this is not conclusive by itself given the uncertainties

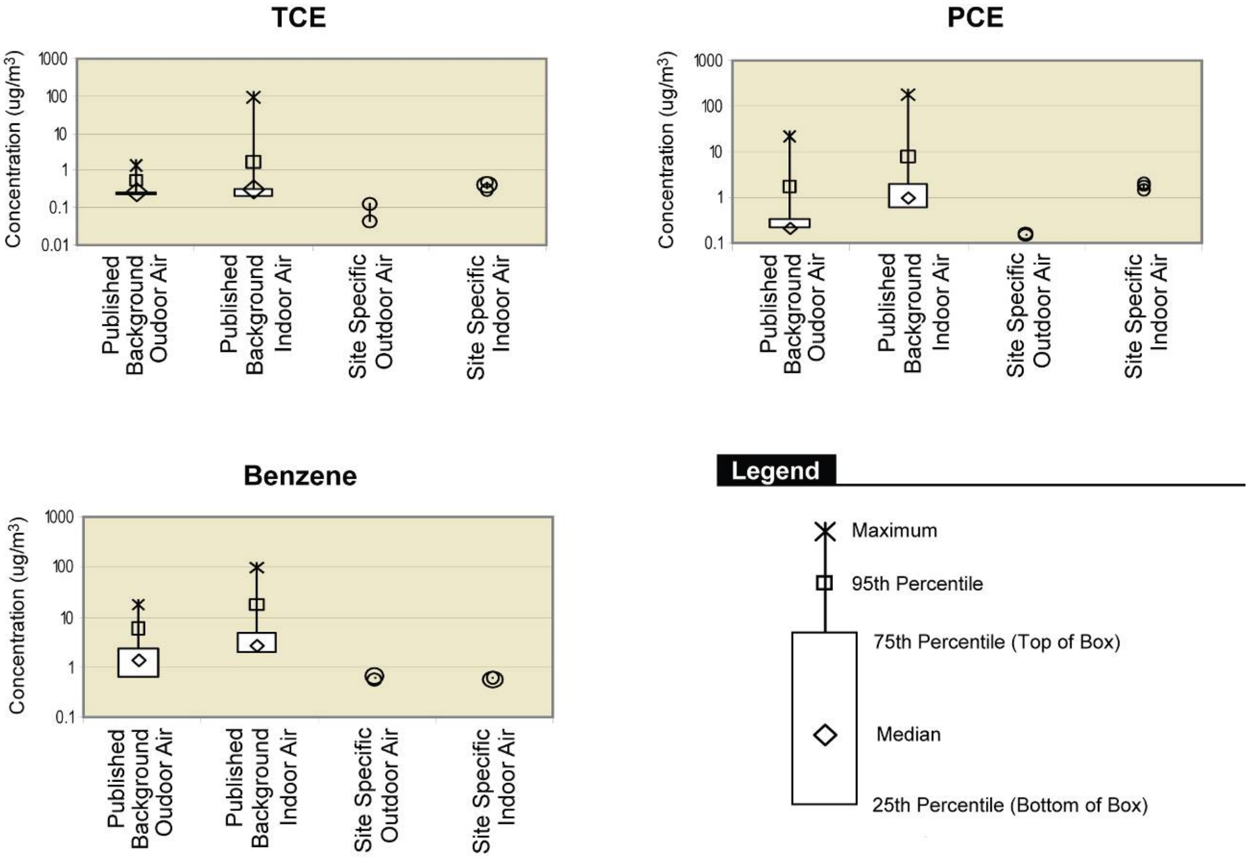


FIGURE 3-2. Indoor/outdoor comparison (box and whisker and dot plots)

associated with published background concentrations and the considerable variability in building or product use and occupant activities.

The comparisons of the hypothetical Alpha Naval Base data presented in Table 3-1 and Figure 3-2 can be used to assess the strength and weight of evidence for each chemical. For example, the results for benzene suggest background outdoor air as a likely source. On the other hand, results for some of the chlorinated solvents suggest a possible subsurface source. Neither finding is conclusive by itself, but considered in combination with the other lines of evidence can yield conclusive results (Section 3.6).

3.1 Constituent Ratios between Indoor Air, Groundwater, and Soil-Gas Samples

Attenuation factors are defined as the ratio of indoor air-to-subsurface concentrations (U.S. EPA, 2002; U.S. EPA, 2008; ITRC, 2007).

Attenuation factors (empirical or modeled) are most commonly used in vapor intrusion investigations to predict indoor air concentrations from groundwater, exterior soil gas, and sub-slab soil-gas data. The procedures used to calculate empirical attenuation factors are described in U.S. EPA (2002 [Appendix F]; 2008) and are not repeated here.

U.S. EPA (2002; updated in 2008) presents a range of published attenuation factors for indoor air versus groundwater, soil gas, and sub-slab soil gas as order statistics (mean and 5th, 25th, 75th, and 95th percentiles). These attenuation factors generally span orders of magnitude and are likely due to factors that include, but are not limited to (1) differing building characteristics (e.g., residential versus industrial, air handling, size, building use, number of doors/windows, etc.); (2) spatial and temporal variability associated with subsurface characteristics and lithology, and (3) different sampling methods over the years.

BOX 3-5. Practical Tips: The Size of Site-specific Datasets

The size of site-specific datasets is an important factor that must be considered. In many instances, one or two indoor and sub-slab samples are collected to represent large structures. Results derived from one or two samples should not be considered conclusive without other supporting lines of evidence.

Building-specific, empirical attenuation factors may also be calculated using the data collected during a site-specific vapor intrusion investigation. A comparison of building-specific and published attenuation factors for specific VOCs may provide an additional line of evidence for background evaluations.

The ratios of indoor and subsurface contaminant concentrations are commonly discussed as "attenuation factors". The use of the term *attenuation* in this context implies that the contaminant present in the indoor air is in fact coming from the subsurface and its concentration in indoor air is reduced (attenuated) relative to the subsurface concentration as a function of (1) vapor transport in the vadose zone, (2) the rate at which it is transferred across the slab, and (3) mixing with indoor air. At the outset of the background evaluation it is unknown whether the indoor air contamination is derived from the subsurface or another source. Thus, this document will use the term *constituent ratios* to express the same concept as the attenuation factor, minus the assumption that indoor air contamination results from vapor intrusion.

Refer to Box 3-6 for a succinct summary of the method, rationale, limitations and uncertainties, and considerations for improving the evaluation when calculating and comparing attenuation factors.

3.2.1 Compile and Determine Adequacy of Site Data

Attenuation factor calculations require concurrently collected soil-gas (exterior or sub-slab) and indoor air samples from the investigated structure. Groundwater data may also be used if collected within a reasonable time (depending on the stability of the groundwater plume) before or after the indoor air sampling. If exterior soil-gas or groundwater data are used to characterize the subsurface, care is required to ascertain that results are representative of conditions near the structure of interest.

Ideally, a sufficient number of samples in each medium is available to ensure the representativeness of the results. However, absence of a large dataset should not prevent proceeding with the attenuation factor computations and comparisons, as long as data uncertainties and their potential impacts are considered and documented.

Datasets with multiple nondetects limit the utility of the computed attenuation factors. Non-detect values in the indoor air result in calculated attenuation factors being reported as "less than" values. Consistent with U.S. EPA (2008), attenuation factors should not be calculated for VOCs that are not detected in the subsurface. Such results often yield artificially high attenuation factors.

3.2.2 Evaluate Data

A comparison of building- and chemical-specific empirical attenuation factors to each other as well as to those presented in the U.S. EPA Vapor Intrusion Attenuation Factors Database (2008) may provide an additional line of evidence in a background evaluation. Chemical-specific attenuation factors can be calculated and presented in a tabular (or graphical) format as part of a background indoor air EDA. Using the representative sample data from Tables 2-3 and 3-1, chemical-specific indoor to soil gas and indoor air to groundwater ratios have been

BOX 3-6. Constituent Ratios between Indoor Air, Groundwater, and Soil-Gas Samples

How does it work?	The ratios of VOC concentrations between different media (e.g., indoor versus sub-slab) are calculated. If the vapor intrusion pathway is likely to be complete, the computed ratios are considered as attenuation factors. For non-hydrocarbon VOCs, these attenuation factors are expected to be (1) similar between the VOCs and (2) within the published range of values (e.g., U.S. EPA, 2008). Attenuation factors for hydrocarbons are generally higher than most other VOCs because of bioattenuation.
How does this help?	It provides site-specific information about the likelihood of background sources.
Limitations and uncertainties	Elevated detection limits or a large number of nondetects in the dataset can make the analysis impractical. Insufficient knowledge about variability can result in poorly supported conclusions.
How to improve the evaluation	Collect a sufficient number of representative samples. Develop DQOs, laboratory procedures, and data reduction schemes to limit unnecessarily high quantitation limits.
Minimum Data Requirements	The minimum is at least an indoor air sample paired with a soil-gas or groundwater sample. However, a minimum of three samples are needed to begin assessing data variability and its potential impact.
How often will this method be used?	Frequently since the data will likely be available by the time a background vapor intrusion evaluation takes place.

calculated and are shown in Table 3-2, along with the range of attenuation factors from U.S. EPA (2008). Bar, box and whisker, or dot plots can also be used to present the same results in graphical form.

U.S. EPA (2008) recommends considering the following when calculating site-specific empirical attenuation factors: (1) data quality, (2) handling of data reported below a given quantitation limit, (3) differences in site conditions, (4) spatial and temporal variability, and (5) contribution of background sources to indoor air concentrations. Consistent with U.S. EPA (2008), empirical attenuation factors are not calculated for VOCs with non-detect results in the subsurface (e.g., 1,1- and 1,2-DCA, 1,1-DCE, and ethylbenzene in Table 3-2). This is because it is assumed the chemical is either absent in the subsurface or present below levels of concern; however, that same chemical can be present in the indoor air due to background sources, which would result in calculated site-specific attenuation factors that are biased artificially high. Attenuation factors can also be biased high (by up to orders of magnitude) if ratios are calculated without considering the subsurface (soil gas or groundwater) source strength (i.e., the magnitude of subsurface VOC concentrations).

The computed attenuation factors in Table 3-2 can be used to highlight some of the common issues encountered when using site-specific attenuation factors in a background indoor air EDA. For example, if the attenuation factor for a particular chemical is significantly higher than the attenuation factors for other VOCs, it may be an indication of background contributions. As an

TABLE 3-2. Comparison of ratios (attenuation factors) for indoor air, sub-slab, and groundwater samples

	Indoor Air (µg/m^3)	Sub-slab (µg/m^3)	GW (µg/L)	Empirical AF (unitless)		U.S. EPA (2008) AF (unitless)		
Volatile Chemical	**IA 1**	**SSG 1**	**Well 1**	**Sub-slab**	**GW**	**Percentile**	**Sub-slab**	**GW**
Benzene	0.65	31	11	2E-02	1E-01	Min	7E-05	1E-06
Dichloroethane, 1,1-	<0.04	<24	<0.1	NC	NC	5%	5E-04	1E-05
Dichloroethane, 1,2-	0.18	<24	<0.1	NC	NC	25%	2E-03	4E-05
Dichloroethene, 1,1-	<0.04	<24	<0.1	NC	NC	50%	5E-03	1E-04
Dichloroethene, *cis*-1,2-	1.1	15,000	3	8E-05	4E-04	75%	1E-02	3E-04
Dichloroethene, *trans*-1,2-	<0.04	18,000	30	2E-06	7E-06	95%	2E-01	2E-03
Ethylbenzene	0.89	<120	<0.1	NC	NC	Max	9E-01	7E-02
Tetrachloroethene	1.7	33,000	98	5E-05	7E-05			
Toluene	3.2	<120	<0.1	NC	NC			
Trichloroethane, 1,1,1-	0.083	<24	<0.1	NC	NC			
Trichloroethene	0.35	5,200	39	7E-05	2E-04			
Vinyl Chloride	<0.04	<24	<0.1	NC	NC			
Xylenes, *m,p*-	1.3	310	<0.1	4E-03	NC			
Xylene, *o*-	0.56	<120	<0.1	NC	NC			

NOTES:
AF = attenuation factor
GW = groundwater
µg/L = micrograms per liter
µg/m^3 = micrograms per cubic meter
NC = not calculated

example, the building-specific sub-slab (0.02) and groundwater (0.1) attenuation factors for benzene in Table 3-2 are orders of magnitude higher than the attenuation factors for the chlorinated solvents, which raises the question of whether benzene is primarily related to a background source. The benzene indoor air to groundwater attenuation factor also exceeds the attenuation factors reported in U.S. EPA (2008). Using the sample calculations shown in Table 3-2, the observations provide further evidence that background sources are contributing to the measured indoor air concentrations for select VOCs: (1) the VOC being detected in the indoor air sample but not in the sub-slab sample (e.g., 1,1-dichloroethane), (2) the chemical-specific attenuation factor (e.g., benzene) being significantly (e.g., orders of magnitude) higher than the attenuation factors for other chemicals, (3) relatively low sub-slab soil-gas source strengths (e.g., see benzene in Table 3-2), and (4) consistency with other lines of evidence (e.g., comparisons with background indoor and outdoor air concentrations [Section 3.1.3], constituent ratios within a single sample [Section 3.3.2], and the additional lines of evidence discussed in Section 3.5).

3.3 Comparison of Constituent Ratios within Samples

As discussed in ITRC's *Vapor Intrusion Pathway: A Practical Guideline* (ITRC, 2007) and mentioned in the *DoD Vapor Intrusion Handbook* (DoD, 2009), the ratios of chemical concentrations within samples can be calculated and compared between media (e.g., TCE/*cis*-1,2-DCE concentrations in sub-slab versus indoor air samples) to help identify potential sources (background or subsurface). A detailed constituent ratio analysis is a primary component of a forensic analysis (Section 4); however, an examination of ratios within samples for a select number of VOCs can be performed during a background EDA.

The constituent ratios for select VOCs from aboveground background sources are often distinctly different from subsurface sources (e.g., soil gas or groundwater). For example, ITRC's *Vapor Intrusion Pathway: A Practical Guideline* (ITRC, 2007) states:

> *"If the concentration of TCE is 10 times higher than that of PCE in groundwater, deep soil gas, and/or sub-slab soil gas but PCE has a higher concentration than TCE in indoor air, it is reasonable to conclude there is an interior or background source of PCE (e.g., dry-cleaned clothes, carpet spot remover)."*

The ratios within soil-gas or air samples can be calculated directly; however, the ratios of VOCs within groundwater samples should only be calculated after applying Henry's Law adjusted for temperature. This adjustment is necessary to account for differing chemical volatilities.

Refer to Box 3-7 for a succinct summary of the method, rationale, limitations/uncertainties, and considerations for improving the evaluation when calculating and comparing constituent ratios within samples.

BOX 3-7. Practical Tips: Comparison of Constituent Ratios within Samples

How does it work?	The chemical ratios (e.g., PCE to *cis*-1,2-DCE) within each medium are calculated and compared between media to see if they are similar. This is a simplified version of the forensics methods presented in Section 4.
How does this help?	Similar ratios (i.e., chemical compositions) between indoor and outdoor air may suggest an outdoor source. Likewise, similar indoor and sub-slab ratios may indicate a subsurface source (i.e., vapor intrusion may be occurring).
Limitations and uncertainties	Concentrations close to the quantitation limits may be suspect and small differences can cause large changes in constituent ratios. Different constituents may have different results. One comparison may indicate vapor intrusion and another may suggest outdoor sources. This could reflect reality (different sources) or could be the result of inherent variability.
How to improve the evaluation	Collect a sufficient number of representative samples. Avoid using results below the quantitation limit. Assess multiple ratios to assess trends or consistency of conclusions.
Minimum Data Requirements	At least one concurrent sample from each medium being considered. Detections in both media are necessary.
How often will this method be used?	Frequently since the data will likely be available by the time a background vapor intrusion evaluation takes place.

3.3.1 Compile and Determine Adequacy of Site Data

For comparisons of constituent ratios (the gas composition) between different media, the data should be collected as close to the same time as possible. Given the well-documented temporal variability of VOC concentrations in indoor air, soil gas, sub-slab soil gas, and even groundwater in some instances, comparing data from samples collected months or years apart would likely result in significant uncertainties. In some cases (e.g., buildings with highly variable operating pressures or highly variable outdoor air contamination sources), grab or short-term samples collected even hours apart may not be comparable.

The analysis can be done with one sample in each medium. However, as with other EDA methods, usually a minimum of three samples are collected per medium. This small dataset can be useful in exploring the variability of concentrations and their impact on computed ratios. For the same reasons discussed previously, calculating ratios involving nondetects is generally not recommended. Also, ratios calculated using concentrations near the quantitation limit may be unstable and highly sensitive to small changes in reported concentrations.

3.3.2 Evaluate Data

Calculating constituent ratios within samples works best for those chemicals detected in both media (e.g., indoor air and sub-slab soil gas; indoor air and outdoor air) and is particularly effective when the ratios are calculated using a reference VOC without significant aboveground sources (e.g., *cis*-1,2-DCE). Table 3-3 shows example VOC to *cis*-1,2-DCE ratios for those chemicals detected in both the indoor and sub-slab samples. *Cis*-1,2-DCE is selected as the reference VOC in this example for the following reasons: (1) *cis*-1,2-DCE is not likely to have significant indoor or outdoor background sources, as indicated by the prevalence of nondetects in the published background datasets (e.g., NYSDOH, 2006; U.S. EPA, 2008; Dawson and McAlary, 2009); (2) it was detected in the sub-slab samples, indicating a potential subsurface source; (3) it was detected in the indoor air and sub-slab samples, which allows calculation of constituent ratios; and (4) this chemical was not detected in the site-specific outdoor air sample, indicating the likely absence of a background outdoor source.

The benzene and *m,p*-xylene to *cis*-1,2-DCE indoor air ratios listed in Table 3-3 are between 25 to 300 times higher than those in the sub-slab sample, which provides a line of evidence suggesting the presence of an aboveground background source for these two petroleum-related VOCs. Conversely, the concentration ratios of the chlorinated solvents to *cis*-1,2-DCE are similar in the indoor air compared with sub-slab samples (Table 3-3), which is often taken as an indication of a subsurface source. However, such similarities are not necessarily definitive evidence of a subsurface source. Air is exchanged in both directions between the indoors and sub-slab. Sub-slab samples can contain detectable concentrations attributable to an aboveground background source.

Consider the statement in the *Navy's Vapor Intrusion Best Practices* report (DON, 2009):

> *"If vapor intrusion from a subsurface source is occurring, the sub-slab concentrations will generally be higher than the indoor air concentrations by a factor of 100 to 10,000 for residential buildings, and usually even more for commercial buildings because of higher ventilation rates, thicker floor slabs, and HVAC systems that result in a net flow of outdoor air into the buildings with a commensurate positive pressure."*

In the example shown in Table 3-3, the sub-slab concentrations of PCE and TCE are more than 10,000 times higher than the indoor air concentration, which provides another line of evidence suggestive of a subsurface source of PCE and TCE.

The results of the indoor to outdoor air comparisons discussed in Section 3.1 should also be considered when evaluating constituent ratios within samples. For example, the indoor and outdoor air concentrations for benzene and *m,p*-xylene are similar (Table 3-3), suggesting a potential above-ground source. Conversely, the indoor air concentrations for the three chlorinated VOCs listed in Table 3-3 are 2.5 to more than 25 times higher than the site-specific outdoor air concentrations. Additional lines of evidence (e.g., induced pressure differences, tracer compound results, forensic, and/or statistical analyses) would help to strengthen the findings suggested by the comparison of constituent ratios.

3.4 Background Indoor Source Identification and/or Removal

There are numerous potential indoor sources of VOCs. For example, dry-cleaned clothes frequently result in detections of PCE in indoor air. The PCE detections may result from either storing or wearing the clothes in the structure. People may also carry petroleum-related VOCs into buildings on their clothes after servicing or fueling vehicles.

More obvious sources include solvents, fuel-containing products, paints, office supplies, various equipment fluids, solvent-containing cleaners, insecticides, construction materials (e.g., glues), and other industrial or consumer products (U.S. Department of Health & Human Services Household Products Health & Safety Database [http://hpd.nlm.nih.gov/]) stored or used in a structure. However, many of these may not be immediately apparent as VOC sources. As the vapor intrusion practice evolves, the list of products that appear harmless but are found to be sources of indoor air measurements continues to grow. For example, plastic-resin holiday decorations have been found to emit 1,2-DCA, resulting in contamination of indoor air (Doucette et al., 2009). Identifying potential products that may be a background source of VOCs, removing them from the structure, and resampling indoor air can provide definitive data about possible indoor sources, particularly if the VOC concentration in the post-removal indoor air samples is substantially lower.

As strong as this evidence can be, it can be challenging to implement such an effort. For example, using certain products may be intrinsic to the operations in the building, and removing them may not be feasible. In addition, although various sources (e.g., a material safety data sheet, the Internet [e.g., http://hpd.nlm.nih.gov/], and product labels) can be consulted, the information from these sources may be outdated or not representative, may not provide the necessary information, or may not even be available. In the event the product cannot be removed, there is also no accepted method for using this product information quantitatively when reviewing indoor air results. This can result in characterization challenges when trying to determine the relative contributions of subsurface and indoor sources.

In addition, managing potentially hazardous materials or wastes removed from a structure could present a challenge for structures or processes not under direct Navy control. Homeowners and non-Navy entities may be reluctant to retain responsibility for items once they are removed. It is also important to consider the potential benefits versus costs associated with an additional round of sampling.

TABLE 3-3. Comparison of constituent ratios within samples

				Ratio of COPC to cis-1,2-DCE		
Chemical of Potential Concern (COPC)	**Indoor Air ($\mu g/m^3$) IA 1**	**Sub-slab ($\mu g/m^3$) SSG 1**	**Outdoor Air ($\mu g/m^3$) OA 1**	**Indoor Air (unitless) IA 1**	**Subslab (unitless) SSG 1**	**Comparison of Indoor Versus Sub-slab Ratios**
Benzene	0.65	31	0.75	0.6	0.002	300
Dichloroethene, cis-1,2-	1.1	15,000	<0.04	--	--	--
Tetrachloroethene	1.7	33,000	0.18	1.5	2.2	0.7
Trichloroethene	0.35	5,200	0.14	0.3	0.3	1
Xylenes, m,p-	1.3	310	0.88	1.1	0.02	55

This method is typically applied infrequently when there is relatively strong suggestive evidence of an indoor vapor source. It is generally only recommended when the potential indoor source is easily identified during a building survey. Otherwise, real-time analytical methods (Section 2.3.3) may be needed to "sniff out" indoor sources, which will add additional cost and complexity.

Refer to Box 3-8 for a succinct summary of the method, rationale, limitations and uncertainties, and considerations for improving the evaluation for the background indoor source identification and/or removal approach.

3.4.1 Conduct Building Survey

Performing a building survey is the first step in trying to identify potential indoor sources. This can include completing questionnaires with building occupants or operators, reviewing building records, and physically surveying the structure to identify possible VOC-source products. ITRC's *Vapor Intrusion Pathway: A Practical Guideline* (ITRC, 2007) and the *DoD Vapor Intrusion Handbook* (DoD, 2009) provide good examples of building survey questionnaires. The greater the knowledge and training of the personnel completing the building survey, the greater the likelihood will be of identifying less obvious indoor VOC sources.

BOX 3-8. Practical Tips: Background Indoor Source Identification and/or Removal

How does it work?	A building survey may identify indoor VOC sources. Ideally, the sources are identified and removed and follow-up samples collected to assess the effectiveness of the removal.
How does this help?	Significant decreases in post-removal indoor air concentrations provide definitive evidence of an indoor source.
Limitations, uncertainties, and considerations	Indoor sources may be difficult to identify. Minimal or no decrease following removal does not necessarily refute the existence of an indoor source or sources. A plan for managing the products should be developed before removing products from a structure. In most cases, it is best that this responsibility remain with the building's owner or occupants. The Navy may want to avoid becoming the owner of hazardous materials or wastes not directly related to Navy operations.
How to improve the evaluation	Thorough and well-documented building surveys by knowledgeable personnel are necessary when trying to identify indoor sources. Real-time indoor air measurements could potentially be used to help identify specific indoor sources; however, the additional costs should be considered relative to the potential benefits. Longer duration samples reduce the likelihood the post-removal concentration changes are due to temporal variability unrelated to the product removal.
Minimum Data Requirements	At least one pre- and post-removal indoor air sample should be collected. Both should be collected for a similar duration at the same location.
How often will this method be used?	This method is most often used at single structures that have anomalous results, compared with nearby structures or where an obvious indoor source can be identified. It is less applicable or beneficial when extensive investigation or research is needed to identify potential sources.

3.4.2 Evaluate Data

Assuming potential background indoor air VOC sources were identified during the building survey, two basic approaches are used to evaluate their effects on indoor air. The most straightforward and definitive approach is to remove the product, wait a sufficient amount of time (e.g., several days), and resample the indoor air. If the post-removal samples have much reduced VOC concentrations, then this is definitive evidence of a background indoor source.

If concentrations do not decrease, two of the most obvious potential conclusions are that (1) the measured indoor air concentrations are due to a subsurface or outdoor source or (2) the background indoor sources have not been identified adequately (and hence not removed). For example, a textile spot remover containing chlorinated solvents can easily be hidden in a desk. There would be no mention in the building records, and building occupants may not have thought of this when completing the questionnaire.

If indoor sources are still suspected based on other lines of evidence but are not readily identifiable, real-time or near real-time surveys can be done (refer to Section 3.5) to locate possible indoor sources. Both the Trace Atmospheric Gas Analyzer (TAGA; www.epa.gov/ Region6/6lab/ taga.htm) and Hazardous Air Pollutants on Site (HAPSITE) analyzers mentioned in Section 3.5 have been used effectively for this purpose. However, operation of these devices requires trained personnel. Rapid turnaround analyses with an on-site or nearby laboratory may also be an option. All of these alternatives result in additional expenditures, so their use must be weighed against the need to identify indoor sources.

3.5 Additional Lines of Evidence

Several methods in addition to those described in Sections 3.1 through 3.4 may be useful during a background evaluation, including differential pressure monitoring or cycling, tracer compound evaluations, and real-time analyses (ITRC, 2007; DoD, 2009; DON, 2009).

3.5.1 Differential Pressure Monitoring

Air potentially flows from the subsurface into a building when the sub-slab air pressure is greater than the indoor pressure (i.e., a “negative” indoor to sub-slab pressure differential). The reverse condition can result in air flow from the building into the subsurface (i.e., a “positive” indoor to sub-slab pressure differential). Indoor air concentrations under positive pressure conditions are likely to be influenced only by background indoor or outdoor sources since vapor intrusion is prevented.

Example pressure differential and barometric measurements are shown in Figure 3-3. Fluctuations in the indoor to sub-slab pressure differences can correlate with fluctuations in outdoor barometric pressure. During positive indoor to sub-slab pressure periods, no driving force exists for the entry of soil gas into the building, and indoor air concentrations would primarily be related to background sources. Pressure differences are building-specific, and generalization of findings among different buildings is not usually recommended.

The pressure differences between the indoors and the subsurface can be measured continuously at one or more locations using portable differential pressure monitors. These data are commonly collected from a dedicated sub-slab probe located away from the probe(s) used for sampling to avoid interference from the vacuum induced during purging and sampling. Ideally, differential pressure data would be collected during sampling several days before and after sampling to help determine representative pressure conditions. Concurrent indoor-to-outdoor pressure differences or outdoor barometric pressure measurements can also be measured and used in the analysis. Differential pressure data (indoor/sub-slab, indoor/outdoor) have two primary uses in a background vapor intrusion evaluation.

First, the magnitude of the indoor/sub-slab pressure differential and the degree of correlation between indoor/outdoor measurements can be an indication of the “leakiness” of the building envelope and the likely degree of air exchange inside the structure. A close correlation between indoor and outdoor barometric pressure suggests a leaky building and possibly high attenuation of vapors intruding from the subsurface. In contrast, a tighter building envelope is more isolated from the exterior atmosphere and would exhibit greater difference in indoor/outdoor air pressure. Likewise, leaky buildings are also likely to show little indoor/sub-slab pressure differential because induced pressure conditions inside the structure (e.g., turning on a bathroom exhaust fan) are rapidly equilibrated with the atmosphere and soil-gas barometric conditions. Thus, if a very leaky building is suspected based on air pressure monitoring, correspondingly high attenuation of subsurface vapors would also be expected.

Secondly, the magnitude of the indoor/sub-slab differential can also be an important indicator of conditions favorable or unfavorable to vapor intrusion. Table 3-4 provides guidelines developed by U.S. EPA from the study of radon intrusion (U.S. EPA, 1993). Figure 3-3 shows an example of measured differential pressures relative to these ranges. This pattern of pressure variation near the neutral line (zero differential) is typical in older buildings and buildings where frequent opening of the envelope is intrinsic to the operation (an aircraft hangar, for example).

Comparison of sampling results under positive versus negative pressure conditions can provide a line of evidence during a background vapor intrusion evaluation.

It is usually impractical to only use pressure differential measurements collected during the typical 8- or 24-hour indoor air sampling period without intentional forcing (see Section 3.5.2 below) given the fluctuations above and below zero commonly observed. However, longer duration differential pressure data can be useful for identifying seasonal trends and targeting sampling events to match representative seasonal

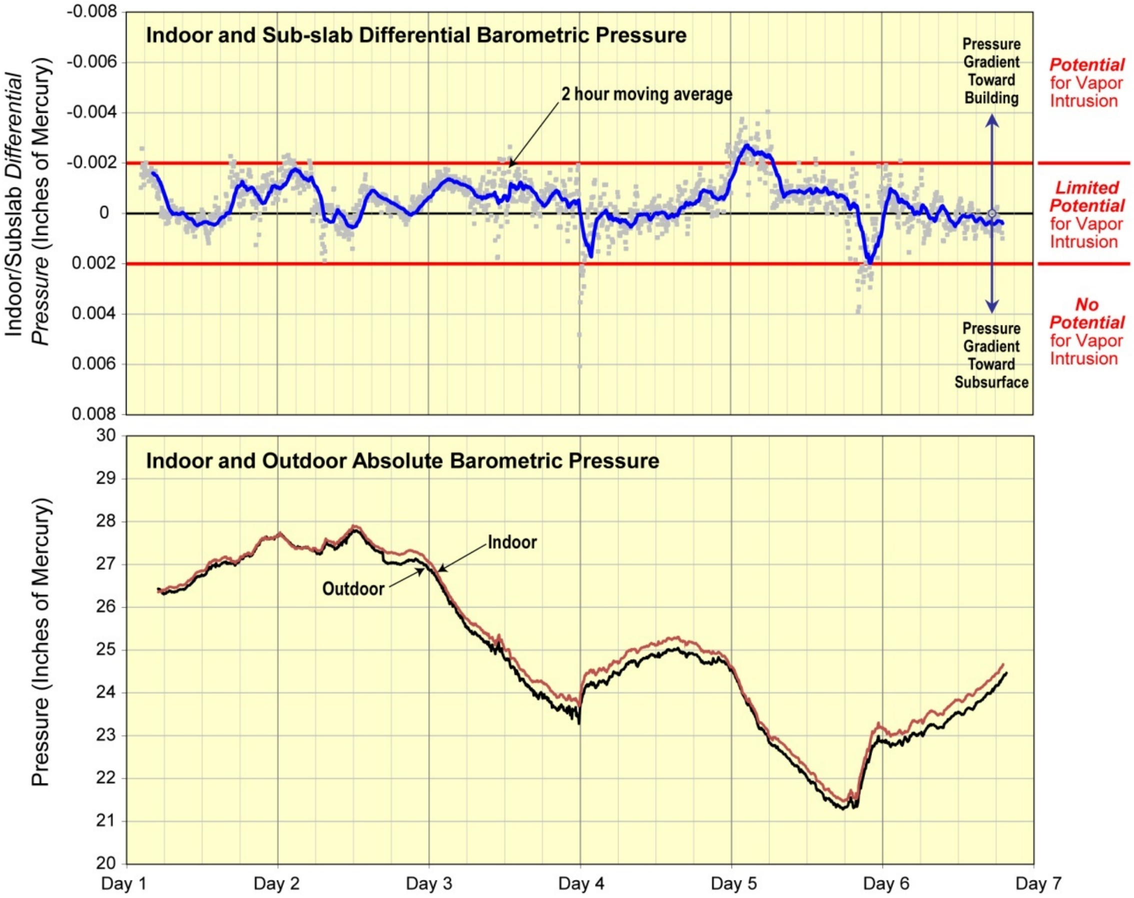


FIGURE 3-3. Sample indoor-to-subsurface pressure differentials

conditions to shed light on potential biases in the dataset resulting from building operation.

3.5.2 Pressure Cycling

Pressure cycling is another approach for assessing the effects of induced pressures on the measured indoor or sub-slab vapor concentrations. Indoor air samples are collected twice, once each with the building under induced negative and positive pressures relative to the sub-slab. The relative contributions from background and subsurface sources can be determined by comparing indoor concentrations for samples collected under induced negative and positive pressures (McHugh et al., 2007; Berry-Spark et al., 2005).

Graphical data evaluation (Figure 3-4) comparisons that can be used to assess the data are presented based on data from the hypothetical Alpha Naval Base. As shown in Figure 3-4, the indoor air concentration for PCE is higher under negative conditions when compared with measurements under positive pressure conditions. Such results suggest the presence of a subsurface source for PCE. In contrast, concentrations of benzene are similar under both negative and positive conditions. This further supports the presence of a background source for the detected petroleum-related VOCs.

TABLE 3-4. Indoor/sub-slab differential pressure measurement interpretation

Condition	Quantitative Measurement Guidelines	Possible Indication	Comments
Positively Pressurized	Consistent indoor pressure measurements greater than 0.002 inHg relative to sub-slab	No apparent driver for vapor intrusion	Pressure difference needed to prevent vapor intrusion in a structure with combined heating and appliance or fan operation effects
Neutral to Positively Pressurized	Consistent indoor pressure measurements between 0 and 0.002 inHg relative to sub-slab or Highly variable indoor pressure measurements typically greater than zero relative to sub-slab	Limited potential for vapor intrusion; an intermittent driver may be present	Minimum acceptable pressure difference needed to prevent vapor intrusion in a structure with either heating effects or appliance/fan effects
Neutral to Negatively Pressurized	Consistent indoor pressure measurements between -0.002 and 0 inHg relative to sub-slab or Highly variable indoor pressure measurements typically less than zero relative to sub-slab	Limited potential for vapor intrusion; an intermittent driver may be present	Range of depressurization that could occur either from heating effects or appliance/fan effects
Negatively Pressurized	Consistent indoor pressure measurements less than -0.002 inHg relative to sub-slab	Potential driver for vapor intrusion pathway	Range of depressurization that could occur from heating effects and appliance/fan effects

NOTES:
inHg = inches of mercury
Table adapted from U.S. EPA (1993).

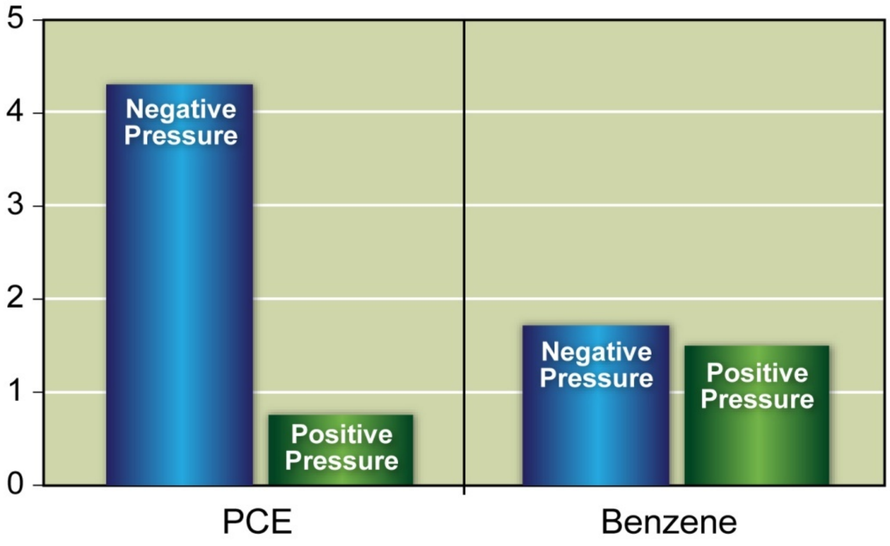


FIGURE 3-4. Example of indoor air comparisons with pressure cycling

3.5.3 Tracer Compounds

Chemicals originating from the subsurface that are rarely detected or not present in indoor air can be used as tracer compounds to help differentiate a subsurface source from a background source (DON, 2009; ITRC, 2007). The ratio of the indoor to subsurface tracer compound is used to estimate a building-specific attenuation factor, which can then be applied to the subsurface concentrations of other VOCs to estimate their corresponding indoor air concentrations. The estimated indoor air concentrations for the potential site-related VOCs can then be compared with measured indoor air concentrations to assess the contribution of background sources. For example, if the estimated concentration is well below the measured concentration, then a background source can be indicated.

Examples of tracer compounds include the following:

- Hexachlorobutadiene and 1,1-DCA have been successfully used as tracer compounds in vapor intrusion investigations (DON, 2009).
- Helium and sulfur hexafluoride have been used as “emplaced” tracers in research applications. More widespread applications of such tracers have been hampered by challenges in achieving a uniform concentration in the subsurface during emplacement.
- Radon has been used successfully as a tracer compound in areas with elevated subsurface levels.

Radon is measured in the indoor and sub-slab samples collected for the hypothetical Alpha Naval Base example. The empirical radon indoor to sub-slab attenuation factors range from 4×10^{-3} to less than 5×10^{-4}. These attenuation factors are far less than those computed for benzene and xylene (Table 3-2). Such differences imply the presence of background sources for these petroleum-related VOCs. As seen with the range of empirical radon attenuation factors, the variability of computed attenuation factors must be acknowledged and documented.

3.5.4 Real-time Monitoring

Real-time or near real-time sampling and analysis techniques, such as the TAGA and HAPSITE analyzers, can be useful in identifying background and subsurface sources. These methods are capable of achieving quantitation limits similar to fixed laboratories. Real-time techniques are often preferred by community stakeholders. Such measurements also allow for relatively quick assessments of the results, creating opportunities to refine the sampling location or approach.

There also are select mobile laboratories that currently offer near real-time analysis; however, they are not capable of continuous readings. Cost or availability of either real- or near real-time sampling and analysis methods often are greater than those associated with the standard fixed laboratory TO-15 methods and prevents their use at most sites.

3.6 Evaluate Lines of Evidence and Assess the Need for Supplemental Analyses

As stated in the introduction, application of all EDA methods is not necessary, nor do these methods need to be applied in any particular order. The cumulative weight of the lines of evidence gathered during a background EDA can be considered at any point during the evaluation. Therefore, the decision to continue with further exploratory methods or more formal analyses can occur at various times during the evaluation process. Such decisions must be consistent with input from all team members or stakeholders.

Figure 3-5 displays a synopsis of the cumulative weight of various EDA lines of evidence discussed in previous sections, based on the dataset from the hypothetical Alpha Naval Base. The project team can create any tabular, graphical, qualitative, or semiquantitative representation that is useful to them. The goal is to bring together the multiple lines of evidence in a way that is meaningful and easy to interpret.

A common observation that emerges from the EDA of the hypothetical dataset is the apparent difference between the petroleum-related and chlorinated VOCs. This is reflected in Figure 3-5, which displays two scales, one for each group of VOCs. The different lines of evidence are symbolized as weights, each applied to the subsurface or background side of the scale according to the outcome of the particular EDA evaluation. The strength of the line of evidence is presented by the size of the symbol associated with the given finding. Such presentations are inherently subjective and are used primarily for communication purposes.

The overall weight of evidence reflected in Figure 3-5 supports the conclusions that (1) chlorinated solvents detected in the indoor air are mainly associated with subsurface soil-gas intrusion and (2) petroleum-related VOCs detected in the indoor air are mainly associated with aboveground (likely outdoor) background sources.

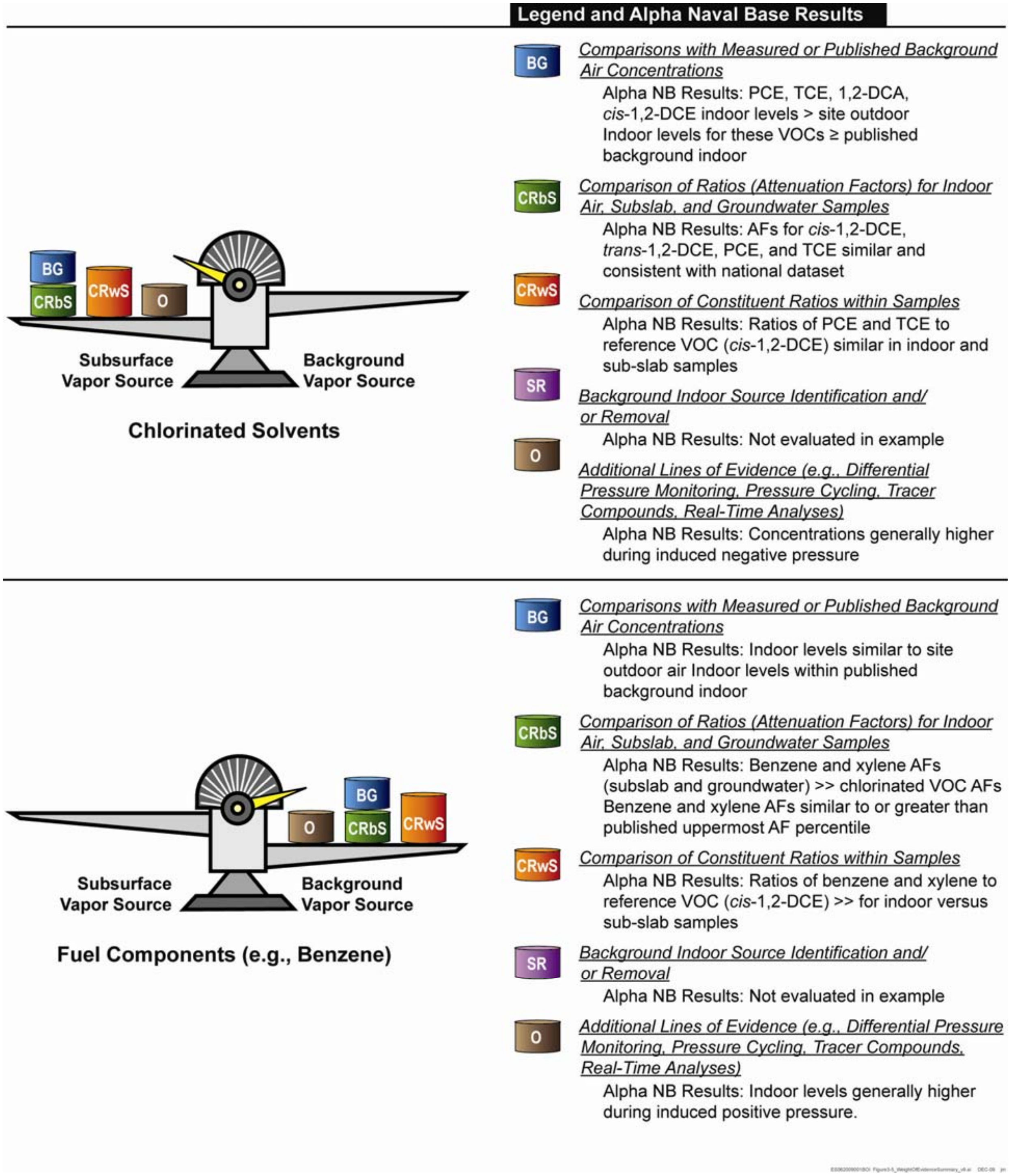
The sizes of the weights are used to suggest which EDA findings provide the strongest evidence. In this case, the comparison of constituent ratios within samples is judged as providing the most definitive evidence of the sources for both the chlorinated solvents and petroleum-related VOCs. Another example of a strong line of evidence is the observation that indoor air concentrations of select chlorinated VOCs (e.g., *cis*-1,2-DCE) are more than 30 times higher than the site-specific outdoor air concentrations, and these VOCs have not generally been detected in the published background datasets.

In this hypothetical case, the project team should conclude that the EDA findings are conclusive for all VOCs of interest. In other cases, however, EDA findings may not be deemed as conclusive, leading to additional background evaluations (e.g., forensics [Section 4] or statistical [Section 5] methods).

3.6.1 Refine Conceptual Site Model

An updated and refined CSM (Figure 3-6) can be generated during any phase of the background evaluation process. Such updates should reflect the observations, conclusions, and lessons learned during the EDA.

As shown in Figure 3-6, the updated CSM reflects the suggested subsurface and background sources of the chlorinated and petroleum-related VOCs. The additional indoor, sub-slab, and outdoor air data are also incorporated into this refined CSM. Question marks on the CSM figure imply uncertainties that can be addressed by follow-on temporal or spatial sampling. In this case,



Legend and Alpha Naval Base Results

BG *Comparisons with Measured or Published Background Air Concentrations*

Alpha NB Results: PCE, TCE, 1,2-DCA, *cis*-1,2-DCE indoor levels > site outdoor
Indoor levels for these VOCs ≥ published background indoor

CRbS *Comparison of Ratios (Attenuation Factors) for Indoor Air, Subslab, and Groundwater Samples*

Alpha NB Results: AFs for *cis*-1,2-DCE, *trans*-1,2-DCE, PCE, and TCE similar and consistent with national dataset

CRwS *Comparison of Constituent Ratios within Samples*

Alpha NB Results: Ratios of PCE and TCE to reference VOC (*cis*-1,2-DCE) similar in indoor and sub-slab samples

SR *Background Indoor Source Identification and/ or Removal*

Alpha NB Results: Not evaluated in example

O *Additional Lines of Evidence (e.g., Differential Pressure Monitoring, Pressure Cycling, Tracer Compounds, Real-Time Analyses)*

Alpha NB Results: Concentrations generally higher during induced negative pressure

BG *Comparisons with Measured or Published Background Air Concentrations*

Alpha NB Results: Indoor levels similar to site outdoor air Indoor levels within published background indoor

CRbS *Comparison of Ratios (Attenuation Factors) for Indoor Air, Subslab, and Groundwater Samples*

Alpha NB Results: Benzene and xylene AFs (subslab and groundwater) >> chlorinated VOC AFs
Benzene and xylene AFs similar to or greater than published uppermost AF percentile

CRwS *Comparison of Constituent Ratios within Samples*

Alpha NB Results: Ratios of benzene and xylene to reference VOC (*cis*-1,2-DCE) >> for indoor versus sub-slab samples

SR *Background Indoor Source Identification and/ or Removal*

Alpha NB Results: Not evaluated in example

O *Additional Lines of Evidence (e.g., Differential Pressure Monitoring, Pressure Cycling, Tracer Compounds, Real-Time Analyses)*

Alpha NB Results: Indoor levels generally higher during induced positive pressure.

FIGURE 3-5. Weight of evidence summary

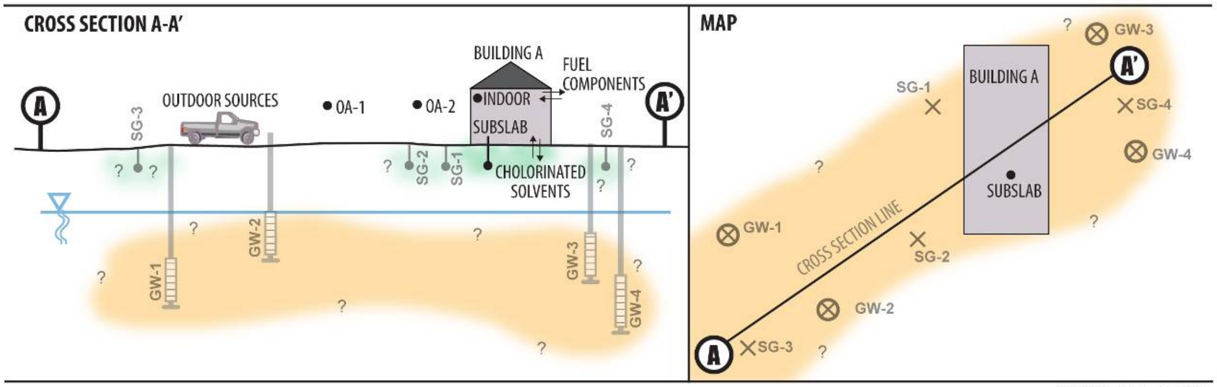


FIGURE 3-6. Updated conceptual site model

additional subsurface characterization of chlorinated solvent soil gas may be warranted, particularly if there are other occupied structures at or near the impacted site.

Examples of other information that can be incorporated into an updated CSM during or following the EDA include (1) the location of known or suspected aboveground sources, (2) the type, location, and use of products identified as potential indoor sources, (3) the location, strength, and chemical composition of subsurface groundwater or vadose zone sources, and (4) chemical-specific sources, such as those related to chlorinated solvents or petroleum-related VOCs. Frequent updating of the CSM fosters further insights and facilitates communication among the project team and other stakeholders.

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4. ENVIRONMENTAL FORENSIC METHOD

NOTE: In some cases, evidence can be derived from forensic and multivariate statistical methods. These methods are advanced procedures, which may not be applicable at many Navy sites. Forensic methods provide analytical procedures to decipher the chemical composition of collected samples to determine the source of detected contaminants. The application of these advanced methods should be considered at sites involving petroleum contamination and out-of-the-ordinary vapor intrusion liabilities.

Environmental evaluations discussed in previous sections primarily focus on the observed concentrations of common chemicals that pose potential indoor risks. In many cases, such data are adequate to reach a conclusive finding concerning the source of detected indoor chemicals of interest. In a few cases, however, a definitive source identification of indoor air contaminants may require a thorough assessment of product chemistry. Such identifications involve the assessment of many chemicals that may not pose any health risks, but are particular signatures of suspect sources. Environmental forensic analysis includes source-specific assemblages of COPCs and many additional chemicals capable of defining ambient vapor plumes and differentiating pattern anomalies caused by vapor intrusion.

Environmental forensic analyses are usually pursued when one or more potential indoor risks linked to vapor intrusion have been identified during the earlier EDA, as described in Sections 2 and 3. This section presents a process for determining if the detected contaminants are caused by soil vapor intrusion based on compositional patterns (i.e., chemical fingerprints) of various field samples.

4.1 Overview

This section discusses chemical fingerprinting methods that help constrain or identify the likely origins of indoor air constituents. The discussion begins with typical conditions that support a forensic analysis, followed by a review of chemical composition of common sources of indoor air vapors.

The discussion continues with an introduction to the advanced chemical fingerprinting methods required for the identification of common hydrocarbon sources. Specific practical aspects of forensic analysis are presented in two case studies. Practical recommendations for environmental practitioners are suggested throughout this section.

4.1.1 Prerequisite Conditions for a Forensic Analysis

Prior to the initiation of a forensic analysis, the RPM must consider its potential costs and benefits. An environmental forensic investigation is usually cost effective when the EDA findings indicate:

- Indoor detections of chemicals of interest are attributed to background sources, although EDA multiple lines of evidence are not considered conclusive.
- The vapor intrusion pathway is believed to be incomplete, although EDA multiple lines of evidence are not considered conclusive.
- The costs of additional characterization and/or mitigation of the alleged vapor intrusion pathway far exceed those associated with the anticipated forensic analysis.

The RPM must evaluate the cost of defining the site-specific background relative to the costs of assuming the indoor contaminants originate from soil gas. The RPM should consider a forensic investigation when the remedy cost or unexpected future costs are unacceptably high. The final decision should be made on a site-specific basis using the best estimates of future costs.

4.1.2 Tiered Forensic Approach

The tiered forensic approach involves two primary phases. First, the forensic investigator conducts a thorough review of EDA findings. This involves an evaluation of historical information, site-specific data, concentration gradients, as well as compositional patterns of samples collected in the vicinity of indoor exceedance locations. Typically, data used in an EDA are adequate to evaluate the chemical composition of halogenated VOCs, including chlorinated solvents and their daughter products. However, in some instances, such data cover a limited number of target analytes, while exhibiting low measurement sensitivity and/or poor quality. These types of chemical data may be inadequate for definitive source identification, especially when investigating vapor emanating from multiple hydrocarbon sources, e.g., petroleum and tar products. More often than not, preliminary data collected during vapor intrusion investigations are suitable for qualitative analyses of tentatively identified compounds (TICs) only. If site conditions warrant a forensic analysis, data gaps identified in the initial review should be subsequently addressed.

The second tier of the forensic investigation involves advanced chemical fingerprinting analyses. The advanced methods expand the target analyte list, lower the detection limits, and improve the measurement accuracy. For this purpose, supplemental sampling may be necessary. For example, vapor intrusion investigations involving VOC sources with complex hydrocarbon patterns, such as gasoline, kerosene, diesel, and manufactured gas plant (MGP) tars, often require advanced chemical measurements of VOCs in air, soil-gas, soil, and groundwater samples. This requirement is particularly acute when differentiating one hydrocarbon source from another, while various forms of chemical partitioning are occurring (Douglas et al., 2007).

Forensic investigators often modify standard laboratory protocols to maximize the dynamic range of laboratory analytical methods. Environmental chemists only recently adapted forensic soil and water methods for air. This incorporates advanced instrumentation capable of measuring chemicals in air over a wide dynamic range. In short, forensic laboratories can now measure hydrocarbon and halogenated VOCs in water, soil, soil gas, and indoor air with an adequate degree of selectivity (large number of compounds) and sensitivity (low detection limits) for source identification purposes (Douglas et al., 2007). The advanced laboratory capabilities are particularly helpful because detected indoor VOC concentrations frequently hover around background ranges, which are attributable to numerous, but indeterminate, sources.

The typical application of advanced forensic methods is the differentiation of one or more petroleum and tar product from background. Advanced methods are also available for expanded lists of halogenated and oxygenated organics. Other methods, such as stable isotopic measurements, help differentiate fixed gases and simple chemical mixtures.

4.2 Compositional Features of Commonly Encountered Chemicals

A central challenge for most vapor intrusion projects is the site-specific nature of the ambient air. The composition of indoor air is typically controlled by human activity and the processes of vapor migration through the building. Human activity influences the indoor air through the use of refrigerants, propellants, adhesives, solvents, respiration, fuel products, cosmetics, cigarette smoke, paints, furniture, and building materials. Appendix A summarizes the composition of commonly encountered products capable of impacting indoor air. Many COPCs are associated with off-gassing or unintended contamination from typical household products. The mixture of COPCs from ambient inside and outside air can vary significantly in terms of concentration and composition as a result of weather events, atmospheric changes, or air handling systems.

4.3 Standard Method TO-15

The laboratory procedures for analysis of air samples is the U.S. EPA TO method for measuring the concentrations of contaminants in ambient air, referred to as Standard Method TO-15 (U.S. EPA, 1999) in this document. The following presents details about Standard Method TO-15 to highlight the modifications that must be performed to yield the necessary measurements for a forensic analysis.

4.3.1 Standard TO-15 Protocol Summary

Standard Method TO-15 utilizes specially treated, certified clean, leak-free canisters for the collection of air and vapor samples. Canisters are shipped to the field under a vacuum of approximately -30 inches of mercury. Flow controllers are calibrated in the laboratory to ensure that air samples are collected over a known time interval. The sampling equipment is simple to use in the field, but field crews must check all fittings in the sampling train to ensure the absence of leaks during sample collection.

The canisters are packaged in the field and shipped to the laboratory for analysis. The laboratory instrumentation draws a known volume of sample into a cryogenic concentrator and then desorbs the sample into a gas chromatograph/mass spectrometer (GC/MS). The MS can be run in two different modes: full scan and selective ion monitoring (SIM). In full scan mode, the MS looks for a range of atomic mass units (amu), which normally ranges from 35 to 300 for the entire analytical run. The largest benefit to running in full scan mode is the ability to acquire a complete mass spectrum of target and non-target analytes. Laboratories typically use Standard Method TO-15 to measure approximately 70 compounds with reporting limits ranging from 0.2 to 0.5 part per billion by volume (ppbv). These reporting limits are generally sufficient for analyzing soil gas.

Manufacturers constantly improve the capabilities of MS instruments to more dynamically measure compounds. SIM is one such innovation worth mentioning, that is permitted, but not required, by Standard Method TO-15. In SIM mode, the MS looks for only two to three ions at each appropriate retention time. Such selectivity makes MS more sensitive and reliable, resulting in lower reporting limits. SIM target analyte lists are approximately 15 to 20 compounds, much shorter than full scan lists. Reporting limits for analytes detected in the SIM mode can be as low as 2 parts per trillion by volume (pptv). These lower reporting limits are especially helpful in cases involving 10^{-6} risk-based criteria. Full scans, in contrast, identify a larger list of analytes and, under appropriate calibration, yield reporting limits in the 10 pptv range.

4.3.2 Standard TO-15 Analytes

The Standard TO-15 analyte list includes an extensive number of halogenated VOCs (Table 4-1). Consequently, Standard Method TO-15 is well suited for evaluating issues related to chlorinated solvents in indoor air. However, only 15 of the Standard TO-15 analytes are petroleum-type hydrocarbons or gasoline additives that would be useful in “fingerprinting” hydrocarbon-rich sources (e.g., gasoline or tars). This list includes:

- MTBE
- hexane
- methanol
- benzene
- ethylene dichloride
- 2,2,4-trimethylpentane (isooctane)
- toluene
- ethylene dibromide
- ethylbenzene
- styrene
- *p*-xylene
- *m*-xylene
- *o*-xylene
- 1,3,5-trimethylbenzene
- 1,2,4-trimethylbenzene

Some laboratories also measure naphthalene as part of the Standard TO-15 analysis. Given that there are potentially hundreds of VOCs in gasoline or other important hydrocarbon sources (e.g., MGP tars or creosotes), the few hydrocarbons among the Standard TO-15 analytes are of limited forensic benefit because they lack the specificity to distinguish one hydrocarbon

TABLE 4-1. Standard TO-15 analytes

Sort (rt)	Class	CAS Number	Analytes	Abbrev	Henry's Law Constant (M/atm)	Raoult's Law Constant (atm)	Solubility (g/l)	Molecular Weight	Molecular Formula	Reporting Limits (ppbv)
1	F	75-71-8	Dichlorodifluoromethane	DCFM	2.1×10^{-3}	5.000	0.29	120.92	CCl2F2	0.20
2	C	74-87-3	Chloromethane	CM	1.0×10^{-1}	4.836	5.33	50.49	CH3Cl	0.20
3	F	76-14-2	Freon-114	F114	5.9×10^{-4}	2.109		170.92	C2Cl2F4	0.20
4	O	75-07-0	Acetaldehyde	ACT	15.0	0.993	always soluble	44.05	C2H4O	2.5
5	C	75-01-4	Vinyl chloride	VC	4.6×10^{-2}	3.395	insoluble	62.5	C2H3Cl	0.20
6	O	106-99-0	1,3-Butadiene	13B	1.6×10^{-2}	2.455		54.09	C4H6	0.20
7	P	106-97-8	Butane	C4	1.2×10^{-3}	2.100	0.06	58.12	C4H10	0.20
8	B	74-83-9	Bromomethane	BM	1.3×10^{-1}	1.875	15.22	94.94	CH3Br	0.20
9	C	75-00-3	Chloroethane	CE	5.1×10^{-1}	1.306	6.00	64.52	C2H5Cl	0.20
10	O	64-17-5	Ethanol	EOH	190.0	0.053	miscible	46.07	C2H6O	1.0
11	B	593-60-2	Vinyl bromide	VB		2.041	insoluble	106.96	C2H3Br	0.20
12	O	107-02-8	Acrolein	ACL	7.40	0.282		56.06	C3H4O	0.50
13	O	67-64-1	Acetone	ACE	30.00	0.238		58.08	C3H6O	0.50
14	F	75-69-4	Trichlorofluoromethane	TCTFM	9.2×10^{-3}	0.871	1.10	137.37	CCl3F	0.20
15	O	67-63-0	Isopropyl Alcohol	IPOH	120.00	0.043		60.1	C3H7OH	0.20
16	P	109-66-0	Pentane	C5	8.1×10^{-4}	0.563	0.10	72.15	C5H12	0.20
17	C	75-35-4	1,1-Dichloroethene	11DCE	7.6×10^{-3}	0.658		96.94	C2H2Cl2	0.20
18	O	75-65-0	Tertiary butyl Alcohol	TBA	84.00	0.041		74.12	C4H9OH	0.20
19	C	75-09-2	Methylene chloride	DCM	3.9×10^{-1}	0.464	13.00	84.93	CH2Cl2	0.50
20	C	107-05-1	3-Chloropropene	3CP	1.1×10^{-1}	0.447		76.53	C3H5Cl	0.20
21	S	75-15-0	Carbon disulfide	CD	5.6×10^{-2}	0.395	2.00	76.14	CS2	0.20
22	F	76-13-1	Freon-113	F113	2.0×10^{-3}	0.375		187.38	C2Cl3F3	0.20
23	C	156-60-5	*trans*-1,2-Dichloroethene	T12DCE	1.5×10^{-1}	0.354		96.94	C2H2Cl2	0.20
24	C	75-34-3	1,1-Dichloroethane	11DCA	1.7×10^{-1}	0.303		98.96	C2H4Cl2	0.20
25	ADD	1634-04-4	MTBE	MTBE	1.70	0.322		88.15	C5H12O	0.20
26	O	78-93-3	2-Butanone	2B	7.10	0.093	290.00	72.11	C4H8O	0.20
27	C	156-59-2	*cis*-1,2-Dichloroethene	C12DCE	1.3×10^{-1}	0.263		96.94	C2H2Cl2	0.20
28	C	67-66-3	Chloroform	CF	2.7×10^{-1}	0.209	8.00	119.38	CHCl3	0.20
29	ADD	107-06-2	1,2-Dichloroethane	12DCA	9.2×10^{-1}	0.080	8.70	98.96	C2H4Cl2	0.20
30	P	110-54-3	Hexane	C6	6×10^{-4}	0.174	immiscible	86.18	C6H14	0.20
31	C	71-55-6	1,1,1-Trichloroethane	111TCA	3.6×10^{-2}	0.132	insoluble	133.41	C2H3Cl3	0.20
32	A	71-43-2	Benzene	B	1.8×10^{-1}	0.099	0.80	78.11	C6H6	0.20
33	S	110-02-1	Thiophene	THIO	4.4×10^{-1}	0.053		84.14	C4H4S	0.20
34	C	56-23-5	Carbon tetrachloride	CT	5.1×10^{-2}	0.119	0.79	153.82	CCl4	0.20
35	N	110-82-7	Cyclohexane	CH	5.6×10^{-3}	0.127	insoluble	84.16	C6H12	0.20
36	C	78-87-5	1,2-Dichloropropane	12DCP	3.4×10^{-1}			113	C3H6Cl2	0.20
37	B	75-27-4	Bromodichloromethane	BDCM	6.3×10^{-1}	0.065		163.83	CHBrCl2	0.20
38	O	123-91-1	1,4-Dioxane	14D	2.2×10^{2}	0.036	highly soluble	88.11	C4H8O2	0.20
39	C	79-01-6	Trichloroethene	TCE	8.2×10^{-2}	0.080	1.00	131.39	C2HCl3	0.20
40	I	540-84-1	2,2,4-Trimethylpentane	224TMP	3.1×10^{-4}	0.054	immiscible	114.23	C8H18	0.20
41	P	142-82-5	Heptane	C7	4.4×10^{-4}	0.053	immiscible	100.23	C7H16	0.20
42	C	10061-01-5	*cis*-1,3-Dichloropropene	C13DCP	4.2×10^{-1}	0.057		110.97	C3H4Cl2	0.20
43	O	108-10-1	4-Methyl-2-pentanone	MIBK	2.60	0.020	19.10	100.16	C6H12O	0.20

TABLE 4-1. Standard TO-15 analytes (continued)

Sort (rt)	Class	CAS Number	Analytes	Abbrev	Henry's Law Constant (M/atm)	Raoult's Law Constant (atm)	Solubility (g/l)	Molecular Weight	Molecular Formula	Reporting Limits (ppbv)
44	C	10061-02-6	*trans*-1,3-Dichloropropene	T13DCP	5.6×10^{-1}	0.045		110.97	C3H4Cl2	0.20
45	C	79-00-5	1,1,2-Trichloroethane	112TCA	8.4×10^{-1}	0.025		133.41	C2H3Cl3	0.20
46	A	108-88-3	Toluene	T	1.5×10^{-1}	0.038	0.47	92.14	C7H8	0.20
47	S	554-14-3	2-Methylthiophene	2MTHIO	4.2×10^{-1}	0.063		98.17	C5H6S	0.20
48	O	591-78-6	2-Hexanone	MBK		0.013	14.00	100.16	C6H12O	0.20
49	S	616-44-4	3-Methylthiophene	3MTHIO				98.17	C5H6S	0.20
50	B	124-48-1	Dibromochloromethane	DBCM	1.10	0.100	2.70	208.29	CHBr2Cl	0.20
51	ADD	106-93-4	1,2-Dibromoethane	12DBE	1.40	0.015		187.86	C2H4Br2	0.20
52	P	111-65-9	Octane	C8	3.4×10^{-4}	0.014	immiscible	114.22	C8H18	0.20
53	C	127-18-4	Tetrachloroethene	PCE	4.4×10^{-2}	0.017	0.15	165.83	C2Cl4	0.20
54	C	108-90-7	Chlorobenzene	CB	2.9×10^{-1}	0.016	low solubility	112.56	C6H5Cl	0.20
55	A	100-41-4	Ethylbenzene	E	1.3×10^{-1}	0.009	0.15	106.17	C8H10	0.20
56	S	872-55-9	2-Ethylthiophene	2ETHIO				112.19	C6H8S	0.20
57	A	108-38-3/106-42-3	p+m- × ylene	mp ×	1.4×10^{-1}	0.028	insoluble	106.17	C8H10	0.40
58	B	75-25-2	Bromoform	BF	1.50	0.007	3.20	252.75	CHBr3	0.20
59	A	100-42-5	Styrene	STY	2.9×10^{-1}	0.006	insoluble	104.15	C8H8	0.20
60	C	79-34-5	1,1,2,2-Tetrachloroethane	1122PCA	2.10	0.011	2.86	167.85	C2H2Cl4	0.20
61	A	95-47-6	o- × ylene	o ×	2.0×10^{-1}	0.009	insoluble	106.17	C8H10	0.20
62	P	111-84-2	Nonane	C9	2.0×10^{-4}	0.013	immiscible	128.25	C9H20	0.20
63	C	95-49-8	2-Chlorotoluene	2CT	1.90			126.58	C7H7Cl	0.20
64	A	622-96-8	4-Ethyl toluene	4ET	2.0×10^{-1}	0.004	insoluble	120.2	C9H12	0.20
65	A	108-67-8	1,3,5-Trimethylbenzene	135TMB	1.7×10^{-1}	0.002	insoluble	120.2	C9H12	0.20
66	A	95-63-6	1,2,4-Trimethylbenzene	124TMB	1.7×10^{-1}	0.001	insoluble	120.2	C9H12	0.20
67	P	124-18-5	Decane	C10	1.4×10^{-4}	0.001	immiscible	142.3	C10H22	0.20
68	C	541-73-1	1,3-Dichlorobenzene	13DCB	2.8×10^{-1}	0.007	insoluble	147	C6H2Cl2	0.20
69	C	106-46-7	1,4-Dichlorobenzene	14DCB	6.3×10^{-1}	0.001	insoluble	147	C6H2Cl2	0.20
70	A	526-73-8	1,2,3-Trimethylbenzene	123TMB	3.1×10^{-1}	0.002		120.19	C9H12	0.20
71	C	95-50-1	1,2-Dichlorobenzene	12DCB	5.3×10^{-1}	0.002	insoluble	147	C6H2Cl2	0.20
72	A	496-11-7	Indan	IN				118.18	C9H10	0.20
73	A	95-13-6	Indene	INE				116.16	C9H8	0.20
74	P	1120-21-4	Undecane	C11	5.5×10^{-5}	0.001	immiscible	156.3	C11H24	0.20
75	A	95-93-2	1,2,4,5-Tetramethylbenzene	1245TMP	4.0×10^{-2}		insoluble	134.22	C10H14	0.20
76	P	112-40-3	Dodecane	C12	1.4×10^{-4}	0.00039	immiscible	170.34	C12H26	0.20
77	C	120-82-1	1,2,4-Trichlorobenzene	124TCB	2.7×10^{-1}	0.00039	insoluble	181.45	C6H3Cl3	0.50
78	A	91-20-3	Naphthalene	N0	2.40		0.03	128.17	C10H8	0.20
79	S	11095-43-5	Benzothiophene	BT0				134.2	C8H6S	0.50
80	C	87-68-3	Hexachlorobutadiene	HCBD	4.0×10^{-2}	0.029		260.76	C4Cl6	0.20
81	A	91-57-6	2-Methylnaphthalene	2MN	2.50	0.001	insoluble	142.2	C11H10	1.0
82	A	90-12-0	1-Methylnaphthalene	1MN	2.30	0.000	insoluble	142.2	C11H10	1.0

source from another within typical background conditions (Stout et al., 2002).

4.3.3 Standard Quality Assurance/Quality Control

A strong quality assurance (QA) program includes numerous QC checks to ensure the attainment of the desired data quality. Appendix E provides a detailed discussion of the QA/QC criteria for the purposes of writing the Quality Assurance Project Plan (QAPP) or Sampling and Analysis Plan (SAP).

4.4 Forensic Method TO-15

Forensic Method TO-15 is a modified version of Standard Method TO-15, customized for the identification of hydrocarbon product sources (i.e., petroleum and tar products). The modification of the standard method allows Forensic Method TO-15 to measure a broader range of VOCs, as listed in Table 4-2. This additional information provides a solid base for distinguishing the source of gasoline, kerosene, diesel, and tar products. The expanded target analyte list provides a powerful tool for distinguishing the source of gas phase constituents in vapor or air samples that is beyond the capability of Standard Method TO-15. The Forensic Method also includes enhanced QA/QC features that meet or exceed those specified in Standard Method TO-15.

4.4.1 Forensic TO-15 Protocol Summary

Forensic Method TO-15 follows the same protocols described for the collection and transfer of Standard Method TO-15 samples onto the instrument. However, Forensic Method TO-15 takes advantage of recent advances in instrument technology. First, the method can simultaneously analyze VOCs in both GC/MS scan and SIM modes. Analyte concentrations are typically measured with the SIM data with sub-ppbv reporting limits for targeted analytes. The GC/MS scan data allow for the identification of unknown (non-target) VOCs and the possible measurement of analyte concentrations above the SIM calibration range. Second, the samples can be simultaneously split in the GC instrument into an MS detector and a flame ionization detector (FID). The GC/FID data generate a standard high-resolution hydrocarbon fingerprint spanning the C_3-C_{13} carbon range. This provides additional chemical fingerprinting information useful for product identification and estimating the concentration of unknown hydrocarbons.

BOX 4-1. Practical Tips: Forensic TO-15 Method

How does it work?	Environmental forensic vapor intrusion investigations typically identify indoor air sources by comparison of concentration gradients and chemical fingerprints among indoor, outdoor, and soil-gas samples.
When is it most beneficial?	Forensics is most beneficial as part of vapor intrusion investigations involving chemicals with multiple subsurface and ambient sources.
Is special testing needed?	Supplemental forensic chemical testing is only recommended when COPCs from petroleum or tar products exceed potential risk screening concentrations.
How much does it cost?	Forensic TO-15 testing costs approximately two times as much as Standard TO-15 test methods. Additional costs may be required for a forensic interpretation.
Laboratory Requirements	The laboratory must use TO-15 modified for the analysis of PIANO compounds. At present, only a few national laboratories perform the Forensic TO-15 method with independent validation.

TABLE 4-2. Forensic TO-15 analytes

sort (rt)	Class	CAS Number	Analytes	Abbrev	Henry's Law Constant (M/atm)	Raoult's Law Constant (atm)	Solubility (g/l)	Molecular Weight	Molecular Formula	Reporting Limits (ppbv)
1	O	106-99-0	1,3-Butadiene	13B	1.6×10^{-2}	2.455		54.09	C4H6	0.025
2	I	78-78-4	Isopentane	IP		0.7828		72.15	C5H12	0.025
3	O	109-67-1	1-Pentene	1P	2.5×10^{-3}	0.694		70.13	C5H10	0.025
4	O	563-46-2	2-Methyl-1-butene	2M1B		0.6789		70.13	C5H10	0.025
5	P	109-66-0	Pentane	C5	8.1×10^{-4}	0.563	0.10	72.15	C5H12	0.025
6	O	646-04-8	2-Pentene (*trans*)	T2P	4.3×10^{-3}	0.5484	insoluble	70.13	C5H10	0.025
7	O	627-20-3	2-Pentene (*cis*)	C2P	4.4×10^{-3}	0.5526		70.13	C5H10	0.025
8	O ×	75-65-0	Tertiary butyl Alcohol	TBA	84.00	0.041		74.12	C4H9OH	0.025
9	N	287-92-3	Cyclopentane	CYP	5.4×10^{-3}	0.3618		70.13	C5H10	0.025
10	I	79-29-8	2,3-Dimethylbutane	23DMB	7.8×10^{-4}	0.2631	negligible	86.18	C6H14	0.025
11	I	107-83-5	2-Methylpentane	2MP	5.8×10^{-4}	0.226	insoluble	86.18	C6H14	0.025
12	O ×	1634-04-4	MTBE	MTBE	1.70	0.322		88.15	C5H12O	0.025
13	I	96-14-0	3-Methylpentane	3MP	5.9×10^{-4}	0.25		86.18	C6H14	0.025
14	O	592-41-6	1-Hexene	1HE ×	2.4×10^{-3}		insoluble	84.16	C6H12	0.025
15	P	110-54-3	Hexane	C6	6×10^{-4}	0.174	immiscible	86.18	C6H14	0.025
16	O ×	108-20-3	Diisopropyl Ether (DIPE)	DIPE	9.9×10^{-2}	0.1565		102.17	C6H14O	0.025
17	O ×	637-92-3	Ethyl Tertiary Butyl Ether (ETBE)	ETBE			12	102.2	C6H14O	0.025
18	I	590-35-2	2,2-Dimethylpentane	22DMP	3.2×10^{-4}		insoluble	100.2	C7H16	0.025
19	N	96-37-7	Methylcyclopentane	MCYP	2.8×10^{-3}	0.1809	insoluble	84.16	C6H12	0.025
20	I	108-08-7	2,4-Dimethylpentane	24DMP	3.2×10^{-4}	0.0107	insoluble	100.2	C7H16	0.025
21	ADD	107-06-2	1,2-Dichloroethane	12DCA	9.2×10^{-1}	0.080	8.70	98.96	C2H4Cl2	0.025
22	N	110-82-7	Cyclohexane	CH	5.6×10^{-3}	0.127	insoluble	84.16	C6H12	0.025
23	I	591-76-4	2-Methylhexane	2MH	2.9×10^{-4}		insoluble	100.2	C7H16	0.025
24	A	71-43-2	Benzene	B	1.8×10^{-1}	0.099	0.80	78.11	C6H6	0.025
25	I	565-59-3	2,3-Dimethylpentane	23DMP	5.8×10^{-4}			100.2	C7H16	0.025
26	S	110-02-1	Thiophene	THIO	4.4×10^{-1}	0.053		84.14	C4H4S	0.025
27	I	589-34-4	3-Methylhexane	3MH	4.2×10^{-4}	0.0809		100.2	C7H16	0.025
28	O ×	994-05-8	TAME	TAME		0.0986	12	102.17	C6H14O	0.025
29	O	592-76-7	1-Heptene	1H	2.5×10^{-3}	0.0742	insoluble	98.19	C7H14	0.025
30	I	540-84-1	Isooctane	ISO	3.3×10^{-4}	0.0539		114.22	C8H18	0.025
31	P	142-82-5	Heptane	C7	4.4×10^{-4}	0.053	immiscible	100.23	C7H16	0.025
32	N	108-87-2	Methylcyclohexane	MCYH	2.3×10^{-3}	0.0605	insoluble	98.19	C7H14	0.025
33	I	592-13-2	2,5-Dimethylhexane	25DMH	3.0×10^{-4}			114.23	C8H18	0.025
34	I	589-43-5/564-02-3	2,4-Dimethyhexane / 2,2,3-TMP	24DMH/223TMP	2.8×10^{-4}			114.23	C8H18	0.050
35	I	565-75-3	2,3,4-Trimethylpentane	234TMP	5.3×10^{-4}		insoluble	114.23	C8H18	0.025
36	I	560-21-4	2,3,3-Trimethylpentane	233TMP	2.4×10^{-4}		insoluble	114.23	C8H18	0.025
37	I	584-94-1	2,3-Dimethylhexane	23DMH	2.6×10^{-4}		insoluble	114.23	C8H18	0.025
38	I	619-99-8	3-Ethylhexane	3EH	2.6×10^{-4}			114.23	C8H18	0.025
39	I	592-27-8	2-Methylheptane	2MHEP	2.7×10^{-4}		insoluble	114.23	C8H18	0.025
40	I	589-81-1	3-Methylheptane	3MHEP	2.7×10^{-4}		insoluble	114.23	C8H18	0.025
41	A	108-88-3	Toluene	T	1.5×10^{-1}	0.038	0.47	92.14	C7H8	0.025
42	S	554-14-3	2-Methylthiophene	2MTHIO	4.2×10^{-1}	0.063	insoluble	98.17	C5H6S	0.025
43	S	616-44-4	3-Methylthiophene	3MTHIO		0.024	insoluble	98.17	C5H6S	0.025
44	O	111-66-0	1-Octene	1O	1.1×10^{-3}	0.0171	insoluble	112.22	C8H16	0.025

TABLE 4-2. Forensic TO-15 analytes (continued)

sort (rt)	Class	CAS Number	Analytes	Abbrev	Henry's Law Constant (M/atm)	Raoult's Law Constant (atm)	Solubility (g/l)	Molecular Weight	Molecular Formula	Reporting Limits (ppbv)
45	N	16747-50-5	1-Ethyl-1-methylcyclopentane	1E1MCP				112.21	C8H16	0.025
46	P	111-65-9	Octane	C8	3.4×10^{-4}	0.014	immiscible	114.22	C8H18	0.025
47	ADD	106-93-4	1,2-Dibromoethane	12DBE	1.40	0.015		187.86	C2H4Br2	0.025
48	A	100-41-4	Ethylbenzene	E	1.3×10^{-1}	0.009	0.15	106.17	C8H10	0.025
49	S	872-55-9	2-Ethylthiophene	2ETHIO			insoluble	112.19	C6H8S	0.025
50	A	106-42-3/108-38-3	p+m- × ylene	mp ×	1.4×10^{-1}	0.028	insoluble	106.17	C8H10	0.025
51	O	124-11-8	1-Nonene	1N	1.2×10^{-3}	0.0071	insoluble	126.24	C9H18	0.025
52	P	111-84-2	Nonane	C9	2.0×10^{-4}	0.013	immiscible	128.25	C9H20	0.025
53	A	100-42-5	Styrene	STY	2.9×10^{-1}	0.006	insoluble	104.15	C8H8	0.025
54	A	95-47-6	o- × ylene	o ×	2.0×10^{-1}	0.009	insoluble	106.17	C8H10	0.025
55	A	98-82-8	Isopropylbenzene	IPB	6.8×10^{-2}	0.01052	slightly soluble	120.19	C9H12	0.025
56	A	103-65-1	n-Propylbenzene	PROPB	1.0×10^{-1}	0.0026		120.19	C9H12	0.025
57	A	620-14-4	1-Methyl-3-ethylbenzene	1M3EB			insoluble	120.19	C9H12	0.025
58	A	622-96-8	1-Methyl-4-ethylbenzene	1M4EB				120.19	C9H12	0.050
59	A	108-67-8	1,3,5-Trimethylbenzene	135TMB	1.7×10^{-1}	0.002	insoluble	120.2	C9H12	0.050
60	O	872-05-9	1-Decene	1D		0.0021	insoluble	140.3	C10H20	0.100
61	A	611-14-3	1-Methyl-2-ethylbenzene	1M2EB				120.2	C9H12	0.025
62	P	124-18-5	Decane	C10	1.4×10^{-4}	0.001	immiscible	142.3	C10H22	0.025
63	A	95-63-6	1,2,4-Trimethylbenzene	124TMB	1.7×10^{-1}	0.0005	insoluble	120.2	C9H12	0.050
64	A	135-98-8	sec-Butylbenzene	SECBUT	8.7×10^{-2}	0.0013	0.015	120.2	C9H12	0.025
65	A	535-77-3	1-Methyl-3-isopropylbenzene	1M3IPB				134.22	C10H14	0.025
66	A	99-87-6	1-Methyl-4-isopropylbenzene	1M4IPB				134.22	C10H14	0.025
67	A	527-84-4	1-Methyl-2-isopropylbenzene	1M2IPB				134.22	C10H14	0.025
68	A	496-11-7	Indan	IN				118.18	C9H10	0.025
69	A	95-13-6	Indene	INE				116.16	C9H8	0.050
70	A	1074-43-7	1-Methyl-3-propylbenzene	1M3PB				134.22	C10H14	0.100
71	A	1074-55-1	1-Methyl-4-propylbenzene	1M4PB				134.22	C10H14	0.100
72	A	104-51-8	n-Butylbenzene	BUTB		0.001359		134.22	C10H14	0.050
73	A	934-80-5	1,2-Dimethyl-4-ethylbenzene	12DM4EB				134.22	C10H14	0.100
74	A	135-01-3	1,2-Diethylbenzene	12DEB				134.22	C10H14	0.100
75	A	1074-17-5	1-Methyl-2-propylbenzene	1M2PB				134.22	C10H14	0.100
76	A	1758-88-9	1,4-Dimethyl-2-ethylbenzene	14DM2EB				134.22	C10H14	0.100
77	P	1120-21-4	Undecane	C11	5.5×10^{-5}	0.001	immiscible	156.3	C11H24	0.100
78	A	874-41-9	1,3-Dimethyl-4-ethylbenzene	13DM4EB				134.22	C10H14	0.100
79	A	934-74-7	1,3-Dimethyl-5-ethylbenzene	13DM5EB				134.22	C10H14	0.100
80	A	4/4/2870	1,3-Dimethyl-2-ethylbenzene	13DM2EB				134.22	C10H14	0.100
81	A	933-98-2	1,2-Dimethyl-3-ethylbenzene	12DM3EB				134.22	C10H14	0.100
82	A	95-93-2	1,2,4,5-Tetramethylbenzene	1245TMP	4×10^{-2}			134.22	C10H14	0.100
83	A	538-68-1	Pentylbenzene	PENTB	1.7×10^{-1}		0.003	148.24	C11H16	0.100
84	P	112-40-3	Dodecane	C12	1.4×10^{-4}	0.00039	immiscible	170.34	C12H26	0.025
85	A	91-20-3	Naphthalene	N0	2.40	0.001	0.03	128.17	C10H8	0.025
86	S	11095-43-5	Benzothiophene	BT0				134.2	C8H6S	0.025
87	ADD	12108-13-3	MMT	MMT				218.09	C9H7Mn03	0.100
88	P	629-50-5	Tridecane	C13	4.3×10^{-4}	0.0000342	insoluble	184.36	C13H28	0.025
89	A	91-57-6	2-Methylnaphthalene	2MN	2.50	0.001	insoluble	142.2	C11H10	0.025
90	A	90-12-0	1-Methylnaphthalene	1MN	2.30	0.000	insoluble	142.2	C11H10	0.025

4.4.2 Forensic TO-15 Analytes

Forensic Method TO-15 measures an extensive hydrocarbon analyte list which includes paraffins, isoparaffins, aromatics, naphthenes, and olefins (PIANO), as well as tar-specific (e.g., styrene) or gasoline-specific compounds (e.g., oxygenate additives) and various thiophenes (Table 4-2). The compounds listed above provide more specificity than Standard TO-15 analytes for distinguishing hydrocarbon sources (Table 4-1). For example, the distribution of paraffins, isoparaffins, and naphthenes helps differentiate gasoline, kerosene, and diesel range materials. The distribution and proportion of aromatics relative to saturated hydrocarbons also helps differentiate petroleum- or tar-derived materials. The presence of olefins and additives typically indicates the presence and approximate age of gasoline and jet fuels.

4.4.3 Forensic Quality Assurance/Quality Control

All of the data quality criteria for Standard Method TO-15 apply to Forensic Method TO-15. In addition, numerous QC checks over and above the Standard Method TO-15 data quality criteria are recommended for Forensic Method TO-15. See Appendix E for examples of these enhanced QC criteria.

4.5 Sample Collection

Given the large array of potential COPC background sources, the sampling design depends heavily on the project-specific objectives. As a general guideline, vapor intrusion investigators benefit from simultaneous sampling of indoor air, outdoor air, and soil gas. These samples explain the basic variation in indoor air for small residential properties. Additional samples are recommended for larger buildings or features of special interest to the investigation.

4.5.1 Indoor Air

It is recommended that one sample be collected from each floor to account for the spatial variability during the sampling period. The sample from the ground floor should be collected in the center of the building. Additional samples can be collected if specific rooms are likely associated with important COPCs (e.g., the attached garage, boiler room, or sump room). Every ground floor sampling location should have a paired soil-gas sample.

4.5.2 Soil Gas

It is recommended that at least three soil-gas samples be collected. The first soil-gas sample should be collected below the center of the building (e.g., sub-slab). All things being equal, this sample is least likely affected by complex soil-gas flow near the threshold of the building foundation. The two additional samples should be collected halfway between the center and edge of the building to assess variability in the soil-gas signature. The secondary sampling locations can be adjusted to intercept soil gas most likely to migrate into the indoor air (e.g., below sumps or foundation cracks) or soil gas approaching the building from a known plume of COPCs.

4.5.3 Ambient Outside Air

It is recommended that one sample be collected upwind from the building. Recognizing that wind direction changes frequently, it is prudent to place the outside sample in the direction of the prevailing wind. Additional outdoor samples are recommended if the study area is potentially influenced by roadways, vehicle parking lots, local industry, or other potential off-site COPC sources.

4.6 Sampling Duration

The variable nature of indoor air necessitates extended sample collection times. Representative samples of indoor and outdoor air are typically collected over approximately 8 hours to account for most of the variation occurring during the exposure period. Soil gas is typically collected over less time (approximately 1 hour) because the volume of soil gas is less than indoor air and sampling artifacts might appear if larger volumes are withdrawn from the ground; for example, the act of collecting the sample might artificially draw soil gas or ambient air into the sampling area.

BOX 4-2. Practical Tips: Forensic Sample Collection

How many samples?	The typical residential dwelling benefits from the simultaneous collection of seven samples including three indoor air, one outdoor air, and three soil gas.
When should samples be collected?	It is generally thought that winter represents the greatest potential for vapor intrusion due to the negative pressure created by closing windows and operating the heating system. Repeat testing may be required initially to evaluate temporal variability.
When would more samples be needed?	More samples are recommended for large buildings or study areas with multiple COPC sources. Careful inspection of the indoor environment might also identify additional potential sources (e.g., garages or boiler room) or preferential pathways (e.g., foundation cracks and sumps) worthy of additional samples.
What equipment is needed?	Six liter (6 L) summa canisters are typically used for the simultaneous collection of the indoor and outdoor samples over an 8-hour period, while the 2.7 L canisters are used for the 1-hour soil-gas samples. The lab can provide pre-calibrated flow controllers that govern the rate at which air is drawn into the evacuated canister. Upon request, the lab can also provide Teflon® tubing to collect samples from confined areas.
Are Canisters Re-useable?	Yes, however, the laboratory is required to clean the cans with heat under a stream of pure gas. The canisters are subsequently tested for COPCs in batches or individually. It is recommended that forensic samples be collected in individually-certified canisters.
Field QC?	One field sample duplicate should be collected per day per 20 or fewer samples. Upon request, the laboratory can provide a sampling "T" that splits the inlet air between two summa canisters.
What field data are needed?	Record the temperature, barometric pressure, precipitation, wind speed, and prevailing wind direction during the sample collection.

4.7 Field Observations

The sample collection team should collect additional data that will help evaluate the results. First, the field team should walk through the study area (inside and outside, if possible) and note the presence of refrigerants, propellants, adhesives, solvents, respiration, fuel products, cosmetics, cigarette smoke, paints, furniture, and building materials. Second, the field team should record meteorological data including the temperature, barometric pressure, precipitation, approximate wind speed, and approximate wind direction during sample collection. Third, the field team should record information about the traffic patterns including periods of automobile and truck congestion, presence of traffic lights (engine idling), and local commercial or industrial activities. These data help contextualize the analytical chemistry results and identify the likely sources of COPCs in ambient air.

4.8 Forensic Case Studies

The following two case studies provide detailed examples of applications of forensic analyses. These case studies highlight the synergistic use of Standard and Forensic Method TO-15 results.

- ❑ The first case study considers the potential vapor intrusions from light, nonaqueous-phase liquid (LNAPL) into a residential dwelling. This multimedia investigation compared the source fingerprints from LANPL and indoor air.

- The second case study considers potential migration of subsurface coal tar vapors into a residential and commercial neighborhood. This forensic investigation hinges on a qualitative comparison of indoor air with background outdoor air and known reference materials.

In both cases, the Standard Method TO-15 results provided enough information to identify a potential problem, but not enough information to determine the actual source. The prevailing CSM could not rule out the vapor intrusion pathway. The forensic analysis demonstrated that the vapor intrusion pathways were incomplete in both cases.

4.8.1 Case Study 1: Multimedia LNAPL Vapor Intrusion Investigation

A routine due diligence investigation during a commercial real estate transaction revealed the presence of low levels of benzene, toluene, ethylbenzene, and xylenes (BTEX) in the indoor air of a commercial building. Site investigators also discovered an LNAPL plume floating on the water table approximately 20 feet away from the building with a depth-to-groundwater of approximately 25 feet. Logistical constraints prevented the collection of soil gas near the property. Site investigators set out to determine if the LNAPL was the source of BTEX and other hydrocarbons in the indoor air of the building.

A forensic investigation was conducted to determine (1) the composition of the LNAPL, (2) the composition of hydrocarbon soil gas that could emanate from the LNAPL, and (3) a high-resolution depiction of the makeup of hydrocarbon vapors in the indoor and outdoor air near the building. These data were then compared to determine if the LNAPL soil-gas chemical signature matched or was distinctive from volatile hydrocarbons found in the indoor air.

The LNAPL sample was analyzed by a modified version of U.S. EPA Method 8015 to develop a GC/FID 'fingerprint' of the LNAPL, from which product composition may be inferred (Stout et al., 2002). Next, the LNAPL was analyzed for volatile C_5-C_{12} PIANO hydrocarbons using GC/MS techniques that were an adaptation of U.S. EPA Method 8260, optimized for low-level measurement of hydrocarbon compounds in petroleum and other hydrocarbon liquids. Indoor and outdoor air samples collected from within and outside the building in question were analyzed using Forensic Method TO-15 GC/MS described earlier in this report.

The GC/FID analysis of the LNAPL revealed that the product was composed of a mixture of petroleum fuels, consisting of about 80% C_{10}-C_{25} hydrocarbons (consistent with the features of diesel/Fuel No. 2), and about 20% C_{25}-C_{40} hydrocarbons (consistent with the features of a heavy fuel oil [HFO]). The concentrations of volatile hydrocarbons measured in the LNAPL were low, i.e., tens of parts per million. The hydrocarbon class composition of the LNAPL was found to consist of paraffins (15%); isoparaffins (1%), aromatics (83%); naphthenes (1%); and olefins (0%). The dominant aromatic hydrocarbon fraction was composed of higher molecular weight alkylated benzenes; there was no benzene found in the LNAPL.

LNAPL-Vapor Phase Fingerprinting

The estimated equilibrium vapor phase composition of the LNAPL at 20°C was computed using basic thermodynamic principles. The vapor phase composition of each volatile hydrocarbon was calculated using Raoult's Law (Uhler et al., 2008):

$$P_{i,v} = P_{i,o}\,\chi_i$$

where

$P_{i,v}$ is the partial pressure of volatile chemical *i* in equilibrium with the LNAPL

$P_{i,o}$ is the partial pressure of pure volatile chemical *i*

χ_i is the mole fraction of volatile chemical *i* in the LNAPL.

Partial pressure data for each of the volatile hydrocarbons measured in the LNAPL were derived from the U.S. EPA SPARC (Sparc

Performs Automated Reasoning in Chemistry) physicochemical database (Carreira et al., 1994). The vapor phase concentrations of each chemical were computed from the estimated partial pressure using the ideal gas law.

The concentrations of volatile hydrocarbons in indoor air were low; i.e., the highest concentration measured in the sample was for toluene at 1.3 ppbv; other compounds detected in the sample were significantly less than 1 ppbv. The hydrocarbon class composition of the volatile hydrocarbons in indoor sample IA101 was found to be paraffins (30%); isoparaffins (27%); aromatics (34%); naphthenes (6%); and olefins (2%). BTEX, dominated by toluene, made up 22% of the volatile organics measured in the indoor air. Benzene was detected in the indoor air at 0.24 ppbv.

The concentrations of volatile hydrocarbons in outdoor air were also low; the highest concentration measured in outdoor air was toluene at 0.27 ppbv. Other compounds detected in the outdoor air sample were generally less than 0.1 ppbv. The hydrocarbon class composition of the volatile hydrocarbons in outdoor air was found to be paraffins (20%); isoparaffins (34%); aromatics (36%); naphthenes (6%); and olefins (4%). BTEX, dominated by toluene, made up 26% of the volatile organics measured in the outdoor air. Benzene was detected in the outdoor air at 0.12 ppbv.

The bulk chemical composition and the relative concentrations of individual volatile chemicals measured in the indoor air were compared with that predicted for the LNAPL vapor to determine if the chemical patterns and features were similar or distinct between LNAPL vapor and indoor air. A comparison between indoor air and outdoor air composition was also conducted to ascertain similarity or difference between the vapor-borne hydrocarbon chemical compositions of these samples.

As shown in Figure 4-1, the volatile hydrocarbon chemical compositions between indoor air and LNAPL vapor, expressed as percentages of PIANO, were significantly different (note that in these charts BTEX chemicals are reported separately from the remainder of other branched chain aromatic compounds). Even at this bulk level, the LNAPL vapor and indoor air hydrocarbon compositions are clearly different — i.e., the LNAPL vapor was dominated by aromatics (47%) and BTEX (11%) compounds, whereas the indoor air was dominated by 2% olefins (relatively unstable hydrocarbons in the environment); the LNAPL vapor contained no olefin chemicals.

Alternatively, the indoor air hydrocarbon composition and the outdoor air composition were much more similar in relative composition (Figure 4-1) — both contained approximately the same proportions of the PIANO chemical classes, including olefins (i.e., the outdoor air contained 2% olefin compounds).

Molecular Chemical Features

Plots of the relative concentrations of individual chemicals (i.e., at the molecular chemical level), are a convenient means to compare and contrast the chemical makeup among samples. Figure 4-2 depicts the relative hydrocarbon composition measured in indoor air compared to that predicted to compose the vapor of the site LNAPL. The compounds are displayed in order of increasing volatility, from left to right. The molecular composition of hydrocarbons between these two samples was significantly different. For example, toluene (T) is the chemical measured in highest concentration in the indoor air sample, while it is absent in the LNAPL vapor. Instead, 1,2,4-trimethylbenzene (TMB) is the chemical that is found in highest concentration in the LNAPL vapor. Further, the indoor air sample contained numerous low molecular weight chemicals, whereas such chemicals were largely absent in the LNAPL vapor.

A quantitative depiction of the differences between the indoor air hydrocarbon composition and the LNAPL vapor composition is shown in Figure 4-3, which depicts the relative differences in composition between the two samples. In this chart, chemicals appearing in the positive (+)

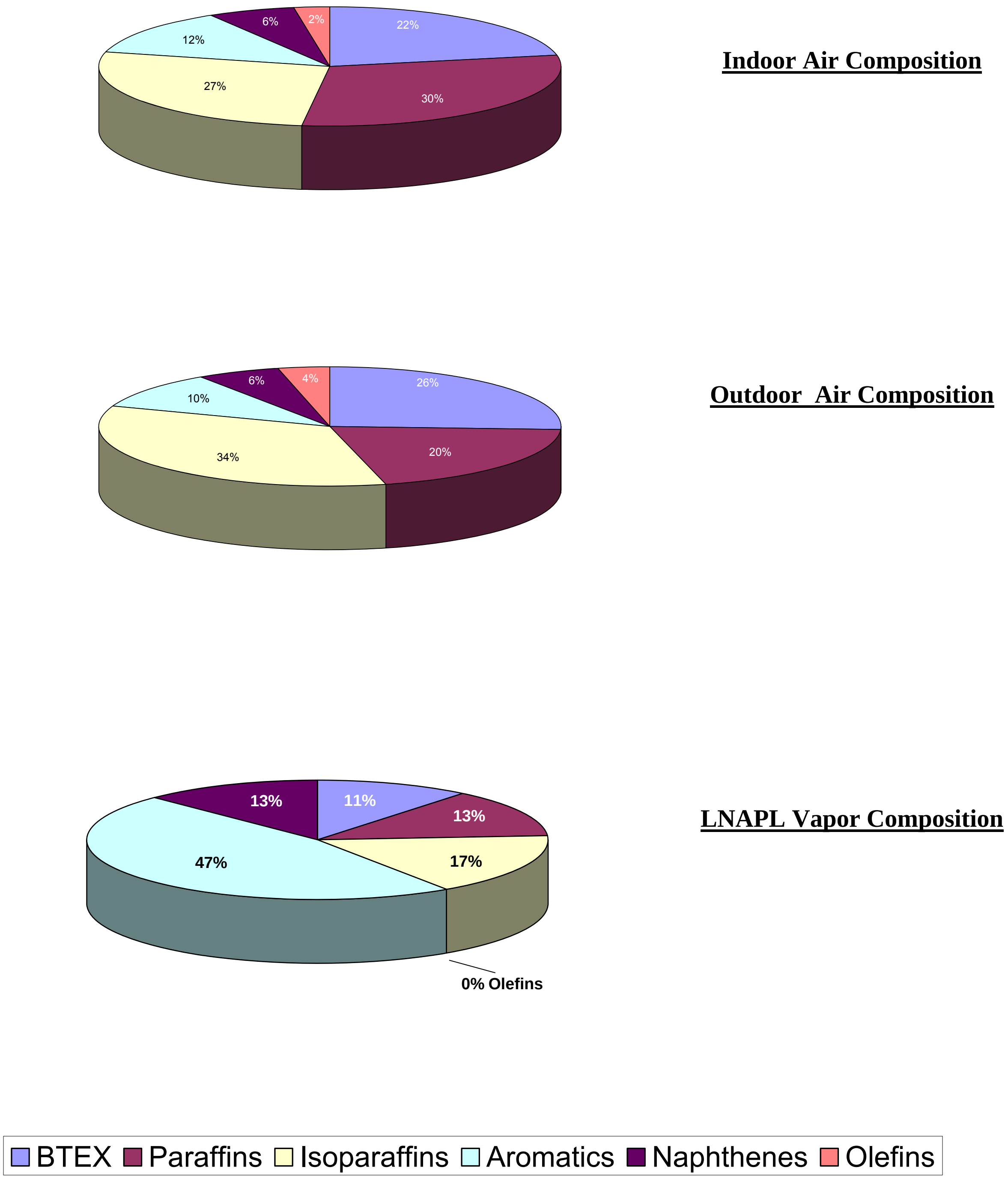

FIGURE 4-1. Relative hydrocarbon class compositions for indoor air and outdoor air, computed for the equilibrium vapor phase for LNAPL found in the subsurface at the study site

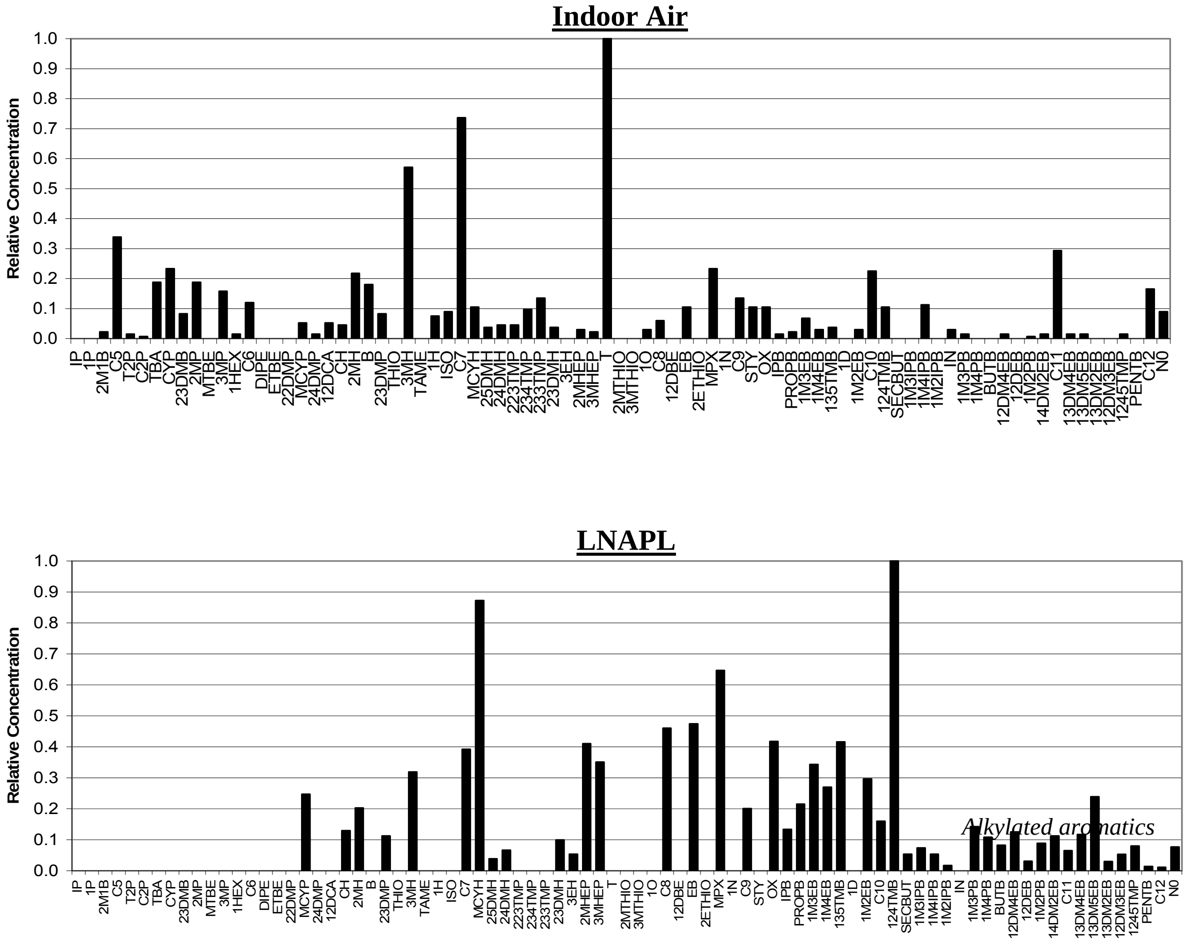

FIGURE 4-2. Relative molecular chemical composition histograms for indoor air sample LNAPL

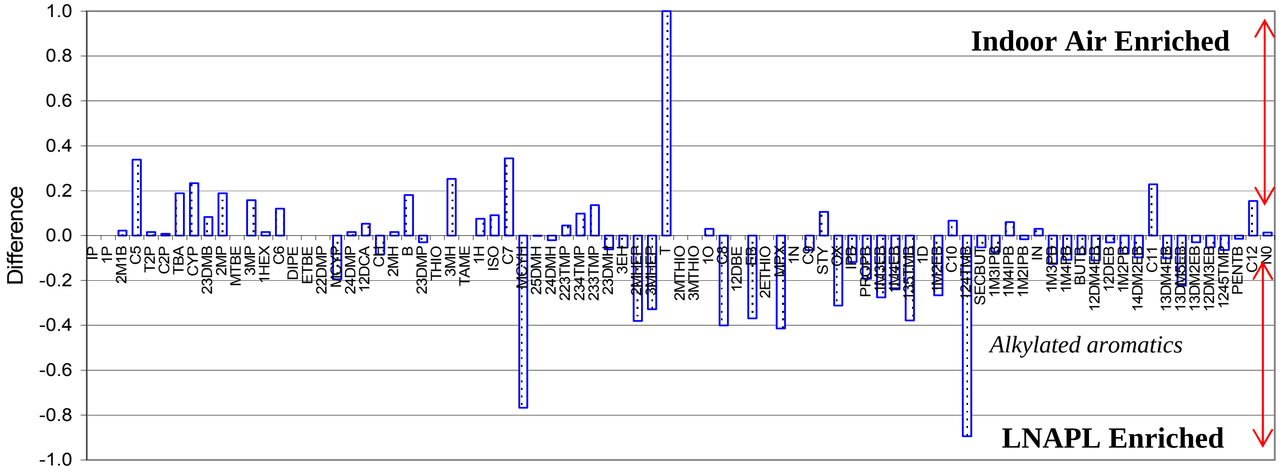

FIGURE 4-3. Compositional difference chart between indoor air and LNAPL found in the subsurface at the site

region of the chart indicate compositional enrichment in the indoor air relative to the LNAPL; chemicals appearing in the negative (-) region of the chart indicate compositional enrichment in the LNAPL vapor relative to the indoor air. This depiction of the data is consistent with the general observations regarding compositional differences noted in Figure 4-2, i.e., the LNAPL vapor was enriched in higher molecular weight aromatics relative to the indoor air, whereas the indoor air was enriched in alkanes, isoalkanes and toluene relative to the LNAPL vapor.

At the molecular chemical level, the hydrocarbon composition of the indoor air sample and outdoor air sample was much more similar than either compared to the LNAPL vapor. Figure 4-4 depicts the relative hydrocarbon composition of the indoor and outdoor air samples. Figure 4-5 presents the relative difference in composition between the indoor and outdoor air samples. Both samples contain toluene as the chemical of maximum concentration, and both have a very similar relative distribution pattern across the hydrocarbon composition range. In fact, the differences in chemical makeup between the two samples are generally small, except in the most volatile range of the hydrocarbon distribution. Overall, it was striking that the indoor and outdoor air samples were of quite similar bulk and molecular chemical makeup.

The investigation revealed that there were clear differences between the hydrocarbon chemistry of the predicted LNAPL vapor and that of the indoor air. The chemical differences — based on both bulk composition and molecular chemistry — indicated that the LNAPL was not the source of the low levels of hydrocarbons found in indoor air at the site. Alternatively, the hydrocarbon composition measured in outdoor air near the building was strikingly similar to that of the indoor air sample. Despite the fact that the concentrations of volatile hydrocarbons in the outdoor air sample were modestly lower than measured in the indoor air, the strong similarity between the hydrocarbon composition of the indoor air and the outdoor air suggested a related source.

4.8.2 Case Study 2: Neighborhood Soil-Gas Vapor Intrusion Investigation

A small residential and commercial neighborhood is located hydrogeologically downgradient from a former MGP site and an automobile service station. Records indicate historical releases of tar from the MGP and petroleum from the service station prior to 1960. An initial round of indoor air testing revealed the presence of low concentrations of BTEX in indoor air.

Site investigators tested soil gas, indoor air, and background outdoor air to determine if vapor intrusion caused BTEX exceedances in the neighborhood. The field team collected source samples as soil-gas grab samples (canister size = 2.7 liter) near the MGP and service station plumes. Additional soil-gas samples were collected near numerous buildings in the neighborhood. The field team collected indoor air and outdoor ambient air over 8 hours (canister size = 6 liter).

Source Signatures

The Standard and Forensic Method TO-15 results demonstrated many differences among the MGP tar, gasoline, and diesel source materials. All of these samples were analyzed by both methods (Figure 4-6). The gasoline sample contained no significant halogenated analytes. The high proportions of isoparaffins and aromatics compared to paraffins suggest gasoline was formulated with alkylate and reformate (a high-octane liquid produced by the catalytic reforming of naphthas). The olefins indicated the presence of cracked petroleum. The presence of 1,2-DCE further suggested the presence of leaded gasoline manufactured in the U.S. prior to 1996 (1,2-DCE is a lead [Pb] scavenger). As discussed below, the absence of 1,2-DCE in indoor air helped differentiate the historical service station release from more modern gasoline vapors detected in the indoor air of downgradient properties.

Standard Method TO-15 results demonstrated that the diesel fuel oil contained heavier hydrocarbons than the gasoline (Figure 4-6) by the dominant abundances of trimethylbenzenes. Forensic Method TO-15 results also demonstrated the

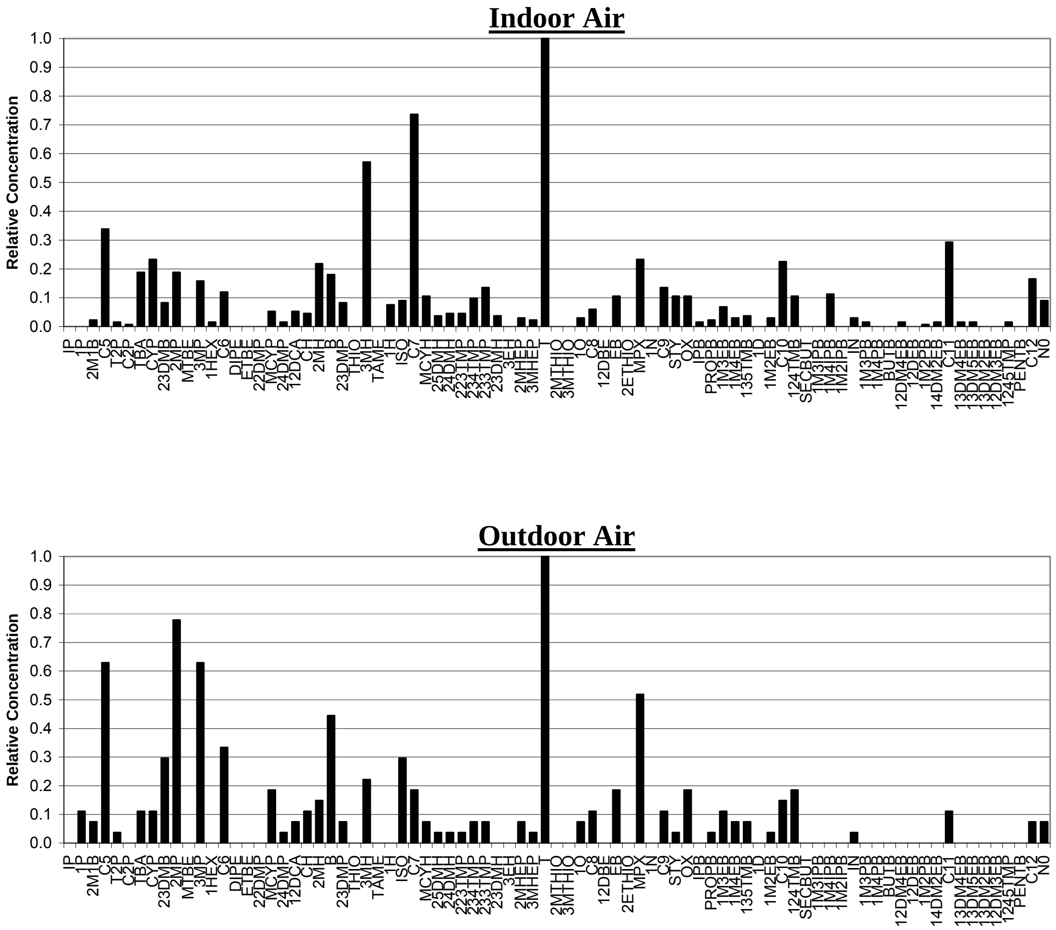

FIGURE 4-4. Relative molecular chemical composition histograms for indoor air and outdoor air at the site

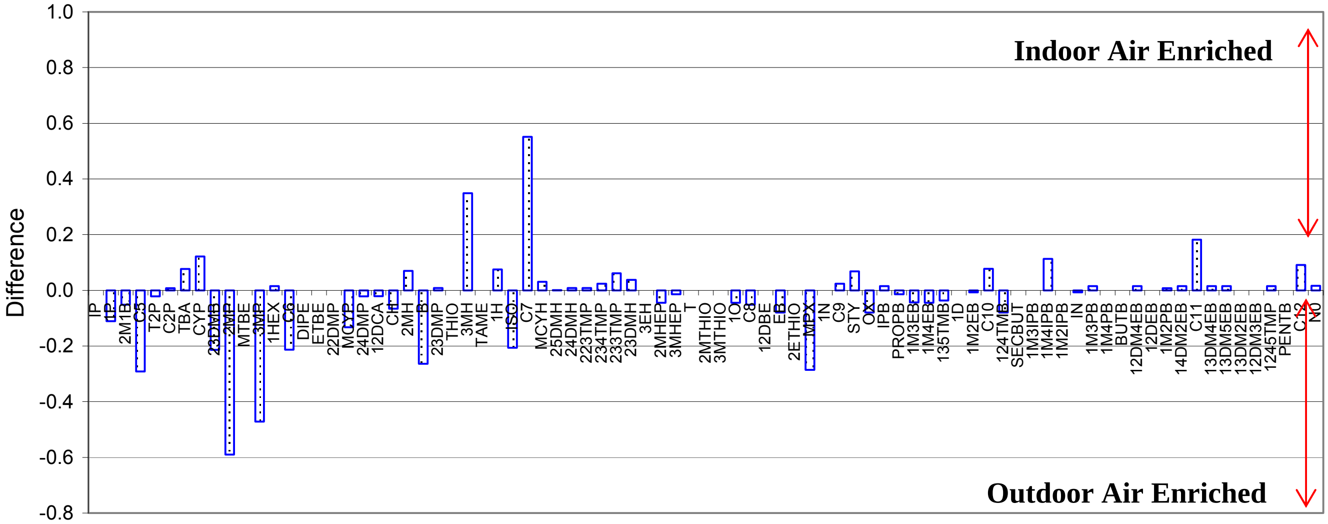

FIGURE 4-5. Compositional difference chart between indoor air and outdoor air at the site

heavy hydrocarbon bias among the paraffins (dominant C_{10} and C_{11}) and isoparaffins (dominant methylheptanes). The absence of olefins and gasoline additives further distinguished the diesel fuel from gasoline. The pattern of heavier hydrocarbons helped identify low-level diesel impacts in outdoor air within the residential study area.

MGP tar contains exclusively aromatics. The process used to generate the tar imprints the aromatic fingerprint with unique features best represented by ratios of two diagnostic compounds. Several features that differentiate MGP tar from petroleum products include high ratios of styrene relative to *o*-xylene (STY/OX), indene relative to 1,2,4-TMB (INE/1,2,4-TMB), and naphthalene relative to tetra-alkylbenzenes (N/B4). The Forensic Method TO-15 results portrayed all three of these compositional relationships while Standard Method TO-15 portrayed only one (STY/OX).

Background Outdoor Air

The field team collected 30 background outdoor air samples throughout the neighborhood over the two-year study period. The results of these analyses helped characterize the concentration and composition of ambient air over time. Most of the Standard Method TO-15 analytes were detected in ambient air (46 detected out of 82 analytes = 56%). The detected VOCs included members of most heteroatomic VOC classes: chlorine, fluorine, oxygen, and sulfur. Most of the pure hydrocarbons were detected frequently with BTEX detects topping the list. The diversity of detected analytes could not possibly have originated from one source. Many chlorinated, brominated, thiophene, and gasoline additives were not detected in ambient air. The presence or absence of VOCs helped constrain the possible origin of indoor air contaminants. Analytes that were detected in indoor air, but not in the outdoor air were attributable to sources other than background outdoor air.

The analytes detected at the highest concentrations in ambient outdoor air included isopropyl alcohol and ethanol, which exceeded 100 $\mu g/m^3$. The maximum BTEX and many normal alkane concentrations ranged from 4 to 75 $\mu g/m^3$. The co-occurrence of BTEX and alkanes in roughly equal proportions plus olefins and low levels of gasoline additives suggested the presence of gasoline vapors attributable to automobile tailpipe emissions or petroleum tank vents (Figure 4-6). The slightly increasing proportions of n-C_9 to n-C_{13} normal alkanes in the median ambient air sample suggested contributions of diesel fuel (Figure 4-6). The remaining mixture of heteroatomic VOCs indicates the possible presence of adhesives, refrigerants, propellants, and others.

The indoor air in the residential property closest to the MGP and service station contained a complex mixture of heteroatomic VOCs and hydrocarbons (Figure 4-7). The oxygenated VOCs dominated the pattern (ethanol, acetone, and acetaldehyde). The hydrocarbons included a mixture of saturated and aromatic compounds consistent with gasoline. The Forensic Method TO-15 results demonstrated the presence of naphthenes and olefins that suggested a gasoline origin. In addition, the pattern of heavy paraffins indicated the presence of weathered gasoline or diesel range hydrocarbons. The first floor sample resembled the outdoor ambient air; however, the match was imperfect (Figure 4-7).

Three features differentiated the indoor and outdoor air. First, the heavier paraffins observed in the outdoor air (1) were not evident in the indoor air (2). Second, the indoor air contained high proportions of isoparaffins relative to aromatics (3). The outside air had low proportions of isoparaffins relative to aromatics (4). Third, unlike the outside air (5), the indoor air (6) contained the oxygenate tert amyl methyl ether (TAME). These differences suggested that the gasoline vapors indoor were not entirely derived from background outdoor air. The composition of the basement air resembled the first floor, except the concentrations were higher. This concentration gradient raised concerns about a potential vapor intrusion pathway. The presence of chloroform on the first floor was attributed to the indoor chlorinated pool and/or household cleansers.

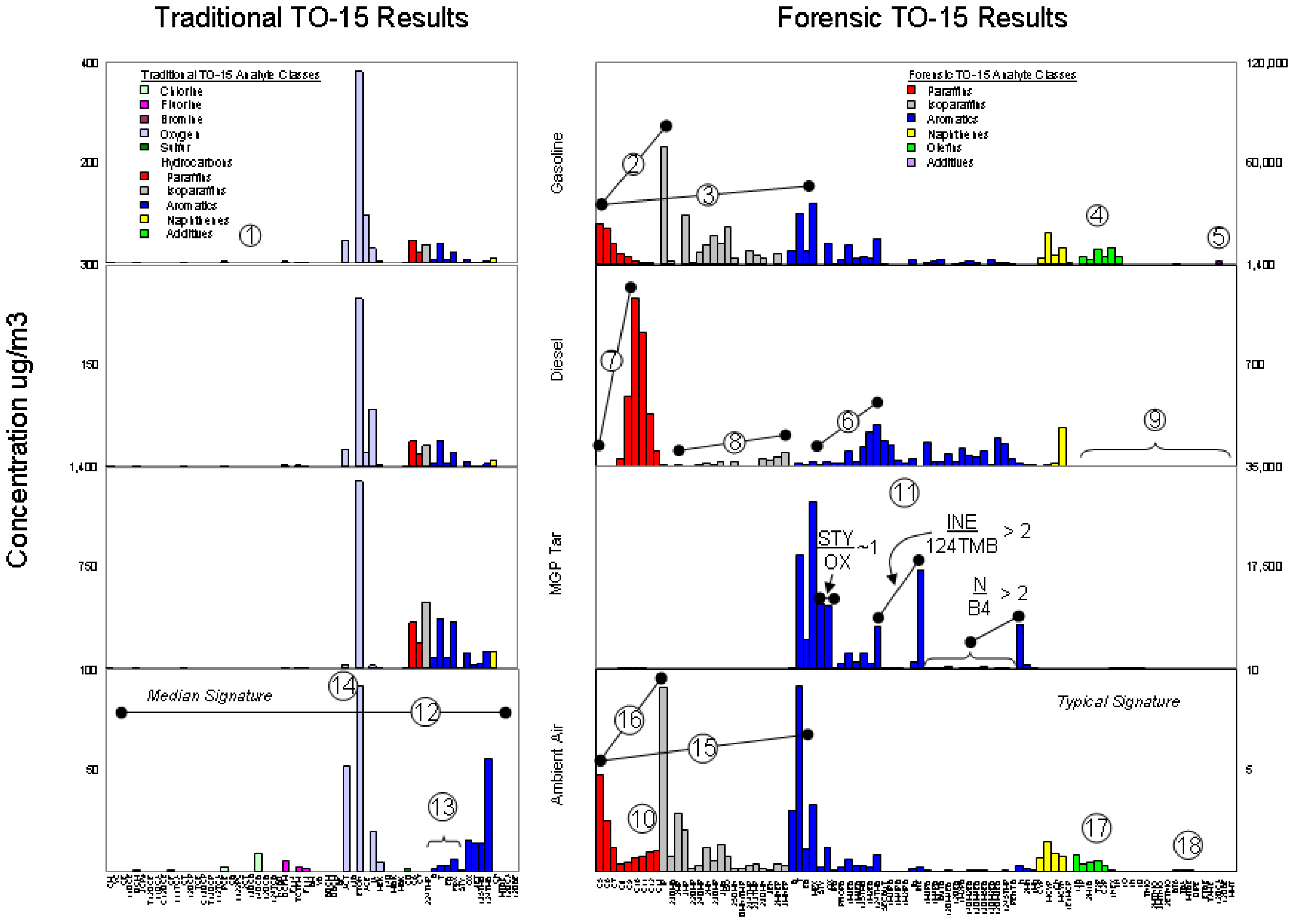

FIGURE 4-6. Concentrations and patterns of standard and forensic TO-15 analytes in source samples (See Tables 4-1 and 4-2 for complete analyte identities.)

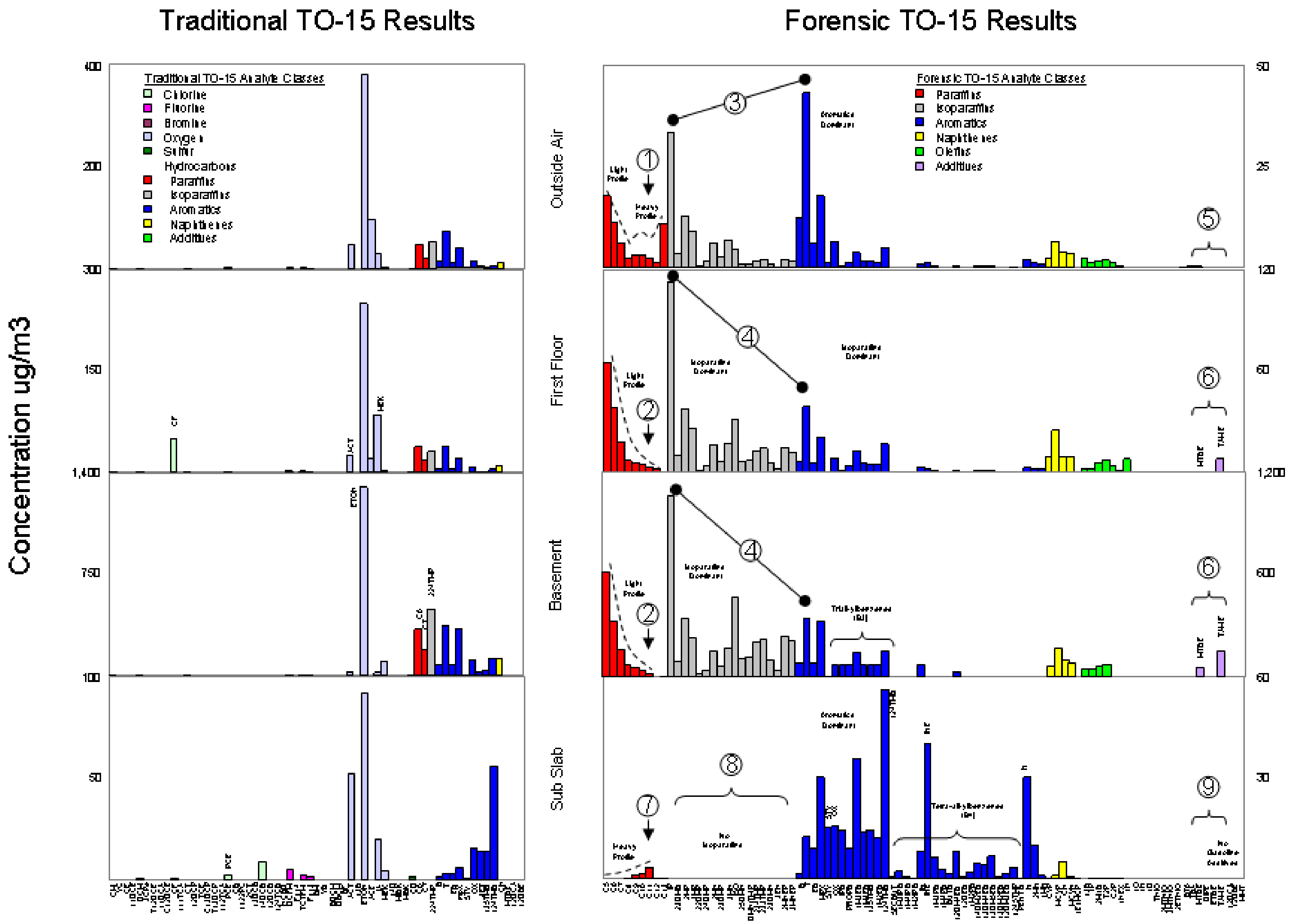

FIGURE 4-7. Concentrations and patterns of standard and forensic TO-15 analytes in residential samples (See Tables 4-1 and 4-3 for complete analyte identities.)

The composition of the sub-slab soil-gas sample differed significantly from the indoor air (Figure 4-7). First, the sub-slab concentrations were much lower than those measured in the basement air. This concentration gradient did not support a vapor intrusion pathway, because vapors should be diluted as they flow from the soil gas to indoor air. Second, the pattern of heavy aromatics in the soil gas (7) did not appear in the indoor air (2). Third, the absence of isoparaffins (8) and oxygenates (9) in the sub-slab soil gas confirmed the incompleteness of the vapor intrusion pathway.

The features listed above, along with the ratios of STY/OX, INE/1,2,4-TMB, and N/B4, could be interpreted as the possible influence of vapor migration from the downgradient MGP site. However, no degree of weathering or mixing could explain the compositional differences between soil gas and indoor air. Indeed, the proportion of tri-alkylated benzenes relative to xylenes was not perceptibly elevated in the basement as it should be if vapor intrusion occurred. These lines of evidence demonstrated that the vapor intrusion pathway was incomplete.

In summary, the compositional patterns and concentration gradients indicated the likely mixture of impacts from background indoor and outdoor sources within the residential property. Collectively, the Standard and Forensic Method TO-15 results demonstrated that vapor intrusion was not a source of indoor air contaminants in the sentinel building immediately downgradient from the historical source areas. This conclusion was based on the finding that (1) the concentrations of COPCs in the soil gas were too low to cause higher level impacts in indoor air and (2) the composition of soil gas differed from indoor air and could not share a common origin. No remedial action was required at this site to control the vapor intrusion pathway. Other buildings in the study area exhibited similar patterns differing most significantly in the composition of chlorinated, oxygenated, fluorinated, and brominated VOCs, attributed to variations in occupant activity and building materials.

4.9 Stable Isotopes

As described in the above case studies, Forensic Method TO-15 helps identify sources of volatile hydrocarbons. The forensic toolbox includes additional methods for identification of other VOC sources. One such technique relies on isotopic measurements that are especially useful when chemical fingerprinting proves inconclusive.

Determining the source of indoor methane (e.g., natural/thermogenic gas versus biogenic gas) typically relies upon stable isotopic parameters ($^{13}C/^{12}C$) (Lundegard, 2006). The carbon isotopic ratio of other target analytes can also be measured for most of the Standard TO-15 analytes. However, some degree of caution is warranted in using these techniques (Stout et al., 1998). They work best when the target analyte is easily separated from all other analytes chromatographically. In addition, isotopic fractionation can naturally alter the isotopic ratio ($^{13}C/^{12}C$) between the source and release areas. Instrument manufacturers and isotopic chemists are developing strategies to control these uncertainties. At present, the use of stable isotopes is not recommended unless all other options have been explored.

Application of stable isotopic methods suffers from several problems. First, most stable isotopic methods are non-standard and thus rarely perform in accordance with well-defined data quality criteria. Second, in many instances, the stable isotopic chromatographic resolution of target analytes is not complete, leading to interferences from other compounds. These resolutions should be demonstrated before, during, and after the sample analyses. Third, the isotopic fractionation typically requires the analysis of many samples along the vapor migration pathway to establish the type and degree of change over space and time. In many investigations, collection of such large datasets is operationally and practically prohibitive.

4.10 Recommended Forensic Analyses

Heightened regulatory scrutiny and increasingly complex modeling options stress the importance of measurement techniques that accurately and definitively confirm or refute vapor intrusion pathways. As the vapor intrusion toolbox grows and evolves, site investigators will face many challenges. The key to successful vapor intrusion evaluations includes:

- ☐ The selection of appropriate tools to substantiate the existence of a vapor intrusion pathway
- ☐ The differentiation of vapor intrusion impacts from confounding sources (including background)
- ☐ The credible protection of human health
- ☐ The satisfaction of regulatory compliance criteria.

Tiered environmental forensic investigations commonly begin with a review of EDA findings. This Tier 1 data review should address the following questions:

- ☐ What VOCs exceed applicable screening limits?
- ☐ What other VOCs are detected?
- ☐ Where have the VOCs been detected?
- ☐ What are the likely sources of the contamination?

These questions may suggest the need for advanced measurement techniques to augment the existing data. The most useful historical data for vapor intrusion investigations are commonly generated by Standard Method TO-15. Other methods provide useful information as well, especially during multimedia investigations. As demonstrated in the case studies, Forensic Method TO-15 proves especially valuable when determining the origin of hydrocarbon impacts for outdoor ambient air, soil-gas, and indoor sources. Other advanced methods, such as stable isotopic analyses, serve as emerging advanced techniques that are best applied within robust QA/QC frameworks. The advanced methods can help define and track the source signatures of the vapor-borne contamination and greatly improve the forensic investigator's ability to confirm or refute the presence of a complete vapor intrusion pathway.

4.11 Limitations of Recommended Procedures

As discussed in Appendix E, in addition to increased cost, analytical testing methods associated with forensic analyses necessitate a strong QA/QC program. The data quality criteria of Forensic Method TO-15 are far stricter than those prescribed for Standard Method TO-15. Although the use of such strict data quality criteria is always preferable, supplemental laboratory resources and capabilities may not be readily available.

4.12 References

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5. STATISTICAL METHODS

NOTE: In some cases, evidence can be derived from forensic and multivariate statistical methods. These methods are advanced procedures, which may not be applicable at many Navy sites. Statistical methods provide analytical procedures that build upon previous methods. The application of these advanced methods should be considered at sites involving petroleum contamination and out-of-the-ordinary vapor intrusion liabilities.

5.1 Overview

Statistical methods consist of procedures for comparing chemical concentrations or properties, measured or estimated, in various locations within the investigated media, including indoor and outdoor air, as well as subsurface soil, soil gas and groundwater. A typical vapor intrusion investigation may involve a variety of comparisons involving background data. The appropriate type and scope of the statistical procedure depends on the objective of the intended comparison.

BOX 5-1. Practical Tips: Recommended Statistical Methods

Statistical methods recommended in this section are multivariate techniques, primarily intended to provide confirmatory evidence for the earlier forensic method.

In general, the comparative statistical testing during a vapor intrusion investigation can be divided into two broad categories:

- ☐ **Individual comparison**: Comparison of a measured or computed value associated with a given chemical to its corresponding range of estimated or published background values – typically performed during EDA. The purpose and definition of individual comparisons are discussed in Section 5.1.1.
- ☐ **Multivariate comparison**: Comparison of chemical profiles of individual air samples – typically performed as part of a forensic analysis involving multiple chemicals measured in a variety of samples, including indoor, outdoor, and soil-gas samples to determine whether the investigated samples display similar chemical profiles. The purpose and definition of multivariate comparisons are discussed in Section 5.1.2.

The statistical comparisons listed above are not intended to be used as sole proofs of presence or absence of vapor intrusion impacts. Instead, they should be considered as complementary lines of evidence along with other physical and chemical observations. Each type of comparison entails specific and unique statistical procedures. None of the above comparisons can be applied without at least a representative set of site-specific samples. This section identifies the statistical methods that are appropriate to achieve each objective, discusses their limitations, and presents guidance for implementing each method.

Note: Background analysis of soil, sediment and groundwater data may involve various forms of statistical distributional comparisons, i.e., the statistical comparison of the entire distribution of measured site concentrations of a given chemical to the distribution of its corresponding background dataset. Distributional comparisons are typically performed to determine whether measured concentrations of a given chemical at a targeted location are significantly higher than those measured at their corresponding background locations. This type of comparison is rarely conducted during a vapor intrusion investigation due to its prohibitive data requirements.

5.1.1 Definition and Purpose of Individual Comparisons

BOX 5-2. Practical Tips: Individual Comparisons

In vapor intrusion investigations, individual measurements are often compared to published or outdoor/ambient concentrations. Results of such comparisons, i.e., exceedance or non-exceedance, should be viewed as preliminary findings, and only in tandem with other observations.

Individual comparisons refer to numeric comparisons of a measured or estimated value associated with a chemical in a given sample to its corresponding range of background values. Section 3 presented a number of individual comparisons used in the EDA process, including examples of appropriate use and application of individual comparisons. The limitations of individual comparisons and their impacts on ensuing findings must be acknowledged and discussed as an integral part of the EDA process.

5.1.2 Definition and Purpose of Multivariate Comparisons

Statistical procedures discussed here involve analyzing one chemical at a time; in statistics, such methods are referred to as *univariate* techniques. *Multivariate* comparison methods, on the other hand, are the general class of statistical procedures that analyze many variables simultaneously. In most vapor intrusion evaluations, investigators are concerned about vapor impact by multiple chemicals. In such cases, the chemical composition of given samples can be viewed as a collection of multiple variables.

Multivariate techniques provide quantitative tools for assessing the similarity of chemical compositions of various samples. These tools can be used to address questions about: (1) the presence or absence of compositional similarity among indoor samples when compared to those observed in outdoor and subsurface samples, (2) the distinct grouping of samples based on their chemical compositions, and (3) the chemical makeup of individual samples relative to known sources.

BOX 5-3. Practical Tips: Multivariate Comparisons

In some cases, evidence can be derived from forensic and multivariate statistical methods. These methods are advanced procedures, which may not be applicable at many Navy sites. Used in tandem with the forensic methods discussed earlier, multivariate comparisons offer confirmatory tools and provide additional lines of evidence.

Multivariate comparisons are statistical methods that simultaneously analyze many variables. In vapor intrusion investigations, these methods are used to assess if detected differences between chemical profiles of collocated/concurrent indoor air, outdoor air and soil-gas samples are statistically significant. In this document, these methods are recommended as confirmatory support of earlier forensic findings.

The application of these advanced methods should be considered at sites involving petroleum contamination and out-of-the-ordinary vapor intrusion liabilities.

Multivariate comparisons are often used as a component of the forensic phase of a vapor intrusion investigation. These comparisons recognize that the impacted indoor or outdoor air concentrations are often substantially attenuated when compared to near-source, subsurface results. To wholly or partially mitigate the attenuation effects, investigated data are usually subjected to pre-analysis data transformation (Johnson et al., 2002), sometimes referred to as "standardization" (Shields et al., 2006).

A common standardization technique is to divide the reported concentration of a chemical in a given sample by the sum of concentrations of all related chemicals in the same sample. Other techniques include dividing chemical concentrations in a given sample by the concentration of a key indicator chemical in the same sample. Such chemical-specific standardization is useful if the vapor source of interest has specific ratios associated with that chemical. Other data transformation options are discussed in various forensics related publications such as Johnson et al. (2002, Section 12.2.2) or Shields et al. (2006, Section 14.4.1), which address dioxin-specific data transformation options.

Through the above transformations, chemical concentrations are converted into dimensionless fractions or ratios. The collection of computed chemical fractions in each sample is regarded as the unique chemical profile of the sample, e.g., dioxin congener profile (Pleil and Lorber, 2007). Unlike measured concentrations, computed profiles are less prone to be affected by attenuation. For example, consider a diluted indoor air sample associated with an intruding vapor from an underlying soil contamination. When compared to the sub-slab soil-gas sample, the indoor sample has substantially lower concentrations. However, the diluted indoor sample still retains the profile of the contaminated soil gas. Multivariate techniques provide tools for simultaneous comparison of many chemicals in order to decipher profile similarities among various samples. These techniques are further discussed in Section 5.2.

5.1.3 Definition and Purpose of Distributional Comparisons

BOX 5-4. Practical Tips: Distributional Comparisons

Distributional comparisons are the most common statistical evaluations used in soil, sediment, and groundwater background analyses. These methods, however, require large site and background datasets, which often do not exist in a typical vapor intrusion investigation. Distributional comparisons are rarely used in background indoor analyses.

Distributional comparison methods refer to parametric and non-parametric statistical tests in which two or more groups of measured data are compared to determine whether their observed differences are statistically significant. These tests are commonly used in site versus background comparisons in soil, sediment and groundwater investigations. Detailed discussions of distributional comparisons in soil, sediment and groundwater are provided in the first three volumes of the DON *Guidance for Environmental Background Analysis* (Vol. 1 – Soil [2002], Section 4; Vol. II – Sediment [2003], Section 4; and Vol. III – Surface and Groundwater [2004], Section 4.2).

Application of the above distributional comparisons requires two conditions. First, available data must be divided into at least two groups, such as a potentially-impacted dataset (often referred to as the site dataset) versus a background dataset. Second, each dataset must contain a statistically adequate number of measurements. Note that the statistical adequacy of a dataset is directly driven by the variability of the investigated concentrations and the desired statistical confidence. Highly variable concentrations and/or stringent confidence levels result in large numbers of required measurements.

During typical vapor intrusion investigations, attaining the above conditions is almost always problematic. Indoor, outdoor, sub-slab and ambient air concentrations usually display large, multiple orders of magnitude variations (e.g., Folkes et al., 2009; Dawson and McAlary, 2009). Such conditions demand excessive numbers of samples (>>30 samples in each medium) to perform meaningful distributional comparisons, even when stringent confidence levels are forfeited. In most vapor intrusion investigations, collecting large numbers of samples compatible with the observed variability of measured concentrations is neither operationally, nor practically, feasible.

Distributional comparisons are rarely pursued in vapor intrusion analyses. An example includes the seven-year long study by NYSDOH (1997), which was conducted from 1989-1996. During this study, indoor and outdoor air samples were collected from 53 residences in the State of New York. All selected residences had neighborhood, construction, and occupancy similar to potentially impacted homes that were being investigated at the time. Despite the length and extent of this investigation, NYSDOH (2006, page 37) concluded that the background results constituted a small dataset.

In rare instances where adequately large site and background datasets can be generated, distributional comparison should be performed following procedures defined in Vol. I, Section 4 (DON, 2002), Vol. II – Sediments, Section 4 (DON, 2003), or Vol. III – Surface and Groundwater, Section 4.2 (DON, 2004), which provide guidelines regarding the following questions:

- What distributional procedures or tests should be used to determine if a chemical is a COPC?
- What testing approaches should be avoided to reduce the probability of falsely concluding that a chemical is a COPC?
- How is the minimum number of measurements needed for the selected statistical test determined?
- How is the selected statistical test performed?

5.1.4 Limitations of Recommended Statistical Procedures

All of the statistical methods discussed and recommended in this section are based on a number of factors that limit their applicability. Prior to any statistical comparisons these factors must be assessed and, if necessary, alternative procedures must be pursued. The main limiting factors are discussed below.

- ***Over-conservative Comparisons:*** Individual comparisons involving a specific numeric benchmark or threshold value are inherently over-conservative, i.e., they tend to incorrectly identify individual measurements as above benchmark, even when the measured values belong to the background population. To avoid this problem, this document recommends individual comparisons involving the range of background values (Sections 3.1 and 3.2). For further discussion, readers are referred to Vol. III – Surface and Groundwater, Section 4.3 (DON, 2004).

- ***Published Background Benchmarks:*** Currently available published background indoor concentrations are based on a few state and national datasets, which are representative of a finite range of site conditions (e.g., NYSDOH, 2006, Appendix C; Dawson and McAlary, 2009). Site-applicability issues of any published dataset must be considered prior to its use in a vapor intrusion investigation.

- ***Disputed or Advanced Procedures:*** In some cases, the application of the selected statistical method is disputed, or site conditions justify the use of more advanced methods. In such situations, involvement of an experienced environmental statistician or geostatistician is highly recommended.

5.2 Multivariate Comparisons

In vapor intrusion investigations, multivariate procedures of interest include the statistical classification methods, which are used to distinguish samples based on their compositional features. Among these multivariate techniques are principal component analysis (Pielou, 1984; Johnson et al., 2002), cluster analysis (Harman, 1970), and finite mixture distributions (Everitt and Hand, 1981). Other methods, such as discriminate function analysis (Hand, 1981; Gibbons, 1994), group investigated sample results according to known patterns associated with background versus site-related releases.

Multivariate comparisons are often used as a component of the forensic analysis. A typical forensic analysis produces findings based on chemical compositions of individual samples about possible sources of detected chemicals. Samples impacted by the same source are expected to share similar chemical profiles. Confirmation of such findings is often performed using statistical classification methods. A suitable confirmatory method should possess the following characteristics:

- The procedure must analyze the data without any biased and/or arbitrary assumptions.
- The procedure must utilize the available data in the most effective manner, i.e., the entire dataset must be considered and analyzed.
- The procedure must have been demonstrated to be an effective and reliable tool for grouping similar multivariate samples.

One of the most common techniques for classification of multivariate samples (and meets the above criteria) is principal component analysis (Jolliffe, 1986; Johnson et al., 2002).

5.3 Principal Component Analysis

Principal component analysis has been applied to numerous multivariate environmental datasets for deciphering similar chemical profiles among the investigated samples. Examples include:

- Grouping of water quality parameters using plots of principal components (Helsel and Hirsch, 1992; page 59)
- Projection of multivariate ecological data onto two-dimensional graphs to reveal their intrinsic patterns (Pielou, 1984; Section 4.2)
- Grouping of monitoring wells based on their time series patterns (Rouhani and Wackernagel, 1990)
- Grouping of dioxin sources based on their congener profiles (Shields et al., 2006; page 309).

Principal component analysis views each investigated chemical as a variable. For example, Table 5-1 lists five petroleum-related VOCs measured in a number of indoor, outdoor, and subsurface samples at the hypothetical Alpha Naval Base. Principal component analysis views this dataset as a five-dimensional dataset. Multivariate analysis of such a dataset, i.e., simultaneous evaluation of five chemicals in a multitude of samples, is a challenging analytical task.

One option is to reduce the dimensionality of the dataset based on the correlations among the investigated variables. For this purpose, the dataset is mathematically transformed into a new set of uncorrelated reference variables, referred to as principal components. This transformation is accomplished based on the correlations exhibited by the investigated variables. The stronger the correlations among the variables, the fewer principal components are necessary to explain the variability of the investigated data.

Each principal component is a linear combination of the investigated variables. The coefficients in these linear combinations are referred to as the *loadings.*[2]

Each principal component explains part of the variability of the investigated data. The principal components are ranked as first to last according to their ability to explain the data variability. The principal component that explains most of the variability of the dataset is referred to as the first principal component. In many cases, the first few principal components can adequately explain the variability of the investigated data. In such instances, the complicated multidimensional problem can be reduced to a simple one or two dimensional graphic problem. For more information about principal component analysis, readers are referred to Horn and Johnson (1985), Golub and Van Loan (1996), and Strang (1998). Appendix F provides an intuitive example to assist RPMs in understanding the intricacies of principal component analysis.

When the investigated variables are correlated, the first two or three principal components account for a large percentage of the variability of the dataset. In such cases, each sample is identified by the values of its first few principal component scores. Therefore, rather than a simultaneous analysis of many variables in a multitude of samples, the relationship between samples can be assessed by simple inspection of a two- or three-dimensional plot, also referred to as the principal components scores plot.

Due to the mathematically complicated nature of principal component analysis, an intuitive example with extensive commentary is provided in Appendix F to introduce the reader to basic elements of principal component analysis.

The following subsections discuss steps taken during a typical principal component analysis.

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[2] In mathematical terms, the loadings associated with each principal component constitute an *eigenvector* of the correlation matrix, and the portion of the variability that is explained by this component is proportional to its corresponding *eigenvalue*.

TABLE 5-1. Site-specific petroleum-related VOC concentrations

Medium	Location	Pressure Condition	Sample ID	Concentrations (µg/m^3)				
				Benzene	**Ethylbenzene**	**Toluene**	**Xylenes, *m,p*-**	**Xylene, *o*-**
Indoor Air	1	Negative	IA-1_Neg	0.65	0.89	3.21	1.31	0.56
		Positive	IA-1_Pos	0.86	0.77	6.90	2.14	0.77
	2	Negative	IA-2_Neg	0.71	1.43	3.69	1.67	0.64
		Positive	IA-2_Pos	0.89	1.55	4.05	3.45	1.12
	3	Negative	IA-3_Neg	0.69	1.67	4.52	1.79	0.70
		Positive	IA-3_Pos	0.87	1.08	4.17	2.38	0.84
Outdoor Air	1		OA-1	0.75	0.33	2.50	0.88	0.35
	2		OA-2	0.67	0.32	1.79	0.89	0.32
Subsurface Soil Gas	1	Negative	SG-1_Neg	31	<120	<120	309	<120
		Positive	SG-1_Pos	<34	<170	<170	<170	<170
	2	Negative	SG-2_Neg	<34	<170	<170	<170	<170
		Positive	SG-2_Pos	<19	<96	<96	<96	<96
	3	Negative	SG-3_Neg	<11	<56	<56	<56	<56
		Positive	SG-3_Pos	<12	<60	<60	<60	<60
	4	Negative	SG-4_Neg	<24	<120	<120	<120	<120
		Positive	SG-4_Pos	<43	<210	<210	<210	<210

5.3.1 Formulate the Problem

Prior to the initiation of principal component analysis, the problem at hand must be clearly formulated. Specifically, the multivariate questions that are being addressed must be verbalized. For example, the building in the hypothetical Alpha Naval Base is situated in the vicinity of a groundwater plume containing various VOCs. As discussed in Section 3.6, the EDA results indicate that petroleum-related VOCs, i.e., benzene, ethylbenzene, toluene, *m,p*-xylenes, and *o*-xylene, are associated with background sources.

If the above EDA finding is correct, then the chemical profiles of indoor samples should be quite distinct from those measured in subsurface samples. Furthermore, the profiles of indoor samples measured under negative and positive pressures should not differ significantly. These outcomes can be verbalized as two multivariate questions: (1) Do indoor samples display distinct VOC profiles when compared to those measured in subsurface samples? (2) Are VOC profiles of indoor samples measured under negative pressure more similar to subsurface profiles than those detected under positive pressure?

The above questions involve chemical profiles of samples, which as discussed before are multivariate measures. Addressing these questions requires simultaneous analysis of five VOCs in 16 different samples. Such multivariate questions are well suited for a principal component analysis.

5.3.2 Conduct the DQO Planning Process

The stakeholders and regulators, with the assistance of an experienced environmental statistician, should use the DQO planning process to agree on:

- The merit and relevance of the formulated multivariate problem and questions
- The representativeness of the available indoor, outdoor, and sub-slab sample datasets
- The list of COPCs and related chemicals (related chemicals are those that do not pose any elevated risk or concern, however, their magnitudes can assist in deciphering the source of detected COPCs)
- The choice of pre-analysis data standardization (e.g., fractions versus concentrations)
- The choice of principal component analysis for statistical classification of the investigated data.

Early concurrence of stakeholders and regulators facilitates communication and improves the chances that the ensuing analytical results are accepted. This is particularly important given the fact that some stakeholders may consider vapor intrusion as an immediate danger, rather than a hypothetical risk.

5.3.3 Implement Principal Component Analysis

The general procedure for conducting a principal component analysis is shown in Box 5-5. Appendix F also presents an intuitive example to highlight the computational steps of a typical principal component analysis.

Principal component analysis is further discussed through the hypothetical case study, introduced in Section 2, which focuses on the chemical profiles of petroleum-related VOCs, as listed in Table 5-2. As noted before, the multivariate questions formulated are:

- ❑ Do indoor samples display distinct VOC profiles when compared to those measured in outdoor and subsurface samples?
- ❑ Are VOC profiles of indoor samples measured under negative pressure more similar to subsurface profiles than those detected under positive pressure?

As a first step, the bivariate plots of the five petroleum-related VOCs are generated, as displayed in Figure 5-1. In this case, each plot displays pairs of measured VOC values in the 16 investigated samples. These plots show strong correlations between paired VOCs, as manifested by linear patterns of their plotted dots. Such correlations indicate that the five-dimensional dataset can be simplified into a much smaller set of principal components.

For this purpose, measured concentrations are converted into fractions, i.e., ratio of a measured VOC divided by the total mass of measured VOCs in the same sample, as listed in Table 5-2. The statistical software then computes the correlation matrix of paired VOC fractions. Subsequently, the correlation matrix is mathematically decomposed using the *eigendecomposition* procedure (e.g., Golub and Van Loan, 1996).

BOX 5-5. Procedure for Conducting Principal Component Analysis

- Formulate the problem at hand; identify the EDA and/or forensic findings that have to be confirmed. Verbalize the issues of interest as multivariate questions. Accordingly, identify the appropriate data transformation that needs to be conducted prior to the initiation of principal component analysis.
- Stakeholders and regulators use the DQO process to agree upon the representativeness of the available data, the use of principal component analysis as a confirmatory procedure in support of the earlier EDA and/or forensic findings, as well as the selected statistical software.
- Perform the appropriate data standardization procedure. For example, convert reported VOC concentrations into fractions of total detected mass of VOCs, i.e., fractions.
- Using the standardized dataset, implement principal component analysis.
- Review various outputs of principal component analysis, including principal component loadings. In some cases, the pattern of computed loadings among the first few principal components may allow chemical interpretations.
- Determine the number of the first few principal components that adequately explain the variability of the dataset. Based on the selected components, compute and plot the individual principal component scores of all investigated samples.
- Inspect the score plot to determine groupings/clustering among the investigated samples. Samples with similar chemical profiles tend to have similar scores.
- Throughout the above steps, involvement of an experienced environmental statistician is required. Care must be taken to focus on specific findings, i.e., presence or absence of profile similarities, while avoiding unsubstantiated and/or speculative conclusions.

TABLE 5-2. Site-specific petroleum-related VOC concentrations and profiles

Sample ID	Concentrations (μg/m^3)					Fractions*				
	Benzene	Ethylbenzene	Toluene	Xylenes, *m,p-*	Xylene, *o-*	Benzene	Ethylbenzene	Toluene	Xylenes, *m,p-*	Xylene, *o-*
IA-1_Neg	0.65	0.89	3.21	1.31	0.56	0.099	0.135	0.485	0.197	0.084
IA-1_Pos	0.86	0.77	6.90	2.14	0.77	0.075	0.068	0.603	0.187	0.068
IA-2_Neg	0.71	1.43	3.69	1.67	0.64	0.088	0.175	0.453	0.205	0.079
IA-2_Pos	0.89	1.55	4.05	3.45	1.12	0.081	0.140	0.366	0.312	0.101
IA-3_Neg	0.69	1.67	4.52	1.79	0.70	0.074	0.178	0.483	0.191	0.075
IA-3_Pos	0.87	1.08	4.17	2.38	0.84	0.093	0.116	0.446	0.255	0.090
OA-1	0.75	0.33	2.50	0.88	0.35	0.156	0.069	0.520	0.183	0.072
OA-2	0.67	0.32	1.79	0.89	0.32	0.167	0.081	0.448	0.224	0.081
SG-1_Neg	31	<120	<120	309	<120	0.059	0.115	0.115	0.595	0.115
SG-1_Pos	<34	<170	<170	<170	<170	0.048	0.238	0.238	0.238	0.238
SG-2_Neg	<34	<170	<170	<170	<170	0.048	0.238	0.238	0.238	0.238
SG-2_Pos	<19	<96	<96	<96	<96	0.047	0.238	0.238	0.238	0.238
SG-3_Neg	<11	<56	<56	<56	<56	0.047	0.238	0.238	0.238	0.238
SG-3_Pos	<12	<60	<60	<60	<60	0.048	0.238	0.238	0.238	0.238
SG-4_Neg	<24	<120	<120	<120	<120	0.048	0.238	0.238	0.238	0.238
SG-4_Pos	<43	<210	<210	<210	<210	0.049	0.238	0.238	0.238	0.238

* Fractions are computed by substituting non-detects by one-half detection limits.

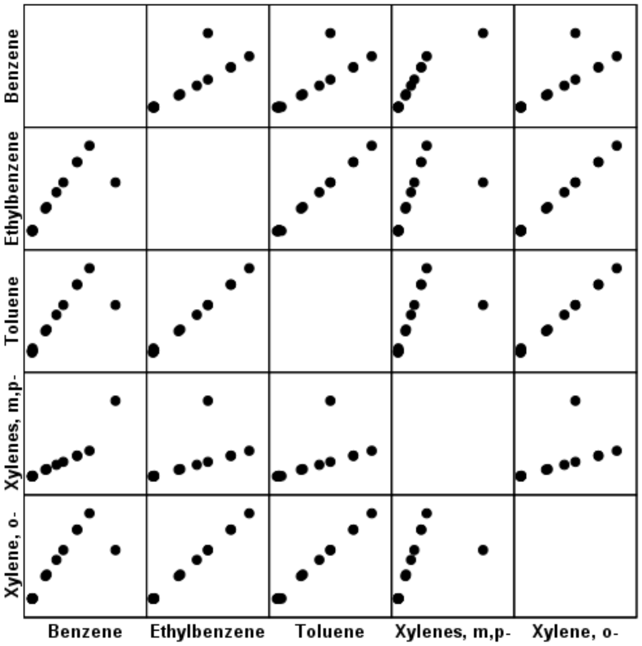


FIGURE 5-1. Bivariate plots of site-specific petroleum-related VOC concentrations

The resulting *eigenvectors* are the loadings of various principal component scores. The principal components associated with the highest *eigenvalues* are those that best explain the variability and patterns exhibited by individual samples.

5.3.4 Interpret Results

Table 5-3 presents the results of the principal component analysis. As indicated in this table, the first two rotated principal components account for 92% of the dataset variability. This implies that the five variables associated with each sample can be replaced by only two principal component scores, without much information loss.

BOX 5-6. Practical Tips: Interpreting Results of a Principal Component Analysis

RPMs should study the example in Appendix F to get acquainted with interpreting the results of a principal component analysis. In vapor intrusion investigations principal component results are primarily used for confirmation of earlier forensic findings. Thorough interpretation of these statistical results, however, requires involvement of experienced personnel familiar with multivariate environmental statistics.

The computed loadings indicate that each principal component is dominated by a specific group of VOCs. For example, the first principal component (PC1), explaining 64% of variances, is dominated by the fractions of benzene, ethylbenzene, toluene and *o*-xylene, where benzene and toluene fractions display patterns opposite to those of other dominant VOCs. The second principal component (PC2), explaining 28% of variances, is dominated primarily by *m,p*-xylenes.

Using the above loadings, Figure 5-2 displays the two-dimensional score plot of investigated samples. Simple inspection of this plot indicates presence of distinct clusters, consisting of indoor, outdoor and subsurface samples, respectively. Such clustering leads to the following findings:

- Measured indoor petroleum-related VOCs have chemical profiles that are clearly distinct from those displayed in subsurface samples. This finding is further confirmed by the comparison of chemical profiles of various sample groups, as demonstrated in Figure 5-3.

- Outdoor samples show profiles that are relatively similar to those measured indoors. This finding is further confirmed by the comparison of chemical profiles of indoor and outdoor sample groups, as demonstrated in Figures 5-3 and 5-4.

Positive or negative pressure condition does not appear to have caused significant alternations in chemical profiles of indoor VOCs. This finding is further confirmed by the comparison of chemical profiles of indoor VOCs measured under positive and negative pressure conditions, respectively, as demonstrated in Figure 5-4.

5.3.5 Summarize Findings

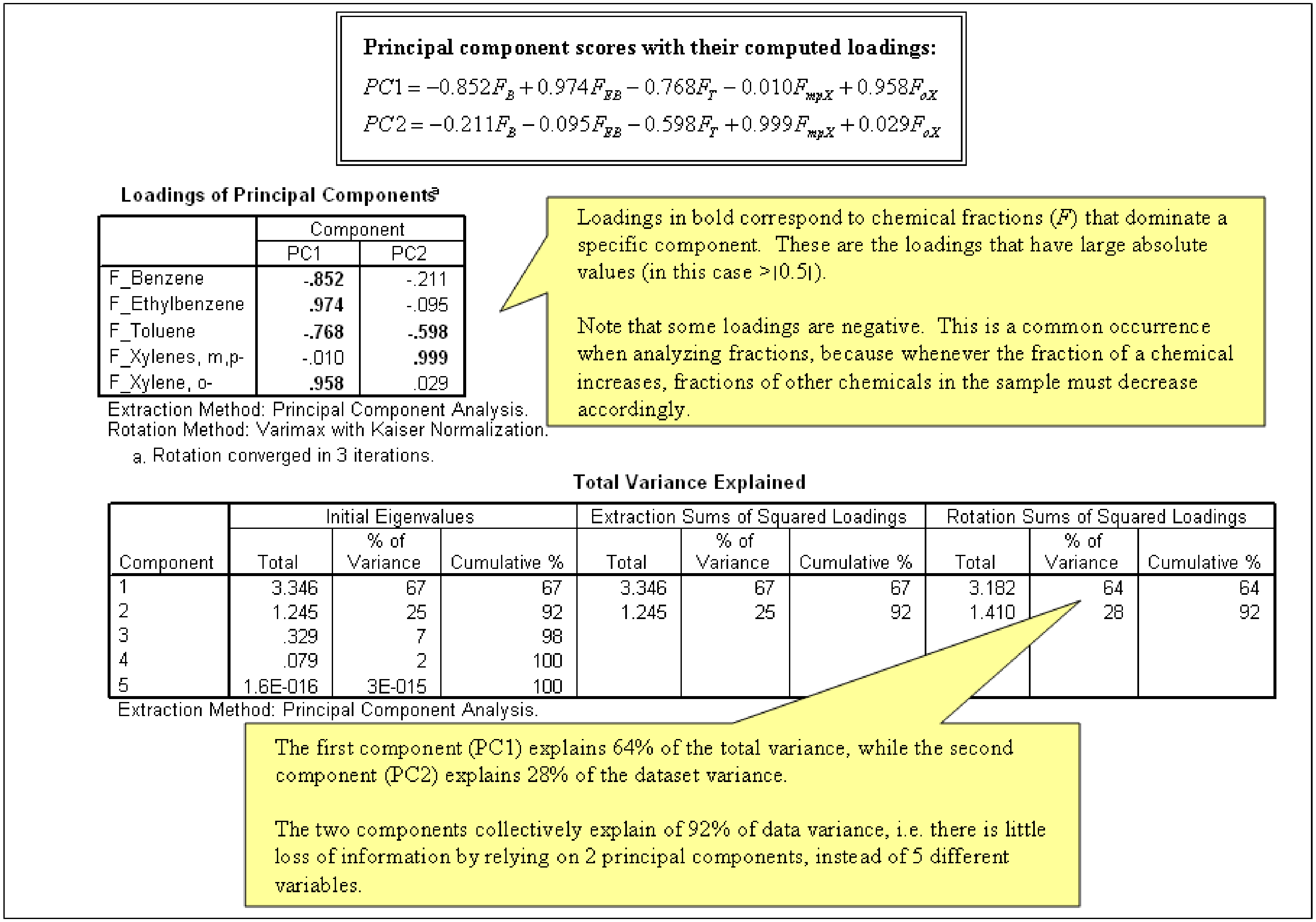
Upon completion of principal component analysis, its results must be summarized to address the formulated multivariate questions. In the hypothetical case study, this summary indicates that the original questions may be answered as follows:

- Indoor samples display distinct VOC profiles when compared to those measured in subsurface samples.

- The chemical profiles of outdoor samples are relatively similar to those measured indoors.

- VOC profiles of indoor samples measured under negative and positive pressure are similar, but clearly distinct from those measured in the subsurface.

The above answers provide further support for the earlier EDA findings (Section 3.6), which indicate that the indoor petroleum-related VOCs are not associated with subsurface sources. In fact, their likely source appears to be outdoor emissions.



Principal component scores with their computed loadings:

$$PC1 = -0.852F_B + 0.974F_{EB} - 0.768F_T - 0.010F_{mpX} + 0.958F_{oX}$$

$$PC2 = -0.211F_B - 0.095F_{EB} - 0.598F_T + 0.999F_{mpX} + 0.029F_{oX}$$

Loadings of Principal Components[a]

	Component	
	PC1	PC2
F_Benzene	**-.852**	-.211
F_Ethylbenzene	**.974**	-.095
F_Toluene	**-.768**	**-.598**
F_Xylenes, m,p-	-.010	**.999**
F_Xylene, o-	**.958**	.029

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.

a. Rotation converged in 3 iterations.

Loadings in bold correspond to chemical fractions (F) that dominate a specific component. These are the loadings that have large absolute values (in this case >|0.5|).

Note that some loadings are negative. This is a common occurrence when analyzing fractions, because whenever the fraction of a chemical increases, fractions of other chemicals in the sample must decrease accordingly.

Total Variance Explained

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	3.346	67	67	3.346	67	67	3.182	64	64
2	1.245	25	92	1.245	25	92	1.410	28	92
3	.329	7	98						
4	.079	2	100						
5	1.6E-016	3E-015	100						

Extraction Method: Principal Component Analysis.

The first component (PC1) explains 64% of the total variance, while the second component (PC2) explains 28% of the dataset variance.

The two components collectively explain of 92% of data variance, i.e. there is little loss of information by relying on 2 principal components, instead of 5 different variables.

TABLE 5-3. Principal component analysis of petroleum-related VOC fractions
(Results produced by SPSS 15.0 for Windows, Release 15.0.1, November 22, 2006.)

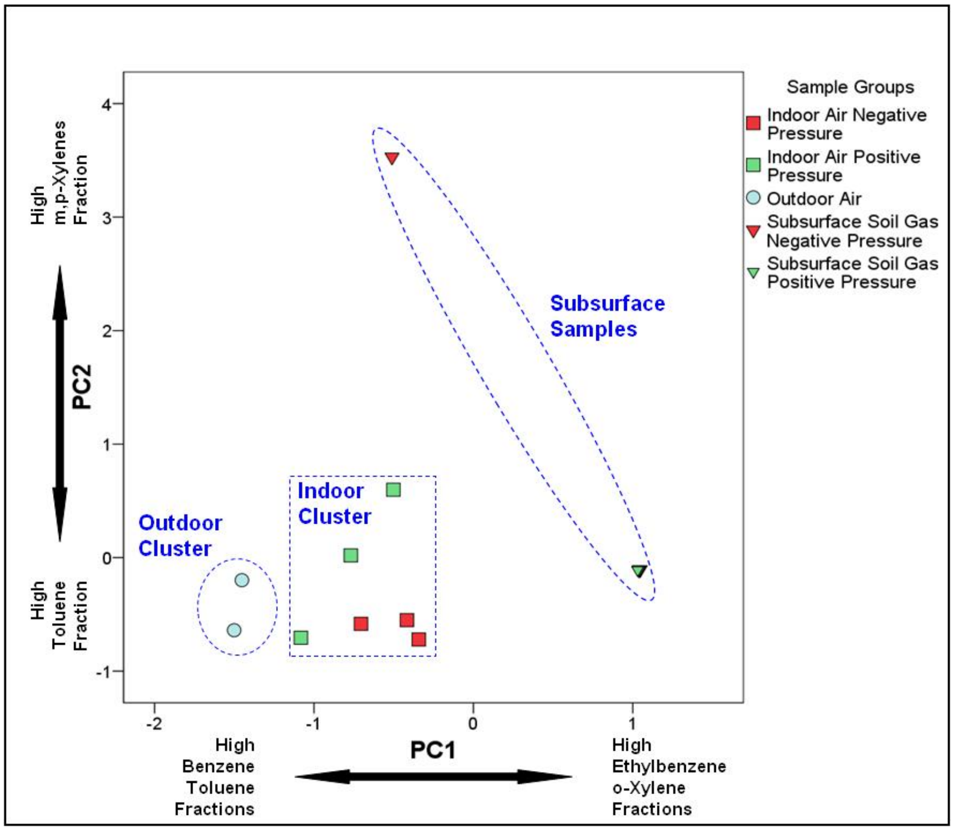


FIGURE 5-2. Principal component score plot of the investigated samples (Dominant chemical fractions are identified along each axis.)

5.3.6 Analytical Limitations of Principal Component Analysis

Principal component analysis provides mathematically effective tools to group investigated air samples in accordance with their multivariate chemical compositions. However, like any statistical procedure, it has certain limitations:

- ❑ Principal component analysis requires a value for each investigated chemicals in every sample considered. Principal component analysis cannot analyze a dataset with any value missing. Non-detects must be substituted by numeric values.
- ❑ Non-detect substitutions can introduce bias and error in the analysis. Datasets with a large percentage of non-detects should not be subjected to principal component analysis.
- ❑ Principal component analysis is conducted through the use of statistical software. Commonly used, QA/QC statistical software packages, such as SAS (www.SAS.com), SPSS (www.spss.com), and Minitab (www.Minitab.com), among others, provide extensive options for various classification methods, including principal component analysis. However, the use of such software often requires special training.
- ❑ Due to the advanced nature of principal component analysis, involvement of an experienced environmental scientist is usually required.
- ❑ Principal component analysis is prone to misuse. To avoid speculative and unsubstantiated findings, principal component analysis should be used as a confirmatory tool for earlier exploratory and forensic results.

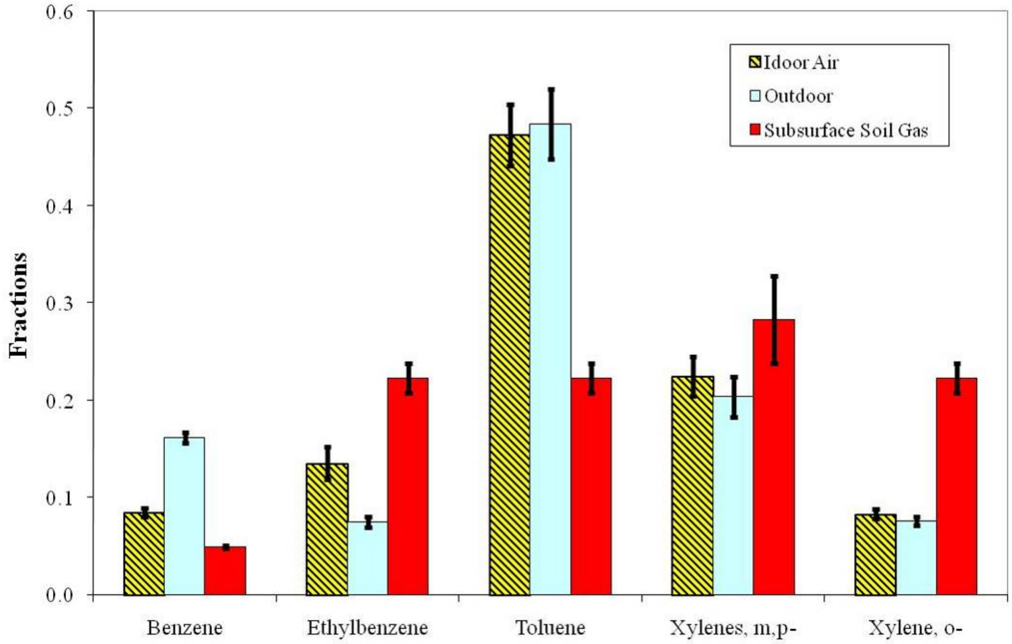


FIGURE 5-3. **Average petroleum-related VOC profiles of investigated sample groups (Error bars represent <u>+</u> standard error.)**

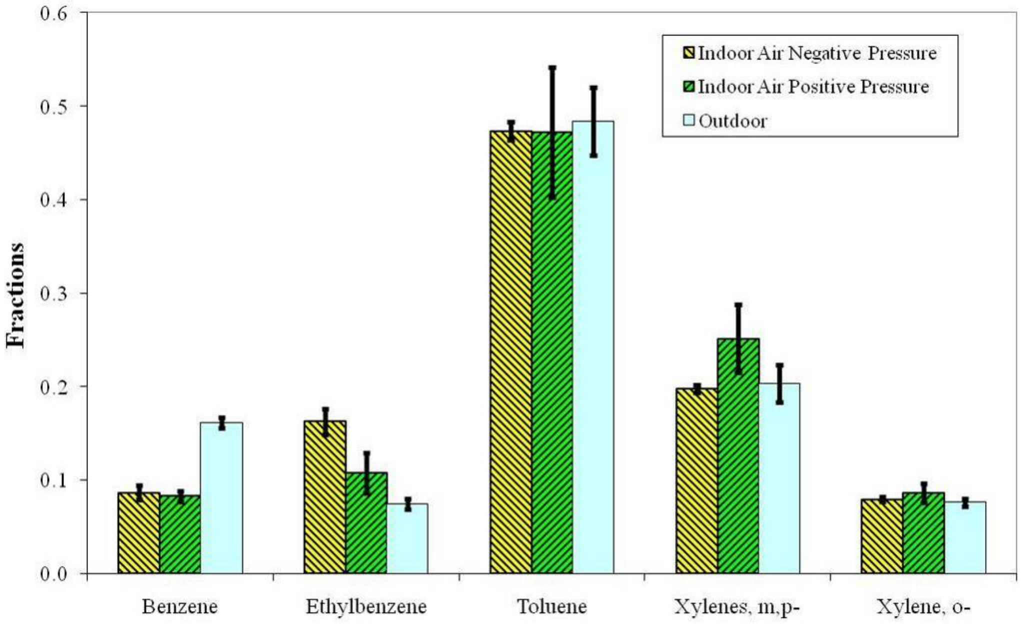


FIGURE 5-4. **Average petroleum-related VOC profiles of indoor sample groups under various pressure conditions**
(Error bars represent <u>+</u> standard errors.)

- The complicated nature of principal component analysis often entails supplementary interactions before stakeholders' concurrence can be attained.

5.4 Advanced Statistical Procedures

As noted earlier, the recommended statistical procedures discussed throughout this section are designed for specific uses in a typical vapor intrusion investigation. The scope of some investigations may require the use of alternative or more advanced comparative methods. For example, some investigations aim at determining the proportions of detected analytes associated with specific sources (i.e., source attribution) or quantifying similarities between sample profiles. These objectives can be addressed by advanced statistical methods, including:

- **Alternative Classification Methods:** In many instances, alternative classifications may be considered for grouping the investigated samples. Among these multivariate techniques are cluster analysis (Harman, 1970), which provides automatic procedures for assigning samples into subsets or clusters. For this purpose, differences between samples are quantified in terms of so-called "distance measures," which determine how the similarity of two samples is calculated. A variety of distance measures can be used for clustering purposes (Pielou, 1984, Section 2). The flexibility provided by distance measures may be advantageous under certain field conditions.
- **Source Attribution Modeling:** Principal component analysis is mainly intended to assess the grouping of the investigated multivariate data. In some cases, quantitative attribution of specific sources in each sample is also desired. Source attribution or "receptor" modeling refers to procedures for inferences of sources and their contributions. As noted by Johnson et al. (2002), the objectives of receptor modeling are to determine (1) the number of sources with distinct chemical profiles in the investigated site, (2) the chemical composition of each source, and (3) the contribution of each source in each sample. Other methods such as discriminate function analysis (Hand, 1981; Gibbons, 1994) also provide procedures to group investigated sample results according to known patterns associated with background versus site-related releases.
- **Geostatistics:** In many cases, site and background data are spatially correlated. Under such instances, geostatistical methods (Journel and Huijbregts, 1978; Isaaks and Srivastava, 1989) can be used. These methods incorporate the spatial correlation of the data into the estimation process. If background data display a strong spatial correlation, location-specific benchmarks may be estimated using geostatistical procedures.

Applications of the above techniques and other advanced statistical procedures require direct involvement and advice of an experienced environmental statistician or geostatistician.

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APPENDIX A: COMPOSITIONAL FEATURES OF COMMONLY ENCOUNTERED CHEMICALS

The identification of ambient background benefits from an understanding of contaminant sources in the indoor environment. Appendix A summarizes the composition of commonly encountered products capable of impacting indoor air.

A.1 Background Air

The composition of air by volume is approximately 78.08% nitrogen, 20.95% oxygen, 0.93% argon, 0.038% carbon dioxide, and trace amounts of other gases (Table A-1). Air also contains variable proportions of water vapor (approximately 1% to 4%). The concentration of airborne anthropogenic substances generally increases with human population density and human activity, i.e., rush hour (Hobbs, 2000).

TABLE A-1. Composition of atmospheric air

Gas	Fraction (ppmv)	Percent	Ref
Nitrogen (N_2)	780,840	78.08%	1
Oxygen (O_2)	209,476	20.95%	1
Argon (Ar)	9,340	0.93%	1
Carbon dioxide (CO_2)	383	0.038%	2
Neon (Ne)	18.18	0.0018%	1
Helium (He)	5.24	0.00052%	1
Methane (CH_4)	1.745	0.00017%	3
Krypton (Kr)	1.14	0.00011%	1
Hydrogen (H_2)	0.55	0.000055%	1
Nitrous oxide (N_2O)	0.3	0.000030%	1
Xenon (Xe)	0.087	0.0000870%	1
Ozone (O_3)	0.07	0.0000070%	1
Nitrogen dioxide (NO_2)	0.02	0.0000020%	1
Iodine (I)	0.01	0.0000010%	1
Carbon monoxide (CO)	trace	trace	1
Ammonia (NH_3)	trace	trace	1

* This is the composition at sea level, 15°C, 101.3 kPa.

(1) *CRC Handbook of Chemistry and Physics*, edited by David R. Lide, 1997.

(2) NASA Earth Fact Sheet. Updated 20 May 2010. http://nssdc.gsfc.nasa.gov/planetary/factsheet/earthfact.html.

(3) IPCC TAR Table 6.1; Available at: http://www.grida.no/publications/other/ipcc_tar/?src=/climate/ipcc_tar/wg1/221.htm.

Common sources of anthropogenic emissions include vehicles, heating equipment, power plants, manufacturing processes, and dry cleaning operations. In addition, many materials off-gas within living spaces (for example, adhesives, paints, fuel storage containers, dry cleaning goods, aerosol spray cans, rugs, and electrical equipment). Other activities, such as bread baking, entail emission of biochemical metabolites such as ethanol. Subsurface soil gas also exhibits background compositional patterns. Subsurface VOCs can originate from natural oil/gas seeps, leaks from oil or gas production wells, natural gas or other pipelines, landfills, and hydrocarbon-contaminated soil and groundwater.

Full identification of background sources can require a prohibitive number of samples. As a result, environmental investigators judiciously select a limited number of samples in key locations based on an inspection of the building and the available historical data. Often these investigations include site-specific background outdoor sampling (NYSDOH, 2006). While such data are useful, they only partially represent background indoor conditions. Indoor air, not impacted by subsurface sources, is influenced by numerous indoor sources, as well as those associated with outdoor emissions.

A.2 Refrigerants

Refrigerants transfer heat by changing phases (e.g., liquid to gas or gas to liquid) during a mechanically assisted vapor compression cycle (Whitman, 2004). In addition to desirable thermodynamic properties, the best refrigerants are noncorrosive, nonflammable, and nontoxic for humans. Early refrigerants (chloromethane, sulfur dioxide gas, and anhydrous ammonia) transferred heat effectively, but possessed varying toxicity.

In 1930, DuPont invented a class of chlorofluorocarbons (CFCs) known as Freons that rapidly replaced earlier refrigerants and propellants because they were odorless, colorless, nonflammable, noncorrosive, and relatively nontoxic (Table A-2) (Stoecker, 1998). As a class of many compounds, CFCs also exhibited a wide range of thermodynamic properties that satisfied almost any application. For example, automobile and small refrigerator manufacturers preferred dichlorodifluoromethane (a.k.a., Freon-12, R-12, or CFC-12), while central air conditioning manufacturers often preferred chlorodifluoromethane (a.k.a., Freon-22, R-22, or HCFC-22). However, manufacturers stopped producing Freon-12 in 1995 and production of Freon-22 will end in 2020 as dictated by Federal environmental regulations.

Alternative refrigerants include 1,1,1,2-tetrafluoroethane (R-134a), difluoromethane (a.k.a., R-32 or HFC-32), and 1,1,2,2,2-pentafluoroethane (a.k.a., R-125 or HFC-125). Some other popular or proposed refrigerants include methyl formate, chloromethane, dichloromethane, and propane. Many additional refrigerants are used in specialized applications. The specific mixture and stability of refrigerants frequently helps forensic investigators track vapor sources.

A.3 Propellants

Propellants are routinely used in spray cans filled with cosmetic products, paints, insecticides, cleansers, static guards, fire extinguishers, and many other products (Rodney, 2004). The propellant is typically a substance with a boiling point slightly lower than room temperature. The low vapor pressure allows the liquid propellant to remain in equilibrium at a safe pressure during storage. When the valve opens, the product vents, the liquid propellant evaporates, and the spray can repressurizes. These steps occur simultaneously until the vaporization of the liquid propellant is complete.

The earliest propellants consisted of compressed air and light hydrocarbons in the 1800s. In the late 1800s and early 1900s, fire extinguishers commonly used carbon tetrachloride propellant. Product manufacturers used CFC propellants extensively from the 1920s through the 1980s (Table A-2). In the 1960s, many fire extinguishers contained bromofluoroalkanes with superior fire suppression capabilities.

Rapid changes occurred in 1989 when the Montreal Protocol and the U.S. Clean Air Act phased out CFCs (United Nations Environment Programme [UNEP], 1999). Chemical engineers developed a variety of new propellants with the understanding that chlorine and bromine degrade atmospheric ozone while fluorine and iodine pose little, if any, ozone toxicity. The non-flammable CFC replacements include nitrous oxide and carbon dioxide for fire suppressants and foods. Halogenated propellants persist for specialized applications, for example, hydrofluoroalkanes (HFAs) in medical devices. The flammable CFC replacements chiefly include propanes, *n*-butane, isobutene, dimethyl ether (DME), and methyl ethyl ether. These flammable substitutes are often blended with mercaptans to safely ensure early leak detection.

A.4 Adhesives

Adhesives are liquid or semi-liquid substances that bind surfaces together. Natural adhesives can be made from animal rendering, egg whites, plant material, and many others (Table A-3). However, most adhesive-related chemicals are associated with the growing number of synthetic glues that offer improved plasticity, toughness, curing speed, and chemical resistance (Ash and Ash, 2004; Petrie and Edwards, 2006).

Drying adhesives are typically polymers dissolved in a solvent that hardens as the solvent evaporates (e.g., rubber cement and wood glue). Contact adhesives are applied to both surfaces and allowed to cure before pressing them together to form elastomers by strain crystallization (e.g., Neoprene). Thermoplastics liquefy when heated and solidify when cooled (e.g., glue gun). Pressure sensitive adhesives (PSAs) are acrylic polymers applied to one surface that stick to other surfaces by applying light pressure (e.g., adhesive tape, masking tape, and stamps). Most adhesives possess some form of solvent to facilitate the manufacturing process and improve product performance. Airborne contaminants are

TABLE A-2. Propellants, refrigerants, and chlorinated solvents

Halomethanes	Haloethanes
Bromochlorodifluoromethane (Halon 1211)	1,1,1,2-Tetrafluoroethane (HFC-134a)
Bromochloromethane (Halon 1011)	1,1,1-Trichloro-2,2,2-trifluoroethane (CFC-113a)
Bromodifluoromethane (Halon 1201)	1,1,1-Trichloroethane
Bromomethane (Halon 1001)	1,1,2,2,2-Pentafluoroethane (HFC-125)
Bromotrifluoromethane (Halon 1301)	1,1,2,2-Tetrafluoroethane (HFC-134)
Chlorodifluoromethane (HCFC22)	1,1,2-Trichloro-1,2,2-trifluoroethane (CFC-113)
Chlorofluoromethane (HCFC31)	1,1-Dichloro-1-fluoroethane (HCFC-141b)
Chloromethane	1,1-Dichloroethane (Freon 150a)
Chlorotrifluoromethane (CFC13)	1,1-Difluoroethane (HFC-152a)
Dibromodifluoromethane (Halon 1202)	1,2-Dichloro-1,1,2,2-tetrafluoroethane (CFC-114)
Dibromomethane	1,2-Dichloroethane (Freon 150)
Dichlorodifluoromethane (CFC12)	1-Chloro-1,1,2,2,2-pentafluoroethane (CFC-115)
Dichlorofluoromethane (Halon 112)	1-Chloro-1,1-difluoroethane (HCFC-142b)
Dichloromethane (DCM)	2-Chloro-1,1,1,2-tetrafluoroethane (HFC-124)
Difluoromethane (HFC32)	Dibromotetrafluoroethane (Halon 2402)
Fluoromethane (HFC41)	Hexachloroethane (CFC-110)
Iodomethane (Halon 10001)	Hexafluoroethane (Halon 2600)
Tetrachloromethane (CFC10)	
Tetrafluoromethane (PFC14)	
Tribromofluoromethane (Halon 1103)	
Tribromomethane (Bromoform)	
Trichlorofluoromethane (CFC11)	
Trichloromethane (Chloroform)	
Trifluoroiodomethane (Freon 13T1)	
Trifluoromethane (HFC23)	

associated with the adhesive solvent and degradation byproducts (Table A-3).

A.5 Household Solvents

A solvent conventionally refers to a liquid that dissolves another liquid or solid substance. In chemical terms, solvents dissolve solutes (Morrison and Boyd, 1992). The universal solvent is water, because it dissolves an extremely wide range of substances. Organic solvents, however, are particularly effective at dissolving organic matter in dirt, oils, and greases commonly encountered in residential, commercial, and industrial settings. Favorable properties of solvents include: high vapor pressure for rapid dissolution, low vapor pressure for rapid evaporation, high purity for minimal residue, and low toxicity for safe application.

Organic solvents fall into several categories. Natural solvents come from vegetable matter (e.g., ethanol or terpenes). Petroleum solvents are typically refined distillates[3] with narrow boiling ranges (e.g., naphtha, mineral spirits, Stoddard solvent, toluene, and xylenes) used in paints, varnishes, and other materials (Table A-4). Halogenated solvents and reagents contain fluorine, chlorine, bromine, and iodine often bonded to an alkyl or aromatic hydrocarbon (Table A-2). Dry cleaners use or formerly used chlorinated solvents to clean clothes (e.g., bleach, tetrachloroethylene, or 1,1,2-trichloro-1,2,2-trifluoroethane). Cosmetic companies often manufacture products with complex mixtures commonly containing oxygenated solvents and oils (e.g., nail polish, perfumes, and fragrances) (Table A-5). Families of solvents, like aldehydes, are used in many capacities such as (1) permanent adhesives in plywood and carpeting, (2) paper resin in facial tissue, table napkins, and roll towels; and (3) foamed resins for insulation and molded products. While individual compounds, like formaldehyde, are commonly detected in indoor air, the compounds that co-occur with formaldehyde help identify its most significant source.

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[3] “Distilled” refers to a product of *distillation*, the method of separating mixtures based on differences in their volatilities in a boiling liquid mixture.

A.6 Respiration Byproducts

Cellular respiration is the process by which food molecules react catalytically with enzymes and oxygen to make biochemical energy. However, the body does not metabolically deconstruct all ingested or inhaled substances equally. For example, the concentration of ethanol in the blood from alcoholic beverage consumption partitions into exhaled air breath with a 2100:1 partition ratio in accordance with Henry's Law (hence, the use and admissibility of blood alcohol tests for the identification of intoxicated drivers). Ethanol also off-gases from bread in many residential, bakery, and brewery settings.

The body absorbs and retains many compounds on the skin and in the blood that experience varying degrees of metabolic alteration. The metabolic breakdown of alcohol forms acetaldehyde notoriously associated with hangovers. The metabolic breakdown of fatty acids forms acetone. Similarly, cigarette smokers inhale thousands of compounds dosing their blood with benzene, toluene, styrene, vinyl chloride, 1,3-butadiene, acetone, methyl ethyl ketone, aldehydes, phenol, PAHs, and many others (Table A-6). Some portions of these compounds and their metabolic byproducts gradually off gas into indoor environments.

A.7 Gasoline

Gasoline is a complex mixture of hydrocarbons whose composition changed significantly since the advent of the automobile in the late 1800s (Table A-7) (Potter and Simmons, 1998; Stout et al., 2005). It contains hundreds of hydrocarbons in the approximate molecular weight range of *n*-pentane (*n*-C_5) to *n*-dodecane (*n*-C_{12}). The specific mixture of hydrocarbons evolved over time in response to changes in the design of the internal combustion engines, antiknock quality (octane), chemical stability, volatility, gum content, and combustion emission standards. Gasoline predominantly contains PIANO. Refiners blend various distillate and refined intermediate products to achieve standard fuel grades. Specific manufacturers mix additive packages and dyes to enhance performance (e.g., isooctane boosts octane), reduce toxic emissions (e.g., MTBE reduces ozone toxins), and mark their products.

Forensic chemists identify gasoline sources by measuring and analyzing the specific PIANO and additive composition. This task proves difficult with Standard Method TO-15 (see Section 4.3) due to the limited number of PIANO constituents measured by most laboratories. Forensic Method TO-15 (see Section 4.4) with numerous target analytes and lower detection limits helps accurately identify the influence of gasoline, especially when present at concentrations approaching background conditions.

A.8 Aviation Gas

Prior to 1945, refiners produced many grades of aviation gasoline (avgas) to optimize the performance of the spark plug aircraft engines (Stout et al., 2002). The proliferation of jet engines after World War II forced the consolidation of avgas into Grades 80, 100, and 100-low lead (ASTM, 2007) with the latter being most common today. Grade 80 avgas contains straight run with paraffins, naphthenes, and some aromatics that can resemble automobile gasoline when weathered.

Grades 100 and 100-low lead contain more isooctane (i.e., extra alkylate) than automotive gasoline. However, automotive gasoline and avgas can be differentiated based on several compositional features. For example, automotive gasoline historically contained a wide range of organic lead and oxygenated compounds while AvGas only employed tetraethyl lead (TEL) and no oxygenates. Forensic chemists often employ advanced hydrocarbon methods to identify avgas in the environment.

A.9 Kerosene and Jet Fuels

Kerosene is commonly used for heating. Refiners manufacture kerosene as a light straight run (distillate) containing hydrocarbons in the *n*-octane (*n*-C_8) to *n*-octadecane (*n*-C_{18}) range (Potter and Simmons, 1998; Stout et al., 2002). It is heavier than gasoline and lighter than middle distillates, like No. 2 heating oil or diesel fuel oil (Table A-7). In general, kerosene is readily

TABLE A-3. Adhesives

Water-based Adhesives	Glue Solvents	Adhesive Solvents
Starch	Formaldehyde	Ethyl-2-cyanoacrylate
Gums	Acetone	Methyl ethyl ketone
Albumen	Vinyl acetate	Acetone
Sodium silicate	Ethyl-2-cyanoacrylate	Toluene
Casein	Carbon Tetrachloride	Petroleum solvent naphtha
Methyl cellulose	Acrylic acid	Vinyl acetate
Lignin	Octodecyl alcohol	Styrene
Polyvinyl alcohol		Hexane
		1,3-Butadiene
		1,2,4-Trimethylbenzene
		Mineral spirits
		Xylene
		Cumene
		Pentane
		Cyclohexane
		2,2-dimethylbutane
		Carbon Tetrachloride
		2-Methylpentane
		3-Methylpentane
		Cyclohexanone
		Butyl alcohol
		Butanol
		Ethyl ether
		Methyl isobutyl ketone

Source: U.S. Department of Health and Human Services
http://householdproducts.nlm.nih.gov/index.htm
Source: Consumer Product Information Database http://whatsinproducts.com

TABLE A-4. Petroleum solvents paint

Paints-Oil Base	Paints-Water Base	Lacquers
Carboxylic Acids	Acrylic resins	Acrylics
Cycloparaffins	Alkyd resins	Cellulosics
Elastomers	Carboxylic acids	Natural resins
Epoxy resins	Cellulose Resins	Natural rubbers
Glycerols	Chlorofluorocarbons	Phosphate alkyds
Glycols	Epoxyl resins	Phthalates
Melamine alkyds	Hydrocarbon resins	Shellac
Pentaerythritols	Natural oils	Styrenated alkyds
Phenolic aldehyde resins	Phthalates	Synthetic rubbers
Phenolics	Plasticizers	Vinylics
Phthalic acids	Rubbers	Zein lacquers
Polyetesters	Syrene-butadiene polymers	
Polyurethane esters	Vinyl resins	
Resins		
Rosins		
Silicone alkyds		
Styrene polyesters		
Urea alkyds		

Reference: Crowne (1968)

distinguished from jet fuels based on (1) its PIANO composition, (2) the absence of additive packages, and (3) its distillation range. Jet fuels can resemble kerosene, but they exhibit greater complexity as discussed below.

The proliferation of jet engines during and after World War II favored kerosene-based products as high performance fuels. Modern commercial jet engines use Jet A comprised almost entirely of *n*-C_8 to *n*-C_{18} hydrocarbons. When distilled from sour crudes with high sulfur concentrations, kerosene requires additional refining (e.g., hydrotreating) before meeting Jet A specifications. Optional Jet A additive packages include antioxidants, metal deactivators, corrosion

TABLE A-5. Cosmetics

Cologne	Perfume
Benzaldehyde	Benzaldehyde
Ethyl acetate	Ethyl acetate
Hexane	Hexane
Methylene Chloride	Ethanol
Ethanol	Benzophenone
Benzophenone	Stearyl alcohol
Stearyl alcohol	Fragrances
Fragrances	
Shampoo	**Lipstick**
Benzaldehyde	Glycerin
Methylene Chloride	Benzoic acid
Benzyl alcohol	Polyethylene
Stearyl alcohol	Polybutene
Dyes	Parabens
Fragrances	Dyes
	Iron Oxides
	Waxes

inhibitors, anti-icing additives, anti-static additives, and lubricity additives. Military jet fuels are compositionally more varied than Jet A, but fall into three general types. Kerosene-based fuels resemble kerosene and Jet A. Wide-cut fuels contain heavy straight run gasoline (naphtha) or cracked[4] gasoline blended with straight run jet. Third, specialty fuels (e.g., rocket fuel) contain only a few selected hydrocarbons.

A.10 Diesel/No. 2 Fuel Oil

The so-called "middle distillates" consist of one or more crude oil distillates collected between 200°C and 350°C at atmospheric pressure (Potter and Simmons, 1998; Stout et al., 2002). They include products, such as diesel, No. 2 fuel oil, home heating fuel, and gas oil. They are sometimes used to improve the fluidity of heavier hydrocarbon products; for example, No. 4 fuel oil is a mixture of No. 2 and No. 6 fuel oils.

Middle distillates generally contain paraffins, isoparaffins, naphthenes, and aromatics in the n-C_8 to n-C_{25} range (Table A-7). Forensic chemists identify middle distillates in air based on the compositional features of the more volatile n-C_8 to n-C_{12} range components, because the heavier material prefers not to partition into air and fall outside the molecular weight range of most air testing methods.

TABLE A-6. Common chemicals in cigarette smoke

Aldehydes [2]
Acetone
Acrolein
Acrylonitrile
Ammonia
Benzene
Benzo(a)pyrene
1,3-Butadiene
Butane
Cadmium
Carbon Monoxide
Catechol
Chromium
Chrysene
Cresol
Ethanol
Hydrogen Cyanide
Isoprene [4]
Lead
Methanol
Methyl Ethyl Ketone
Naphthalenes [1]
Nickel
Nicotine
Nitric Oxide
NNN (N-nitrosonornicotine) [5]
NNK (4-Methylnitrosamino-1-3-Pyridyl-1-Butanone) [5]
NAT (N'-Nitrosoanatabine) [5]
Phenol
Pyridine
Quinoline [3]
Resorcinol
Styrene
Toluene
Vinyl chloride

A.11 Heavy Petroleum Products

Heavy petroleum products contain semivolatile hydrocarbons with vapor pressures that rarely necessitate consideration as part of a vapor intrusion investigation (Potter and Simmons, 1998). Examples of heavy petroleum products include No. 6 fuel oil, Bunker C oil, mineral oils, hydraulic fluids, motor lubricating oil, asphalt, and others.

In some instances, heavier petroleum products are blended with lighter distillates to enhance

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[4] "Cracked" refers to a product of *cracking,* the process whereby large hydrocarbons are broken down into smaller (lighter) hydrocarbons by breaking the carbon-carbon bonds in the precursors in the presence of a metal catalyst under high temperature and pressure.

performance; for example, WD-40® contains Stoddard solvent mixed with a heavier lubricant (Table A-7). However, these materials generally represent residual or highly refined petroleum products that contain little to no volatile hydrocarbons. Consequently, these substances will not be considered further in this discussion of forensic methods.

A.12 Tar Products

Tar vapors contain high concentrations of benzene, alkylated benzenes, and naphthalene in the absence of most other hydrocarbons. Tar was produced historically by the destructive distillation of coal (coal tar), cracking of middle petroleum distillates (carbureted water gas tar), or cracking of heavy petroleum oil (oil gas tar) (Rhodes, 1945). Coal tars were produced by manufactured gas plants or coke plants. Carbureted water gas and oil gas tars were only produced by manufactured gas plants.

Tar refiners fractionally distilled automotive gasoline, light oils, creosote, and many chemical intermediate products from crude tars (Rhodes, 1945). The heavy residual tar was used to make roadway pavement, weatherproofing, roofing tile, paint, and many other products. While some tar products are still available, the modern supremacy of petrochemicals largely replaced historically common coal tar products. Consequently, tar products are most commonly encountered as fill with building debris, weatherproofing around building foundations and pipes, roofing materials, treated wood, and shoe polish.

Passive volatilization from materials containing tar can account for the detection of benzenes and naphthalenes in soil gas and indoor air. Forensic chemists identify tar product emissions by the aromatic signature and absences of other hydrocarbons. Recognizing tar product emissions with Standard Method TO-15 is challenging, because the analyte list contains some aromatics and few saturated hydrocarbons. Consequently, Forensic Method TO-15 often helps investigators pinpoint the effects of tar products.

TABLE A-7. Petroleum distillates

Gasoline	Kerosene	Diesel	Blended Lubricant (WD40)
Butane	Hexane	Octane	Butane
Isobutane	Heptane	Nonane	Methylene chloride
Pentane	Octane	Decane	Stoddard solvent
Isopentane	Nonane	Undecane	Mineral spirits
Hexane	Decane	Dodecane	Petroleum distillates
Heptane	Undecane	Tridecane	Propane
Octane	Dodecane	Tetradecane	Heptane
2,2-dimethylbutane	Tridecane	Pentadecane	Polydimethylsiloxanes
2,2,4-trimethylpentane	Tetradecane	Hexadecane	Ethanol
1-pentene	Pentadecane	Heptadecane	Isobutane
2,2,4-trimethyl-1-pentene	Hexadecane	Octadecane	o-phenylphenol
Cyclopentane		Nonadecane	Pentane
Methylcyclopentane		Eicosane	
Cyclohexane		Heneicosane	
Benzene			
1,2,4-Trimethylbenzene			
Toluene			
Ethylbenzene			
Xylenes			
2-Methylpentane			
3-Methylpentane			
Isopropanol			

Source: U.S. Department of Health and Human Services http://householdproducts.nlm.nih.gov/index.htm
Source: Consumer Product Information Database http://whatsinproducts.com

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APPENDIX B: CONCEPTUAL SITE MODEL CHECKLIST – VAPOR INTRUSION

Conceptual Site Model Checklist – Vapor Intrusion	
Site Name	
Site Description	Location:
	Size:
	Site Status: ☐ Active ☐ Inactive ☐ Unknown
Site Conditions	
Current Conditions (Request maps of site and adjacent areas)	Describe present site conditions using information from checklist as follows: conduct property inspection to identify on-site land use [e.g., residential vs. non-residential] and groundwater use [potable vs. non-potable] conditions as well as land and groundwater use on adjacent property, number and type of structures [do structures have basements], number/type of people [adults, teens, children], distance from base boundary, distance to nearest off-base community [residential and non-residential]; site in investigation, cleanup, or post-cleanup phase.
Future Conditions	Describe potential future conditions (obtain from Base Master Plans or redevelopment plans for property transfers), consider including information as was identified under “current conditions” above
Geology and Hydrogeology	☐ Vadose zone lithology ☐ Depth to bedrock ☐ Characteristics of each stratigraphic unit ☐ Depth to groundwater ☐ Groundwater connection to surface water ☐ Aquifer characteristics (physical and chemical) ☐ Productivity of saturated zone ☐ Water quality and resource use classification (e.g., potable) ☐ Regional aquifer water quality and resource use classification ☐ Local potable water source
Nature and Extent of Contamination	
Impacted Media	☐ Surface soil ☐ Subsurface soil ☐ Groundwater ☐ NAPL ☐ Soil gas
Vapor Intrusion Source Description (Request figures)	List all known or suspected contaminant sources For each source area, record the following information: ☐ Describe history of contamination ☐ Describe previous remedial/removal actions ☐ Depth to top of source/plume ☐ Depth to bottom of source/plume ☐ Source/plume width ☐ Source/plume length parallel to groundwater ☐ Plume orientation, direction, and speed ☐ Is plume migrating under residential or non-residential developments ☐ Identify contaminants/concentrations (typical constituents, components, additives, etc. stored or handled on the property or constituents detected in the environment): ▫ volatile organics ▫ semi-volatile organics ▫ other organics ▫ metals ▫ other inorganics ▫ NAPLs

Conceptual Site Model Checklist – Vapor Intrusion	
Site Name	
Special Considerations for Vapor Intrusion CSMs	
Contaminant Sources for Vapor Intrusion	What are the source(s) of vapor intrusion at the site? ☐ Dissolved Plume ☐ NAPL ☐ Contaminated Soil ☐ Soil Gas Are there contaminants of concern of sufficient volatility and toxicity in subsurface? (Refer to Table A-1 of the *DoD Vapor Intrusion Handbook* [January 2009] for chemical-specific toxicity and volatility assessment) Do concentrations exceed generic screening criteria based on appropriate exposure scenarios/contaminated media? [For generic screening criteria refer to: (1) Appendix H of the ITRC [2007] guidance, (2) Use of U.S. EPA Johnson & Ettinger model for Subsurface Vapor Intrusion to Indoor Air, (3) State-specific screening levels/guidance]
Assess Quality of Data	Are there sufficient data of adequate quality to support a quantitative vapor intrusion assessment? ☐ Age of the data ☐ Sample collection methods ☐ Analyses conducted for all suspected chemicals and degradation products ☐ Reporting limits sufficiently low for comparison to screening criteria ☐ Sampling locations relative to source area and buildings
Background Levels	Identify background contributions to indoor air ☐ Outdoor Sources: ☐ Indoor Sources: What are the background concentrations for each contaminant of concern at the site?
Migration Mechanisms	What are the dominant migration mechanisms at the site? ☐ Diffusion in the unsaturated zone ☐ Diffusion through the capillary zone immediately above the top of the water table aquifer ☐ Advective/convective transport ☐ Migration through preferential pathways
Building Uses and Characteristics	General Information: ☐ Inspection to identify on-site land use (residential and non-residential) ☐ Total number of on-site structures ☐ Distance from source to nearest off-base community (residential and non-residential) Record relevant information for each building: ☐ Building use (e.g., residential, non-residential) ☐ Exposed population (e.g., number of adults, teens, children) ☐ Foundation type/material (e.g., slab on grade, basement) ☐ Distance from base boundary ☐ Distance from source area ☐ Floor thickness ☐ Length of structure

Conceptual Site Model Checklist – Vapor Intrusion	
Site Name	
	☐ Width of structure ☐ Height of structure ☐ Floor-wall seam crack width Evaluate the enclosed inhabited space of the building, “Building Envelope” ☐ HVAC system ☐ Leaky or tight (sumps/open pits) ☐ Differential pressure monitoring
Factors Affecting Vapor Migration	Define the key vadose zone characteristics and vapor migration pathways: ☐ Depth to source ☐ Soil type ☐ Horizontal extent of contamination ☐ Distance of vapor source from buildings ☐ Sufficient delineation of the source area(s ☐ Identify locations and depths of major underground utilities
Risk Assessment Exposure Pathways and Receptors for Vapor Intrusion	
Current and Future Land Use	Current: ☐ residential ☐ industrial ☐ commercial ☐ agricultural ☐ recreational ☐ other Future: ☐ residential ☐ industrial ☐ commercial ☐ agricultural ☐ recreational ☐ other Surrounding: ☐ residential ☐ industrial ☐ commercial ☐ agricultural ☐ recreational ☐ other
Media affected or potentially affected	Source #___: ☐ soil ☐ groundwater Source #___: ☐ soil ☐ groundwater
Identify Potential Receptors	Current Human: ☐ residents ☐ visitors ☐ workers ☐ other_______ Future Human: ☐ residents ☐ visitors ☐ workers ☐ other_______
Identify Appropriate Chemical-Specific Screening Level for Exposure	Human: ☐ generic ☐ site-specific
Is the Vapor Intrusion Exposure Complete?	☐ yes ☐ no Rationale for exclusion of exposure pathway(s):________________________________

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APPENDIX C: SAMPLING AND ANALYTICAL METHODS AND DATA ADEQUACY FOR RISK SCREENING

C.1 Summary of Sampling and Analytical Methods

Various investigative and analytical methods are available depending on the environmental medium being investigated during a vapor intrusion evaluation. It is not the intent of this background indoor air guidance to provide a detailed discussion of each sampling and analytical method. Rather, the objectives of this appendix are to provide (1) a brief summary of the investigative and analytical methods commonly used in vapor intrusion and background evaluations, along with references to other guidance documents that can be reviewed for more detailed discussions, (2) an overview of how the sampling methods and corresponding environmental data will be used when conducting the background evaluations described in subsequent sections, and (3) a discussion of some strengths and weaknesses associated with the various sampling and analytical methods.

The sampling and analytical methods used to conduct a vapor intrusion evaluation have been discussed in the DoD, ITRC, U.S. EPA, and various state vapor intrusion guidance documents (DoD, 2009 [Section 3]; ITRC, 2007 [Appendix D]; U.S. EPA, 2002 [Appendices A and E]; Cal/EPA, 1997, 2003, 2005; NJDEP, 2005; NYSDOH, 2006; MADEP, 2002). The Navy also recently commissioned a study to review and document best practices in subsurface and indoor air sampling methods (among other topics) to improve assessment of the vapor intrusion pathway (DON, 2009). RPMs are referred to these guidance documents for details; however, a brief summary of the most common sampling and analytical methods is provided in subsequent paragraphs.

As discussed in ITRC's 2007 guidance, data collected from one or more of the media listed in Table C-1 are recommended when assessing the vapor intrusion pathway. The general approaches commonly used to evaluate the data in a vapor intrusion assessment are summarized, along with a sampling of issues for consideration. These considerations highlight the challenges associated with vapor intrusion evaluations that also affect the usability and interpretation of the data in a background evaluation. Brief discussions related to the sampling strategies for each medium are provided in subsequent paragraphs.

Groundwater

Groundwater impacted by site-related activities is often a primary source of VOCs evaluated in vapor intrusion investigations. In areas distant from the primary release (e.g., the residence shown on Figure C-1), groundwater is the likely sole source of subsurface vapors. As discussed in DON (2009) and ITRC (2007), the methods for conducting groundwater sampling have been researched and developed for many years, and practitioners are relatively experienced and trained to collect samples that meet site-specific data quality needs. ITRC (2007) highlights a number of recommendations for collecting groundwater data suitable for vapor intrusion evaluations (and potential background indoor air evaluations). Refer to U.S. EPA, ITRC, and other state documents for specific guidance and procedures for the installation of groundwater monitoring wells and the acquisition of high-quality groundwater data that can be used in vapor intrusion evaluations (U.S. EPA, 2002 [Appendix E]; ITRC, 2007 [Appendix D]; NJDEP, 2006; and Cal/EPA, 2005).

Vapor intrusion investigations often arise based on a review of existing groundwater data; hence, the characterization of groundwater contamination is one of the first components to be incorporated into a CSM. The potential for significant

TABLE C-1. General Sampling Strategies for Vapor Intrusion Evaluations

Medium	Method Used to Evaluate the Data	Issues Relevant to the Background Evaluation
Groundwater	Modeled or empirically based groundwater to indoor air ratios can be used to predict indoor air levels	• Constituent ratios between groundwater and indoor air may help distinguish groundwater, soil, and background sources of vapors. • Modeled or empirically based attenuation factors may span three or more orders of magnitude, which can complicate interpretation of the data. • Some agencies prefer one type of subsurface data over another or do not allow use of data from a single subsurface medium. • Since groundwater is rarely, if ever, characterized under buildings, it is important to account for spatial variability when using groundwater to predict vapor intrusion.
Soil Gas	Modeled or empirically based soil gas to indoor air constituent ratios can be used to predict indoor air levels	• Constituent ratios within or between soil gas and other media may help differentiate between the vadose zone, groundwater, and background sources. • Modeled or empirically based attenuation factors may span three or more orders of magnitude, which may complicate interpretation of the data. • Some agencies question use of exterior soil-gas data to predict indoor air concentrations. • Historical soil-gas monitoring methods were not designed for vapor intrusion assessments. • Empirical data show the poorest correlations between soil-gas and indoor air data (U.S. EPA, 2008). • Soil-gas results are spatially or temporally variable.
Sub-slab Soil Gas	Modeled or empirically based sub-slab soil gas to indoor air constituent rations may be used to predict indoor air levels	• Constituent ratios within or between sub-slab soil gas and other media may be used to distinguish subsurface versus background sources. • Modeled or empirically based attenuation factors may span three or more orders of magnitude, which may complicate interpretation of the data. • Concurrent indoor and outdoor air data are highly recommended when implementing a background evaluation. • Potential for orders of magnitude spatial or temporal variability. • Intrusive and sometimes not feasible due to access limitations, engineering constraints, or disturbances to occupants.
Indoor (and Outdoor) Air	Can use measured indoor air concentrations to estimate exposure	• Indoor air sampling may provide the most direct measurement for assessing inhalation exposure to occupants. • Background indoor and outdoor sources can confound interpretation and use of indoor data. • Indoor sampling is intrusive and sometimes not feasible due to access limitations or disturbances to occupants. • Spatial and temporal variability is often significantly less than variability in subsurface media data.

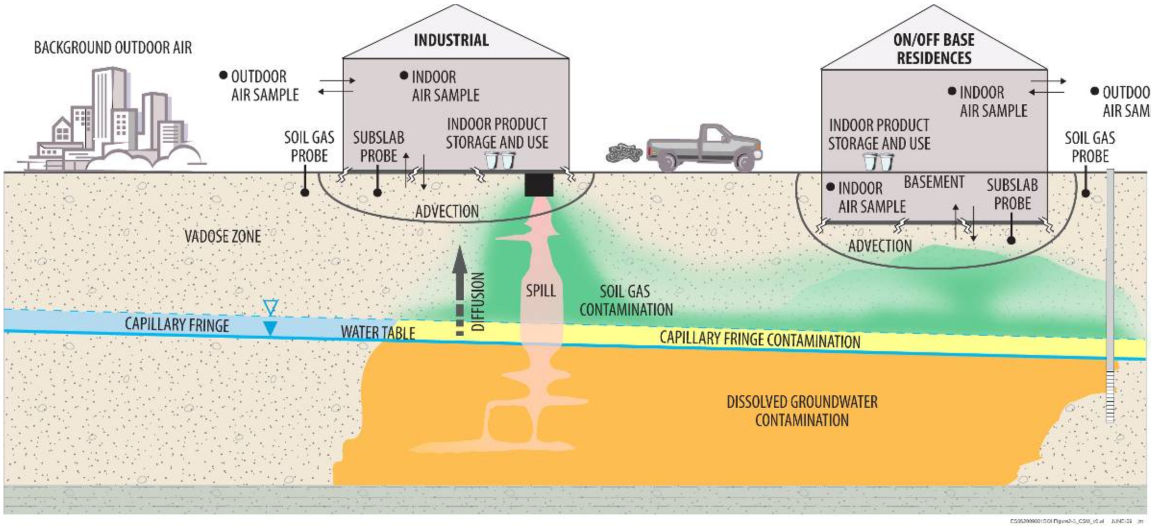

FIGURE C-1. Sample Conceptual Site Model

BOX C-1. Practical Tips: Monitoring Well Design, Installation, and Sampling for Vapor Intrusion

RPMs should consider the following when designing and sampling groundwater monitoring wells:

- **Proper screen intervals** to measure chemical concentrations at the top of the water table since this is where volatilization from groundwater occurs.

- **Proper screen lengths** to minimize the effect of chemical concentrations from deeper groundwater on the overall average groundwater concentration. Wells with screen lengths that are longer than 10 feet within the aquifer introduce substantial uncertainty in the water-table contaminant characterization.

- **Proper well installation, development, purging, and sampling** are required to obtain representative, high-quality groundwater data.

- **Selecting or installing wells as close as possible to the structure** since concentrations may not be uniform within a plume.

vapor intrusion resulting from VOCs volatilized from groundwater is often predicted based on conservative assumptions about attenuation as the vapors migrate vertically and enter a building.

Characterization of the water table is critical for a reliable vapor intrusion assessment, and monitoring wells have not typically been installed or sampled for this purpose. Strong increasing or decreasing vertical concentration gradients are common in the saturated zone. Therefore, samples from below the water table or samples derived from long-screen wells that penetrate well below the water table may mischaracterize water table concentrations and result in either false positive or negative conclusions.

The representativeness of the water table samples can be affected by the sampling methodology. Grab samples collected during drilling frequently do not correlate well with samples collected from a developed and purged monitoring well. Groundwater data can be spatially variable and, to a lesser degree, temporally variable. Since monitoring wells are virtually never located beneath buildings, it is necessary to document uncertainties related to delineation of groundwater contamination, especially if large changes in concentration are expected over distances on the scale of the building footprint. Additional factors for consideration also include the distance from the release, variable geochemical conditions and lithology, the presence and timing of clean water recharge and contaminant source loading, the location and rates of contaminant degradation, and groundwater and solute velocities. Hydrogeologists need to be aware of and incorporate the objectives of the vapor intrusion investigation when aiding CSM development. Even with these considerations, groundwater investigations provide many useful inputs to the vapor intrusion CSM.

"Exterior" Soil Gas

The term "exterior" means that the samples were not collected beneath structure (see "Sub-slab soil gas"). Some regulators (e.g., NYSDOH, 2006) have expressed a strong preference for using indoor and sub-slab data as the primary lines of evidence given concerns about the uncertainties in using soil-gas data collected outside a building to predict sub-slab concentrations. However, it is important to consider where the structure of interest is located within the CSM when selecting the sampling medium. In areas distant from known or suspected primary releases, VOCs are likely present due to groundwater transport and typically there is less spatial variability than what is observed near the primary release area. Therefore, sampling of exterior soil gas (or groundwater) may provide a defensible characterization of conditions under a structure. Closer to known or suspected primary releases, orders of magnitude variability in subsurface contamination can be observed over very short distances and data collected outside the building footprint may have little bearing on conditions beneath the structure. Furthermore, historical releases inside the building are increasingly documented during vapor intrusion investigations and exterior data are much less useful. This highlights the need for a sound CSM developed in consultation with practitioners having knowledge of site conditions and contaminant fate and transport.

There is no consensus on the most appropriate protocol for sampling soil gas. Of the three general methods for collecting soil-gas samples (active, passive, or surface-flux chambers), there continues to be a preference for active soil-gas samples. However, there is recognition that more than one method may be needed to address the wide range of data quality needs, uncertainties, and variability associated with soil- gas sampling.

Two types/locations of exterior soil-gas samples are commonly collected:

- ☐ Shallow soil-gas samples are typically collected from 5 feet bgs. This depth is considered sufficient to minimize barometric pumping effects from the atmosphere, which can bias soil-gas concentrations low. Shallow soil-gas samples collected away from buildings may help evaluate the overall contaminant distribution. A shallow soil-gas sample collected near buildings can sometimes be used as a surrogate for sub-slab samples. This use is limited with large building footprints or buildings with potential contaminant releases under the building, which is common in current or former industrial or maintenance buildings.
- ☐ Deep soil-gas samples are typically used to characterize the relationship between vapor sources (groundwater or vadose zone) and sub-slab or shallow soil gas. While deep soil-gas data are not directly applicable to the methods described in this document, deep results may be used to refine the CSM.

A range of soil-gas sampling methods are in use today (e.g., ASTM, 1992; American Petroleum Institute [API], 2005; Electrical Power Research Institute, 2006; Cal/EPA, 2003, 2005; Arizona Department of Environmental Quality, 2008; Geoprobe, 2005). However, and as discussed in DON (2009), some of these protocols were developed for less stringent data quality purposes, and most do not provide enough detail to prevent the results from being biased or minimize variability due to factors such as leaks, sorption/desorption biases, incomplete purging, and so forth. A list of several QC procedures has been presented in DON (2009) and is reproduced as Appendix D. These QC procedures are recommended for consideration when collecting soil-gas samples for the following reasons (DON, 2009):

- ❑ Risk-based target soil-gas concentrations are very low for select VOCs, and there is an increased likelihood of false positives that may be attributed to equipment and cross-contamination.
- ❑ A review of the empirical soil-gas data indicates there is a high degree of spatial and temporal variability, and it is not clear if this is due to natural variability or sampling bias.
- ❑ Selecting sampling locations, depths, frequencies, sampling methods, and target analytes is site-specific, and available guidance is limited.
- ❑ There is no consensus on the most appropriate analytical methods and target analyte lists.

Sufficient, high-quality soil-gas data are also critical in refining the CSM. The location and magnitude of soil-gas impacts provide information about (1) the attenuation of soil gas in the vadose zone, (2) the locations of vadose zone sources (site-related or not) that can easily be missed when only soil and groundwater are sampled, (3) the effects of natural and manmade features (clay layers, streams, roads, buildings, etc.) on soil-gas migration and attenuation, and (4) temporal and spatial variability. It is important not to view temporal and spatial variability as an impediment of CSM development. Rather, these uncertainties should be documented as a sound scientific practice, particularly since they may prove valuable when interpreting other data.

Sub-slab Soil Gas

Sub-slab soil-gas sampling is used to estimate concentrations of volatile contaminants immediately beneath a structure. As stated in ITRC's *Vapor Intrusion Pathway: A Practical Guideline*, "Sub-slab soil gas sampling is the preferred approach of many regulatory agencies for investigating vapor intrusion, primarily because of the proximity of the sample location to the receptor and the elimination of background interferences (when proper sampling methods are employed)" (ITRC, 2007). Sub-slab sampling is often intrusive and disruptive to building occupants. However, these data can be very usefully for assessing the vapor intrusion pathway and helping to differentiate subsurface contributions from other volatile compounds detected in indoor air samples (i.e., the background evaluation).

There are fewer published sub-slab soil-gas sampling protocols than exterior soil-gas sampling procedures. U.S EPA and select states have published draft sub-slab soil-gas sampling protocols (www.epa.gov/region8/r8risk/sampling.html; ITRC, 2007; NJDEP, 2005; NYSDOH, 2006; CDPHE, 2004; Cal/EPA, 2005). As discussed in the *DoD Vapor Intrusion Handbook* and ITRC's *Vapor Intrusion Pathway: A Practical Guideline*, sub-slab sampling results can be compared with risk-based screening values to assess the vapor intrusion pathway during the preliminary screening phase and to identify site-related VOCs for a targeted background indoor air evaluation (DoD, 2009; ITRC, 2007). The following are select examples of factors discussed in DoD (2009) and ITRC (2007) that should be considered when collecting sub-slab samples (refer to the guidance documents for details):

- ❑ Avoid sampling in areas where groundwater and the associated capillary fringe are shallow (e.g., <5 feet bgs) and might come into contact with the slab.
- ❑ Identify locations of underground utilities (e.g., electric, gas, water, tension rods, or sewer lines) beneath the slab to avoid sampling in these locations.
- ❑ Existing vapor barriers (if present) may be damaged by sub-slab sampling and sampling through them should be avoided to the extent possible.

- ❑ Reseal all sub-slab entry points when the soil-gas probe is removed to help minimize creating potential preferential vapor migration pathways into the structure.
- ❑ Ensure the sensitivity of the reporting limits meet data quality needs and project action limits when developing the sample design. To the extent practical, it is also preferable if reporting limits meet RBC requirements. However, RBCs are not enforceable standards and may represent low concentrations that are not achievable using current analytical technologies.
- ❑ Consider spatial and temporal variability. Multiple presentations and articles have focused on the variability associated with sub-slab soil-gas sampling (http://iavi.rti.org/; Folkes et al., 2009; Luo et al., 2009).

Sub-slab data characterize the potential subsurface source of vapors and are very useful in refining the CSM. Site-related chemicals can flow into buildings when air pressure in the building is lower than the soil-gas air pressure (the requisite conditions for vapor intrusion). However, the converse is also true — volatile chemicals may flow from the building into the subsurface (see Section 3.5.1). Thus, the presence of a site-related chemical in a sub-slab soil-gas sample above a target concentration cannot alone support the conclusion that vapor intrusion is occurring, particularly given the uncertainty in the assumed attenuation. It is also important to consider the spatial variability in sub-slab vapor concentrations, which can span orders of magnitude (http://iavi.rti.org; Folkes et al., 2009; Luo et al., 2009). Therefore, other components of the CSM should be considered to minimize false negative or positive conclusions. In particular, the known or potential presence of primary releases beneath or immediately next to the structure, and the associated high degree of spatial variability, should be taken into account when designing a sub-slab investigation. Since the range of detected sub-slab concentrations can span orders of magnitude, this may confound the background evaluation methods discussed in Section 3 of the main document, particularly those relying on the concentration ratios between indoor and sub-slab analytical results.

Indoor Air

Indoor air sampling is the most direct approach for measuring concentrations of volatile contaminants in the indoor air inhaled by building occupants; however, the volatile concentration may be associated with background concentrations. The advantages and limitations associated with indoor air sampling as part of a site-specific vapor intrusion investigation are discussed in DoD (2009). Assuming the practical constraints (e.g., intrusiveness to building occupants) do not prevent indoor air sampling, site-specific indoor (and outdoor) air results may be used in both vapor intrusion and background indoor air evaluations.

Several methods can be used to collect indoor air samples, including (1) grab or time-integrated active sampling into evacuated canisters, glass bulbs, or Tedlar® bags with analysis by U.S. EPA Methods TO-15, TO-14A, TO-3, or others, (2) active adsorptive sampling (drawing air or gas through a tube filled with adsorbent media at a fixed flow rate for a measured time) and analysis by U.S. EPA Methods TO-17, TO-10A, TO-13, or others, (3) passive sampling using adsorbent media to sequester VOCs over time by passive uptake followed by laboratory analysis (see DON, 2009 [Section 3.2]) and (4) real-time monitoring using a portable field instrument or mobile laboratory (e.g., U.S. EPA's Trace Atmospheric Gas Analyzer mobile lab [www.epa.gov/earth1r6/6lab/taga.htm]). Although there are advantages and disadvantages to each of these methods, collecting indoor air (or outdoor air, sub-slab, or soil gas) samples into evacuated canisters has generally become the accepted industry standard. Active indoor air sampling methods using canisters and flow controllers result in high-quality, consistent air concentrations. The methods for collecting active indoor (and outdoor) air samples using canisters are described in detail in ITRC's *Vapor Intrusion Pathway: A Practical Guideline* (ITRC, 2007

BOX C-2. Practical Tips: Factors Contributing to Variability

Spatial and temporal variability of analytical results is a recurring topic throughout this document, particularly for air and soil gas. Both natural and manmade factors contribute to this variability.

Contaminant concentrations in soil gas are sensitive to spatial variations in soil texture (fine versus coarse grain size) and gas permeability.

Temporal and spatial changes in moisture content likewise affect both diffusive and advective vapor transport.

Wind, temperature, and barometric pressure in the atmosphere can cause rapid variability in vapor concentrations in the upper vadose zone.

Near primary releases, vapor-phase contaminant concentrations can change by many orders of magnitude over just a few feet.

Biodegradation, particularly of petroleum hydrocarbons, can result in similar orders-of-magnitude variability over short distances.

Building characteristics and operations also result in variability in the indoor air contaminant concentrations, particularly temporal variability.

A building's air exchange rate with the atmosphere, which is a major factor in vapor attenuation, is influenced by daily use patterns (e.g., opening and closing doors and windows during work hours) as well as seasonal changes in operation (e.g., changing from heating to cooling).

Natural factors such as wind and barometric pressure can also cause rapid changes in the atmospheric air exchange rate as well as the indoor/sub-slab pressure differential, thereby affecting indoor air contaminant concentrations.

Sources of variability in air can include the following:

- ☐ Human activities, such as the daily arrival and departure of workers wearing dry-cleaned clothing
- ☐ Outdoor sources, such as the operations of a nearby industrial or manufacturing facility

In the same way that pressure changes can affect indoor air concentrations, they can also affect sub-slab/crawl space concentrations as indoor air is exchanged with these matrices.

These are just some of the factors that contribute to the observed variability of indoor air and soil-gas contaminant concentrations. The *DoD Vapor Intrusion Handbook* (2009) offers some guidance on addressing variability when collecting and interpreting data. This is likely to remain a topic of ongoing research in the coming years. It may not be possible, or even useful, to precisely characterize the cause and effect of the factors that result in variability.

When planning, collecting, and interpreting data, users of this guidance should remain cognizant that such temporal and spatial variability exists and be aware of some of the major factors behind it.

[Appendix D]) and MADEP (2002) and are not repeated here.

Concurrent indoor, sub-slab, and outdoor air results provide the results needed to conduct site-specific vapor intrusion background evaluations. A minimum of two rounds of indoor air data are recommended in most vapor intrusion guidance documents (e.g., DoD, 2009; ITRC, 2007; U.S. EPA, 2002; Cal/EPA, 2005; NYSDOH, 2006; NJDEP, 2005). Folkes et al. (2009) have demonstrated that indoor air results can vary by a factor of two to three times above or below the annual average. This is consistent with the findings of a detailed Environmental Security Technology Certification Program study on spatial and temporal variability of air concentration data (McHugh, 2008). The spatial variability of sub-slab soil-gas concentrations is significantly greater than indoor (and outdoor) air results and can vary by 10 to 100 times or more (McHugh, 2008; Luo et al., 2009; Wertz, 2007). The number and frequency of indoor (and concurrent sub-slab or outdoor) air samples, along with the anticipated (or measured) variability should be considered during the EDA, forensic, or statistical components of a vapor intrusion background indoor air evaluation.

Indoor air results are used to refine the CSM. However, it is critical that background sources be adequately addressed to minimize false negative or positive conclusions. This may include comparing indoor air concentrations with measured or published background air levels or evaluating VOC ratios within or between indoor, outdoor, and subsurface (sub-slab, soil gas, groundwater) samples (Section 3). Indoor air (and concurrent outdoor and/or subsurface) results can also be used in the background forensic (Section 4) and statistical methods (Section 5).

C.2 Data Adequacy for Risk Screening

The data used for risk screening should represent a reasonably accurate and current characterization of the site. Many of the data adequacy and data quality considerations for specific media were presented above. Additional considerations are discussed below.

Data should be reasonably current. For example, use of 10-year-old data to characterize media as variable as soil gas or indoor air is not recommended. In addition, data collected pre-remediation at sites with ongoing or past remediation are not recommended for use during the risk-screening step. The known or expected rate of changing conditions in other media should also be considered when assessing data usability. Data that are 1 year old and collected over a relatively stable groundwater plume may be usable but would not be adequate for a recent release or fast-moving dissolved plume. Other factors in the CSM, including building operations and climate conditions, may also be factors when considering the usability of older data.

Data should be validated for quality in accordance with the UFP-QAPP (Intergovernmental Data Quality Task Force, 2005), which provides the framework for developing project-specific data validation requirements. In addition, the *Navy Installation Restoration Chemical Data Quality Manual* (DON, 1999 [Appendix H]) defines data qualifiers that give the end users a qualitative measure of data usability. Data may be assigned the following typical qualifiers:

- ☐ "J": Estimated concentration
- ☐ "N": Presumptive evidence of the identification of an analyte
- ☐ "R": Rejected data (unusable)
- ☐ "B": The analyte was detected above one-half the reporting limit in an associated blank
- ☐ "U": Not detected (at the predefined quantitation limit)

Validated and unflagged data are considered fully usable in the risk screening. Both "J" and "N" flagged data are assumed to represent a detection of the analyte with uncertain quantification. "N" flagged data indicate the concentration is between the method detection limit (MDL) and the reporting limit. "R" flagged data are not suitable for risk screening. "U" flagged data provide useful information about the adequacy of the quantitation limits relative to the screening levels.

Data flagged with a "J" typically indicate that an analyte was detected below the project-specific reporting limit but above the MDL and the concentration is estimated. If the concentrations in such samples are close to the risk-based screening level, it may be possible to review data validation documentation to determine if the "J" flag suggests a high or low bias in the reported concentration. When data with a potential low bias (reported concentrations are thought to be below the true concentration) are present and the concentration is close to the screening level, the given analyte may be retained for further evaluation in order to err on the side of conservatism.

Data flagged with a "U" indicate that the analyte was not present above its quantitation limit (e.g., MDL or reporting limit). If the quantitation limits are below risk-based screening levels, analytes may be screened out using "U" flagged results. However, quantitation limits above screening levels are common and are the result of a number of factors. Ideally, this would be avoided by considering the screening levels when establishing the quantitation limits with the laboratory. Sometimes higher detection limits are caused by interferences — most commonly the presence of another analyte at a much higher concentration; at other times, the laboratory technique may result in higher detection limits. There is no prescriptive solution to resolving cases of quantitation limits above screening levels. Factors such as waste history, process knowledge, and detections in other media should be considered before eliminating analytes from further consideration.

Knowledge or expectations about the spatial and temporal variability for each medium should be considered. Indoor air concentrations typically vary less spatially than subsurface concentrations. There is no "rule of thumb" solution to resolving these uncertainties in the risk-screening step. Certainly, a single round of measurements from a limited number of samples provides the highest degree of uncertainty. Collecting samples from multiple locations and across multiple sampling events can help determine and account for variability in the CSM and risk screening.

Use of data from other media to predict indoor air concentrations introduces additional uncertainties associated with the assumed attenuation factors or modeling assumptions. Use of upper-percentile attenuation factors from sources such as U.S. EPA (2008) can mitigate the possibility of prematurely eliminating chemicals during risk screening. Even so, the CSM should be reviewed to determine if there are factors warranting further consideration. For example, in the case of shallow water tables in contact with basements, published attenuation factors may underpredict indoor air contaminant concentrations.

In summary, the representativeness, quality, and uncertainty associated with environmental data need to be considered and documented in the risk-screening evaluation. In the best case, these factors would be considered as part of the sampling and analysis plan, which could include elements to improve the overall data usability; examples include (1) designing the monitoring well so samples are collected from the top of the water table, (2) installing exterior soil vapor probes close to buildings of interest, and (3) determining if multiple rounds of data are warranted.

C.3 References

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APPENDIX D: SUGGESTED QUALITY CONTROL PROCEDURES FOR SOIL - GAS SAMPLING (AFTER DON, 2009)

Soil-gas sampling during vapor intrusion investigation is challenging due to the typical low concentrations of the investigated chemicals. To avoid some of the common problems associated with such sampling, several QC procedures should be considered.

1. **Equipment blank sample:** Assemble a soil-gas probe, and collect a sample before installing it in the ground. Repeat the process for each probe.
2. **Coring:** Collect soil core for visual inspection of texture and moisture at a minimum, also consider laboratory index tests for bulk density, grain density (collectively used to determine porosity), moisture content, and grain size distribution in select samples to provide information to support conceptual and mathematical models of the transport pathway.
3. **Probe installation:** If site geology is well known and highly permeable, temporary probes can be used. Otherwise, coring a hole followed by installation of the probe with a sand pack and annular seal is recommended. The preferred seal is a slurry of bentonite and water; however, alternating lifts of granular bentonite and water may be equally effective. Sealed permanent probes provide much higher protection against leaks and thus more representative samples when compared to temporary devices. Probes should be handled with clean hands. Use of new pairs of nitrile gloves before each probe installation is recommended. Adding dry granular bentonite above a sand pack helps prevent slurry from invading the sand pack.
4. **Multilevel probes**: If multilevel probes are installed in a single borehole, exert a vacuum on each probe in turn, and monitor the vacuum in adjacent probes to assess the integrity of seals.
5. **Probe Development**: Entrained air during probe installation should be purged as soon as practicable after seals are placed. Sampling can proceed if sufficient flow can be achieved with a modest vacuum. Otherwise, an overnight delay in sampling is recommended to re-equilibrate. If flow is too low to remove at least one pore volume of the sand pack and tubing, allow several days or more for equilibration before sampling.
6. **Pre-sampling Monitoring:** Purge standing volume in the probe and sand pack prior to sample collection: monitor total VOCs with a photoionization detector or FID, as well as O_2, CO_2 and CH_4 with a landfill gas meter; and review the field screening data. Monitored parameters should be relatively stable before sampling is performed.
7. **Flow Measurements:** Measure flow and vacuum during purging to assess permeability, and verify whether special procedures may be required for low-flow probes.
8. **Sample collection:** Conduct vacuum leak check prior to sample collection; adjust fittings as necessary. Assemble all sampling fittings, and apply pressure or vacuum to the lines. Close valves at each end, and monitor pressure or vacuum over time for at least a minute. If the applied pressure or vacuum does not hold, there is a leak, which should be fixed before sampling.
9. **Tracer:** In low-permeability soils, sub-slab samples, or very shallow soil-gas samples (<5 ft deep), the potential for leaks is high. In such cases, use of a tracer, such as helium is recommended.

Place a shroud over the Summa canister, flow controller and top of the probe, add ≥ 10% helium. Afterwards, purge through T-fitting to Tedlar® bag using a lung box. Record field parameters, including helium. If helium is <10% of the concentration in the shroud, the sample can be used for laboratory analysis.

APPENDIX E: FORENSIC QUALITY ASSURANCE/ QUALITY CONTROL

E.1 Standard Quality Assurance/Quality Control

A strong QA program includes numerous QC checks to ensure the attainment of the desired data quality. This appendix provides a detailed discussion of the QA/QC criteria for the purposes of writing the QAPP or SAP. Table E-1 summarizes the DQOs for Standard Method TO-15.

The sample holding time is 30 days from the date of sample collection. This holding time criterion ensures that the samples are analyzed in a timely fashion. In theory, the holding time also ensures that analytes are measured before any degradation. Speedy analyses of samples are always advantageous because it allows for re-analyses within the holding time, if necessary. Standard Method TO-15 employs re-useable stainless steel sample containers (Summa canisters). All containers must be rigorously decontaminated after use in the field to avoid sample cross contamination. After cleaning the containers in batches, the stainless steel canisters are analyzed individually or in batches to demonstrate the effectiveness of the decontamination procedure. At a minimum, the sample canister that contained the highest concentrations of VOCs before decontamination is usually tested for cleanliness. If the tested canister contains no target analytes above the calibration limit of the method, the canisters are approved for re-use.

TABLE E-1. TO-15 DQ criteria

Sample	TO-15	TO-15 Mod (PIANO)
Procedure Blank (PB)	Blank criteria for acceptable data: no target analyte at or above the reporting limit	Blank criteria for acceptable data: no target analyte at or above the reporting limit
Surrogate (Sur)	%Recovery to be established by laboratory control points	70% - 130% recovery
Laboratory Control Sample (LCS)	Not Required	70%- 130% recovery
Laboratory Control Sample Duplicate (LCSD)	Not Required	70%- 130% recovery
LCS/LCSD Relative Percent Difference (RPD)	Not Applicable	<25% RPD
Sample Duplicate (Dup)	< 25% RPD	< 25% RPD for those analytes > the reporting limit
MS Tune (Bromofluorobenzene)	50ng injected every 24 hours or less	50ng injected every 24 hours or less
Initial Calibration (Ical)	%RSD ≤ 30% for all analytes; up to two analytes may be ≥30% and ≤40%	%RSD ≤ 30% for 90% of analytes; %RSD ≥30% and ≤50% for 10% of analytes allowed
Continuing Calibration (CCV)	CCV analyzed at the beginning of the sequence; percent detection ≤ 30% for analytes	CCV analyzed at the beginning and end of sequence; percent detection ≤ 30% for analytes; ≤40percent detection for analytes from naphthalene to 1-methylnaphthalene
Internal Standard (IS)	60% - 140% of the area of the IS in the associated calibration standard; Retention times within +/- 0.30 min	60% - 140% of the area of the IS in the associated calibration standard; Retention times within +/- 0.30 min
Initial Calibration Verification (ICV)	Not Required	Following the ICAL (secondary source), %D ≤ 30% for analytes; %D between 50% and 130% for naphthalene through 1-methylnaphthalene allowed
Holding Times	30 days from sampling (SUMMA canister)	30 days from sampling (SUMMA canister)

Prior to initiating any data collection it is necessary to demonstrate that the GC/MS instrument is working properly. The instrument condition is initially demonstrated by tuning the MS detector and evaluating the standard mass spectral abundances. The tune is accomplished by injecting bromofluorobenzene (BFB) into the Standard TO-15 GC/MS instrument.

An acceptable BFB analysis initiates a 24-hour analytical period during which standards and samples are analyzed. Once injected and analyzed the BFB is evaluated through the data system to determine if the acceptance criteria are met.

Once tuned, the instrument is calibrated by analyzing a "calibration standard" at multiple concentrations. The instrument operator calculates relative response factors (RRFs) from the results of the multilevel initial calibration (ICAL) curve and establishes the linear or quadratic relationship between the magnitude of the instrument response relative to a known target analyte concentration. The operator then calculates the percent relative standard deviation (RSD) among the ICAL RRFs. The stability of the instrument is demonstrated by analyzing a continuing calibration verification (CCV) standard containing a mixture of target analytes at a known concentration every 24 hours.

To monitor for possible laboratory contamination, a procedure blank is analyzed with each analytical sequence. This method blank is a certified canister that is pressurized with humidified, ultra-pure air or nitrogen and carried through the same analytical procedure as the field samples.

Field samples are analyzed following the procedure blank for a 24-hour period starting with the instrument tune. Internal standards are injected into the procedure blank and field samples and their area responses are monitored. Instrument operators typically reanalyze samples if the procedure blank is contaminated or spike sample recoveries fail the applicable data quality criteria.

On a daily basis, a new sequence begins with a BFB tune followed by a CCV. The CCV is analyzed to verify the continued accuracy of the initial calibration curve. The RFs of the target analytes in the CCV are compared against the average RFs of the target analytes from the initial calibration and to determine the percent difference (%D). Analysis of a procedure blank and field samples may then be performed if the %D criterion is met. Failure of the %D criterion may be an indication that a new initial calibration curve needs to be performed.

E.2 Forensic Quality Assurance/Quality Control

All of the data quality criteria for Standard Method TO-15 apply to Forensic Method TO-15. In addition, there are numerous QC checks over and above the Standard Method TO-15 data quality criteria that are recommended for the Forensic Method TO-15. This section discusses these enhanced QC criteria.

Forensic Method TO-15 includes an Initial Calibration Verification (ICV) sample after the ICAL. The ICV is a mixture of target analytes formulated at a known concentration from a source different than the ICAL standards. The percent recoveries are calculated and used to determine the accuracy of the method.

Another QC enhancement includes the analysis of a laboratory control sample (LCS) and laboratory control sample duplicate (LCSD). The LCS and LCSD samples are blank samples fortified with target analytes of known concentration. The ICV solution from a source that is independent of the ICAL standards is typically used as the LCS spiking solution. The percent recovery (%R) of the target analytes demonstrates the capability of the method to accurately measure the target analytes.

The RPD between the LCS and LCSD demonstrates the precision or reproducibility of the method under ideal conditions.

A field sample duplicate is also analyzed with each Forensic Method TO-15 sequence to further monitor the precision and accuracy of the analytical method. The RPD of the sample and duplicate demonstrates the precision of the method for the site conditions.

Finally, a closing CCV is analyzed at the end of a sequence to help measure performance of the instrument through the complete period of analysis. This is not a requirement of Standard Method TO-15. Collectively, these method enhancements ensure that Forensic Method TO-15 analyses are as good as or better than the Standard Method TO-15 results.

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APPENDIX F: INTRODUCTORY EXAMPLE OF PRINCIPAL COMPONENT ANALYSIS

Note: ***The following is an introductory example, presented in a series of text boxes, to familiarize the reader with various computational elements of principal component analysis.***

BOX F-1. Example of a Multivariate Dataset

Consider a class of 10 students, graded in six different subjects, as listed below.

Subject	**Student_1**	**Student_2**	**Student_3**	**Student_4**	**Student_5**	**Student_6**	**Student_7**	**Student_8**	**Student_9**	**Student_10**
Science	B	A	C	B	A	D	B	C	B	B
Math	B	B	C	A	A	D	A	C	A	B
Social Studies	A	B	D	B	B	C	A	B	A	C
English	A	B	D	A	B	B	A	C	A	C
Art	A	C	B	C	A	B	A	C	C	D
PE	B	D	A	B	A	A	B	C	A	A

Each subject may be thought of as a *variable*. In that case, the grading chart above becomes a six-dimensional multivariate dataset. The table below is the same chart, where letter grades are converted into their equivalent numeric grade points.

Subject	**Student_1**	**Student_2**	**Student_3**	**Student_4**	**Student_5**	**Student_6**	**Student_7**	**Student_8**	**Student_9**	**Student_10**
Science	3	4	2	3	4	1	3	2	3	3
Math	3	3	2	4	4	1	4	2	4	3
Social Studies	4	3	1	3	3	2	4	3	4	2
English	4	3	1	4	3	3	4	2	4	2
Art	4	2	3	2	4	3	4	2	2	1
PE	3	1	4	3	4	4	3	2	4	4

BOX F-2. Use of *Scores* to Summarize Multivariate Datasets

Analyzing a six-dimensional multivariate dataset can be difficult. To simplify this process, each student's grades are summarized by a single ***score***. The obvious option is the ***average grade***, as listed below.

Subject	**Student_1**	**Student_2**	**Student_3**	**Student_4**	**Student_5**	**Student_6**	**Student_7**	**Student_8**	**Student_9**	**Student_10**
Science	3	4	2	3	4	1	3	2	3	3
Math	3	3	2	4	4	1	4	2	4	3
Social Studies	4	3	1	3	3	2	4	3	4	2
English	4	3	1	4	3	3	4	2	4	2
Art	4	2	3	2	4	3	4	2	2	1
PE	3	1	4	3	4	4	3	2	4	4
Average Grade	***3.5***	***2.7***	***2.2***	***3.2***	***3.7***	***2.3***	***3.7***	***2.2***	***3.5***	***2.5***

Average grade is a score, which is mathematically written as a ***linear combination*** of each student's grade in various subjects, or

$$\overline{G} = \frac{G_{Science} + G_{Math} + \cdots + G_{PE}}{6} = \frac{1}{6}G_{Science} + \frac{1}{6}G_{Math} + \cdots + \frac{1}{6}G_{PE}$$

The weight assigned to each subject in the above equation is referred to as its ***loading***. Substituting the grades of a student in the above equation yields his or her unique average grade.

BOX F-3. Alternative Scores for Summarization of Multivariate Datasets

Despite its simplicity, average grade is usually viewed as an inadequate score because all subjects are weighted equally, regardless of their academic significance. The average grade also masks the strengths of individual students in particular subjects.

Another score is the weighted ***grade point average***, or GPA, in which each subject is weighted (w) based on predetermined values. For example, in colleges, the grade in each subject is weighted according to its "credit hours." The general formula for GPA is

$$GPA = \frac{w_{Science}G_{Science} + w_{Math}G_{Math} + \cdots + w_{PE}G_{PE}}{w_{Science} + w_{Math} + \cdots + w_{PE}}$$

As with the average grade, GPA has also been criticized. Some claim it is biased toward certain subjects, while masking students' performances in other subjects.

BOX F-4. Principal Component Analysis

Principal component analysis offers a statistical procedure for producing unbiased scores that can adequately reflect the class performance.

In this technique, the range of student performance in any subject is measured in terms of a ***variance,*** i.e., the square of the standard deviation of students' grades in a given subject, as listed below.

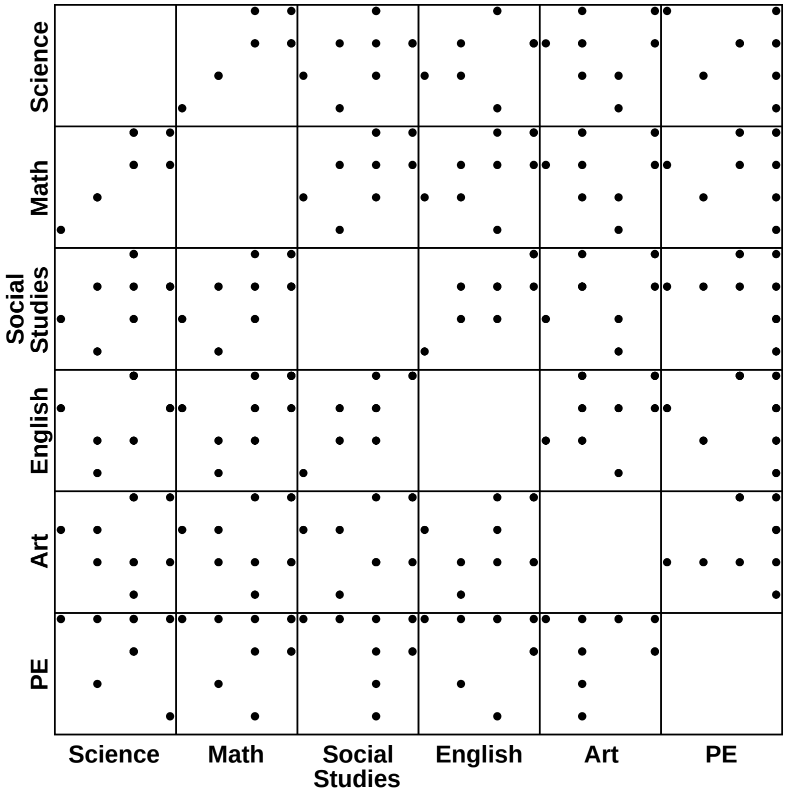
Subject	**Student_1**	**Student_2**	**Student_3**	**Student_4**	**Student_5**	**Student_6**	**Student_7**	**Student_8**	**Student_9**	**Student_10**	**Subject Variance**
Science	3	4	2	3	4	1	3	2	3	3	**0.84**
Math	3	3	2	4	4	1	4	2	4	3	**1.11**
Social Studies	4	3	1	3	3	2	4	3	4	2	**0.99**
English	4	3	1	4	3	3	4	2	4	2	**1.11**
Art	4	2	3	2	4	3	4	2	2	1	**1.12**
PE	3	1	4	3	4	4	3	2	4	4	**1.07**

Principal component analysis automatically calculates the ***total variance***, which is the variance of the sum of all subject grades. Total variance is the sum of all subject variances (listed above), but discounted for any correlation among the investigated variables. In this case, the computed total variance can be viewed as the measure of the overall class performance variations.

Principal component analysis identifies scores that capture the largest percentages of the total variance in a descending order. In many cases, the first few principal components explain the vast majority of the total variance.

BOX F-5. Bivariate Correlations

To identify the best-representative scores, principal component analysis explores the correlations among the grades students received in various subjects. These correlations are displayed in the following *bivariate* matrix plots, which show comparisons of students' grades in one subject versus those received in another.



Some plots display linear patterns (e.g., Math vs. Science, English vs. Social Studies). This means student grades in these subjects are highly correlated. Such correlations suggest that the information about each student can be summarized by only a few scores.

BOX F-6. Computing Principal Component Scores

Using a statistical software package, the above matrix plots are converted into a correlation matrix, as shown below.

	Science	Math	Social Studies	English	Art	PE
Science	1	0.80	0.46	0.34	0.05	-0.30
Math	0.80	1	0.64	0.60	0.10	0.00
Social Studies	0.46	0.64	1	0.85	0.28	-0.30
English	0.34	0.60	0.85	1	0.30	-0.10
Art	0.05	0.10	0.28	0.30	1	0.16
PE	-0.30	0.00	-0.30	-0.10	0.16	1

In this case, each element of the above matrix is the ***Pearson's correlation coefficient (r)*** of the specified paired subject grades. r^2 is also known as the ***coefficient of determination***.

Having the correlation matrix, the statistical software package will calculate the set of principal component scores that best explain the total variance, i.e. scores that best reflect the overall class performance. For this purpose, principal component analysis uses the *eigendecomposition* of the correlation matrix. In this process, the correlation matrix is decomposed into a series of *eigenvectors*, each associated with an *eigenvalue*. Each eigenvector defines one of the principal components. The eigenvalue of a principal component quantifies how much of the total variance is captured by that particular component. The sum of eigenvalues is equal to the total variance. The eigenvectors are ranked according to their associated eigenvalues.

PC1 or the first principal component is associated with the highest eigenvalue, while PC2 or the second principal component has the second highest eigenvalue. PC1 and PC2 are the top two scores. In this case, the resulting PC1 and PC2 are:

$$PC1 = 0.75G_{Science} + 0.86G_{Math} + 0.90G_{SocialStudies} + 0.84G_{English} + 0.31G_{Art} - 0.25G_{PE}$$
$$PC2 = -0.38G_{Science} - 0.07G_{Math} + 0.06G_{SocialStudies} + 0.23G_{English} + 0.74G_{Art} + 0.71G_{PE}$$

As shown above, the computed "loadings" of PC1 (i.e., coefficients of subjected grades in the PC1 equation) for Science, Math, Social Studies and English are much higher than those for Art or PE. These loadings imply that the PC1 score is heavily driven by the student's grades in Science, Math, Social Studies, and English. In contrast, the PC2 score is more influenced by the student's grades in Art and PE.

Substituting the actual grades of a student into the above equations will yield the unique scores of that student.

BOX F-7. PC Scores: Information-Effective Summaries

Principal component analysis computes the percentages of the total variance explained by each PC. In this case, PC1 and PC2 explain 50% and 21% of the total variance, respectively. In contrast, the average grade only captures 17% of the total variance.

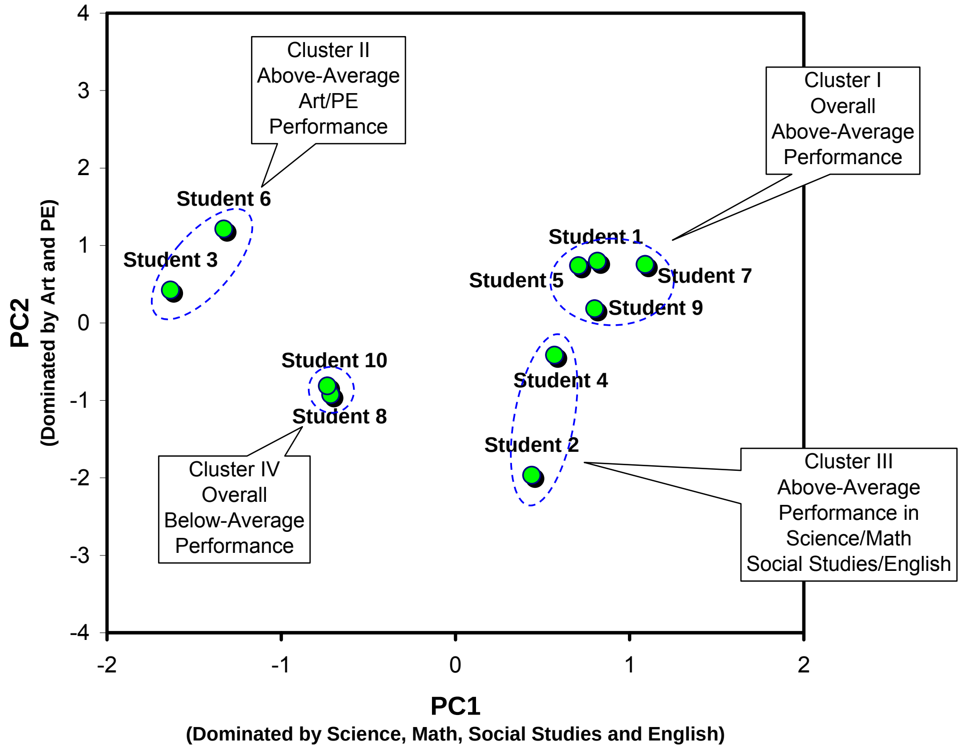
The above information-effective scores collectively explain 71% of the class performance. In other words, these scores summarize class performance without much loss of information.

Use of additional principal components increases the percentage of explained variance. For example, addition of a third score to the first two, i.e., PC1, PC2 and PC3, would explain 86% of the class performance. However, such an addition complicates the analysis and defeats the purpose of data summarization.

BOX F-8. Score Plots and Sample Grouping

Now, the unique PC1 and PC2 scores of each student can be calculated by simply substituting his or her grades in the above PC1 and PC2 equations. The plot of these student-specific scores is called the ***score plot***, as displayed below.

Visual inspection of the score plot allows the identification of students with similar patterns. Such students will have ***clustered*** scores.



In the above score plot, students in Cluster I, i.e., Students 1, 5, 7 and 9, display above average performance in all subjects. In contrast, students in Cluster II, i.e., students 3 and 6, are primarily strong in Art and PE, while students in Cluster III, i.e., students 2 and 4, are mainly strong in the more academic subjects.

The above principal component scores provide a far more comprehensive summary of each student's performance than the average grade or GPA.

BOX F-9. Environmental Application

In environmental investigations, the above analysis can be repeated with the following replacements:

- School Subjects ⇨ Chemicals
- Students ⇨ Samples
- Students' Grades ⇨ Chemical Concentration Measures (e.g., Chemical Fraction)

For example, in the hypothetical case considered in Section 5.3, the fractions of petroleum-related VOCs in different samples are the variables, as listed below.

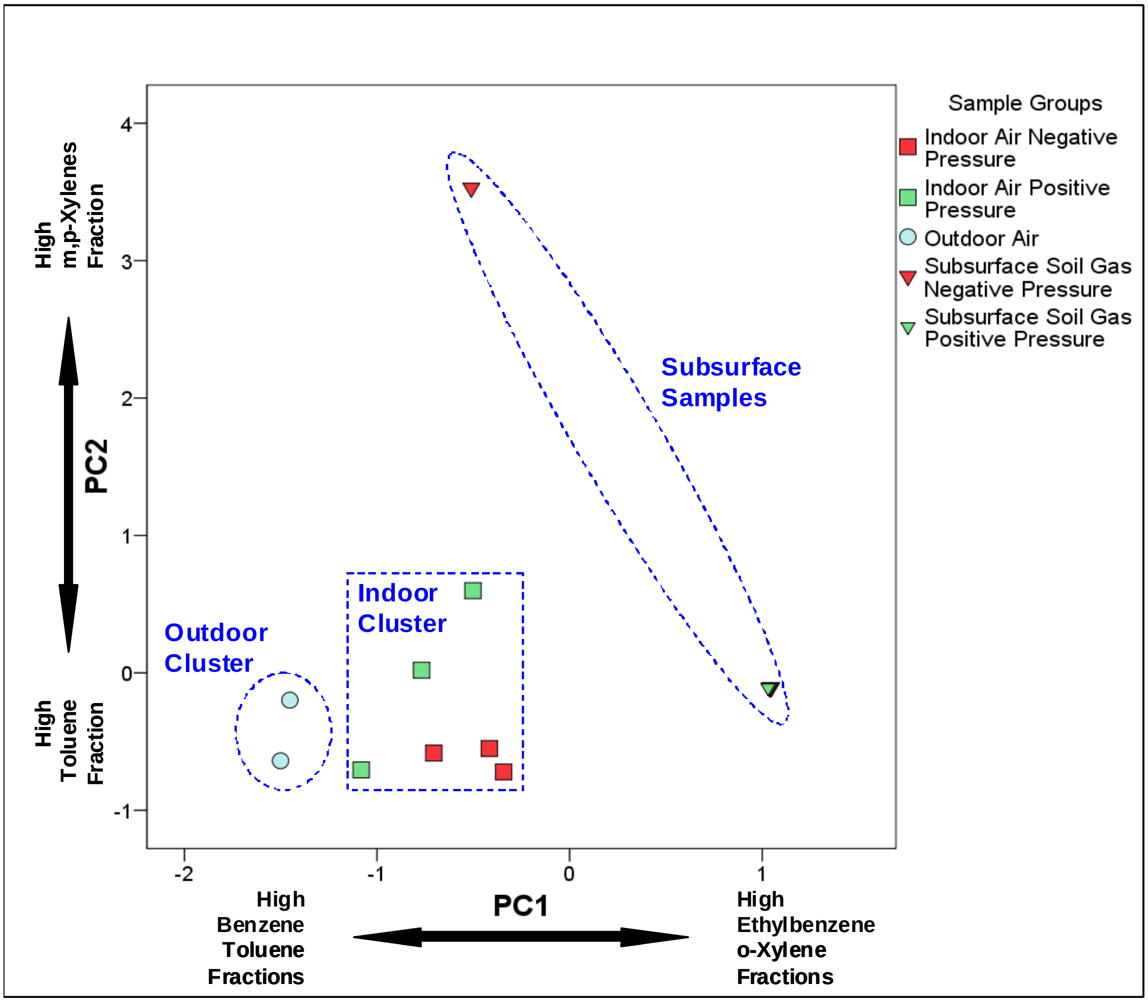
Petroleum-related VOC Fractions in Varoius Indoor (IA), Outdoor (OA), and Subsurface Soil Gas (SG) Samples

	Samples															
Chemicals	IA-1_Neg	IA-1_Pos	IA-2_Neg	IA-2_Pos	IA-3_Neg	IA-3_Pos	OA-1	OA-2	SG-1_Neg	SG-1_Pos	SG-2_Neg	SG-2_Pos	SG-3_Neg	SG-3_Pos	SG-4_Neg	SG-4_Pos
Benzene	0.10	0.07	0.09	0.08	0.07	0.09	0.16	0.17	0.06	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Ethylbenzene	0.13	0.07	0.18	0.14	0.18	0.12	0.07	0.08	0.12	0.24	0.24	0.24	0.24	0.24	0.24	0.24
Toluene	0.48	0.60	0.45	0.37	0.48	0.45	0.52	0.45	0.12	0.24	0.24	0.24	0.24	0.24	0.24	0.24
Xylenes, m,p-	0.20	0.19	0.20	0.31	0.19	0.25	0.18	0.22	0.59	0.24	0.24	0.24	0.24	0.24	0.24	0.24
Xylene, o-	0.08	0.07	0.08	0.10	0.07	0.09	0.07	0.08	0.12	0.24	0.24	0.24	0.24	0.24	0.24	0.24

The collection of fractions of VOCs in each sample is defined as its unique chemical ***profile***.

BOX F-10. Indoor, Outdoor and Subsurface Sample Clusters and Groupings

The goal is to use principal component analysis to summarize the multivariate chemical profile of each sample by a few scores. Having determined the loadings of these scores, as discussed in Section 5.3, unique scores of each investigated sample can be computed and plotted, as shown below.



The above score plot clearly indicates that the scores of indoor samples form a cluster distinct from those of subsurface samples. In contrast, indoor and outdoor clusters are near each other. These observations further confirm the earlier EDA findings that (1) indoor petroleum-related VOCs are not caused by subsurface sources, and (2) indoor petroleum-related VOCs are likely linked to outdoor emissions. For more discussion, refer to Sections 3.6 and 5.3.