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1 October 1997

US Army Corps
of Engineers

ENVIRONMENTAL QUALITY

DESIGN, INSTALLATION AND UTILIZATION OF FIXED-FENCELINE SAMPLE COLLECTION AND MONITORING SYSTEMS (FFMS)

ENGINEER MANUAL

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DEPARTMENT OF THE ARMY
U.S. Army Corps of Engineers
Washington, D.C. 20314-1000

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Manual
No. 200-1-5

1 October 1997

Environmental Quality
DESIGN, INSTALLATION AND UTILIZATION OF
FIXED-FENCELINE SAMPLE COLLECTION
AND MONITORING SYSTEMS

1. Purpose. This Engineering Manual (EM) provides air monitoring guidance for designing and conducting real-time, fixed-fenceline air quality monitoring programs for site investigation and remediation projects. Specifically, the Manual addresses the selection, set-up, and operation of sampling and analytical equipment, data management, and quality assurance/quality control (QA/QC). Guidance for developing sampling and analysis plans and standard operating procedures is also presented.

2. Applicability. This EM applies to all USACE Commands having responsibility for hazardous, toxic, and radioactive waste (HTRW) projects.

3. References. References are presented in Appendix A.

4. Distribution Statement. Approved for public release distribution unlimited.

5. Discussion. This EM provides details for the development and implementation of a real-time, fixed-fenceline monitoring system (FFMS) for the collection and measurement of both background and fenceline migration of onsite generated volatile air contaminants. The EM addresses the sample collection design requirements based on site environment, site specific contaminants, and the data quality objectives (DQOs) established for the monitoring. Management and technical personnel can use this EM to provide scope and contract language as well as oversite direction for the actual installation and operation of such fenceline monitoring systems. This EM addresses requirements for a perimeter air monitoring program during site investigation, feasibility studies, and remedial actions.

FOR THE COMMANDER:

OTIS WILLIAMS
Colonel, Corps of Engineers
Chief of Staff

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App A - References
App B - Acronyms & Definitions
App C - Guideline SOPs
App D - Technical Source Listing
App E - Conversion Factors
App F - Equipment Listing
App G - Target Compound List

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Chapter 1
Introduction

1-1. Purpose

The U.S. Army Corps of Engineers (USACE), as part of their hazardous, toxic, and radioactive waste (HTRW) programs, conduct site investigation and remedial action projects in an efficient, cost-effective, and technically-sound manner. This Engineer Manual (EM) assists in this process by providing guidance to USACE personnel responsible for designing and conducting real-time, fixed-fenceline sample collection and monitoring systems (FFMS) as part of an air quality monitoring programs at (HTRW) sites. The EM specifically addresses the selection, set-up, and operation of sampling and analytical equipment; quality assurance/quality control (QA/QC) and data management requirements. Guidance for developing standard operating procedures and associated information is also presented, in applicable appendices.

1-2. Applicability

This EM applies to USACE commands having responsibility for ambient air measurements associated with HTRW site investigation and remediation projects. This EM is intended to present its users with the requirements necessary to monitor the release of volatile organics and other compounds at the perimeter of an HTRW site using a FFMS monitoring system. The requirements for such a system normally address six technical areas: 1) Monitoring location, 2) Monitoring frequency, 3) Instrumentation, 4) Action limits, 5) Meteorological monitoring and 6) Documentation and recordkeeping.

This EM can provide technical support to USACE design and/or construction personnel responsible for the requirements involved in the design, implementation, and operation of a real-time, fixed-fenceline sample collection and monitoring system for HTRW projects including: 1) Ordinance and Explosive (OE), 2) Defense Environmental Restoration Programs (DERP), 3) Base Realignment and Closure (BRAC), 4) Installation Environmental Compliance, 5) Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) or Superfund, 6) Resource Conservation and Recovery Act (RCRA) and, 7) Applicable civil and military projects.

1-3. References

The references used in the text of this EM along with additional references which may support the design, installation and operation of a FFMS are included in Appendix A.

1-4. Scope

This EM can be useful to USACE personnel responsible for the development and implementation of a real-time, fixed-fenceline monitoring system for the collection and measurement of both background and fenceline migration of onsite generated volatile air contaminants. The EM assumes the decision has been made to use such a real-time, fixed-fenceline monitoring approach either as a stand alone monitoring system or as part of a more extensive air monitoring program. NOTE: Perform an Air Pathway Analysis (APA), as specified in EPA-450/1-89-001a and EP 1110-1-21, before designing an air monitoring system. Results of the APA should be used to determine the need for ambient air monitoring and if so determined would assist in the development of an appropriate HTRW Air Monitoring Plan. The EM includes the sample collection design requirements based on site environment, site specific contaminants, and the data quality objectives established for the monitoring. The EM will assist in providing an understanding as to which design approaches are best suited for a given project data requirement. This EM addresses the design of a perimeter air monitoring system which can be used during site investigation, feasibility studies, and remedial actions and provides direction for the actual installation and operation of such fenceline monitoring systems.

1-5. Overview of Manual

The EM is organized into eight chapters and seven appendices. Chapter 1 is the *Introduction*. Chapter 2, *How to Use This Manual*, describes the relationship between the EM and the major steps in planning and executing a fenceline ambient air monitoring program. Chapter 3, *Monitoring Objectives and Technological Options*, discusses the tasks that are crucial to the planning process, including determining data quality objectives, identifying regulatory limits and action levels, investigating properties of any hazardous air contaminants at the site, and assessing technical considerations and constraints in designing a monitoring program. Chapter 4, *Function of the Analytical Center*, describes the analytical center's components and design, operational options, contingency and reference method monitoring, and communication between system components. Chapter 5, *Requirements for the Collection System*, discusses all aspects of the collection system, including design, construction, and operation; sample conditioning and transportation; preventative maintenance and corrective action; and time-integrated and real-time monitoring requirements. Chapter 6, *Meteorological Monitoring System*, presents the objectives of sampling system control, meteorological monitoring concepts, integration of the analytical center with the meteorological monitoring system, and program action levels and response. Chapter 7, *Data Management System*, highlights all aspects of a data management system, including design and operation of the data acquisition system; data compilation, storage, transmission, and reporting; and data validation and quality assessment. Chapter 8, *Quality Assurance/Quality Control Requirements*, presents basic QA/QC principles, the approach to quality planning, data characterization, and specific applications to fenceline monitoring.

The appendices of this EM play an important part in the design and implementation of a FFMS at a HTRW site. They provide additional guidance and information useful to the design and operation of the monitoring program. Following is a brief discussion of each appendix provided in this EM.

- **Appendix A--References**. Appendix A contains an up-to-date list of references supporting citations in this manual and associated literature sources relevant to establishing a FFMS at a HTRW site

.

- **Appendix B--Acronyms and Definitions**. As with any document which uses acronyms and technical terminology, an accurate and reliable list of acronyms and technical definitions must be provided. Appendix B provides a list of acronyms and definitions used in this EM along with additional terms unique to the technical field of air monitoring.

- **Appendix C--Guidelines for Developing Standard Operating Procedures (SOPs) for Fenceline Monitoring**. To obtain reliable results, adherence to prescribed methodology is imperative. Appendix C provides guidelines for preparing and implementing SOPs relative to the FFMS program. Example format and content of typical USACE approved SOPs are provided.

- **Appendix D--National Technical Guidance Series, Bulletin Boards, and Electronic Data Bases**. The efficiency with which a fenceline air monitoring program can be developed and implemented is highly dependent on the extent and quality of technical information available during the development phases of the program. Appendix D provides information on assessing various federal, state and commercial databases, electronic bulletin boards and fact sheets pertinent to FFMSs at HTRW sites.

- **Appendix E--Conversion Factors for Common Air Pollution Measurements and Other Useful Information for HTRW Sites**. Appendix E provides convenient conversion tables and factors associated with air monitoring measurement systems used at HTRW sites. Information in this appendix assist the USACE engineer in confronting a multitude of confusing and conflicting emission units presented in various project documents.

- **Appendix F--Manufacturers of Sampling and Analytical Equipment**. This appendix provides examples of some of numerous commercially available sampling and analytical systems and equipment which could be available and suitable for monitoring both time-integrated and real-time emissions from HTRW sites as part of a FFMS program.

- **Appendix G--Development of a Target Compound List**. Development of a site-specific target compound list (TCL) as part of a FFMS at a HTRW site is a key factor in the success of the program. Appendix F provides guidelines and details on how to develop a site-specific TCL using a simple algorithm involving health effects data, emission data, risk information, availability of sampling/analytical methodologies and regulatory requirements.

Chapter 2
How to Use This Manual

1-1. Introduction

Designing an air monitoring program for a HTRW site is not a difficult task if one approaches the project in a systematic way. The real difficulty lies in selecting the most appropriate approach, establishing the data quality objectives (DQOs), and selecting the proper sampling and analytical methodology. As with other monitoring programs, no two HTRW sites have the same site characteristics and project demands. Consequently, a successful project requires proper planning and organization for the collection of accurate and reliable data. Planning and organization are essential to attaining the data collection goals of minimizing data collection costs and ensuring that data are defensible, and are of known and acceptable quality to meet the needs of the primary data user (decision maker).

Figure 2-1 depicts the major project planning and execution steps needed in the successful design of a FFMS at a HTRW site. This approach should be thought of as a flow chart or a guide that is useful, but not necessary, to follow steps sequentially. This Chapter depicts (explains) how personnel responsible for air monitoring at HTRW sites may use this EM to select and design the FFMS technology and to implement it as part of air monitoring program. The relationship of various paragraphs of this EM to a project=s planning and execution steps in implementing this program is discussed below.

1-2. Defining Monitoring Program Objectives, Intended Use of Data, and Data Quality Objectives

This EM can assist with the initial planning phase of a project by helping to identify monitoring program objectives, intended use of the data, and project DQOs. Although the EM itself cannot determine the specific objectives and data uses for a given project, it defines the capabilities of applicable technology, thereby ensuring that a project's objectives and data uses are realistic and achievable for the selected measurement system. For example, if one objective of a project is to measure minute quantities of some trace contaminant, the EM can help determine whether system detection limits are sufficiently low to allow measurement of the contaminant within acceptable accuracy and precision limits.

Paragraphs of the Manual that may be most useful during the initial planning phase of a project include:

- 3-2 Data Quality Objectives.
- 3-3 Regulatory Limits, Action Levels, and Site Specific Alert Levels and Triggering Mechanism.
- 3-5 Chemical and Physical Properties of Hazardous Air Pollutants.
- 3-6 Technical Considerations in the Development of a FFMS.
- 7-0 Data Management.

$ 8-2 Quality Planning.

DEFINING MONITORING PROGRAM OBJECTIVES, INTENDED USE OF DATA, AND DATA QUALITY OBJECTIVES

- Needs and Expectations of Data Users and Regulators
- Protection of Public Health and Safety
- Technical, Physical, and Resource Limitations

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PREPARATION / PLANNING AND DOCUMENTATION

- Scope of Services (SOS) Documentation
- Plans and Specifications (for remediation projects)
- Work Plan
- Sampling and Analysis Plan (SAP);
  - -- Equipment Purchase
  - -- Quality Assurance Project Plan (QAPP)
- Standard Operating Procedures (SOPs) (if not already available)

↓

SITE SET-UP AND OPERATION

- Analytical Center Set-Up
  - -- Equipment Purchase
  - -- Environmental Needs (electricity, security, etc.)
  - -- Installation and Operation
- Monitoring Points Set-Up
  - -- Heat-trace line installation/operation
  - -- Probe location and maintenance
- Routine Monitoring
- Contingency Monitoring

↓

OPERATION AND MAINTENANCE OF EQUIPMENT

- Routine Maintenance and Corrective Action
- System Checklist and Evaluation
- Field Evaluation and Performance
- Corrective Action and SOP Update

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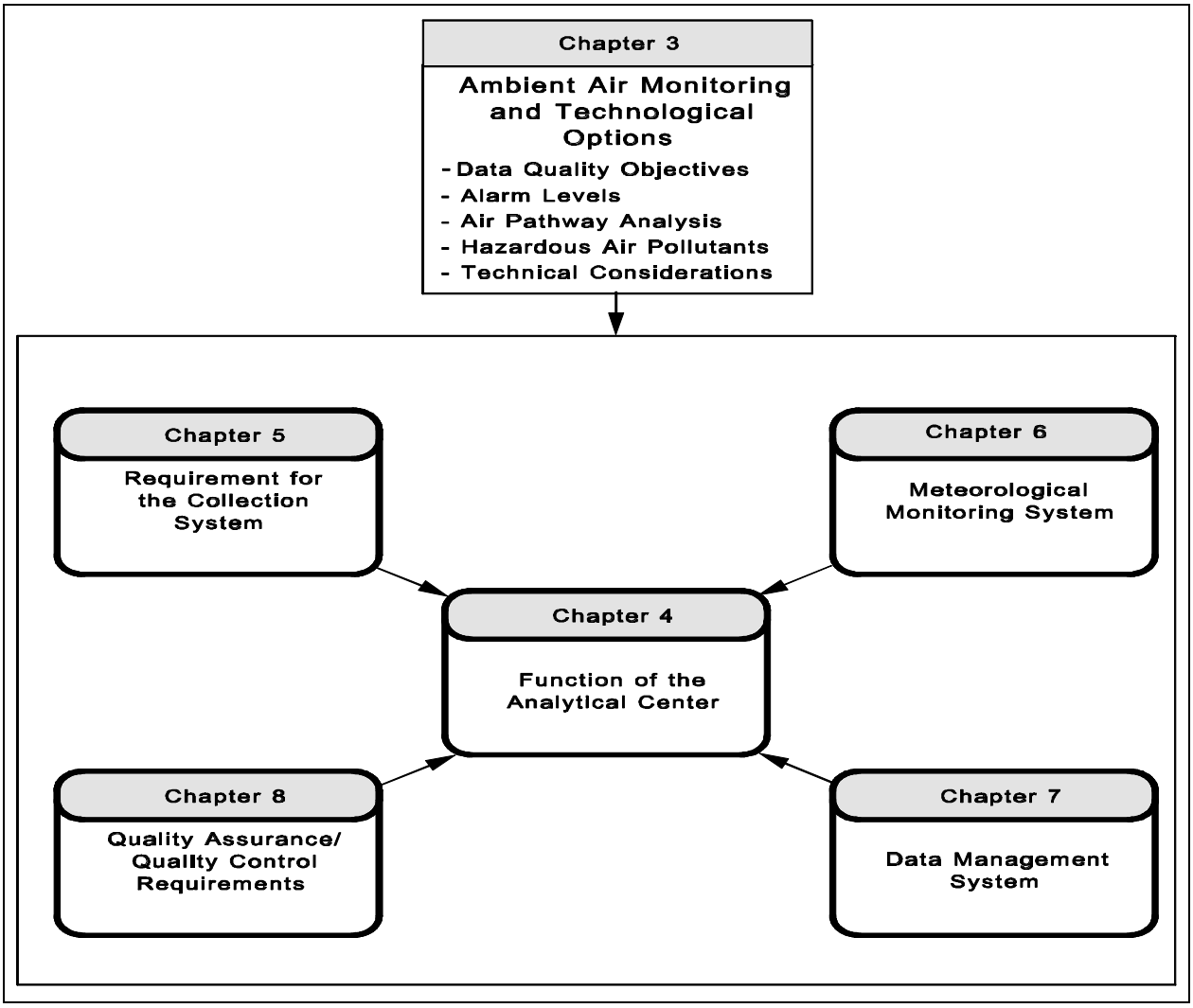
DATA ANALYSIS AND REPORTING

- Data Acquisition System and Design
- Data Compilation, Storage and Transmission
- Data Validation Procedures
- Data Reporting Requirements

1-3. Preparing Planning and Execution Documents

This EM can serve as a valuable tool in preparing the various planning and execution documents that are required before field work commences. This EM is useful in preparing the SAP, consisting of the FSP and the QAPP, and



SOPs. Additionally, it may be appropriate under certain circumstances to incorporate by reference portions of this EM into certain planning and execution documents. Figure 2-2 depicts the relationship between key chapters of the EM and the critical elements in designing, implementing, and operating a FFMS at a HTRW site, while Table 2-1 cross-references the manual with specific project planning and execution steps.

TABLE 2-1
Relevance Of Manual Chapters To Project Planning And Execution Steps

Manual Chapters		Program Objectives, Intended Use of Data, and DQOs	Planning and Execution Documents	Site Set-Up and Operation	Operation and Maintenance of Equipment	Data Analysis and Reporting
1.	Introduction	!				
2.	How to Use This Manual	!				
3.	Monitoring Objectives and Technical Options	!	!			
4.	Function of the Analytical Center		!	!	!	
5.	Requirements for the Collection System		!	!	!	
6.	Meteorological Monitoring System		!			
7.	Data Management System		!			!
8.	Quality Control Requirements	!	!	!	!	!
Appendices						
A.	Abbreviation/ Acronyms and Glossary	!				!
B.	References		!			!
C.	Guidelines for Developing Standard Operating Procedures (SOPs) for Fence-Line Monitoring		!			
D.	National Technical Guidance Series, Bulletin Boards, and Electronic Data Bases		!			
E.	Conversion Factors for Common Air Pollution Measurements and Other Useful Information		!			!
F.	Manufacturers of Sampling and Analytical Equipment		!			
G.	Development of Target Compound List	!				

1-4. Site Set-Up and Operation

Even with good planning, challenges in the field will still occur. The sections of the Manual that address site set-up (especially in Chapter 4, *Function of the Analytical Center*, and Chapter 5, *Requirements for the Collection System*) are intended to help avoid unpredictable events through implementation of a careful planning process that has been implemented at previous HTRW projects. Additionally, Paragraph 8-4 contains a discussion of *Special concerns*, in which some common operational challenges are described and recommendations made for avoiding them during site set-up are presented.

1-5. Operation and Maintenance of Equipment

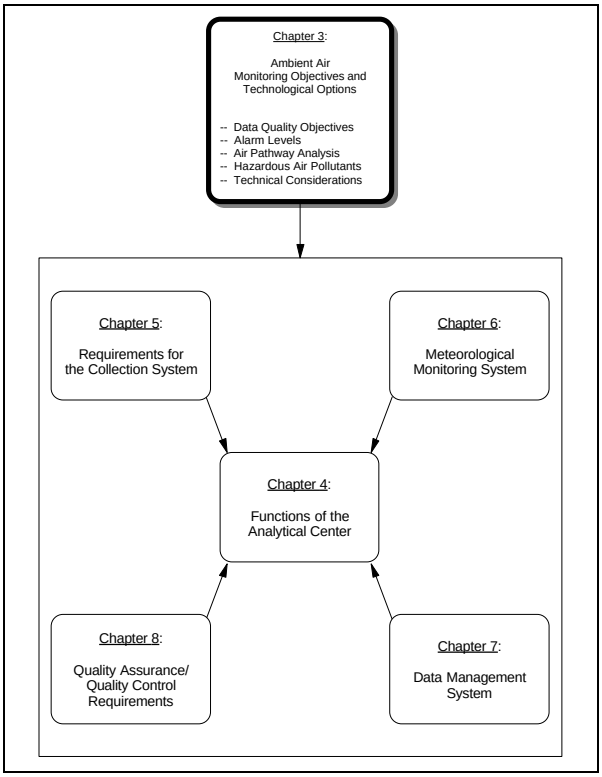
Paragraphs in Chapter 4, *Function of the Analytical Center*, and Chapter 5, *Requirements for the Collection System*, describe critical operating parameters and provide guidance on the operating and maintenance procedures needed to ensure the success of the program. Chapter 8, *Quality Assurance/Quality Control Requirements*, describes the checks and audits needed to demonstrate whether the correct operating and maintenance procedures have been followed.

1-6. Data Analysis and Reporting

Automated data acquisition systems are essential due to the large volume of data collected and the frequent need for quick turn-around in analyzing data and reporting results. Chapter 7, *Data Management System*, discusses the design and operation of these systems and the preferred procedures for documenting data and reporting results. Also discussed in Chapter 7 are calibration and validation procedures, data quality assessment, and reporting. The characterization of data quality, including the use of QC samples and data quality indicators, is described in Chapter 8, *Quality Assurance/Quality Control Requirements*. Finally, Appendix E, *Conversion Factors for Common Air Pollution Measurements and Other Useful Information for HTRW Sites*, provides useful information for manipulating and reporting data.

SUMMARY REQUIREMENTS FOR MONITORING OBJECTIVES AND TECHNOLOGICAL OPTIONS

Defining monitoring objectives is the first important step in the design and operation of a FFMS at a HTRW site. The purpose of Chapter 3 of EM 200-1-5 is to discuss the objectives and DQOs of a FFMS with respect to quantifying emissions during different phases of the remediation program. By clearly defining the objectives and DQOs, the Corps is able to successfully assess and characterize effects of pollutant transport via the applicable exposure pathway from the HTRW site.



SECTION I: INTRODUCTION

SECTION II: DATA QUALITY OBJECTIVES (DQOs)
- Introduction
- DQO Process

SECTION III: REGULATORY LIMITS, ACTION LEVELS AND SITE SPECIFIC ALERT LEVELS
- Introduction
- Regulatory Limits
- Action Levels (I-IV)

SECTION IV: EPA's AIR PATHWAY ANALYSIS
- Superfund Process
- Air Pathway Analysis

SECTION V: CHEMICAL AND PHYSICAL PROPERTIES OF HAPs
- Air Emission Mechanism
- Technology for Monitoring HAPs
- Defining HAPs
- Site Specific Target Compound List (TCL)

SECTION VI: TECHNICAL CONSIDERATION IN DEVELOPING A FFMS
- Acceptable Risk-Specific Concentrations
- Monitoring Strategy
- Cost Factor
- Site Characteristics
- Quality Assurance

Chapter 3 discusses the tasks that are crucial to the planning process, including determining data quality objectives, identifying regulatory limits and action levels, investigating properties of HAPs at the

Panel 3-1. Overview of Monitoring Objectives and Technological Options

site, and assessing technical considerations and constraints in designing the FFMS program at the HTRW site.

Panel 3-1. Overview of Monitoring Objectives and Technological Options

3-1. Introduction

The purpose of this Chapter is to discuss the objectives, nature, and mechanisms for quantifying emissions from HTRW sites during different phases of investigation or remediation utilizing a real-time FFMS for applicable volatile organic compounds (VOCs) or particulate-related contaminants. For the assessment and clean-up of HTRW sites, it is necessary to characterize and quantify potential and actual effects of pollutant transport from the site. Clean-up of HTRW sites is performed to assure general environmental protection and the health and safety of the population in close proximity of the site. Contamination at a given site may pose a current or future risk by exposure from a number of potential pathways, which include direct contact with the in-situ pollutants, subsurface migration of the contaminants via vapor plumes or ground-water plumes, contamination of surface waters, and atmospheric transport (and deposition) of gaseous, aerosols, or wind-blown contaminants. To successfully assess and clean up a HTRW site, it is necessary to characterize the potential effects of pollutant transport via the applicable exposure pathways for each step of the assessment and clean-up process. Verification of these exposures must be included in the establishing of the project DQOs.

3-2. Data Quality Objectives (DQOs)

a. Introduction. DQOs are qualitative and quantitative statements derived from the DQO process that clarify study objectives, define the appropriate type of data, and specify the tolerable levels of potential decision errors that will be used as the basis for establishing the quality and quantity of data needed to support decisions. The DQO process is an important planning tool to determine the type, quantity, and quality of data needed to support decisions. The DQO process helps develop statements of the level of uncertainty a decision maker is willing to accept when making decisions based on the air monitoring data. DQOs differ from data quality indicators, (such as measurement precision and accuracy), in that they express the limits of the overall uncertainty of a project's results in terms of the probability and consequences of making a wrong decision (rather than as the limits of uncertainty about specific measurements). DQOs play an important role in setting the stage for data quality assessment (DQA).

When environmental data are used to support a decision, for example, the decision maker needs to ensure that the data will support the decision with satisfactory confidence. If the data exhibit a large amount of variability, then the decision maker may be faced with some difficult questions. Do the data indicate that the environmental characteristics of interest are exhibiting a large amount of natural or inherent variability? If so, how does this variability complicate the task of making a sound decision? On the other hand, does the variability in the data indicate that there are problems with the measurement system used to generate the data? If so, what can be learned from this data, and what can be done to improve the quality of data collected in the future? These kinds of questions can be answered by the DQA process. The DQA process is a statistical and scientific evaluation of the data set to assess the validity and performance of the data collection design and statistical test, and to establish whether a data set is adequate for its intended use.

b. DQO process. The DQO process begins with the statement of a potential or real ambient air problem at a HTRW site and defines one or more decisions that will be made to resolve the problem. The subsequent

DQO steps define why and how the ambient air monitoring measurements are being performed and concludes with optimizing the FFMS which will provide the required data and acceptable data quality. EPA defines the DQO process as: "A scientific planning tool to facilitate the efficient and effective planning of environmental data collection activities." For application to FFMS and off-site monitoring the environmental data includes the project defined contaminants of concern that are migrating both on-site as background concentrations and at the fence-line or off-site as fugitive emissions. EPA also defines DQOs themselves as "Qualitative or quantitative statements developed by the data user to specify the quality of data needed to support decisions." For this application the data will be used to support such action decisions as the implementation of engineering controls, a cessation of site activities, initiation of contingency sampling, public required information, system performance monitoring, etc.

Implementation of the DQO process effects three benefits, which include: (1) optimization of sampling and analysis design. (2) maximization of resource efficiency and; (3) improved decision making. The use of real time monitoring in the SAP design can optimize the real time contaminant concentration measurement and identify the need for more accurate real-time contaminant quantification. The sampling and analysis design should include the threshold or action level concentrations at which an action such as contingency sampling and/or site activity corrective actions must be implemented.

Figure 3-1(a) presents the seven major elements of EPA's DQO process, while Figure 3-1(b) presents this process as applicable to HTRW ambient air monitoring program requirements.

(1) Step 1: State the problem. This first step of the DQO process involves the identification and involvement of the DQO team members and stating the problem that results from the HTRW project site and site activities. The DQO process team should involve project directors, engineers, chemists, geologists, risk assessors, air monitoring personnel, regulators, etc. For all ambient air monitoring decisions which are driven by regulatory requirements, the Federal, state or local project related regulatory personnel should be included in the DQO process team. For HTRW projects, the problem can be generically stated as "Activities at the site will generate air emission problems which must be dealt with by one or more decisions." These decisions can be made with a sufficient amount of ambient air monitoring data of a specified quality. Such decisions may be required for sites at which contaminants of concern are present and at which site activities will occur that have the potential for a release or for the transfer of airborne contaminants off-site. The activities may involve site investigation, material removal or contaminated material remediation.

The need for perimeter and off-site ambient air monitoring may also be dictated by the results of an APA, a state or local regulatory air monitoring requirement or as a result of negotiations with local citizens who may be impacted by the off-site contaminant migration. It should be kept in mind that some air monitoring may involve background air monitoring in the absence of any activities at the site as support data for some anticipated future activity. The project/site description statements must include terrain, climate, remoteness, meteorology (both known and unknown), surroundings, etc. The DQO process will also require identification of the type of site activities that will be conducted or that can be anticipated to occur. This first step should result in information upon which the rest of the DQO process will be conducted. As a working example, a site contaminated with benzene, ethyl benzene, toluene and xylene (BETX) is to be excavated.

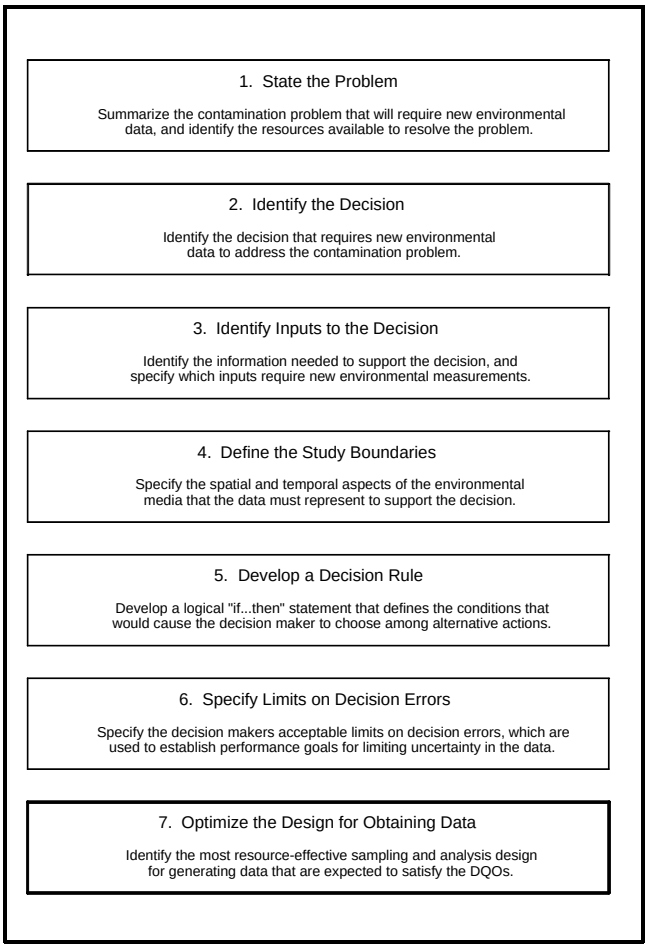


Figure 3-1(a). Seven steps associated with EPA's DQO process.

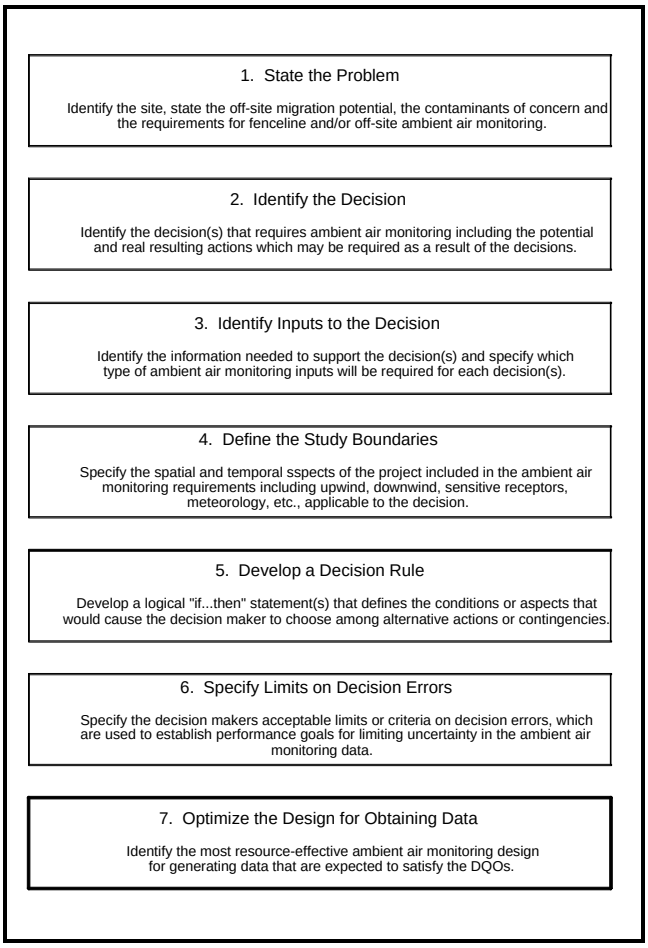


Figure 3-1(b). Seven steps associated with the DQO process as applied to air monitoring at HTRW sites.

The site is located in a remote area with two private households within an area that could possibly be affected by a plume originating from the site. The local regulatory agency has indicated that any site generated VOC emissions must be measured by monitoring at the fenceline. To implement Step 1, the problem simply stated, is "*Emissions, which may adversely affect the health and safety of the nearby environments and residents, may be generated from a site contaminated with BETX during the site excavation activities, and consequently BTEX or an indicating parameter must be monitored.*"

(2) Step 2: Identify the decision. The second step in the DQO process involves the identification of the decision which will solve the potential or real ambient air problem. This step also establishes the alternative steps that may be implemented based on the outcome of the ambient air measurements. This step should be used to generate subdecisions which support the principle decisions. These subdecisions are a part of the

iterative nature of the DQO process and are often generated as part of Step 7, which are steps to optimize the air monitoring system design without compromising the initial decision. It should be noted that for each subdecision, Step 5 should generate additional "if...then" statements which are compatible with the previous statements and which default to the higher level decision. A subdecision may involve the monitoring of NonMethane Organic compounds (NMOCs) as an indicator of the presence of BETX.

Continuing with the example, monitoring for the off-site migration of BETX will assure the health and safety of the two receptors of concern, the two private household occupants. Should the off-site migration of BETX components be detected during the excavation activities when either of the receptors of concern are within the meteorological plume, a corrective action must be implemented. The results of Step 2, can be stated in the example as *"The detection of any BETX component migration off-site during excavation that impacts either receptor of concern will require corrective action"*. The appropriate corrective action will be defined later in the DQO process.

(3) Step 3: Identify Inputs to the Decision. Identification of the decision inputs requires identification of the applicable data users and regulators and the information that they will require to solve the decision statement. Regulators typically provide or should confirm compound and/or parameter action levels based on emission factors, risk-determined action levels, ambient air requirements, etc. Citizen groups often demand concentration data that assures the site activities are not resulting in adverse health affects to area residents. These groups also require that the monitoring data be a direct reflection or a reliable indicator that a site activity is being conducted according to design or in a manner which assures the health and safety of the local residents on a continuing basis. This data can also be used by the personnel with oversight responsibilities for the activities to assure the activities are being performed in the planned or contractually required manner. An important part of the decision process is identifying who the decision makers are and where they are located. Real-time ambient air monitoring data can be transmitted electronically from a remote site location to a contractor's or regulator's office. Such needs will impact the air monitoring system design.

The use of real-time monitors as part of a FFMS offers immediate on-site, perimeter and off-site contaminant concentration data that can be used to make decisions that require immediate implementation of contingency plans. The detection of specific compounds on a real-time basis can determine if engineering control practices must be implemented, site activities must be decreased or halted, action levels have been reached or exceeded that require contingency sampling.

For the BETX excavation example, monitors may only be required which detect BETX migration off-site during excavation which impact on the residences. It may be feasible however to monitor for NMOC with a BETX confirmation measurement as a contingency. Identifying inputs to the decision would therefore require monitoring NMOC/BETX at the fenceline during excavation whenever the receptors of concern are within the site plume. Determination of whether the receptors are within the plume at any given time however, requires that site meteorology be monitored or obtained from an acceptable near-by meteorological monitoring station. The meteorological data must include the atmospheric stability class to determine the receptor impact. The regulators should provide required method detection limits based on existing regulations, risk based dispersion modeling, or measurement based technology. The results of Step 3 for the example site can be stated as: *"Meteorological and NMOC/BETX monitoring must be performed to indicate whether the BETX emissions are having an impact on the receptors of concern during excavation activities."*

(4) Step 4: Define the Study Boundaries. Identification of the boundaries requires defining both the spatial and temporal project boundaries. Identification of the spatial boundaries is often difficult for some projects and is contingent on the decision makers domain. The project boundaries are not confined to the site for air monitoring and often involve off-site air monitoring and tracer release, detection and modeling activities. Air monitoring may involve either or both volatile and semi-volatile compounds or particulate related matter. Boundaries often are variable with changing meteorological conditions. A receptor of concern which is in the site plume during certain meteorological conditions will not necessarily be within the boundaries when the conditions change. For regulatory purposes, the boundaries may be defined by the specific project emissions source types while the boundaries defined by citizen groups may include sensitive receptors. For this reason, the DQO process team established in Step 1 should be involved in defining the spatial and temporal boundaries.

The spatial boundaries of the example BETX contaminated site during excavation activities will be a function of when the site plume can impact on either receptor of concern. Depending on whether the regulator or other data user specifies that the results of a total BETX concentration measurement at the site fenceline requires a corrective action or specifies that the determination of BETX generated exclusively by the on-site excavation requires the action, will dictate whether background measurements are required. The spatial boundaries can therefore, include background air contaminants migrating on-site in addition to those migrating off-site. The temporal boundary for this example may include two boundaries, one for the entire duration of the excavation activities and one for monitoring periods in which the receptors of concern are within the site plume. The results of Step 4 for the example may be stated as; "*Monitoring will be performed both at the upwind and downwind perimeter of the HTRW site for NMOC/BETX, whenever the receptors are impacted by the BETX emissions, for the duration of the excavation.*"

(5) Step 5: Develop a Decision Rule. The development of a decision rule often requires the establishment of one or more "if,...then" statements. Each decision rule should be composed of four elements: The parameter of interest, the scale of the decision, the action level for that decision, and the alternative action. Sometimes the decision rule is composed of a series of prioritized subdecision statements. A subdecision statement for air monitoring could be "*If a threshold limit is exceeded for a specified measurement, then a confirmation measurement must be performed*." This action may then be followed by a second subdecision statement that "*if the threshold limit exceedence is confirmed, then compound speciation must be performed, on-site corrective action taken or site activities terminated*."

The development of the decision and subdecision rules is an important part of the DQO iterative process. While the iterative process should not change the primary decisions, Steps 5, 6, and 7 should generate additional subdecisions and additional "if....then" statements as the measurement program is optimized. Each subdecision should contain the parameter of interest, the action level, the alternative action appropriate to the subdecision, and the scale of the decision when different from the principle decision.

For the BETX example project, implementating Step 5 may result in the statement; "*If the NMOC concentration exceeds the action level and a BETX measurement confirms the NMOC results during the time when the receptors are impacted by BETX emissions, <u>then</u> either engineering controls to diminish the BETX emissions are applied or the excavation activities are halted*.

(6) Step 6: Specify Limits on Decision Errors. The decision errors will likely rely on the specific component measurement requirements and how near the measurements must be to the true values. This step of the DQO process often generates the Project DQOs in terms of precision, accuracy, representativeness, comparability, completeness, method sensitivities (method detection limits) and data validation and reporting requirements.

For the DQO process for ambient air monitoring at HTRW sites, precision and accuracy are often key elements in the iterative subdecision-optimization process steps. The precision of an air contaminant measurement is taken as the variance between two or more measurements. This often results in "if...then" statements which require a repeat of a given measurement. If the result of the repeated measurement is averaged with the initial measurement, the result must be within an acceptable (and defined) variance. The variance between the measurements is expressed as relative standard deviation (RSD). The acceptable RSD of a required measurement should always be defined and stated as one of the project DQOs.

The confidence the decision maker has in the measurement technology or technique relies on the accuracy of the measurement. The accuracy of the measurement can be defined in numerous ways including the measurement result relative to a standard reference method measurement, the result of the measurement when subjected to a well known standard contaminant concentration or the result of a measurement audit procedure. Relative accuracy is usually expressed as the percent deviation from the accepted method result or analysis of a standard. The accuracy of each required measurement should be clearly defined during this step of the DQO process and should include the method of determining accuracy.

An additional characteristic of data quality is representativeness. Representativeness is not expressed quantitatively but relies on project specific and good scientific judgments. A major part of measurement representativeness for HTRW FFMS is the spatial boundaries defined by the fourth DQO process step. Due to the nature of the variability of ambient air, representativeness must address site micrometeorology, monitor siting, diurnal and climatic changes, etc. Comparability is another key DQO element when optimizing the SAP. With the addition of more "if...then" statements which may involve differing contaminant measurement technologies, the resulting data must be comparable to and support the higher decision statement and its requirements.

Completeness as applied to an HTRW project DQO involves a set number of contaminant measurements. The number of measurements may be defined within a decision statement with its measurement requirements or may be applicable to continuous monitoring or the sampling schedule.

Method detection limits are involved in the component of concern threshold or action level monitoring. Regardless of whether the measurement method is instrumental or a manual sample with subsequent laboratory analysis, the minimum detection limit must always be stated. The ambient air measurement detection limit should always be made known to an analytical laboratory and analytical evidence required that the decision limit can be achieved. For instrumental monitoring, the detection limit stated by an instrument manufacturer may not be applicable to the specific project. A calibration or audit gas at or near the required detection limit will provide evidence that detection limits are achieved.

Data validation and reporting can be key components to the decision maker. The probability that a false positive or false negative decision will be made increases as the data validation decreases. The timeliness of the data reporting also can be key to the decision maker. For decision alternatives which require immediate actions, real time air monitoring data will be a requirement.

Decision error limits often involve the verification of a contaminant detection beyond an action level. The DQO process must define the measurement precision and accuracy acceptable to make the decision. One method of assuring that precision and accuracy are defined project DQOs for all measurements is to include them in the "if...then" statements, as in the example case below. The decision maker must also agree that the measurement is representative of the air media for which the action level applies. For real-time air monitors the detection of an action limit exceedence is typically confirmed with a duplicate measurement or by the use of a manual reference measurement method. Such decision rules may involve complex contractual details that must be well defined, such as the implementation of dispersion modeling, the implementation of on-site engineering controls or activity limitations that impact the contractors efficiency.

In order to assure the detection of NMOC and BETX off-site migration at the example site, the decision maker must define the accuracy and precision of the measurements. This may be accomplished by including the required precision and accuracy in the "if...then" statements. Step 6 should provide statements such as; *" If the measurement values for NMOC and BETX meet a precision of ±30% and an accuracy of 70 to 130% , and are supported by documented representativeness and comparability during the time the receptors are impacted by BETX emissions, then the specified corrective action must be implemented*

(7) Step 7: Optimize the Design for Obtaining Data. The optimization of the data acquisition design is typically necessitated by project funds and air monitoring cost effectiveness. Cost reductions and air monitoring efficiency can often be achieved without precision and accuracy compromise. Any compromises must always be acceptable to the decision maker. The optimization can also be achieved by fine-tuning sample representativeness, sampling data reporting, acceptable levels of data quantity and data validation limitations. Air sampling is best optimized by avoiding unnecessary data quality, measurement methods, detection limits, QC requirements, etc. Air monitoring can nearly always be optimized considering the absence of receptors when meteorological conditions are considered. When the on-site activities are of extensive length the use of automated monitors provides an optimization not achievable using manual sampling and sample analysis.

Optimization must always be accomplished with the generation of additional "if...then" statements which support the additional subdecisions. The lowest subdecision and the related air monitoring requirements can often involve low cost acquisition and analysis using screening measurements. The rationale that "<u>if the concentration of a class of components is less than a defined action level then the components of concern within that class must be less than the action level</u>" allows for the use of cost effective measurement methods. Such methods may measure an entire class of compounds and provide a result in terms of concentrations less than the action level. The associated "if...then" statement must include the "then" portion, the alternative which reverts to the next higher decision statement. This iterative process of optimization maintains the integrity of the initial decision statement(s) defined in step two of the process. Several of the more common factors to consider in optimizing air monitoring plans for HTRW site activities include the following:

- The systematic monitoring of a chemical compound class (i.e., NMOCs using a photoionization detector (PID)) rather than using a gas chromatograph (GC) to separate the NMOCs for individual compound quantification can significantly reduce monitoring and calibration apparatus requirements and can also reduce manpower requirements for data reduction and reporting.

- The collection and analysis of specific compounds which are representative of a total class of compounds of concern needed by the decision maker can optimize the air monitoring approach. If the decision maker requires the concentration of semi-volatile organics for example, the need may be satisfied by the measurement of the most volatile (i.e., naphthalene) or the measurement of benzo(a)pyrene, which is one of the most carcinogenic compounds of the semi-volatile group, and thus represents the greatest risk. In such an instance, the field sampling and/or laboratory analysis could be greatly simplified.

- The use of historical site related meteorological data can greatly effect the temporal boundaries of the project established in the fourth step of the DQO process . For project specific receptors which drive the decisions, the absence of any receptors in the downwind plume of the site emissions can alleviate the need for air monitoring. A typical dispersion model will address concentrations based on the yearly wind rose. However, if the dispersion modeling is performed on a monthly basis it may be clear that the receptors are not affected during certain time intervals and thus the temporal boundaries can be lessened.

- Not all site activities are performed on a continued basis. Where the activities are limited to certain seasons, daytime hours or weekdays, the air monitoring activities can be optimized accordingly. This can be accomplished by the selection of measurement methods which are not based on 24-hour sampling time intervals, using automated samplers which can be programmed to sample during prescribed time intervals, or using low cost portable measurement devices which can be easily maneuvered into the downwind plume during the activities. The optimization process may involve the acceptance of short-time measurement methods which require a compromise of sensitivity due to shorter sampling intervals.

- The most relevant factor in the optimization step can be the decision error probability for real-time instrumental monitoring versus manual grab sampling and laboratory analysis. Depending on the "if...then" statement that supports the primary decision, it may be necessary to require real time ambient air monitoring. Depending on project specific spatial boundaries, the decision maker may have to implement immediate corrective actions when threshold values are met or exceeded. For such projects real-time ambient air monitoring will be a must and can be accomplished using a fixed fence-line monitoring system, long path fourier transfer infrared spectroscopy (FTIR) monitoring, or other real-time measurement technology.

For the example BETX site, the results of optimizing the design in Step 7, may result in a subdecision statement such as; *" If, during the time when the receptors can be impacted by BETX emissions, NMOC measurements which meet a precision of ±30% and an accuracy of 70 to 130% using a confirmation measurement, exceeds the threshold limit, then BETX speciation and quantification measurements must be performed." The higher decision statement then reads; "If the BETX measurements which meet a precision*

of ±30% and an accuracy of 70 to 130% , using a confirmation measurement exceed the threshold limit, then the corrective action must be implemented." This succession of decision and subdecision allows for both the optimization of acquiring air monitoring data while maintaining the decision maker's acceptable decision error limits.

c. DQOs and incorrect decisions. DQOs are expressed in terms of acceptable probabilities that the measurement results will not lead to incorrect decisions. Two general types of incorrect decisions can occur: false positive errors and false negative errors. False positive errors result in decisions to take action to reduce pollutant exposures when the true concentrations are actually below levels of concern. False negative errors result in not taking action when, in fact, concentration levels are above those thought to pose a serious risk. While false negative errors are usually more detrimental because of the health risks that might unknowingly be imposed on the public, false positive errors are also counterproductive because of the money and time wasted taking unnecessary action. DQOs, therefore, place limits on the acceptable probabilities that either a false positive or false negative error will be made. The acceptable probability that a measurement result will lead to an incorrect decision should depend on the seriousness of the consequences of the incorrect decision. The following examples of APA data quality objectives demonstrate the relationship between acceptable probability rates and the seriousness of the incorrect decision

- At a true concentration of ½ the level of concern, the probability of a **false positive** finding should be less than 10% (i.e., at least 90% of the time, the data would correctly indicate that there is no problem).

- When the true concentration is 1½ times the level of concern, the probability of a **false negative** finding should be less than 5% (i.e., at least 95% of the time, the monitoring data would correctly indicate that there is a problem).

The probability of a false finding is directly and quantitatively related to the accuracy and precision of the measurement method. For instance, in the examples above, a measurement method with a precision of 20% (expressed as relative standard deviation) and no systematic biases would be needed to satisfy each of the these conditions.

In addition to quantitative limits of data quality, DQOs must also be defined qualitatively in terms of representativeness and comparability. Representativeness refers to the specific conditions of space and time to which measurement value is intended to relate. For example, if data are to be compared within 30-minute inhalation-based action levels, the measurement values must be representative of conditions in the typical breathing zone (i.e., approximately 5' to 6' above ground in an area with unrestricted air flow) and averaged over 30-minute intervals. Comparability refers to assurances that the measurement results are expressed in a manner and format that enables direct comparison with applicable action levels (i.e., standardized units) or, if necessary, with other, similar types of data.

3-3. Regulatory Limits, Action Levels, and Site Specific Alert Levels and Triggering Mechanism

a. Introduction. One important purpose for conducting a real-time, fixed-site perimeter monitoring program is to demonstrate compliance with Federal, State, and local regulatory limits during site investigation and remediation activities. Additionally, monitoring data are used to determine whether *action levels* intended to protect worker and public health have been exceeded. Thus, an understanding of the regulatory framework surrounding site activities and the potential for exposure to harmful air contaminants is essential for designing and conducting the monitoring program.

The relevance of regulatory limits and action levels to the design of the USACE fenceline monitoring programs is described below.

b. Regulatory limits. Many fenceline monitoring programs involve Superfund site remediation. Under CERCLA and Superfund Amendments and Reauthorization Act (SARA), on-site remedial actions must attain (or have waived) Federal and more stringent State applicable or relevant and appropriate requirements (ARARs) for environmental protection. Additionally, the revised National Oil and Hazardous Substances Pollution Contingency Plan (NCP) requires compliance with ARARs during remedial actions as well as at completion and compels attainment of ARARs during removal actions to the extent practicable. (Although the NCP exempts CERCLA sites from obtaining permits for on-site actions, all remedial actions as well as removal actions must identify and comply with the substantive provisions of the permit regulations that are determined to be ARARs.) Even if USACE fenceline monitoring program does not involve a Superfund site, most, if not all, of the ARARs probably apply.

To determine what regulatory limits are considered ARARs and whether they apply to a USACE site, the following information is needed:

- Air quality designation of the site's location (i.e., attainment, nonattainment, unclassified, or transport) for each National Ambient Air Quality Standard (NAAQS).

- Classification of each designated nonattainment area (i.e., marginal, moderate, etc.).

- Required control measures, including emission limitations and emissions offsets.

- Baseline emission estimates at the site and estimated (i.e., modeled) air pollutant emissions associated with site investigation and remediation activities.

Once obtained, this information can be used to identify the ARARs that are applicable to the site.

Many air regulatory programs may be identified as ARARs or could otherwise be applicable to USACE site investigations and remediations. Many of these programs are driven by the Clean Air Act (CAA), whereas others, especially at the State and local levels, are independently developed. These regulatory programs are described below.

(1) NAAQS. For each of the six Federal criteria pollutants (CO, Lead, NO_2, PM_{10}, Ozone, and SO_2), EPA has established primary and secondary NAAQS. The primary standards are designed to protect public

health with an adequate margin of safety, whereas the secondary standards are intended to protect public welfare (e.g., soil water, crops, vegetation, animals, property, and visibility).

NAAQS themselves are not enforceable. Instead, the emission standards that are developed to attain the NAAQS that are enforceable. These emissions standards are generally incorporated into the State Implementation Plan (SIP) prepared by each State. In addition to emission standards, a SIP may include monitoring, recordkeeping, enforcement, and other requirements as well as measures such as economic incentives. All of the elements within a SIP are enforceable and, thus, would constitute ARARs.

Although not enforceable, CERCLA allows requirements such the NAAQS to be used as other criteria or guidelines to be considered (TBC) on an appropriate basis. For example, in cases where a SIP does not specifically address a criteria pollutant emission at a site, the pollutant's NAAQS can be used to derive acceptable emission or exposure levels. However, such use must be justified on the basis of protecting public health or the environment.

(2) Other potential standards.

(a) Resource Conservation and Recovery Act (RCRA) Standards. Regulations under RCRA address air pollutant emissions from several activities that may occur at CERCLA sites, and these regulations may be considered ARARs. Examples of affected activities include hazardous waste incineration; hazardous wastes burned in boilers and industrial furnaces; other thermal treatment operations; waste pile, land disposal, and landfill operations; hazardous waste treatment, storage, and disposal facilities; air stripping; and containment buildings.

(b) Non-Attainment Areas. To construct a major new source in an area not attaining a NAAQS, the owners or operators must ensure a net decrease in emissions in the area. Thus, existing sources must agree to reduce their emissions below that which would otherwise be required for them to offset the anticipated new emissions from the proposed new source. Additionally, the new source must apply lowest achievable emission rate (LAER) emission control technology. Also, under a SIP, existing sources in non-attainment areas may be required to apply reasonably available control technology (RACT). Under certain circumstances, both LAER and RACT may be ARARs for CERCLA sites meeting the definitions of major and new.

(c) Prevention of Significant Deterioration (PSD) Areas. For areas that are attaining NAAQS levels, the PSD program allows industrial growth while ensuring that air quality will not significantly deteriorate in these areas. To achieve this objective, the application of best available control technology (BACT) is required for new source construction and major modifications. PSD requirements would be considered ARARs in cases where a CERCLA action involves a major source or modification located in (or possibly upwind of) an attainment area.

(d) Title V Operating Permits Program. The 1990 CAAA require that states develop an operating permits program that incorporates all air emission permit requirements for major sources into a single permit for an industrial source. Examples of applicable permit requirements would be NESHAP, NSPS, MACT, and state-specific requirements (e.g., associated with a SIP). Although CERCLA on-site actions are not subject to

administrative procedures and permit requirements, CERCLA sites will have to comply with any substantive standards associated with the permit programs that are determined to be ARARs.

(e) State Air Toxics Regulations. Some state air pollution control agencies have developed their own regulations for controlling air toxics emissions. These regulations are likely to be considered ARARs for most CERCLA sites. Because requirements differ widely from state to state, the rules for the state where the site is located must be carefully examined.

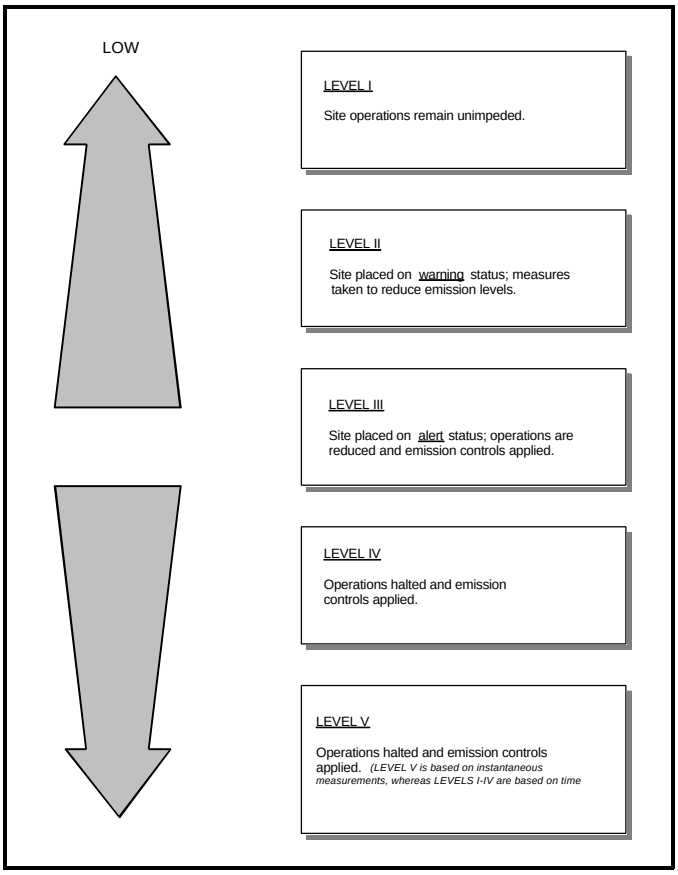
c. Action levels. Action levels are derived from regulatory limits and/or health exposure criteria and are intended to provide an exposure concentration level below which exposure is safe. In situations where the action level is exceeded (i.e., exposure occurs at unsafe levels), some action is required, such as shutting down the operation and/or removing personnel from the site until the problem is resolved. Because action levels are not regulatory limits, they are not ARARs. Instead, they are exposure levels that are established on a case-by-case basis and may differ from site to site, depending on the pollutants of concern and the potential for exposure to the workers and the public.

Action levels are usually established for two exposure scenarios: (1) the immediate working area within the site and (2) the fenceline (i.e., property boundary) of the site. The action levels associated with the working area are designed to protect the health of the on-site workers, whereas the perimeter action levels (PALs) associated with the fenceline are designed to protect the surrounding population and environment. (The fenceline is assumed to represent worst-case exposure for persons in nearby homes, businesses, and other public access areas.) Several time-averaging periods may be applied, depending on the time period associated with the applicable action level or ARAR, the specific compounds present and their health effects, and the capabilities of the air monitoring equipment. Typical averaging periods include 15-minute, 1-hour, 24-hour, 1-month, and 1-year averages, and instantaneous values.

Three types of action levels are often specified, based on the compounds of interest, the operating life of the source, the type of emission sources, and the potentially exposed population. These levels are described below:

(1) Long-term action levels for carcinogens. Long-term action levels for exposure to human carcinogens are usually based on inhalation unit risk factors published by EPA. The duration of exposure is generally assumed to be the expected operating life of the source or 30 years, whichever is less, and receptors are usually assumed to be constantly present during this period. The level of risk that is generally considered to be acceptable is in the range of 10^{-6} to 10^{-4} as an upper limit for the lifetime of the remediation effort. (A 10^{-6} risk represents a 1 in 1 million chance that a representative individual who is continuously exposed to site emissions will develop cancer over a lifetime.)

(2) Long-term action levels for non-carcinogens. Long-term action levels for non-carcinogenic effects are usually based on chronic reference concentrations (RfCs), which are estimates of the level of continuous exposure that can occur without adverse health effects during a person's lifetime. Chronic oral reference dose (RfD) values can also be used to derive action levels; however, care must be taken in extrapolating oral data to inhalation scenarios.


LOW
LEVEL I
Site operations remain unimpeded.
LEVEL II
Site placed on warning status; measures taken to reduce emission levels.
LEVEL III
Site placed on alert status; operations are reduced and emission controls applied.
LEVEL IV
Operations halted and emission controls applied.
LEVEL V
Operations halted and emission controls applied. (LEVEL V is based on instantaneous measurements, whereas LEVELS I-IV are based on time

- Greater specificity in contaminant analysis.
- Correlation of analytical and meteorological data to evaluate source direction.
- Calculation of net upwind/downwind concentration.
- Investigation and documentation of probable causes of exceedance.
- Implementation of site management controls, if necessary.

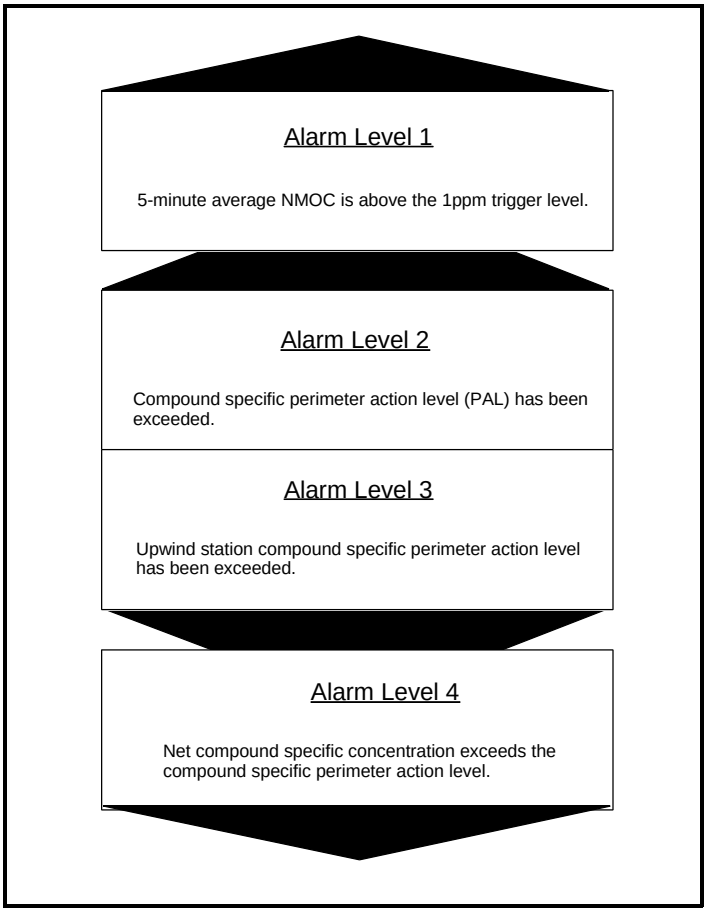


Figure 3-3. Example of site-specific alert levels involving NMOC and speciated organics, associated with an FFMS at HTRW sites

Alarm levels for all target analytes are preprogrammed within the gas chromatograph microprocessor as are the sampling and rest intervals. During any sampling interval, exceedances of either a total non-methane organic compounds threshold and/or specific target analyte thresholds may be determined depending on the specific mode of chromatograph operation. In operation, the microprocessor should cycle through the established sampling schedule, log the individual instrument measurements to the data storage system, and compare the measurements with the preset alert levels. When an exceedance is identified, the microprocessor should trigger audible alarm mechanisms within the analytical center and generate a report as well as initiate further analyses, data storage, and data correlation. An example “quickscan/speciated” operational scheme is described in the following sections.

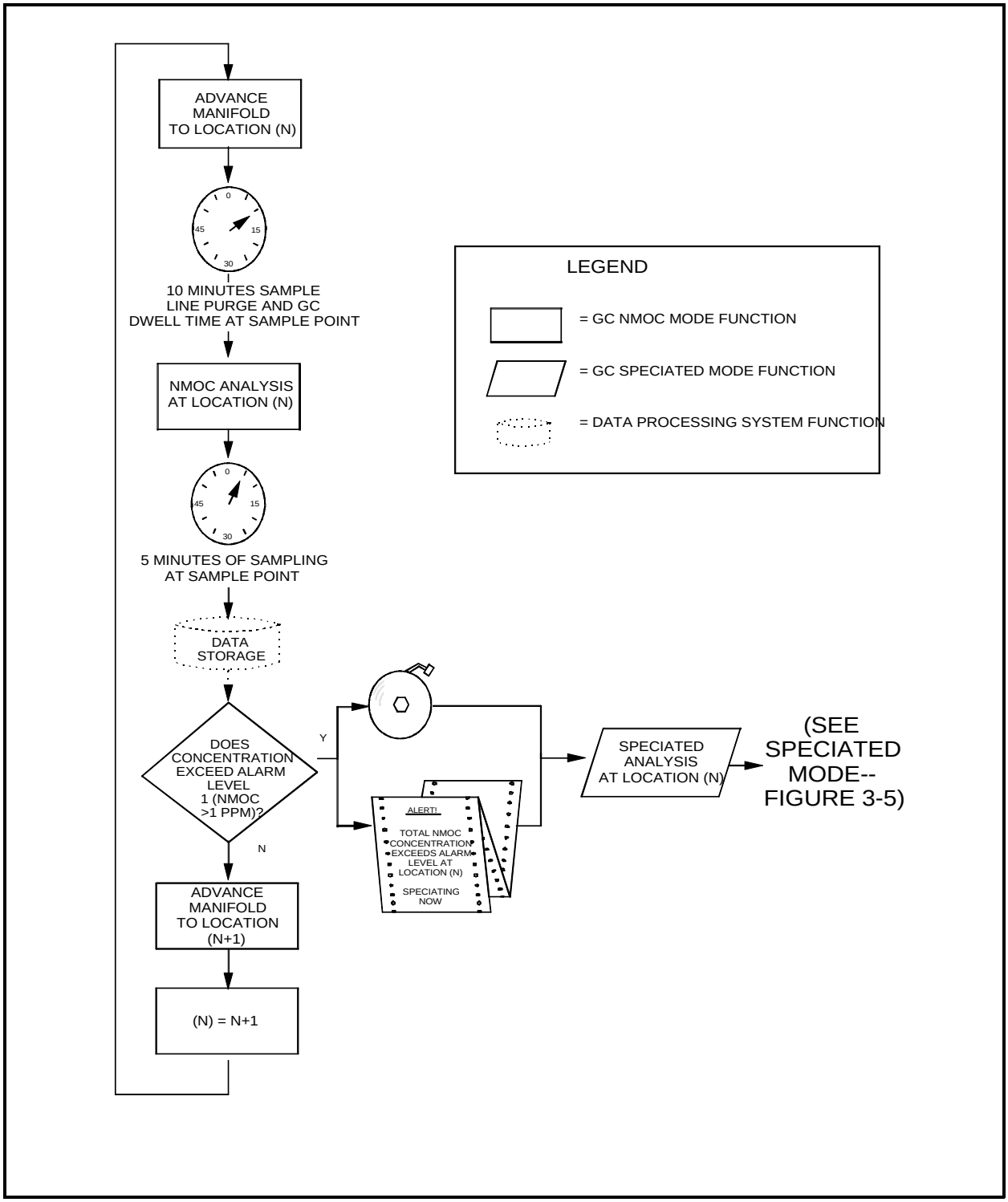


Figure 3-4. Example of decision for alarm level 1, NMOC mode

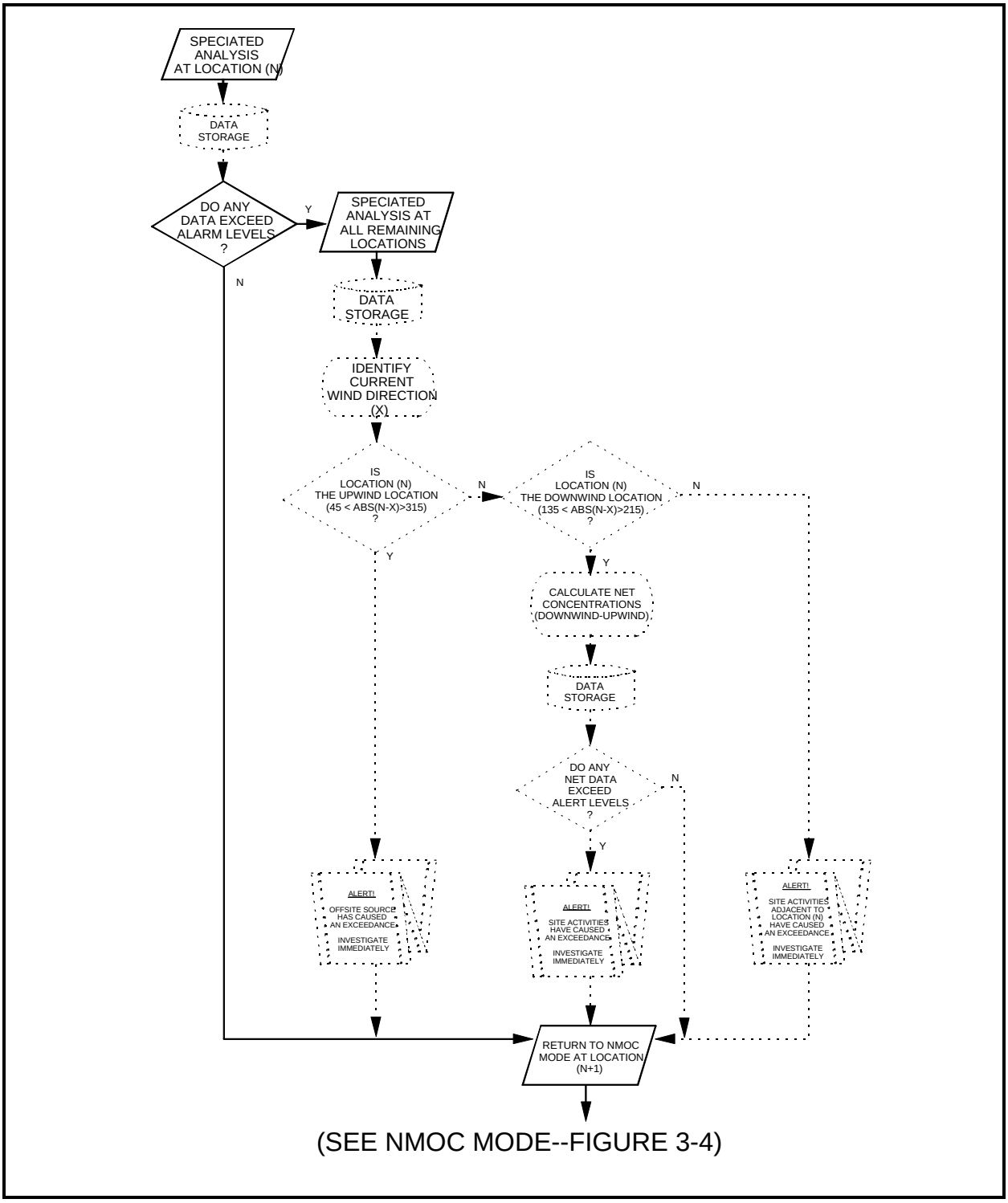


Figure 3-5. Example of decision for alarm levels 2, 3, and 4, speciated mode.

(1) Alarm level 1 — NMOC exceedance. The network of heated sample lines transport sample gas from locations around the waste site to the manifold sampling apparatus and the gas chromatograph. The microprocessor controlled manifold apparatus allows sequential sampling of each sample line. During routine sampling, the gas chromatograph is typically operated in a "Rapid Analysis Mode (RAM)" mode for total NMOCs. As such, the GC column is bypassed, and sample gas from each sample line is isolated and directed to an appropriate GC for gross quantification. Resultant data are automatically logged to the data storage system. When the total NMOC concentration in a given sample is below the alarm level, manifold apparatus simply proceeds to the next sample line. When total NMOC concentration exceeds the preset alert Level 1, the microprocessor generates a written report, and a speciated analysis of the sample is typically initiated, as illustrated in Figure 3-4.

(2) Alarm level 2 — compound specific exceedance. In the speciated mode, the sample gas is directed to the GC column wherein a gas chromatographic separation is performed. Individual contaminants elude from the GC column and are directed to a second GC detector for quantification. Specific analytes are identified on the basis of chromatograph retention time as compared to regular, multi-point calibrations of the system. Again, all data are logged to the data storage system. If the concentrations of all of the target compounds are below the preset alarm Level 2, the microprocessor signals the manifold apparatus to proceed to the next sample line, and analytical operation is shifted back to the RAM mode. If the concentration of any target compound exceeds the preset alarm Level 2, the microprocessor typically generates a report and initiates a sequence of speciated analyses of sample gas from each of the remaining sample lines. All resultant data are logged to the data storage system. Once a complete circuit of speciated analyses has been completed, the microprocessor signals the manifold apparatus to proceed to the next sample line and shifts analytical operation back to the RAM mode, as illustrated in Figure 3-5.

(3) Alarm level 3 — meteorological data evaluation and upwind compound specific exceedance. Subsequent to the speciated analysis for each sample line, the microprocessor queries the data storage system to determine the location of the upwind sample line. If the concentration of any target compound at the upwind location exceeds the preset alarm Level 3, the microprocessor typically generates a report indicating further investigation with a portable organic vapor analyzer in the area of the exceedance if necessary.

(4) Alarm level 4 - meteorological data evaluation and compound specific exceedance (net concentration). If the concentration of all target compounds at the upwind location are below the preset alarm Level 3, the microprocessor typically subtracts the upwind concentrations from those reported for the downwind line to determine the net concentrations. If the net concentration of all target compounds at the downwind location are below the preset alarm Level 4, the microprocessor typically generates a report indicating that no response is necessary. If the net concentration of any target compound at the downwind location exceeds the preset alarm Level 4, the microprocessor typically generates a report indicating the necessity for further investigation with a portable organic vapor analyzer in the downwind area.

3-4. EPA's Air Pathway Analysis (APA) Mechanism

a. Introduction. The primary motivations for clean-up of HTRW sites are to protect the general environment and to protect the health and safety of persons in proximity to the site. Contamination at a given HTRW site may pose a current or future risk by exposure from direct contact with the in-situ pollutants, subsurface migration of the contaminants via vapor plumes or ground-water plumes, contamination of surface waters, and atmospheric transport (and deposition) of gaseous, aerosols, or wind-blown contaminants. To successfully assess and clean up an HTRW site, it is necessary to characterize the potential effects of pollutant transport via the applicable exposure pathways for each step of the assessment and clean-up process.

b. Superfund process. Superfund sites are potential sources of air emissions that can impact onsite/offsite health and safety. Therefore, it is important to identify site-specific air emission sources and conduct follow-up air pathway analyses to characterize the potential impacts. The Superfund process consist of three (3) phases as identified in Figure 3-6. They are:

- Pre-remediation.
- Remediation.
- Post-remediation

Air emissions can occur during all phases of site investigation.

(1) Pre-remediation phase. The pre-remediation phase is concerned with evaluating the potential risk to public health and the environment posed by the Site. The pre-remediation phase begins with site discovery. From there, a Preliminary Assessment (PA) is conducted to collect as much information as possible about the pollutants present and their physical state. This activity is meant to be a relatively quick and inexpensive undertaking that involves collecting all relevant documentation about the site. The EPA uses the information gathered in the PA to determine if further investigation or action is warranted.

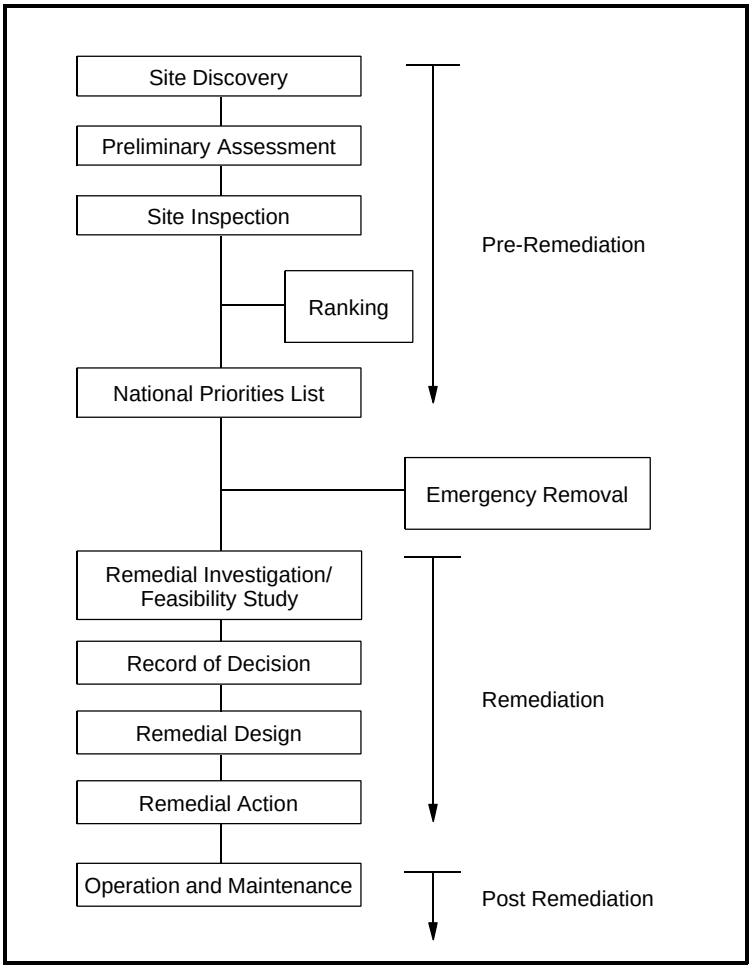


Figure 3-6. Example of EPA's air pathway analysis mechanism

If further investigation is warranted, a Site Inspection (SI) is conducted. The SI is the first action that involves some form of sample collection. This inspection is concerned with determining the immediacy of the health risk posed by the site. Samples are collected from the various media present and analyzed, and the results are used to rank the site within the Hazard Ranking System (HRS) model. The HRS model ranks the relative hazard the site poses over five pathways: air, direct contact, groundwater, surface water, and fire/explosion (the direct contact and fire/explosion pathways are evaluated but not currently included in the ranking). If the site scores higher than a predetermined amount, it is placed on the National Priority List (NPL).

Once on the NPL, the necessity of an Emergency Removal (ER) is evaluated via a site inspection by personnel from the Removal Program. This site inspection may take place during the Remedial Investigation (RI). If the site is believed to pose an immediate and significant health risk, actions are taken to ameliorate the problem. These actions may entail removing or covering exposed surface wastes, removing compressed gas cylinders, fencing the site to reduce public access, etc. Following the SI and emergency removal actions, if any, the remediation phase begins.

(2) Remediation phase. The remediation phase consists of the RI and Feasibility Study (FS), production of a Record of Decision (ROD), Removal Design (RD), and Remedial Action (RA). This phase lasts longer than the pre-remediation phase and is designed to take the site from a known health risk to a clean site in a controlled fashion. This phase is the main focus of USACE's activities at HTRW Superfund sites.

The RI and FS are separate steps but are typically conducted simultaneously and interactively. During the RI, data are collected to determine more precisely the types of compounds present at the site and the location and extent of contamination. The data gathered during the RI are used for any risk assessment that is performed. The data also are used to help identify appropriate cleanup procedures and remedial alternatives. The FS is concerned with identifying the preferred cleanup alternative. In making this identification, several alternative cleanup methods are considered and, when warranted, developed. Once the FS is completed, a ROD is issued, which serves as the official EPA decision about the preferred course of subsequent action.

The next actions are the design and implementation of the remediation alternative. The RD is detailed plan for site remediation, and the RA can take a variety of forms--from short-term activities to long-term activities that can take several years to complete.

(3) Post-remediation phase. Once the remedial activity has ended, a brief monitoring period takes place during which the effectiveness of the cleanup is determined. This period is called the post-remediation phase; it may also be referred to as the Operations and Maintenance (O&M) phase. If the monitoring shows that the site no longer poses a health or environmental threat, the site may be removed from the NPL.

c. Air pathway analysis. The evaluation of these emissions are part of EPA's APA's for quantifying emissions associated from a site during all stages of remediation. An APA is a systematic approach involving a combination of modeling and monitoring methods to assess actual or potential receptor exposure to air contaminants. Therefore, an APA is an exposure assessment for the air pathway, and it provides input to the Superfund risk assessment process. The primary components of an APA are:

- Characterization of air emission sources (e.g., estimation of contaminant emission rates).
- Determination of the effects of atmospheric processes (e.g., transport and dilution).
- Evaluation of receptor exposure potential (i.e., what air contaminant concentrations are expected at receptors of interest for various exposure periods).

The overall goal of an APA is to evaluate the site's actual or potential effects on air quality. The specific goal of any associated air monitoring network is typically to evaluate the exposure of on-site workers and the off-site population and surrounding environment.

CERCLA and SARA mandate the characterization of all contaminant migration pathways from the waste or hazardous material to the environment and evaluation of the resulting environmental impacts. However, air pathway analyses are often overlooked because many sites have little or no perceptible air emissions in their baseline or undisturbed state. Even low-level emissions, however, may be significant if toxic or carcinogenic compounds are present. From a health-risk perspective, the dominant exposure pathway over the lifetime of a site will, in many cases, be due to air exposure during remediation. Failure to perform an adequate air pathway assessment may result in an underestimate of the risk posed by the site and, in some cases, can ultimately result in work stoppages, added costs, and public relation problems.

Air pathways have several unique characteristics. Most other pathways require extended time periods for exposure to first occur, and exposure can be minimized by limiting site access (e.g., by putting a fence around the site) or by getting local residents to forgo use of contaminated resources. With the air pathway, however, any on-site releases of emissions can have an almost immediate downwind impact. The point(s) of impact can change relatively quickly as the wind direction and wind speed shift; therefore, the effects of atmospheric plumes may cover a wider area than those of groundwater plumes. If local residents are within an air emission plume, they have little choice but to breathe the air. The exposure rate, however, may vary greatly from receptor to receptor. The factors cited above cause, in many cases, exposure via the air pathway to be harder to predict than exposure via other pathways.

The potential for air releases from a site can be difficult to determine in some cases. If unplanned-for air releases occur during remediation activities (e.g., the release of subsurface pockets of toxic gases), it may be necessary to suspend remediation activities until further site investigation or remedial design work can be completed to address air emission concerns. Such delays can be costly and also may affect the public's confidence in the selected remediation approach.

(1) Evaluate exposure of on-site workers. On-site workers at a hazardous waste site may be exposed to significant amounts of air pollutants in the course of performing their jobs. Any source of emissions at a site will result in an emissions plume. Fugitive air emission releases usually occur at ground level and are not thermally buoyant; therefore, the maximum ambient air concentrations for such sources occur immediately downwind of the source and at ground level. Point sources, such as Soil Vapor Extraction (SVE) units, can have relatively short stacks and nonbuoyant plumes which can result in the maximum ground level ambient air concentrations from such sources occurring within the site boundaries. Frequently, on-site workers may have to operate equipment or otherwise work in contact with such emission plumes.

(2) Evaluate pollutant levels at fenceline and exposure of off-site community/environment. A major concern at hazardous waste sites is the potential exposure via the air pathway of residents and workers in the areas surrounding the site. The degree of concern depends on the nature of the contamination, the proposed remedy, and the proximity of the off-site populace (receptors). The exposure of off-site receptors typically is evaluated in several steps in the APA process, and both modeling and monitoring approaches may be employed as part of the exposure assessment.

The evaluation of human exposure (due to inhalation) using a monitoring approach generally involves measuring the concentrations of target analytes at the fenceline of the site for ground-level emission sources and at the areas of maximum estimated ground-level impacts for elevated emission sources (e.g., incinerator stacks). Additional ambient air monitoring may be conducted at selected receptor locations in the surrounding community (e.g., at nearby schools) or on-site, if there is public access. Data is also usually collected at locations upwind and downwind of the site. The data are compared with action levels to determine if there is cause for concern at downwind locations. If downwind concentrations exceed levels of concern, actions must be taken to reduce pollutant emissions. The difference in the concentrations measured downwind and upwind of the site yield adjusted concentrations considered to represent the contribution of the site emissions to the local air quality.

The evaluation of off-site exposure generally requires that monitoring be performed whenever significant air emissions may be released from the site. At sites that have the potential for adversely affecting the air, this requirement is often addressed by performing a short baseline study prior to remediation, followed by continuous monitoring during remediation. Usually, a fixed network of point samplers is located around the perimeter of the site, samples are collected continuously, and all samples are analyzed. Additional samplers may be located near the working areas. The number of samples and their placement is therefore important to ensure that emissions are properly characterized, which requires a basic understanding of the sources of the emissions at the sites and their mechanisms for release and subsequent impact to the surrounding community.

3-5. Chemical and Physical Properties of Hazardous Air Pollutants (HAP)

a. Air emission mechanism from HTRW sites. Emissions from HTRW sites may be classified as either point or area sources. Point sources include stacks (process emissions) while area sources are generally associated with fugitive emissions (e.g., from landfills, lagoons, material handling and contaminated surface areas).
Air contaminant emissions can be classified into two basic categories (i.e., gas phase emissions and particulate matter emissions). The emission mechanism associated with gas phase and particulate matter releases are quite different.

(1) Gas phase emissions. Gas phase emissions primarily involve organic compounds but may also include certain metals. Gaseous emissions from an HTRW site can be released through a variety of mechanisms, including:

- Volatilization.

- Biodegradation.
- Photodecomposition.
- Hydrolysis.
- Combustion.

Volatilization is typically the most important mechanism for air releases and occurs when molecules of a dissolved or pure substance escape to an adjacent gas layer. For wastes at the surface, this action results in immediate transport into the atmosphere. Volatilization from subsurface wastes results in a concentration gradient in the soil-gas from the waste to the surface. The rate of emissions is usually limited by the rate of diffusion of contaminants to the soil-air interface. Volatilization is thus an important process for the release of gaseous emissions from both surface contamination and contaminants in the shallow subsurface. The rate of volatilization of contaminants at a soil-air boundary is a function of the concentration and properties of the escaping chemical, soil properties (moisture, temperature, clay content, and organic content), and properties of the air at soil level (temperature, relative humidity, and wind speed). The rate of volatilization from liquid surfaces is dependent on the concentration of the contaminants in the boundary layer of liquid at the liquid-air interface. Any factors that enhance mixing in the bulk liquid and replenishment of contaminants in the boundary layer will enhance the volatilization rate.

(2) Particulate emissions. Particulate matter (PM) emissions from hazardous waste sites can be released through wind erosion, mechanical disturbances, and combustion. Hazardous substances, such as metals, can also be adsorbed onto particulate matter and thereby transported with the inert material.

The importance of each of these mechanisms varies as a function of source type. The hazardous constituents of concern in a particulate release may involve constituents that are either absorbed or adsorbed onto the particulate or constituents that actually comprise the particulate. These constituents may include volatile and semi-volatile organic compounds, metals, and non-volatile toxic organic compounds.

Significant atmospheric dust can arise from the disturbance of soil exposed to the air. Dust generated from these area sources is referred to as “fugitive” because it is not discharged to the atmosphere in a confined flow stream. The dust generation process is caused by two basic physical phenomena: entrainment of dust particles by the action of wind erosion of an exposed surface under moderate-to-high wind speeds, and pulverization and abrasion of surface materials by mechanical disturbances.

For airborne particulates, the particle size distribution plays an important role in inhalation exposure. Large particles tend to settle out of the air more rapidly than small particles, but may be important in terms of non-inhalation exposure. Very small particles (i.e., those that are less than 10 microns in diameter) are considered to be respirable and thus present a greater health hazard than the larger particles.

(3) Transport and diffusion. Once released to the ambient air, a contaminant is subject to simultaneous transport and diffusion processes in the atmosphere. Atmospheric transport/diffusion conditions are significantly affected by meteorological, topographic, and source factors.

The contaminant will be carried by the ambient air, following the spatial and temporal characteristics of the wind flow field (as determined by wind direction and speed conditions). The turbulent motions of the atmosphere (as characterized by atmospheric stability conditions) promote diffusion of airborne gases and particulate matter. Thus, the local meteorology during and after the release determines where the contaminant moves and how it is diluted in the atmosphere.

(4) Transformation, deposition, and depletion. Contaminants emitted to the atmosphere are subjected to a variety of physical and chemical influences. Transformation processes can result in the formation of more hazardous substances, or may result in hazardous constituents being converted into less harmful ones. A variety of inorganic and organic materials may be present along with the natural components of the air. The emissions may remain in the atmosphere for a considerable time and undergo a myriad of reactions. Both primary and secondary products are exposed to further changes through oxidation and photochemical reactions. In general, however, these effects are secondary to transport and diffusion in importance and are subject to more uncertainty.

b. Defining hazardous air pollutants. Ambient air around a hazardous waste site is a very complex, dynamic system of interacting chemicals. As previously discussed, the pollutants can be found in the gas phase, in the particulate phase, or in a liquid aerosol surrounded by a gaseous atmosphere. The complex nature of the dynamic air system around a site controls the complexity of the solution of sampling method and analytical requirements in the identification and quantification of these chemicals. Each pollutant has its own unique characteristics, yet many fall within basic classes such as volatiles, semi-volatiles, aromatics, halogenated compound, etc.

(1) Volatile organic compounds. VOC is a general term used to describe the gaseous nonmethane organic emissions from a hazardous waste site. These compounds have vapor pressures greater than 10^{-1} mm Hg and boiling points <200 C and, thus, are predominantly found in the gaseous state in the atmosphere, as identified in Table 3-1, and illustrated in Figure 3-7. Much of the present work dealing with samples and analysis or organic compounds from hazardous waste sites has been done on VOCs utilizing SUMMA® whole air canisters followed by or utilizing on-site real-time analyzers that separate and quantify the individual organic constituents by gas chromatography/flame ionization detection (GC/FID).

Table 3-1
Defining Hazardous Air Pollutants

Category	Vapor pressure, mm Hg	Boiling point, C
• Particulate matter	$<10^{-7}$	>500
• Semi-volatile compounds	10^{-1} to 10^{-7}	200-500
• Volatile compounds	$>10^{-1}$	<200

(2) Semi-volatile organic compounds. Semi-volatile organic compounds (SVOC) are not as easily collected or analyzed as the VOCs. However, attention has been focused at resolving the problems associated with SVOCs found around hazardous waste sites. Members of this class include polynuclear aromatic hydrocarbons (PAHs) with four or fewer fused rings; halogenated compounds such as polychlorinated

biphenyls (PCBs); organopesticides with chlorine and phosphorus; and various pesticides and herbicides. Vapor pressures of these compounds range from 10^{-1} to 10^{-7} mmHg. These less volatile compounds are present in the atmosphere, both in the gaseous phase and in a particle-bound phase. Sampling from this type of pollutant usually involves a filter followed by polyurethane foam (PUF) or XAD-2 resin in a high-volume sampler.

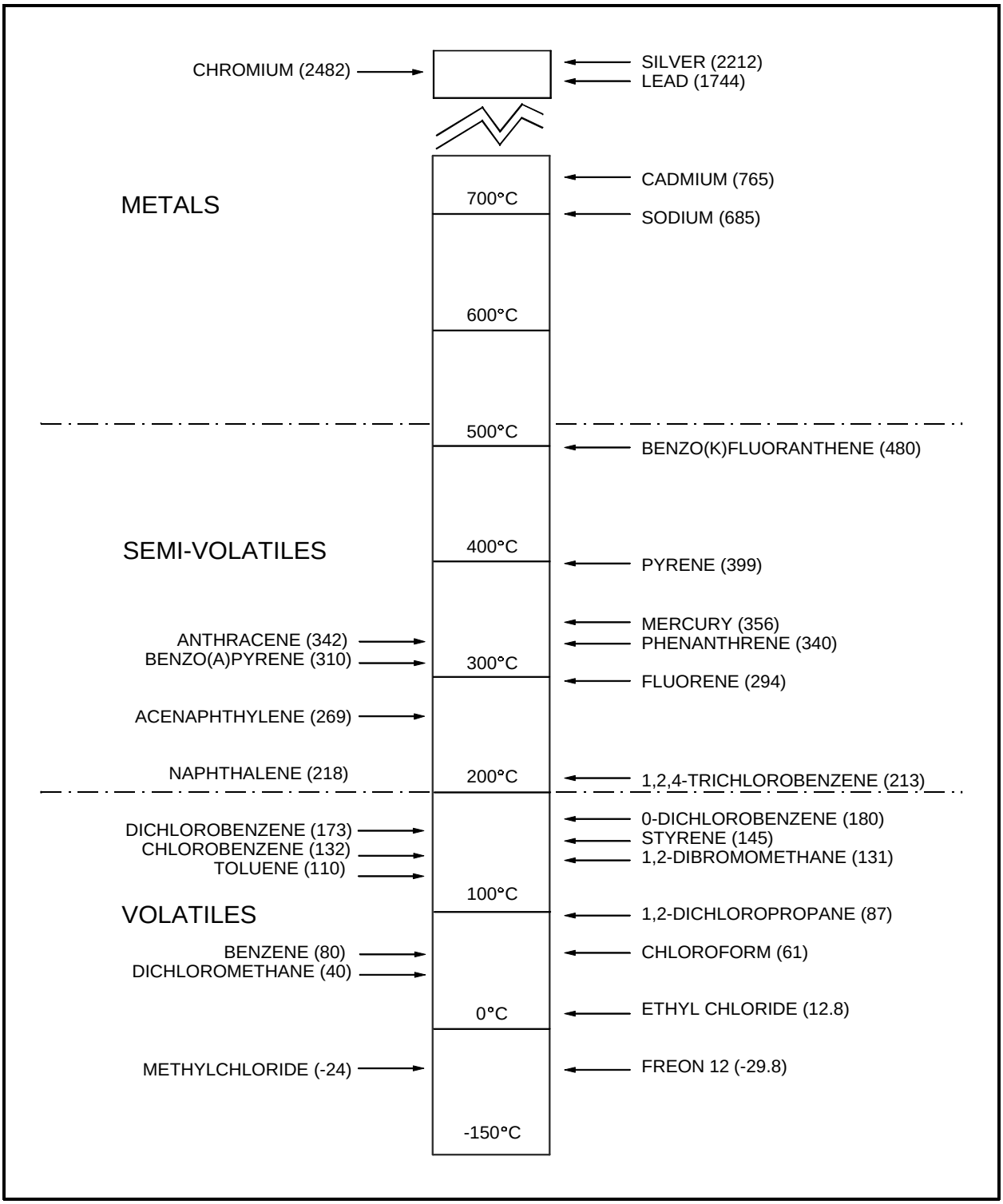


Figure 3-7. Example of EPA's defining hazardous air pollutants by boiling point.

(3) Non-volatile organic compounds. Ambient air contains relatively low amounts of non-volatile organic compounds, which are organic compounds with vapor pressures less than 10^{-7} mmHg. These compounds are almost always found in the condensed particle-bound state. Polynuclear hydrocarbons with more than four rings, their nitrogenous and oxygenated derivatives, are the major constituents of this category. A high-volume sampler containing a quartz filter is used to monitor non-volatile organic compounds.

(4) Inorganic compounds. Inorganic compounds are those compounds with vapor pressure less than 10^{-12}mm Hg. These compounds are almost always found in the particle state. Heavy metals, such as lead, chromium, cadmium, zinc, beryllium copper, and other earth metals represent this category of HAPs. Once again a high-volume sampler containing a quartz filter is used to monitor inorganic compounds.

c. Technology for monitoring hazardous air pollutants at HTRW sites. A variety of sampling methods can be used to monitor hazardous air pollutants at HTRW sites. The methods vary according to sample type (i.e., volatile compounds, semi-volatile compounds, inorganics, and particulate borne compounds), sample duration and detectability, and applicability to the monitoring objectives of the program. The greatest number of available methods for any one type are for the volatile fraction. Semi-volatile pollutants exist in both the vapor and particulate phases, so the sampling methodology must address both. Finally, the concentration of particulate-borne contaminants (inorganic and non-volatile organic) can be monitored by collection of the total mass loading during sampling.

Sampling techniques may be divided into these broad classes, regardless of the analytes of concern. They are time-integrated sampling, grab sampling and real-time monitoring.

- **Time-Integrated sampling**--time-integrated sampling involves collecting a sample over a fixed time period (e.g., 8- hour or 24-hour) and provides a single, integrated value. Methods included in time integrated are whole air canister sampling, solid adsorbent tube monitoring, and most particulate matter and semi-volatile collection systems.

- **Grab sampling**--grab sampling involves collecting an instantaneous air sample. This technique usually requires some form or type of container to contain the instantaneous sample.

- **Fixed-site real-time monitoring**--real-time monitoring involves sample extraction, conditioning, analyzing, and reporting within a fixed time period, usually less than 15 minutes.

- **Passive sampling**--passive sampling involves collecting a sample over an extended period of time without assistance from a pump. This sampling techniques is usually exclusively associated with monitoring volatile organics.

- **Portable real-time monitoring**--portable GC systems provide sampling and analysis of a limited target compound set. The use of portable systems allows one to “survey” the site and identify “hot spots,” thus making it a very feasible tool during investigating phase of a site.

Each of these sampling techniques has certain advantages and disadvantages, depending on the monitoring objectives, the required detection limits, and the duration of the monitoring program. The different techniques are described below.

(1) Grab sampling. Grab sampling involves extracting a sample at a single point-in-time. As discussed earlier, the hardware for accomplishing this sampling is usually a whole air sample container (i.e., SUMMA® canister, glass sampling bulb, tedlar bags, or solid adsorbent tubes for colorimetric gas detection). In the grab sample mode, a sample is taken over a very short period of time, from a few seconds to a few minutes.

Grab sampling is usually used in EPA's APA program as a screening technique to identify contaminants that might be present in an area of interest and to determine their approximate concentration. As an example, grab sampling can be used to collect volatile organics during the site investigation stage using tedlar bags or SUMMA® canisters to help develop the target compound list for future long-term monitoring or to assess the preliminary risk at the site.

Some of the advantages of grab sampling are that the methodology is simple to apply and sampling costs are at a minimum. Several disadvantages, however, are associated with grab sampling. One major disadvantage is that the value acquired is a single point in time and cannot be related to typical ambient air regulations involving 8- and 24-hour limits. Another disadvantage is that the sample volume acquired is relatively small, thus requiring very sensitive analytical techniques if the data is to be used for comparison with ambient air regulatory limits. Finally, inward and outward diffusion of gases in some of the collection containers has been observed, thus creating uncertainty in the data.

(2) Time-integrated monitoring. This category of monitoring is the most commonly used technique in monitoring HAPs at HTRW sites. Time integrated is most applicable if the pollutant is present in very low concentrations because sampling can be conducted long enough to provide the analytical system sufficient sample to meet required detection limits. Appropriate time-integrated sampling techniques are available for collecting volatiles, semi-volatiles, inorganic, and particulate matter (PM) in the ambient air.

In time-integrated sampling, the sampling period can be as short as minutes or as long as weeks or months, depending upon the detection limits needed to be reached associated with the analytical system. The results from the analysis of integrated samples are expressed as average concentrations over the sampling period.

Integrated sampling for PM can be accomplished by means of total suspended particulate (TSP) samplers, dichotomous samplers, or size-select inlet samplers. The sophistication of the samplers ranges from manually operated hand-held units to fully automated units that can run for weeks unattended.

Integrated sampling for gaseous pollutants can be accomplished by extracting a sample over a period of time through solid adsorbents, SUMMA® canisters, impingers, or other collection devices that can capture the analytes of interest over a period of time. In general, the greater the sampling time the more analyte is trapped on the collection media, thus allowing for lower detection limits. Thus, integrated sampling methods may not be adequate for evaluating compliance with short-term (e.g., 15-minute, 1-hour) action levels. As an example, a high-volume particulate monitor may not be adequate to determine compliance with a 1-hour emission limit for selected inorganic metals. Integrated sampling methods are therefore useful for determining pollutant

concentration when the regulatory limit is based on a time similar to the 8-hour PEL or EPA's 24-hour NAAQS. For some analytes, like dioxins, a sampling period of 72 hours may be required to obtain adequate sample to meet desired detection limits.

Integrated sampling techniques offer additional advantages. They can be cost effective, require fewer personnel than continuous monitoring and are sufficiently flexible to achieve the detection sensitivity to meet the health base detection limits needed in most regulatory monitoring programs. In addition, samples can be analyzed at a more convenient time or place off-site. Several drawbacks of integrated sampling include the lack of immediate feedback on the data that is acquired, thus preventing modification of remediation activities on site. In addition, time-integrated sampling methods typically do not give site decision makers timely data so that they can determine worker and community exposure to pollutants or the need for implementing emission controls. Another disadvantage is that short term temporal information is also lost. Finally, time-integrated monitoring requires the collected sample to be transported to another location for analysis, thus leading to possible sample integrity problems involving sample deterioration, losses of analytes, and contamination for the surround environment.

(3) Real-time monitoring. Real-time monitoring refers to methods that provide nearly instantaneous values, thus allowing multiple measurements over a very short time period of several minutes. In general, real-time means the ability to extract, condition, concentrate, analyze, and report data nearly instantaneously. The samples may be analyzed directly at the collection point, or the sample may be transported through hundreds of feet of heat-trace lines to a central analytical center for analysis. In the former situation, a single analytical system is used at each of the sampling points around the site. In the latter case, a single analytical device is used to analyze samples from multiple sampling points around the site. In this case, the analytical system cycles through each of the sampling points in the network. Automated analytical systems may involve GC, GC/MS, mass spectrometry/mass spectrometry (MS/MS), infrared spectroscopy (IR), fourier transform infrared spectrometry (FTIR), or open-path optical monitoring (OPOM).

The use of real-time monitoring usually occurs when site regulatory personnel must make timely decisions on the emissions from the site during periods of active remediation. Real-time monitoring also enables the regulators to "see" peak short-term concentrations that may have important health effects associated with site remediation. Variations in concentration as a function of time can be correlated with source emissions. The major advantage that real-time monitoring has over portable real-time monitors is that most portable monitors react with entire classes of compounds and tend not to be specific for a given compound that might be on the target compound list. As an example, photoionization detectors (PID) are very sensitive to aromatic hydrocarbons but significantly less sensitive to aliphatic hydrocarbons. In essence, if the portable system does not have a GC column attached to it, it does not have the capability to differentiate between the two compounds like the real-time monitoring system.

Although real-time monitoring systems have numerous benefits, they also have disadvantages. Such systems are expensive and require frequent calibration and routine maintenance. In addition, real-time systems are usually complex, requiring highly trained field personnel, rigorous quality-control (calibration) procedures, and independent performance audits of routine monitoring and data handling operations. Finally, securing electrical power and a suitable location for housing the real-time system and the adaptation of sampling lines and cables for the system can require long-term planning and entail considerable expenses.

(4) Passive sampling. In recent years, the development of passive sampling devices (PSD) has drawn much attention. These devices sample by means of gas diffusion or permeation of VOCs on an adsorbent (i.e., Tenax®, charcoal) rather than by means of a pump. They have been shown to be simple, convenient, inexpensive, and valid alternatives for assessing time-weighted average concentrations for personal exposure monitoring.

Analysis of adsorbed compounds on sampling tubes is accomplished by thermal desorption and chromatographic separation. Specificity can be introduced into a passive sampling technique by choice of a suitable adsorbent substrate which is unique to capturing a specific compound. As an example, a passive sampler using chemically-coated glass fiber filter has been developed for formaldehyde. A comparison of recoveries of trichloroethylene from active charcoal tubes and a thermal desorbable personal monitor revealed the passive sampler to exhibit better recovery efficiency. A personal dosimeter based on molecular diffusion and direct detection by room temperature phosphorescence has been developed to monitor vapors of polynuclear aromatics.

(5) Portable gas chromatographic sampling techniques. Probably one of the most attractive sampling and analysis approaches is that of portable sampling methods based upon real-time monitoring. Portable sampling techniques are mostly used in a "screening" application at HTRW sites during both pre-remediation and remediation activities. Portable monitoring allows instantaneous results to be acquired so on-site decisions can be made in the protection of workers and off-site communities. Portable monitoring allows rapid turn-around of data with relatively inexpensive instrumentation.

Two of the most common detectors utilized in portable gas chromatographics are portable FID and PID. These detectors, used in conjunction or separate, are generally used to give background levels of total VOC and to identify "hot spots" of VOCs within a test locale. Two of the most important attributes of these detectors are their ever-increasing levels of sensitivity, and when used in conjunction with a chromatographic column, the ability to specifically characterize and/or identify VOCs at the HTRW sites.

The operation of an FID portable GC involves the pollutant entering the flame where it is mixed with hydrogen and burns. Ions and electrons formed in the flame enter the electrode gap, decreasing the gap resistance, thus permitting a current to flow. The flow of electrons determines the pollutant concentration. The FID is a universal detector, responding to a whole host of organic compounds and classes. One of the major advantages of the FID is its lack of response to air and water. The FID therefore serves as a basis for most commercially available "total hydrocarbon" and "non-methane hydrocarbon" analyzers. The detection limits for most FIDs is 100 ppb.

Portable PIDs operate on the principle of photoionization. In operation, the gas stream is subjected to a high-intensity beam of ultraviolet (UV) radiation from a lamp of a particular energy. If the molecule ionization potential is lower than that of the lamp, absorption occurs by the gas molecule, leading to the formation of a positive ion and free electron. The positive ion is collected at the electrode and the resultant current is directly proportional to the analyte concentration.

Consequently, the ionizational potential of the lamp is very important in the detection of certain classes of compounds. Compounds having high ionization potential will be less easily detected than those of lower

ionization potential. This ability allows one to readily detect aromatic hydrocarbons, but will not detect aliphatic hydrocarbons having a higher ionization potential.

The manufacturers of photoionization lamps usually provide lamps in four (4) energy levels. They are:

- 8.3 eV.
- 9.5 eV.
- 10.2 eV
.
- 11.7 eV.

It is more difficult to ionize an alkane (i.e., butane) than a chlorinated aromatic (i.e., chlorobenzene). The selection of the lamp therefore allows the user to "screen out" certain organics based upon their ionization potential. If the lamp does not have enough energy to ionize the molecule, it therefore does not "see" it. Consequently, aromatics can be selectively detected in the presence of halogenated hydrocarbons with a low-energy lamp (e.g., 9.5. eV), whereas both groups can be detected with a high-energy lamp (11.0 eV).

The sensitivity of the PID is considerably better than the FID in most cases (10 ppb or better). Recent models have shown sensitivity to the sub-ppb range.

d. Developing a site-specific target compound list (TCL).

(1) Introduction. The developing of a site-specific TCL is a key factor in the development of a FFMS for HTRW sites. HTRW sites often contain a complex mixture of contaminants, and not every contaminant will pose a significant risk via the air pathway. Selection of too broad a range of compounds can lead to excessive cost, whereas selection of too few may result in not meeting the project objectives. In most cases, the selection of a TCL at a HTRW site is a compromise between technical feasibility and environmental significance.

The objective of developing a site specific TCL is to provide a prioritized list of compounds for which there are sampling and analytical protocols, and as a tool for optimizing the air monitoring design. The TCL includes compounds most commonly found at the HTRW site which pose the most significant threat to human health and are most likely to enter the air pathway.

Certain compounds typically are considered to "drive" both the listing of target compounds and the risk assessment as part of the APA. These compounds pose the most significant risk during the remediation program. Consequently, the objective of the APA is to focus available resources and effort on those compounds thought to pose the most significant risk at a site, rather than including an evaluation of every compound found at the HTRW site. The selected analytes are sometimes referred to as target compounds or compounds of potential concern.

(2) Classification of target compounds. Compounds of interest for FFMS program are categorized, based on the compound and its physical and chemical properties, into four broad classifications, as discussed in Paragraph 3-5. The four classifications once again are:

- VOC, especially benzene and chlorinated solvents such as vinyl chloride, methylene chloride, chloroform, etc.
- SVOC, such as PCBs, PAHs, pesticides., and other semi-volatile inorganic compounds such as those containing mercury.
- Non-volatile compounds such as asbestos and cyanides.
- Heavy metals, such as lead, chromium, cadmium, zinc, beryllium, copper, and arsenic.

Table 3-2 summarizes the compound classes and the representative compounds in each class of the four classifications. Table 3-3 provides typical concentrations of the different categories of hazardous air pollutants in the atmosphere.

As previously discussed, an attempt to monitor all emissions at the HTRW site is not realistic. Consequently, the selection of target compounds to represent either a broad classification, or a specified class of compounds is usually performed in developing an air monitoring program at an HTRW site. The selection of target compounds (i.e., indicator compounds) at a minimum should include all contaminants with concentrations greater than or equal to 10% of the appropriate health based action level at the site. These contaminants are expected to represent the greatest contributors to potential health impacts. This approach provides a practical basis to address the large number of potential emission compounds at the site. Many factors should be reviewed in the decision process for selecting tracer species, including:

Table 3-2
Example Of Classification Of Organic And Inorganic Compounds For Air Monitoring At HTRW Sites

Contaminant type	Compound class	Representative compounds	
Volatile organics	Aromatics	benzene toluene ethylbenzene	total xylenes styrene chlorobenzene
	Halogenated species	carbon tetrachloride chloroform methylene chloride chloromethane 1,2-dichloropropane trans-1,3-dichloropropene cis-1,3-dichloropropene bromoform bromomethane	bromodichloromethane dibromochloromethane 1,1,2,2-tetrachloroethane 1,1,1-trichloroethane 1,1-dichloromethane chloroethane tetrachloroethane trichloroethane vinyl chloride
	Oxygenated species	acetone 2-butanone	2-hexanone 4-methyl-2-pentanone
	Sulfur containing species	carbon disulfide	

	Nitrogen containing species	benzonitrile
Volatile (inorganics)	Acid	hydrogen cyanide hydrochloric acid
	Sulfur containing	hydrogen sulfide

Table 3-2 (Continued)

Contaminant Type	Compound Class	Representative Compounds	
Semi-volatile organics	Phenols	phenol 2-methylphenol 4-methlphenol 2,4-dimethylphenol 2-chlorophenol 2,4-dichlorophenol 2,4,5-trichloropheno	2,4,6-trichlorophenol pentachlorophenol 4-chloro-3-methylphenol 2-nitrophenol 4-nitrophenol 2,4-dinitrophenol 4,6-dinitro-2-methylphenol
	Esters	bis(2-ethylhexyl)phthalate di-n-octyl phthalate di-n-butyl phthalate diethyl phthalate vinyl acetate	
	Chlorinated	1,2-dichlorobenzene 1,3-dichlorobenzene 1,4-dichlorobenzene 1,2,4-trichlorobenzene hexachlorobenzene	nitrobenzene 2,6-dinitrotoluene 2,4-dinitrotoluene 3,3-dichlorobenzidine
	Amines	n-nitrosodimethylamine n-nitrosodi-n-propylamine n-nitrosodiphenylamine aniline	2-nitroaniline 3-nitroaniline 4-nitroaniline 4-chloroaniline
	Ethers	bis(2-chloroethyl)ether bis(2-chloroisopropyl)ether	
	Alkadienes	hexachlorobutadiene hexachlorocyclopentadiene	
	Miscellaneous and aromatics	benzoic acid benzyl alcohol bis(2-chloroethoxy)methane dibenzofuran hexachloroethane isophorone	
	Polynuclear aromatic hydrocarbons (PAHs)	acenaphthene acenaphthylene benz(a)anthracene benzo(b)fluoroanthene benzo(k)fluoroanthene benzo(g,h,i)perylene benzo(a)pyrene chrysene dibenz(a,h)anthracene	fluoroanthene fluorene indeno(1,2,3-c,d)pyrene naphthalene 2-methylnaphthalene 2-chloronaphthalene phenanthrene pyrene
	Pesticides	alpha-BHC beta-BHC delta-BHC gamma-BHC heptachlor haptachlor epoxide 4,4'-DDT 4,4'-DDD 4,4'-DDE endrin	endrin ketone endrin aldehyde endosulfan I endosulfan II endosulfan sulfate aldrin dieldrin chlordane methoxychlor toxaphene

Table 3-2 (Continued)

Contaminant Type	Compound Class	Representative Compounds	
	Polychlorinated biphenyls (PCBs)	Arochlor 1016 Arochlor 1221 Arochlor 1232 Arochlor 1242	Arochlor 1248 Arochlor 1254 Arochlor 1260
Non-volatiles	Inorganic metals and nonmetals	aluminum antimony arsenic asbestos barium beryllium cadmium calcium chromium cobalt copper iron	lead magnesium manganese nickel potassium selenium silver sodium thallium tin vanadium zinc

Table 3-3
Example of Typical Concentrations of HAPs in the Atmosphere

Category	Concentration range
PAHs	10-100 ng/m^3
PCBs	1-10 pg/m^3
Pesticides	10-100 ng/m^3
Particles	10-50 g/m^3
Volatiles	0.5-5.0 ppb

- Variety of types of air contaminants (organic, inorganic, biohazard, radioactive).
- Physical state of air contaminants (gas, liquid, solid).
- Level of air contaminant emissions.
- Air monitoring objectives.
- Potential availability of standard sampling and analytical techniques.
- Homogeneity of the waste material.
- Potential analytical interferences from the site.

The rate at which soil contaminants are emitted to the air depends in part on their volatilities (for gaseous contaminants only), which in turn depend on vapor pressures and Henry's Law constants. Highly volatile compounds will typically be emitted at a higher rate than compounds of similar concentration in the soil but lower volatility. Computer models that rely in part on compound vapor pressure and Henry's Law data as input are often used to estimate potential emissions to the air. Emission rates can then be used as input to an atmospheric dispersion model to gauge both short-term (e.g., 1-year) concentration levels at the facility fenceline and off-site receptors. Semi-volatile and nonvolatile compounds may also be of concern when they exist in significant concentrations and there is the potential for the dispersion of wind-blown dust.

It often is not practical to monitor for every compound present in the soil or ambient air because of the limitations of available technical or financial resources. In these cases, potential target compounds should be ranked in terms of predicted concentration levels and applicable health-based action levels. Note that the potential adverse health effects vary from compound to compound, and the health-based action levels may vary by orders of magnitude between compounds with relatively similar structures and physical properties. For example, 1,2-dichloroethane is considered to be a much more potent carcinogen than 1,1-dichloroethane, and benzene is considered to pose a much more significant risk than equal amounts of toluene or xylene. Therefore, the most significant compounds at the site from a health risk standpoint might not necessarily be those present in higher concentrations in the soil or water.

Table 3-4
Relationship Between Ambient Air Monitoring Design Elements and the Three Phases of Remediation at a HTRW Site

	Three Phases in the Remediation of a HTRW Site		
	Phase I:	Phase II:	Phase III:
Design element	Pre-remediation or baseline study	Remediation study	Post-remediation study
Number of target compounds	Multiple compound classes; full analyte list	1-20	<10
Data quality objectives	Identify compounds accurately; semi-quantitatively	Quantify level of specified compound(s)	Quantify level of specified compound(s)
Sampling			
Period	24-hour	8-24 hours	24-hour
Duration	5 days to 1 year	Duration of remediation	5 days to 1 year
Frequency	Daily to once every 6 days	Daily	Daily to quarterly
Number of sampling locations	4-12	4-12	4-12
Monitoring method characteristics	Low detection limits Applicable to broad range of compounds	Rapid data turnaround Low detection limits Specific target compound list	Low detection limits Specific target compound list

Basically, the objective is to find the type and/or species that could be used to assess air quality impacts from the site during investigation and/or remediation activities. The ideal target compound should be:

- Found in air emissions from the site in a fixed ratio to other constituents.
- Non-reactive or stable species.
- Found at levels above analytical detection limits.
- Unique to the site.
- Known toxicity and acceptable exposure criteria.

Consequently, the objective of developing a site specific TCL is to provide a prioritized list of compounds for which an FFMS can be developed. The TCL should be comprised of those compounds that are most commonly found at the site, pose the most significant threat to human health, and that are likely to enter the air pathway. The number of target compounds to be monitored vary depending upon which phase the HTRW site remediation program is occurring, as identified in Table 3-4,

(3) Ranking of target compounds utilizing a basic algorithm. To assist personnel in developing a TCL, the EPA has developed a simple algorithm to rank compounds at HTRW sites in order of importance. Considerations in developing the ranking scheme were health effects, regulatory needs, potential for human exposure through the air pathway, and use of available data bases.

Table 3-5
Example of Components of the RIA Program for a HTRW Site

Rank	Descriptor
1	Health effects index
2	Analyte identified at the site and on the Hazardous Substance Priority List (HSPL)
3	Regulated by State agency
4	Listed in California Air Resource Board (CARB) List of Lists
5	Listed in New York Air Guide One
6	Frequency of occurrence at NPL sites
7	Volatility index (VI)
8	Listing in SARA Title III
9	Availability of analytical methodology
10	Availability of reference standard

The ranking index algorithm (RIA) is comprised of 10 components, as listed in Table 3-5 in order of their ranking. Following is a brief discussion of each of the components of the algorithm.

(a) Health effects index. In considering health effects, available data developed by EPA's Pollutant Assessment Branch (PAB) and generally contained in the list of unit risk factors for the inhalation of carcinogenic air contaminants should be used. This list is maintained by PAB for air assessments performed

within EPA's Office of Air Quality Planning and Standards (OAQPS). The PAB also maintains a separate list of compound "cancer potency slopes" that, in most cases, are based upon ingestion routes of exposure. Because in many cases these cancer potency slopes have been, and will continue to be, converted to inhalation factors for use in air toxics risk assessments, data could be included in the health effects index ranking.

For those compounds that are non-carcinogens, EPA has determined a RfD value. The RfD's are used by EPA as threshold values in evaluating non-carcinogenic health effects. For other compounds on the list not described by any of these data bases, one can rely on various health effect indicators such as threshold limit values. As a last resort, consult reportable quantity data from SARA Title III listing.

(b) Regulated by State agency. The National Air Toxics Information Clearinghouse should be used as an indicator of state regulatory activity for specific HAPs. For the various states regulating on the basis of reference ambient levels (RALs), frequency of occurrence of regulations for specific chemicals should also be an important ranking criteria.

(c) Regulatory list. Frequency of occurrence on lists of hazardous materials should also be considered as a useful ranking indicator. The California Air Resources Board (CARB) publishes a "List of Lists" that shows the frequency with which specific chemicals are listed in 12 authoritative lists of hazardous chemicals. The New York Air Guide II also categorizes specific air toxics compounds at high, medium, or low toxicity. SARA Title III, Section 313 also lists hazardous pollutants. Frequency of occurrence in each of these lists should be used as an indicator of relative importance of these compounds, occupying the 2nd, 4th, 5th, and 8th positions in order of importance of ranking criteria.

(d) Potential for human exposure through air pathways. Indicators for the potential for human exposure should be incorporated by considering both the frequency of occurrence at the HTRW site and the volatility of each of the listed compounds. Frequency of occurrence at different sites can be obtained directly from the EPA list entitled "Frequency Distribution of Substances Present at Final and Proposed NPL Sites." A volatility ranking number between 0.5 to 3 for each compound should be derived from boiling point and/or vapor pressure data, as available. These indicators are generally considered to represent potential for human exposure though the air pathway at the site and was assigned the 7th position in the ranking scheme.

(e) Availability of analytical methods and reference standards. The 9th and 10th weighing positions were assigned to availability of analytical method and reference standard, respectively. For marginal compounds, the availability or lack of analytical methods and reference standards should be a factor in the decision to include or exclude such compounds from the TCL.

In summary, the following considerations should be used to develop the site-specific TCL:

- Frequency with which compounds have been found at the sites.
- Compounds that present a risk of exposure by inhalation and that are highly toxic or carcinogenic.
- Frequency with which compounds are requested under Federal or State regulations (ARARs and TBCs) to meet cleanup goals.

- Availability of sampling/analysis methods and reference standards for the target compounds.
- Relative volatility of the candidate compounds.
- Availability of health-based data (unit risk, reference doses and acceptable ambient levels) for the target compounds.

To complete the ranking process, each of the candidate analytes should be entered into a spreadsheet and arrayed with corresponding numerical data describing each of the 10 ranking criteria. A RIA is then devised that positions the maximum value of each of the ranking criteria terms in its relative weight positions. The algorithm, the ranges of the numerical data in the spreadsheet, and the relative maximum term values are shown in the following equation:

$$RIA = 10G + 11.3B + 120M + 7.5D + 23.3F + 10K + 20L + 40E + 35C + 15J$$

where:

G = health effects;
B = analyte identified at a site or on Hazardous Substance Priority List (HSPL);
M = analyte regulated by state or Federal agency;
D = listed into CARB list;
F = listed into Air Guide II list;
K = frequency of occurrence at NPL sites;
L = volatility index;
E = listing in SARA Title III;
C = availability of analytical methods; and
J = availability of reference standards.

Health effects, for example, should be designated as the most important of the descriptive criteria and accordingly ranked number 1; availability of a reference standard should be the least important, ranked number 10.

For convenience in developing a RIA ranks are assigned corresponding maximum values of the algorithm terms representing the descriptors. For health effects, a maximum term value of 100 should be selected, while for availability of reference standard, a maximum term value of 30 should be selected. Intermediate term values for other descriptors should be selected so that each algorithm term representing a descriptor that can be retained in the relative position.

For health effects, each chemical should be assigned an index value between 1 and 10, with 10 being the maximum value of the health effect descriptor and representing the greatest level of health hazard. For availability of reference standard, each chemical should be assigned an index value between 0 and 2, with 0 representing no standard available and 2 representing availability of EPA-certified standard. The algorithm constant is derived by dividing the maximum term value by the maximum numerical index value arrayed in the

spreadsheet. For health effects, the algorithm constant was 10 (100/10), while for the availability of reference standard, the algorithm constant was 15 (30/2).

Table 3-6
Example Of RIA And Deviation Of Term Values
RIA = 10G + 11.3B + 120M + 7.5D + 23.3F + 10K + 20L + 40E + 35C + 15J

Data source			Computer spreadsheet range of numerical data			Derived constant for algorithm (a ÷ b)
Descriptor	Rank[a]	Selected max. value of descriptor[a]	Algorithm variable	Minimum value	Maximum valuable[b]	
• Health effects index	1	100	G	1	10	10
• Analyte identified at site and on Hazardous Substances Priority List (HSPL)	2	90	B	0	8	11.3
• Regulated by State agency	3	80	M	0	0.667	120
• Listed in CARB list of lists	4	75	D	0	10	7.5
• Listed in New York Air Guide II	5	70	F	0	3	23.3
• Frequency of occurrence at NPL sites	6	65	K	0	6.5	10
Volatility index	7	60	L	0.5	3	20
Listing in SARA Title III	8	40	E	0	1	40
Availability of analytical method	9	35	C	0	1	35
Availability of reference standard	10	30	J	0	2	15
Maximum value of algorithm		645				

[a]Relative importance of descriptor.
[b]Numerical data expressed as decimal fraction.
[c]Numerical data expressed a decimal fraction x 100, for multiple listings only.

Utilizing the RIA for a series of EPA Superfund sites nationwide, the first twenty (20) ranked compounds are calculated as:

Rank	Compound	Rank	Compound
1	Vinyl chloride	4	Chloroform

2	Trichloroethylene	5	Benzene
3	Cadmium	6	Carbon Tetrachloride
7	Arsenic	14	Heptachlor/Heptachlor epoxide
8	Tetrachloroethylene	15	1,2-dichloroetheneFormaldehyde
9	Chromium	16	Acrylonitrile
10	Mercury	17	Benzo(a) pyrene
11	Beryllium	18	1,2-Dichloroethane
12	Selenium	19	Chlorobenzene
13	Nickle	20	Lead

The ranking index should be designated as the sum of the descriptor terms with a maximum value of 645, as illustrated in Table 3-6.

Table 3-7 illustrates a sample calculation for ranking vinyl chloride. The complete target compound list developed for EPA nationwide for Superfund sites consists of approximately 257 target compounds. Of the 257 compounds, 43% are volatiles having vapor pressure greater than 0.1 mm Hg. Approximately 32.4% of the target compound list are classified as semi-volatiles with vapor pressure ranging from 10^{-1} to 10^{-7} mm Hg. Finally, inorganic metals comprise approximately 28% of the target compound list. Appendix G contains the full target compound list of 257 compounds as developed for EPA to be used at Superfund sites utilizing the algorithm.

Table 3-7
Example of Sample Calculation For Vinyl Chloride

Value of variable in algorithm[a]	Descriptor	Vinyl chloride term value[b]
G = 4	Health effects index	40
B = 8	Analyte identified at site and on HSPL	90
M = 0.5	Regulated by State agency	60
D =10	Entered in CARB list of lists	75
F = 3	NY Air Guide List	70
K = 1.51	Frequency of occurrence at NPL sites	15
L = 3	Volatility index	60
E = 1	Listing in SARA Title III	40
C = 1	Availability of analytical method	35
J = 2	Availability of reference standard	30
	Total algorithm value for vinyl chloride	515

RIA = 10G + 11.3B + 120M + 7.5D + 23.3F + 10K + 20L + 40E + 35C + 15J
= 10(4) | 11.3(8) + 120(0.5) + 7.5(10) + 23.3(3) + 10(1.51) + 20(3) + 40(1) + 35(1) + 15(2)
= 40 + 90 + 60 + 75 + 69.9 + 70 + 15 + 60 + 40 + 35 + 30
= 515

[a]Values for vinyl chloride terms from spreadsheet.
[b]Rounded off to nearest whole number.

(4) Summary. The process of developing a site specific TCL from a general universe of compounds is critical in meeting the project's objectives. The overall objective of the site specific TCL is to identify species that are common to the waste, likely to be present in emissions and can be sampled and analyzed by the FFMS. The target compound list should be composed of compounds that are:

- Found uniformly in the waste and at a relatively constant ratio to other contaminants.
- Relatively non-reactive and stable in ambient air.
- Found in the downwind plume well above the analytical detection limit of the sample collection/analytical technique.
- Unique to the site and not found in the upwind air at significant levels.

Representativeness of these compounds should be demonstrated at the onset of the program and perhaps throughout the program. This verification of target compounds is critical for demonstrating the applicability to the FFMS at the site. Figure 3-8 summarizes the steps one should perform in developing a site specific target compound list using the RIA system.

3-6. Technical Consideration in the Development of a Fixed-Fenceline Sample Collection and Monitoring System.

a. Introduction. To achieve the objectives of a real-time FFMS, proper planning and organization are required that attain the data collection goals, minimizes cost and ensures that the data is defensible and is of known and acceptable quality to meet the needs of the primary data user (decision maker). An effective way to accomplished these objectives is to implement EPA's DQO process as outlined in Paragraph 3.2. This process applies to all HTRW remediation projects where monitoring data is to be used to make project decisions. DQOs are qualitative and quantitative statements produced when implementing the program.

The overall goal of an APA is to estimate the site's actual or potential effects of emissions to the surrounding air quality. A major objective of the APA is to estimate the pollutant levels from the site at the fenceline and their transport to the off-site community and environment. The evaluation of off-site exposure generally requires that monitoring be performed whenever significant air emissions may be released from the site. At sites that have the potential for adversely affecting the air, this requirement is often addressed by establishing a fixed network of sample points around the perimeter of the site where samples are extracted on a continuous basis. Collecting samples on a continuous basis allows for an evaluation of the effectiveness of the hazardous pollutant control options installed at the HTRW site during remediation activities, and allows for immediate corrective action based upon real-time pollutant concentration data coupled with on-site meteorological data. It is therefore imperative that specific technical considerations be given when implementing a real-time, volatile FFMS because the output of this system will be used for both health and safety considerations at the site and for documenting the achievement of complying with regulatory emission limits.

To achieve the above objectives, a number of crucial areas need to be considered in the design and implementation of a real-time volatile FFMS. They are:

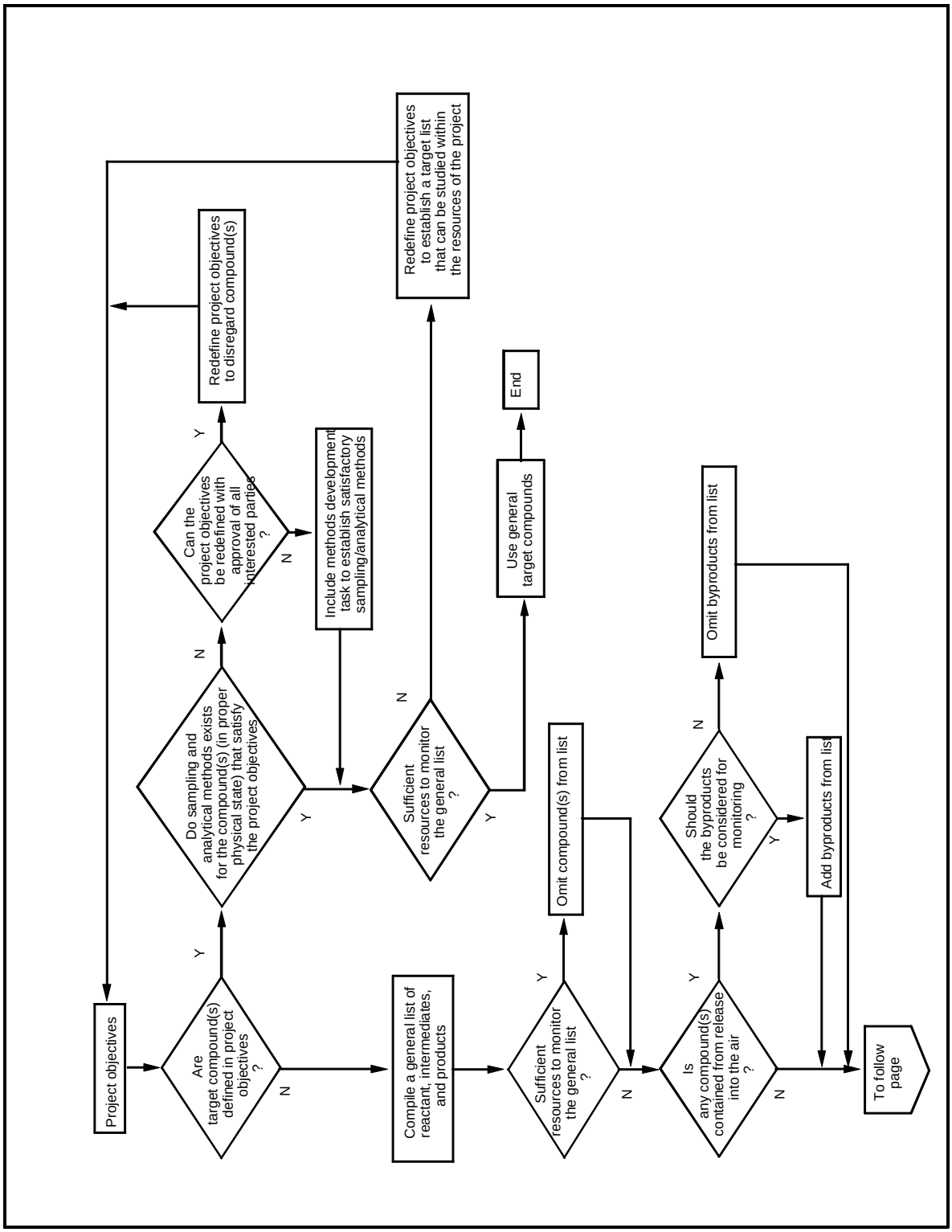


Figure 3-8. Example of flowchart for defining a site specific target compound list at a HTRW site.

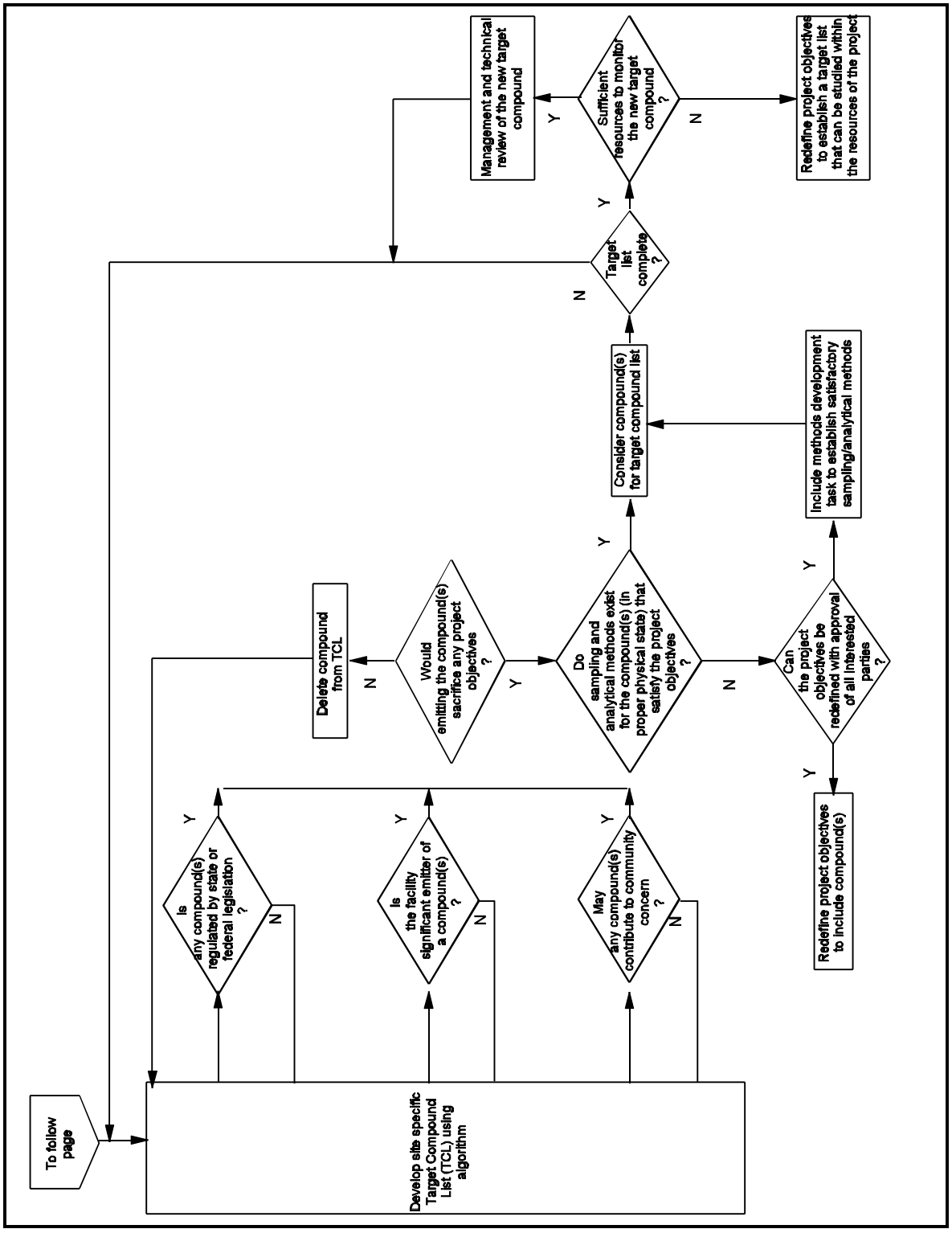


Figure 3-8. (continued)

- The selection of toxic compounds for analysis, based on toxicity and the likelihood of human exposure.
- The applicability of sampling techniques to specific target compounds or classes of compounds.
- The design and implementation of the FFMS.
- Long term performance of the analytical system to meet project DQOs.
- Site characteristics associated with the location of inlet probes and analytical center.

b. Designing monitoring strategy. The first step in designing a monitoring strategy is to determine the overall objectives of the sampling program. Most problems in sampling program design can be traced directly to misunderstandings about overall sampling objectives. The importance of a well thought-out set of sampling program objectives cannot be overstated.

In developing a monitoring strategy to meet sampling program objectives, several crucial items should be provided. These include:

- Processes and/or sources to be characterized.

- Any relevant rules that require the monitoring program to be conducted, and any specific Agency requirements.

- The intended use of the monitoring data.

- A summary of DQOs and other QA concerns.

- Any cost, physical, and time constraints.

The purpose for specifying the above items up-front is to allow plan preparers to clearly understand the technical requirements of the sampling program and to allow plan reviewers to critically evaluate the technical specifications of the plan and the data that the program will generate.

The development of a monitoring strategy also forces interested parties to “think through” the purposes of the program and to reach a consensus on critical requirements before the commitment of funds. An example of sampling program objectives for an HTRW site assessment study is presented in Figure 3-9.

c. Acceptance air risk specific concentration. One of the primary purposes for conducting a real-time FFMS program is to provide the data required for an inhalation risk assessment for both on-site and off-site receptors. The concept of the “acceptable air risk specific concentration” (acceptance concentration) was developed by EPA to assist in the identification of methods capable of detecting airborne HAPs concentrations low enough to permit a meaningful risk assessment to be performed at various levels. The acceptable risk concentration specified by EPA is 10^{-6}, which means that to detect HAPs at an inhalation risk of 1-in-1 million (10^{-6}) level, the selected sampling method must be capable of quantifying concentrations at least as low as the acceptance risk concentration. (In other words, the acceptance concentration equals a maximum individual risk of 10^{-6}.) The EPA’s Superfund Public Health Evaluation Manual defines an acceptable level of cancer risk as being in the range of 10^{-7} to 10^{-4}. (This range represents the acceptable level of risk for an adult exposed to maximum predicted ambient air concentration for a 70-year period, 24 hours per day. A 10^{-7} risk is a 1-in-

10 million chance of death from cancer, whereas a 10^{-4} risk is a 1-in-10 thousand chance of death from cancer.) Obviously, air sampling methods must be capable of measuring ambient contaminant concentrations corresponding to risks within the 10^{-7} to 10^{-4} range.

As an example of how acceptance concentrations can be used in selecting sampling methods, consider the compound vinyl chloride, whose acceptance concentration is 0.024 µg/m^3. A vinyl chloride concentration in ambient air of 0.024 µg/m^3 represents an inhalation-based cancer risk of 10^{-6} (i.e., for every 1 million adults who are exposed to this concentration over 70 years, one adult would be expected to die from cancer related to vinyl chloride exposure). If vinyl chloride is present in the ambient air at a concentration of 0.024 µg/m^3, and if the air sampling system used to measure vinyl chloride concentrations is not designed such that concentrations as low as 0.024 µg/m^3 can be detected, then the risk of cancer would not be detected. (Instead, the analytical results would be reported as "below detection limit.") Obviously, if the characterization of risk levels as low as 10^{-6} is a DQO of the sampling program, the sampling method must be capable of detecting concentrations as low as the acceptance risk concentration. (The same argument also holds for acceptance concentrations based on other risk levels of interest.)

Derivation of the acceptance concentrations is straight-forward and can be performed at any risk level of interest and for any compound having an inhalation unit risk factor for cancer. The derivation formula is as follows:

$$\text{Ambient Air Level (AAL)} = \frac{\text{Risk level of interest}}{\text{EPA's unit risk factor}}$$

where:

Risk level of interest = The lowest level of inhalation risk at which site investigators wish to characterize the risk of death from cancer for an adult exposed to ambient air concentrations of the contaminant of interest, for a 70-year period, 24 hours per day (i.e., 10^{-4}, 10^{-5}, 10^{-6}, etc).

EPA's unit risk factor = A common measure of a compound's carcinogenic potency via the inhalation route of exposure, in units of m^3/µg. Appendix G contains many unit risk numbers for several hazardous air pollutants. The unit risk factor times the ambient air concentration of the compound equals the risk of cancer for an exposed individual.

Again using vinyl chloride as an example, the acceptable AAL concentration at a 10^{-6} risk level is calculated as follows:

$$\text{AAL for vinyl chloride} = \frac{10^{-6}}{4.2 \times 10^{-5}}$$

$$= 0.024 \ \mu g/m^3$$

SAMPLING PROGRAM OBJECTIVES

The objective of this FFMS program is to assess compliance with Rule XXX by measuring HAPs emissions from the HTRW site. The Rule provides a list of toxic compounds which must be assessed (see Table X), and specifies concentrations that will be monitored as 24-hour average concentrations. The intended use of the data will be to perform an HAPs risk assessment for both nearby residents and on-site workers at the one-in-a-million (i.e., 10^{-6}) risk level. Both carcinogenic and non-carcinogenic, acute health effects are to be assessed.

USACE has determined that the following data quality objectives are necessary to assure that the sampling results are meaningful:

Accuracy:	±30%
Precision:	±30%
Completeness:	At least 80% of validated data must be acquired. The expected failure rates of the selected sampling methods should be considered in determining the number of separate measurements to plan for.
Representativeness:	Emission measurements should reflect normal conditions at the site over a 24-hour period. The data will be used to calculate emission rates.
Comparability:	The selected methods and procedures should be similar to those recently used at the USACE site so that emissions from the two sites can be compared.

All measurements and analyses must be completed by the end of physical year 19XX. Due to site access problems during the rainy season, it is preferred that all measurements be made during the summer months, provided that this can be accomplished without seriously sacrificing the representativeness of the sampling program. Costs should be minimized through the use of screening techniques wherever possible.

Figure 3-9. An example of sampling program objectives for a HTRW site assessment study

The risk level of 10^{-6} has been chosen as the basis for AALs concentration values presented in Appendix G because this is the level of risk most often monitored by EPA's Regional Offices. Similar calculations can be performed at other risk levels of interest.

Unfortunately, for some of the more hazardous air pollutants, it will not be possible to design a practical real-time volatile FFMS that is capable of detecting the very low ambient air concentrations corresponding to a 10^{-6} risk. In these situations, it will be necessary to modify the objectives of the risk quatification as defined in the DQOs of the USACE sampling program. For example, it may be necessary to be satisfied with a risk quantification goal of 10^{-5} or even 10^{-4}, which would raise the detection limit of the real-time volatile FFMS to a detectable level. Alternatively, if a number of hazardous compounds are present in the ambient air, it may be possible to use an easily-measured compound as an "indicator" of a more difficult-to-measure compound. Another alternative would be to calculate risk for the compound using the worst-case assumption that concentrations are present at the lower limit of detection for the real-time volatile FFMS.

When applying the AAL concept, it is important to allow for the presence of multiple carcinogenic compounds. Inhalation risks are usually assumed to be additive. Thus, if an objective of a USACE HTRW program is to quantify inhalation risk at levels as low as, say, 10^{-6}, and if more than one carcinogenic air contaminant is present, then the *sum* of risks for the individual compounds must be determined. Although the sum of risks may exceed 10^{-6}, the contribution to total risk by each of the individual compounds may be less than 10^{-6}. The sampling method must be capable of detecting concentrations associated with these low risk values (i.e., less than 10^{-6}), thereby making detection at levels *below* the AAL concentrations outlined in Appendix G desirable.

d. Site characteristics. One of the most important aspects to consider when evaluating site characteristics is the site terrain. The geometry of the site and the contour of the location directly influence the extent and the design of the FFMS program. Extremely complex terrain will complicate the migration of contaminants and make evaluation techniques complex with uncertain results. Fixed-point monitors may not be as effective as the application of open-path optical remote sensing devices because of the likelihood of the fixed-point monitors missing the "site plume." To compensate, one can increase the number of fixed-point monitors as part of the FFMS program on both the horizontal and vertical plane in an attempt to characterize the site plume. Another option is to use air dispersion modeling to map the site plume; however, air dispersion modeling is often difficult to implement and results are often inaccurate and non-representative.

Local meteorological conditions will also play a major role in the design of a perimeter air monitoring program. The placement of inlet extractive probes or time-integrated monitoring systems must be such that the gas sample analyzed is truly representative of the site emissions regardless of wind direction. Historically, the evaluation of the 5-year wind rose is used to help locate inlet probes in an upwind/downwind scenario based upon the dominant wind direction. However, the uncertainty of the meteorological conditions at the site would require, at a minimum, four inlet probes around the site with the first inlet probe placed in the upwind quadrant based on the 5-year wind rose and the remaining probes at 90 around the site. This placement allows for appropriate coverage at a reasonable cost. Paragraph 5-3 discusses in greater detail the placement of inlet probes in association with site specific meteorological conditions.

Accessibility to sampling sites and inlet probes is also a consideration when designing the perimeter air monitoring system. Under best conditions, the site will have an access road around the perimeter where the inlet probes are located for ease of maintenance and auditing functions. The access road saves time and labor when performing probe tip audits because equipment can be transported to the site by vehicle over rough terrain rather than hand-carrying to the location. Finally, a perimeter air monitoring station should be located outside the exclusion zone to minimize the personal protection equipment (PPE) requirements as part of the site health and safety program. If the sites are located in the exclusion zone, then a level A or B may be required. Working under these levels of protection is extremely difficult, requiring considerably more time and expense to complete a simple task. Again, depending on the project, road accessibility and locating the inlet probes outside the exclusion zone may be important to the successful completion of the project within a defined timeframe and restricted budget.

Available utilities are not as important for an FFMS program as they would be for a time-integrated network of samplers. As part of the heat-trace line component of the extractive system (see Paragraph 5-4), all electrical needs are self-contained in the umbilical cord. Consequently, the probe inlet, filter, and lines are heated to operating temperatures by electrical connections extending from the analytical center to the probes via the umbilical cord. However, if the program requires collocated volatile samples or other time-integrated systems (i.e., PM-10/TSP samplers, semi-volatile samplers, etc.) at the probe perimeter locations, it may be wise to establish line power to operate these systems rather than using portable generators or battery powered instruments. This requirement is especially essential if the perimeter air monitoring program is to be operated over several years rather than months. If the program is short in duration and the air pathway can be monitored using simple, battery-powered instrumentation, line power is not needed.

e. Evaluation of available information. A substantial savings in sampling time and costs can be realized by evaluating existing information. While such information seldom satisfies the objectives of the sampling program, the information can provide valuable insight into what analytes to sample, when and where sampling should be performed, and what sampling techniques are likely to be successful. For example, data from a past sampling program at a similar site may indicate which compounds are likely to be present and at what concentrations. Historical data from a nearby site might indicate the extent to which background concentrations may contribute to the on-site concentration measurements. Additionally, information may be available on contaminant phase distribution characteristics and monitoring equipment performance. The time devoted to locating and reviewing information on past test programs usually pays for itself in the development of a more efficient sampling strategy. Appendix D, Hazardous Air Pollutants Data Bases, provides guidance on proper methodology selection for over 1,000 HAPs detected at hazardous waste sites.

f. Meteorological data. Ordinarily, the monitoring strategy will include the collection of meteorological data. An important reason for evaluating these data is to determine whether the atmospheric condition and pollutant concentration have an impact on the surrounding community and are truly “representative” of conditions at the site. For example, because the volatilization of toxic compounds from contaminated soil is influenced by soil temperature and moisture, temperature and rainfall measurements may be especially important to monitoring strategies where the volatilization of contaminants from the soil is to be characterized. In this example, an effort would be made to conduct the monitoring program during periods when temperatures and rainfall are within normal ranges for the locale under study. At a minimum, the following meteorological parameters should be monitored on a continuous basis:

- Wind speed and direction.
- Temperature (10-meter and 2-meter).
- Relative humidity.
- Barometric pressure.
- Precipitation.
- Solar radiation.

Meteorological data are also important in determining where to site inlet probes and monitoring equipment, and in assuring that siting decisions remain appropriate throughout the test period. The usual strategy for siting inlet probes is to establish monitoring locations downwind of the source, with possibly one or two locations upwind of the source for background measurements. The use of an on-site specific meteorological station both before and during the sampling period will provide the information necessary to make intelligent decisions about monitor siting. Chapter 6 discusses in greater detail the meteorological system and its role in a real-time, fixed-fenceline real-time FFMS program.

g. Selection of instrumentation and analytical methods. An obvious factor in the selection of instrumentation and analytical sampling methods is the ability of the method to measure the compound of interest at a specified concentration, typically in the low ppbv range for highly toxic compounds. The ability of a sampling method to measure low concentrations will depend on several factors, including:

- The sensitivity of the sampling method for the particular compound of interest.
- Applicability of the method to monitor all target analytes.
- Ability of the instrumentation to collect, speciate and detect specific analytes.
- Cost constraints.
- Instrumentation performance and reliability.
- The detection limit of the chosen instrumentation and analytical method.
- Ease of set-up and operation.

Other important factors to consider in the selection of sampling methods are (1) the potential for artifact formation, (2) the minimization of erroneous data due to interfering compounds, (3) the ability of the method to achieve desired data quality objectives, (4) the ability to simultaneously measure other compounds of

interest, and (5) the compatibility of the sampling method with available analytical methods. Questions that should be answered in the selection of instrumentation are:

- Can the selected instrument detect the probable target compounds?
- Does the sampling methodology sample the analyte effectively and quantitatively?
- Does the instrument transfer the analyte quantitatively from the inlet to the analytical detector?
- Can the instrumentation produce precise, accurate, and quantitative results for all of the analytes listed in the monitoring program goals?
- Does the selected instrumentation have detection limits low enough to meet the overall objectives of the sampling program?
- Would the methodology be hampered by any interfering compounds?

h. Selection of compounds for measurement. Compounds should be selected for measurement based upon the program objectives and evaluation through the APA program. For example, if the perimeter air monitoring program is intended to assess compliance with Federal, state or local rules or policies, these rules or policies may specify the compounds for which measurements are required. Additional factors to be considered in selecting compounds for measurement include:

- Expected presence in the atmosphere based on the presence of soil or groundwater analyses or on historical material usage records.
- The potential for adverse health effects by the inhalation route of exposure.
- The technical feasibility of the monitoring and measurement systems.
- The likelihood that atmospheric degradation or formation processes may alter compounds concentrations in the atmosphere.
- Sampling cost considerations.
- Regulatory requirements.

As illustrated in Table 3-8, the selection process should also consider ranking of the compounds (see Paragraph 3-5), depending on whether they are regulated, whether dependent on percentage of positive hits in the soil, whether the compounds were detected in the air during background monitoring, or whether they were detected during bore hole testing. Once the larger list of compounds is identified, then that list needs to be reduced to a more manageable number (less than 5) of compounds that can be monitored by a real-time GC system. As an example, Table 3-9 identifies the three target volatile organic compounds that were selected from a larger list of compounds (Table 3-8) for real-time monitoring at an HTRW site.These compounds were

selected because they represent an aromatic, an alkene, and a chlorinated aromatic. Table 3-9 also identifies the OSHA PELs, PALs and the AAL (at 10^{-6} risk level) for the three selected analytes. Using Table 3-9, one can determine that an on-site GC system can detect the target analytes at 10^{-6} risk levels or if another risk level needs to be evaluated as part of the DQO process.

In situations where the available sampling methods are not capable of measuring an analyte at concentrations as low as desired (as often occurs with some of the more toxic compounds), it may be reasonable to measure a surrogate compound instead. This surrogate would be a compound that ordinarily co-exists in the atmosphere with the compound of concern, but is more easily measured. Thus, the presence of the surrogate compound would"indicate" the presence of the compound of interest.

Table 3-8
Example of Compilation Of Analytes Of Interest As Part Of The Selection Process at a HTRW Site

Ranking	Analyte	Boiling Point (C)	OSHA PELS (ppm)	State regulated	% positive soil samples	Detected in background monitoring	Detected in bore hole monitoring
1	Acetone	56	--		48		
2	Benzene	80	10	**M**	2	**M**	**M**
3	Toluene	111	50		21	**M**	**M**
4	Xylenes	144	100		26	**M**	**M**
5	Methylene chloride	40	--		12	**M**	**M**
6	Trichloroethylene	87	50		20	**M**	**M**
7	Chloroform	132	--	**M**	4		
8	Chlorobenzene	132	10	**M**	60	**M**	**M**
9	Dichlorobenzene	174	25		20		
10	Tetrachloroethylene	121	25	**M**	20	**M**	**M**

Table 3-9
Example of Three (3) Site Specific Target Compounds Selected from Table 3-8 as Results From the Selection Process

Compound	On-site GC instrument quantitation limit, ppb	Instrument calibration range, ppb		OSHA PEL, ppb	Perimeter action level (PAL), ppb	Acceptable ambient level (AAL) at 10^{-6} risk, ppb
		Minimum	Maximum			
Toluene	0.2	0.5	2,000	91,463	914	1.9
Chlorobenzene	0.2	0.5	2,000	77,777	777	1.6
Tetrachloroethylene	0.2	0.5	2,000	25,110	251	0.9

Another consideration concerns the data quality likely to be associated with a particular measurement approach. For example, if measurements are made at concentrations close to the limit of detection for a given compound, the accuracy and precision associated with these measurements may be unacceptably poor and may not meet the program DQOs. In these situations, it may not be worthwhile to proceed with that measurement method.

A final scenario would be to monitor NMOC at a PAL of 1 ppm. Then, if exceeded, require the GC system to speciate the NMOC peak at detection limits below the 10^{-6} AAL value, as illustrated in Figure 3-10. This requirement would allow maximum flexibility for an on-line GC system design by allowing alarm levels at 1 ppm and risk levels (10^{-6}) determined at ppb levels, thus meeting USACE program DQOs.

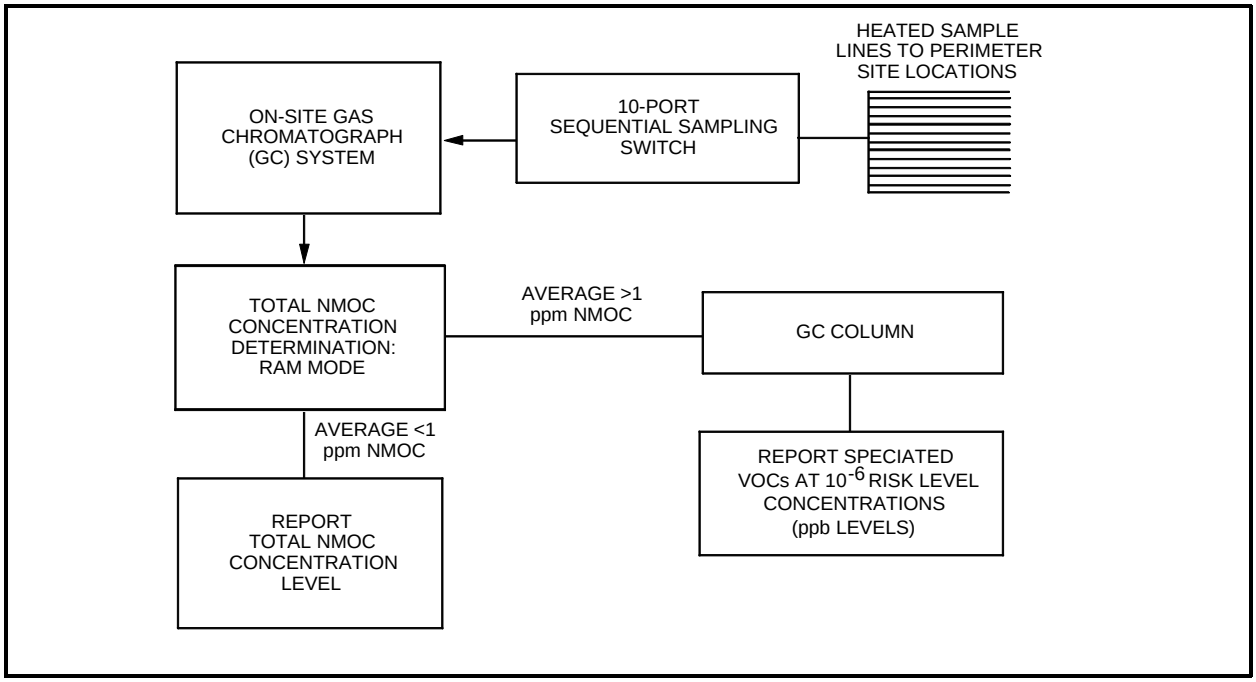


Figure 3-10. Example of application of monitoring NMOC/speciated organics at the site perimeter as part of the selection process.

i. Number and location of sampling sites. A variety of factors influence the number and location of probe inlets around a hazardous waste site. Factors that influence the required number and location of inlets at the site are:

- Evaluation of 5-year wind-rose for predominant wind direction.
- Location of potential on-site emission sources (i.e., process emissions, waste handling facilities, etc.).

- Location of topographic features that affect the dispersion and transport of site emissions.

- Location of sensitive receptors at the site perimeter and off-site.

- Location of off-site sources that might contribute as background contributors to on-site concentrations.

- The level of confidences needed to ensure that the maximum concentration levels are obtained.

In determining the number and location of sampling sites, dispersion models (screening and refined) should be used to assist in calculating ground-level concentrations in the site vicinity and to determine locations of maximum calculated concentrations for short-term (up to 24 hours) averages and long-term (monthly, seasonal, and annual) averages. Inputs into the dispersion model should include stack height for the treatment system, hazardous waste constituent concentration, previous 1-year on-site meteorological data, population close to the site, and sensitive population. The model outputs should be plotted as isolpeths of concentration. This information will assist in siting of monitoring stations. The first priority, however, should be to locate inlets that:

- Provide information on possible high impact of emission plume on sensitive receptors (i.e., concerned citizen, downwind communities, schools, hospitals, etc.).

- Are positioned in the plume of expected high concentrations of source constituents based upon historical meteorological data and dispersion model results.

Typically, programs designed for determining long-term concentration levels (e.g., annual or lifetime exposures) will require fewer probe inlet locations than those intended to monitor compliance with short-term action levels. The long-term prevailing wind directions are usually more predictable than day-to-day wind patterns, and inlet sites, therefore, can be more accurately situated for measuring significant long-term effects.

For determining concentration levels with respect to short-term effects, a fixed network of sample inlets ideally should be located around the perimeter of the HTRW site, with additional samplers located near working areas and near sensitive receptors. The number of sampling sites will depend, in part, on the size of the HTRW site. For large sites surrounded by nearby residences, a 12-station network would provide nearly complete spatial coverage at the fenceline (i.e., one sampling station every 15), as illustrated in Figure 3-11. However, cost considerations may not allow this

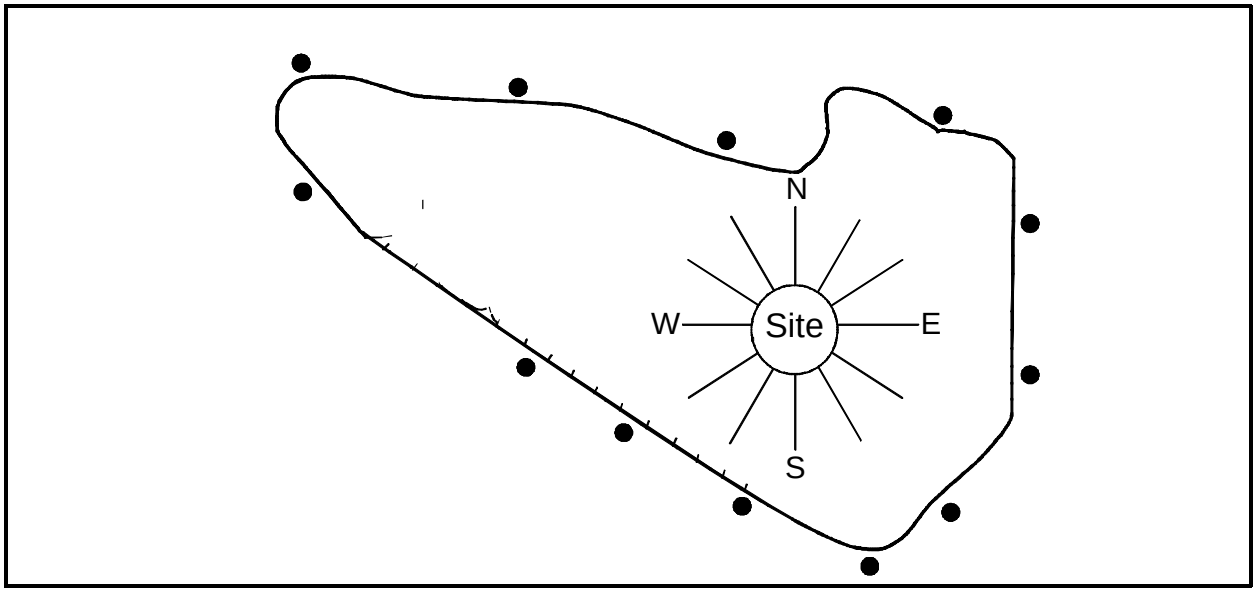


Figure 3-11. Example of a 12-point monitoring network HTRW site

arrangement. Another example would be to determine the predominant 5-year wind rose and place one inlet probe upwind and three inlet probes downwind. A better application of the four station arrangement would be to locate an inlet probe at the centroid of each of the 90 quadrants of a circle based upon the 5-year wind rose, as illustrated in Figure 3-12.

Each of the inlet probes serve specific objectives as part of the FFMS program:

- Inlet probe #1: Inlet probe #1 is the predominant upwind site based upon the previous 5-year wind rose. This inlet should identify specific constituents entering and impacting the site.

- Inlet probe #2: Inlet probe #2 is the second probe that provides data on the impact of emissions from the site.

- Inlet probe #3: Inlet probe #3 is the predominant downwind site based upon the previous 5-year wind rose. It should be located approximately 180 from inlet probe #1. Working with probe #1, a predominant upwind/downwind concentration of the emissions from the site can be instantaneously calculated.

- Inlet probe #4: Inlet probe #4 monitors the impact of emissions from the site.

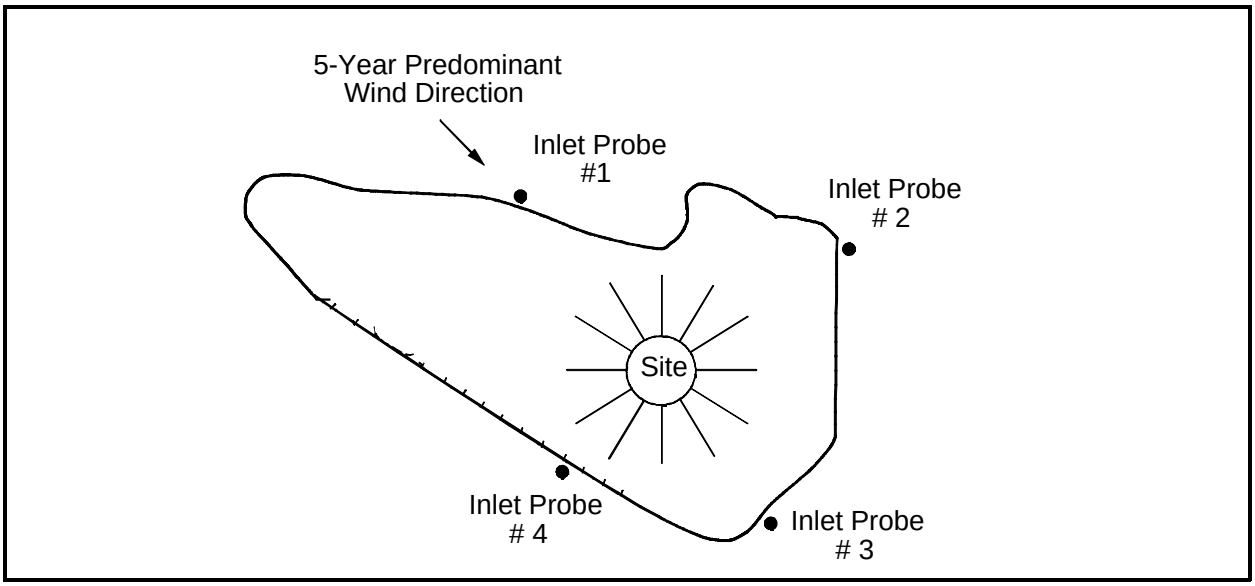


Figure 3-12. Example of a 4-point monitoring network with inlet probes at 90 location

After the number of stations have been determined, the placement of probes must be considered. In many cases, constraints on placing inlet probes can be encountered because of wind flow obstructions caused by nearby buildings, trees, hills, or other obstacles. Other constraints might be related to security, the accessibility of electrical power, as well as the proximity to roadways or other pollution sources that might affect the representativeness of the sample for measuring the waste site's effects on air quality. Specific guidelines for probe siting for sampling representative conditions are given in Table 3-10.

j. Cost factors. A number of issues affect the cost of establishing and conducting a FFMS at a HTRW site. Those issues are:

- Objectives of the perimeter air monitoring program.
- Analytes to be monitored and the program required detection limits.
- Frequency and duration of the monitoring program.
- Assessibility for installation of the perimeter system.
- Contingency monitoring.

Table 3-10
Example of Summary of Key Probe Siting Criteria for FFMS Program

Factor		Criteria
Vertical spacing above	•	Representative of the ground breathing zone and avoiding effects of obstructions, obstacles, and HTRW on-site traffic. Height of probe intake above ground in general, 2-3 m above ground and 2-15 m above ground in the case of nearby roadways.
	•	1 m or more above the structure which supports the inlet probe.
Horizontal spacing from	•	Minimum horizontal separation from trees acting as an obstruction must be >10 m from the dripline.
	•	Optimum horizontal separation from trees should be >20 m from the dripline.
	•	Distance from probe inlet to an obstacle such as a building must be at least twice the height the obstacle protrudes above the inlet probe.
	•	If the inlet probe is located on a roof or other structures, there must be a minimum of 2 m separation from walls, parapets, penthouses, etc.
	•	There must be a sufficient separation between the inlet probe and a furnace or incinerator flue. The separation distance depends on the height and the nature of the emissions involved.
Unrestricted airflow	•	Unrestricted airflow must exist in an arc of at least 270 around the inlet probe, and the predominant wind direction for the monitoring period must be included in the 270 arc.
Spacing from roads	•	A sufficient separation must exist between the inlet probe and nearby HTRW on-site roadways to avoid the effect of dust and vehicular emissions on the inlet.
	•	Inlet probe should be placed at a distance of 5-25 m from the edge of the nearest HTRW on-site roadway depending on the vertical placement of the probe inlet which could be 2-15 m above ground.

The objectives of the FFMS program will most certainly be affected by costs. Whether the program is established to monitor PALs, evaluate/document off-site exposure for protection of the surrounding community, or monitor on-site workers as part of an industrial hygiene program, overall costs are affected. The primary objectives will dictate the type of sampling equipment and analytical requirements to meet the DQOs of the program. Even the level at which emissions are to be monitored will affect cost. For example, if the alert level at the perimeter is measured in terms of NMOC rather than speciated organics, then the analytical equipment is less complicated, thus less costly. If, however, the purpose is to monitor at the risk level of 1-in-1 million, the analytical system must be far more sensitive, thus increasing the cost of the FFMS program substantially.

The number of type of analytes to be monitored will also affect the cost of the program. If the requirements are to monitor on a real-time basis for a large group of speciated organics, the program cost will increase. A larger analytical system will be required to be installed to give a full "chromatogram" of the analytes to be monitored. On the other hand, if one is able to select an appropriate subset of the compounds to be monitored and limit their number to less than five, cost savings can be achieved.

The frequency of sample collection will have a significant cost effect on the FFMS program. While real-time, on-site automated monitoring helps reduce the cost by the fact that analysis is on-site, the implementation of concurrent quality assurance monitoring using time-integrated systems must be taken into account, which

brings into issue data turnaround and laboratory responsiveness as a factor in the decision for the implementation of the time-integrated monitoring techniques. Moreover, one must consider capital equipment, maintenance, and operational costs.

The duration of the monitoring program may influence the selection and implementation of the real-time program. Consideration must be given in the application of GC to the field environment. One must consider the ruggedness of the system, its ability to operate 24 hours per day, and the ability to maintain the system. While there are numerous systems on the market, many are "portable" and used for screening purposes rather than for long term FFMS application.

Assessibility of the FFMS must be taken into consideration when projecting cost. If the analytical center is within the exclusion zone, it will be more difficult to perform daily functions due to the level of protection. Likewise, the installation of up to 1,000 feet per sampling point of heat-trace lines must be considered as part of the overall cost estimate of the system. These lines must be protected from on-site traffic during activities at the hazardous waste site, which may require burying the lines or encapsulating them for protection from on-site heavy vehicle traffic. In addition, long term maintenance of the heat-trace lines must be considered as part of the operating cost of the system.

Finally, contingency monitoring must be considered when implementing a real-time FFMS program. Many regulatory agencies require that the monitoring system be available for a certain percent of the time (i.e., 80%). To address system downtime, contingency monitoring must be implemented, which may require temporary manual sampling procedures or may require a separate system which has been certified similar to the primary system. Costs can be a major factor for determining the sampling contingencies.

For USACE projects, costs should be developed delineating labor, material, and equipment costs for each FFMS. Each component of the FFMS should be costed out separately, since each system and the applicable technologies selected during system design will be different for each project/designer. Vendor information, (including company, point of contact, and cost quote) should be provided with each cost element. Providing this level of detail will facilitate loading the cost information into USACE cost estimate databases. The costs should be structured using the HTRW Remedial Action Work Breakdown Structure (RAWBS) format shown in Figure 3-13.

The example cost estimates given in Table 3-11 are an expansion of Section 331XX.02.03.01 of the USACE HTRW RAWBS and are based on the assumption that all capital equipment is bought and not leased. In addition, costs are provided on a per-unit basis, both for equipment and analytical work as part of the QA program. Other expenses, such as labor requirements for network operation and data management and reporting, are given as estimated number of man-hours/cost. The unit cost for labor and actual man-hours may vary significantly, depending on the level of personnel involved and the charge rates of the individuals or organizations actually performing the work. Therefore, these estimates are guidelines only. In addition, program cost and site preparation cost can vary from site to site. These costs will depend on the distances involved and the complexity of providing electrical service to the monitoring location, site security needs and other requirements for site preparation.

The costs presented are reflective of a sophiscated FFMS for a HTRW remediation. The cost presented in Table 3-11 are associated with both administrative/management and hardware/operation of a real-time, FFMS at a HTRW site for a 5-year monitoring program. Table 3-11 outlines cost for program man-hours, equipment cost, and other direct costs.

k. Perimeter air monitoring program mobilization. As identified in Chapter 1, recent remedial actions have required the implementation of a real-time, fixed fenceline volatile organic monitoring system to characterize emissions from hazardous waste sites. The monitoring program normally consists of three basic components:

- Meteorological monitoring system.
- Sample collection system (probe inlet, filter, pump, and heat-trace lines).
- Analytical center real-time gas chromatograph, data management system, and contingency system).

Prior to field deployment, all components of the monitoring program must be evaluated under control conditions to verify their performance and ability to meet design specifications. Experience has shown that time spent "up front" in a program dealing with system evaluation is well spent and saves considerable time in the field. Compare your needs to the manufacturers specifications and determine if the equipment meets the DQO objectives of the project. To assist with the certification of purchased equipment, Table 3-12 identifies component specification checklist to be completed prior to receipt of equipment.

Once the equipment has passed certification at the manufacturer's facility or your facility, it is time to mobilize to the site. It is important to allow sufficient time in the field to receive, assemble and calibrate the various components of the monitoring system. Based upon field experience, a five week mobilization program is not an uncommon length of time. Figure 3-14 illustrates a typical timeline for the mobilization and installation of a real-time, FFMS program.

l. Quality assurance. The purpose of a QA program is to assure that the monitoring results are *of known quality* and that the results are *appropriate for the intended use of the data*. It is important that a clear distinction be made between *quality assurance* and *quality control*. *Quality control* is performed by project management and staff as part of their routine monitoring activities; *quality assurance*, however, must be performed by individuals who are entirely detached from the project and its staff.

Ideally, the QA program should be executed by a "third party" that is not controlled or influenced by the organization conducting the monitoring program. For example, if one contractor has been hired to conduct a monitoring program, a second contractor should be hired to provide a QA evaluation of the work performed by the first contractor. Unfortunately, due to budgetary and/or contractual constraints, it is often not feasible for the second "third party" contractor to be hired.

A more common approach for executing a QA program is for the contractor conducting the FFMS program to also provide its own QA program. While not strictly within the spirit of the QA concept, it is permissible for the monitoring contractor to provide its own QA, provided that the QA personnel (1) are organizationally separated from the project team, and (2) report directly to the higher levels of management. An example of a

contractor organizational chart showing the relationship of QA to other organizational functions is illustrated in Figure 3-15.

WBS No.				Description	UOM English/Metric	
331XX	01	06		Temporary Relocations/Roads/Structures/Utilities	EA	EA
	01	07		Construction Plant Erection	EA	EA
	01	08		Institutional Controls	EA	EA
	01	09		Alternate Water Supply	EA	EA
	01	10		Population Relocation	EA	EA
	02			MONITORING, SAMPLING, TESTING, AND ANALYSIS		
	02	01		Meteorological Monitoring	EA	EA
	02	02		Radiation Monitoring	EA	EA
	02	03		Air Monitoring and Sampling	EA	EA
	02	03	01	Real Time	MO	MO
	02	03	02	Non-Real Time	MO	MO
	02	03	03	Asbestos	MO	MO
	02	03	9x	Other (Use Numbers 90-99)		
	02	04		Monitoring Wells	EA	EA
	02	04	06	Gravel Pack Material	CF	M3
	02	05		Sampling Surface Water/Groundwater/Liquid Waste	EA	EA
	02	06		Sampling Soil and Sediment	EA	EA
	02	07		Sampling Asbestos	EA	EA
	02	08		Sampling Radioactive Contaminated Media	EA	EA
	02	09		Laboratory Chemical Analysis	EA	EA
	02	10		Radioactive Waste Analysis	EA	EA
	02	11		Geotechnical Testing	EA	EA
	02	12		Geotechnical Instrumentation	EA	EA
	02	13		On-Site Laboratory Facilities	EA	EA
	02	14		Off-Site Laboratory Facilities	EA	EA

Figure 3-13. HTRW remedial action work breakdown structure (RAWBS)

Table 3-11
Example of Cost Associated With a Real-Time Volatiles FFMS Program For Five (5) Years as Documented by the Corp's HTRW Remedial Action Work Breakdown Structure (RA WBS)

WBS No. 331.XX.02.03.01	YEAR 1	2	3	4	5
1.0 Program Man-hours					
1.1 Organization					
Project Management	200	200	200	200	200
Monthly Reports	96	96	96	96	96
Quality Assurance/Quality Control Project Revised Activities	120	60	60	60	60
1.2 Pre-Mobilization					
Documentation Perimeter Air Sampling Plan (PASP)	100				
-Quality Assurance Project Plan (QAPP)	100				
Purchasing of Equipment	60				
Instrument Calibration in Laboratory	200				
1.3 Mobilization					
Set-up (80 hr/wk x 3 wks x 3 people)	720				
Quality Assurance/Quality Control	40	80	80	80	80
1.4 Monitoring					
Yearly (40 hr/wk x 52 wks x 1 person)	2,080	2,080	2,080	2,080	2,080
1.5 Demobilization					
Break-down (80 hr/wk x 2 wks x 2 people)					320
1.6 Quality Assurance/Quality Control Evaluation	160	160	160	160	160
TOTAL LABOR, MAN-HOURS	3,876	2,676	2,676	2,676	2,996
(continued)					14,900

Table 3-11. (Continued)

B. Program Equipment	Unit Cost, $	No. Of Units	Total Cost, $
Meteorological Station			
Wind Speed Sensor	450	1	450
NIST Calibration of Sensors	150	1	150
Wind Directional Sensor	450	1	450
Temperature Sensor	350	2	700
Solar Radiation Sensor	450	1	450
Precipitation Gauge	400	1	400
Barometric Pressure Sensor	450	1	450
10 Meteorological Tower	1,000	1	1,000
Data Logger	2,500	1	2,500
Modem	430	1	430
Data Logger Software	400	1	400
Stability Class Software	600	1	600
System Engineering	2,000	1	2,000
Back-up Power Supply	300	1	300
Keyboard Display	400	1	400
Wires, Support to Data Logger	1,000	1	1,000
Recorder, 6 Channel	2,000	1	2,000
Freight	700	1	700
Relative Humidity Gauge	700	1	700
TOTAL			$15,080
Analytical System			
Real-time Gas Chromatograph with "RAM" Option and Speciation Capability	45,000	1	45,000
System Application and Engineering	7,000		7,000
Calibration Gases for 5 years	10,000	1	10,000
Support Gases for 5 years	5,000	1	5,000
System Software for four (4) Level Alarm	2,500	1	2,500
GC Columns for 5 years	4,000	1	4,000
Freight	500	1	500
Supplies for 5 years	2,500	1	$2,500
TOTAL			$76,500
Data Logger			
Data Logger	3,500	1	3,500
Input Channels Engineering	1,500	1	1,500
Input Communication with Other Systems (Meteorological station, real-time GC system and computer)	150	1	150
Relays	280	1	280
Keyboard	680	1	680
Modem	225	1	225
Instrument	125	1	125
Rack	2,970	1	2,970
Personnel Computer	3,900	1	3,900
Software for Calculating "Net" Concentration	4,000	1	4,000
Start-up Application	500	1	500
Freight	500	1	$18,330

Table 3-11 (Continued)

	Unit Cost, $	No. Of Units	Total Cost, $
Perimeter Sampling Stations (5 Year Program)			
Central Analytical Center with Environmental Controls	15,000	1	15,000
Four (4) Perimeter Sampling Stations Set-Up and Operational	3,000	4	12,000
Office Equipment (chairs/tables, etc.)	1,000	1	1,000
TOTAL			$28,000
Other (5 Year Program)			
Tools	5,000	1	5,000
Calibration Gases	4,500	1	4,500
Express Mail	1,000	1	1,000
Supplies	3,000	1	3,000
Electricity	3,000	1	3,000
TOTAL			$16,500
Heat-Trace Lines			
Four Stations up to 1,000 ft per Station ($25/ft)	25,000	4	100,000
Temperature Controller	2,000	1	2,000
Installation	5,000	1	5,000
Protective Conduit ($0.50/ft)	500	4	2,000
TOTAL			$109,000

	YEAR				
C. Other Direct Cost	1	2	3	4	5
Project Management					
Telephone	3,000	1,000	1,000	1,000	1,000
Postage & Shipping	800	200	200	200	200
Photocopying	1,500	500	500	500	500
Computer Supplies	300	100	100	100	100
Safety Supplies	500	200	200	200	200
Medical Training	750	750	750	750	750
Other Supplies	250	125	125	125	125
Support	2,000	500	500	500	500
	$9,100	$3,375	$3,375	$3,375	$3,375
Pre-Mobilization					
Telephone	150	---	---	---	---
Postage & Shipping	300	---	---	---	---
Photocopying	500	---	---	---	---
Other Supplies	100	---	---	---	---
Support	400	---	---	---	---
	$1,450				

Table 3-11 (Continued)

	Year				
	1	2	3	4	5
Mobilization					
Airfare	3,000	---	---	---	---
Truck (Leasing: $700/month)	700	---	---	---	---
Room and Board	4,158	---	---	---	---
($66/day x 21 days x 3 people)		---	---	---	---
Telephone	300	---	---	---	---
Car (Leasing: $500/month)	500				
	$8,658				
Quality Assurance/Quality Control Evaluation					
Airfare	5,000	2,000	2,000	2,000	2,000
Car Rental	500	500	500	500	500
Room and Board	1,386	1,386	1,386	1,386	1,386
($66/day x 21 days x 1 person)					
Telephone	200	200	200	200	200
Postage & Shipping	1,000	500	500	500	500
	8,086	4,586	4,586	4,586	4,586
Demobilization					
Room and Board	---	---	---	---	1,848
($66/day x 14 days x 2 people)	---	---	---	---	630
Car ($45/day x 14 days)	---	---	---	---	2,000
Airfare (2 x $1,000)	---	---	---	---	100
Telephone	---	---	---	---	200
Other Supplies	---	---	---	---	300
Freight					5,078

With reference to the real-time, FFMSs, the USACE may require a QA sample (see Paragraph 4-5) using EPA's Compendium Methods as the method in calculating project relative accuracy. The two systems would once again be compared and evaluated against each other. An example of this application might be a collocated sampling canister (Compendium Method TO-14A) at a sampling inlet of a FFMS on-site extractive GC system. The canister would be analyzed for NMOC and speciated organics and compared to the real-time system. Another example may be the requirement for the design, construction, and operation of a mobile trailer containing real-time and time-integrated systems to be used on a prescribed frequency as QA sampler collocated with the on-site FFMS sampling inlets. In operation, the trailer could be rotated between on-site perimeter stations on an established frequency (i.e., 50% of sampling events or one, 24-hour sample per week) to evaluate the accuracy and precision of analytes monitored by the FFMS program. Design considerations for such a trailer must address such consideration as:

- Power requirement (use propane generators to minimize contamination from power source).

Table 3-12
Example of Checklist Associated With Certification of Manufacturer's Guarantees Associated With a FFMS Program

Analytical System (GC)	
Q	Provide "back purge" capability for sample lines.
Q	New "RAM" software verified operational.
Q	Modification of bulkhead fitting to allow heating to prevent condensation.
Q	Implementation and certification of GC detectors.
Q	Software package updated to allow documentation of real-time chromatography.
Q	Development of "practical quantitation limits" for the target compounds.
Q	Manufacturer cleanliness certification of <2 ppb total volatile organics.
Q	Manufacturer development of: -Retention time windows for the targeted organics. - Documentation of peak geometry for each analyte. -Guidelines to evaluate pre-column breakthrough and column deterioration.
Q	Incorporation and validation of perma-purge dryer into sample conditioning system for moisture control.
Q	Pump capacity to pull sample from up to 1,000 ft away at a flow rate of 39.6 ft/sec at 25" Hg vacuum for an exchange rate of 2.0 units.
Q	System capable of sequencing between perimeter points as specified in the Solicitation (sample 5 minutes, dwell 10 minutes).
Q	Gas chromatographic system able to report data to analytical center data management system.
Sample Transport System Heat Trace Lines	
Q	Use of stainless-steel at each junction coupled to Teflon® tubing.
Q	Documentation of stability of heat-trace line to maintain temperature at 212 F ± 20 F.
Q	Incorporation of direct-readout of temperature in the analytical center for each sample line central trailer.
Q	Ability to read temperature in each section by a hand-held thermocouple reader.
Q	Provide output for alarm functions from controller data system.
Q	Construction of sample inlet system to design specifications. - Stainless steel shroud. - Heated sintered stainless steel filter (212 F ± 20 F) with efficiency of 99.99%. - Filter size of ½" x 2¼" element.
Q	Teflon® tube, 0.25" I.D. size for sampling lines, thick wall of 0.375" O.D.'
Q	Variable controller in analytical center so heat-trace lines can be adjusted on demand.
Q	Lines and J-boxes designed for inclement weather.
Data Management System	
Q	Ability to accept 0-10V signals from meteorological system and GC system.
Q	Ability to initiate four levels of alarm. Alarm 1 - 5 minute average NMOC > 1 ppm. Alarm 2 - Compound specific perimeter action level. Alarm 3 - Compound specific perimeter action level upwind. Alarm 4 - Net compound specific (upwind/alarm level).
Q	Capability of performing upwind/downwind determination and calculations using real-time meteorological and analytical data.
Q	Ability to produce histograms etc. for data review and interpretation.
Meteorological System	
Q	Ability to provide battery-backed power supplies.
Q	Equipped with an RS-232C port for direct communication.
Q	Dial-up modem for remote interrogation.
Q	Digital-to-analog converters for data logger access.
Q	All measurement components (wind speed, direction, stability class, relative humidity, temperature, etc.) NIST certified.

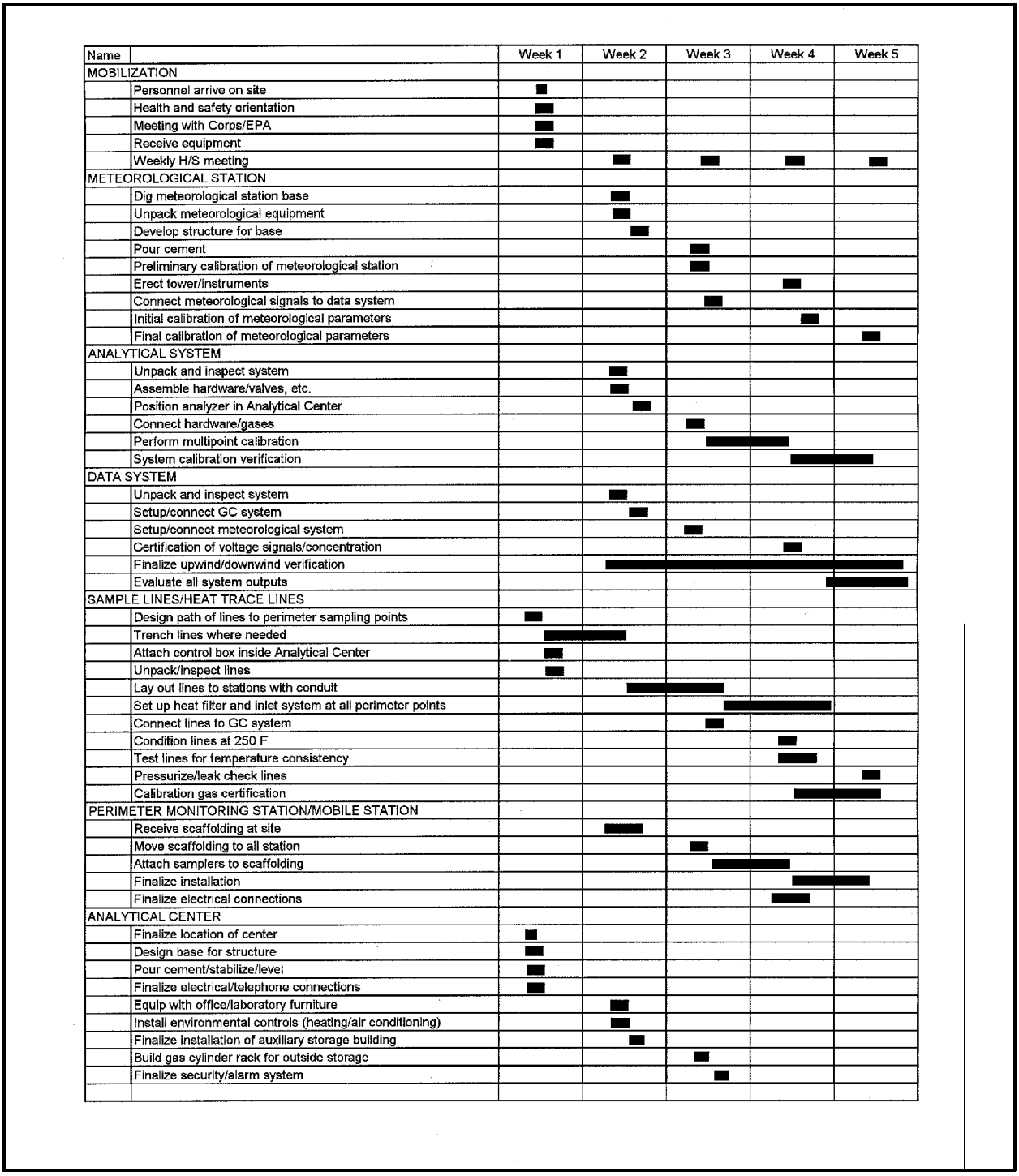


Figure 3-14. Example of a program timeline for establishing a real-time volatile FFMS at a HTRW site

- Mobility (use large oversize tires for better traction during movement on the HTRW site).
- Stability (provide leveling scopes at all four corners of the mobile unit).
- Safety (provide entrance steps and railings completely around the mobile unit).

Finally, a quality assurance plan (QAP) should be prepared as a separate document to the HTRW sampling and
analysis plan. It is important that the QA plan be prepared well before the start of the monitoring program so that there will be sufficient time for the Plan to be reviewed and approved by all interested parties. The important elements of a QAP are listed below and discussed extensively in Chapter 8.

- Project description, including intended use of the data.
- Project organization and QA/QC and responsibilities.

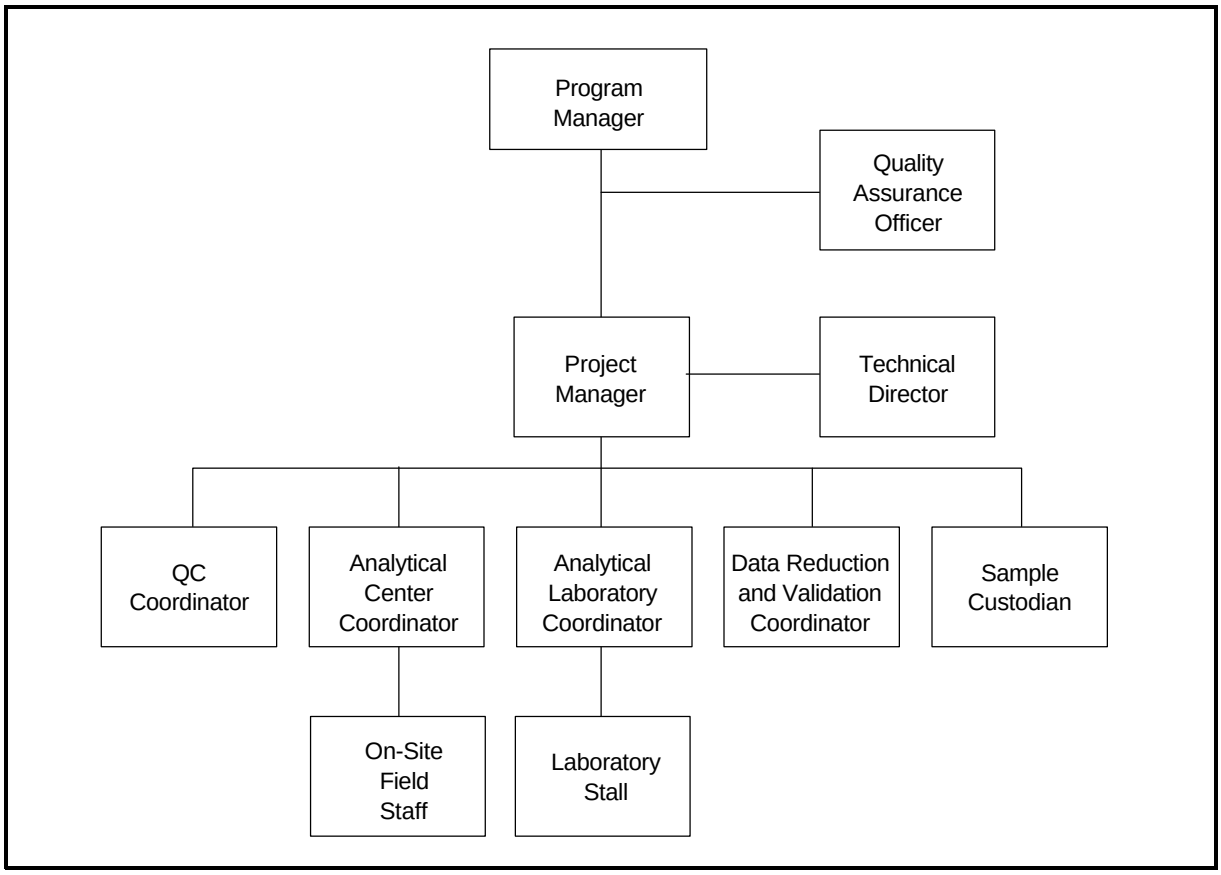


Figure 3-15. Example of contractor organization chart showing relationship of quality assurance to other organizational functions for a real-time volatile FFMS

- Data quality objectives for critical measurements, in terms of precision, accuracy or bias, completeness, representativeness, and comparability, or qualitative acceptance criteria when quantification is not practical.

- Site selection and sampling procedures.

- Sample custody.

- Calibration procedures and frequency.

- Analytical procedures.

- Data reduction, validation, and reporting, including handling of invalid/missing data.

- Internal QC checks and audits.

- Results of performance and systems audits.

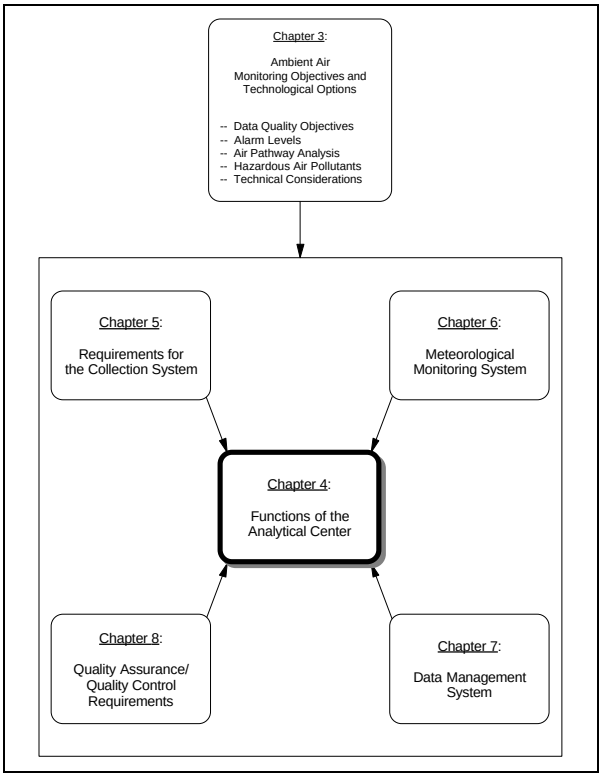
- Preventative maintenance (procedures and schedules).

- Calculation of data quality indicators; specific procedures and statistical methodology to be used in routinely assessing and evaluating data precision and accuracy or bias (both QC and measured), representativeness, comparability, and completeness of the specific measurement parameters involved.

- Corrective action (criteria and procedure).

- QC reports to management.

SUMMARY REQUIREMENTS FOR ANALYTICAL CENTER



The Analytical Center serves as the nerve center for the FFMS at the HTRW site. Operation of the perimeter air monitoring system will be continuously evaluated in the Analytical Center. Consequently, the proper design and operation of the Analytical Center is important to meeting the project's DQOs.

SECTION I: ANALYTICAL CENTER OBJECTIVES

SECTION II: ANALYTICAL CENTER SYSTEM COMPONENTS

- Structural Requirements
- Location, Utilities, Instrumentation Operation

SECTION III: ANALYTICAL SYSTEMS AND OPTIONS

- NMOC Monitoring
- GC Monitoring
- GC Detectors

SECTION IV: SUPPORTING MEASURING METHODS

- EPA Compendium Methods Introduction
- Organic Compendium Methods
- Inorganic Compendium Methods

SECTION V: SYSTEM ALARM CONFIGURATION

The Analytical Center is a multiple use Center. It is therefore important that the Center be well designed, with sufficient space to allow for required operational and analytical activities, apparatus/reagents and supporting data acquisition and processing functions. This chapter addresses the various design options available in implementing an Analytical Center at a HTRW site.

Panel 4-1. Overview of Requirements For The Analytical Center.

4-1. Introduction

The Analytical Center serves as the nerve center for the real-time perimeter air monitoring program. All real-time data will be received, processed, and reported at the Center. Operation of the perimeter air monitoring system will be continuously evaluated here. Hence, most day-to-day monitoring activities will be focused in this area. The Center requires a laboratory-clean, environmentally controlled space in which to operate real-time monitoring instrumentation, collect reference method samples, perform audits, and store all electronic data and storage systems. Ideally, all power and data transmission lines should originate or route through the Center to ensure stable, continuous operation. The Analytical Center can be designed to accommodate office facilities for air monitoring personnel and house related data processing and communications equipment.

For some projects, it may be necessary for the Analytical Center to function as a self-contained, ambient-air laboratory. In addition to housing instrumentation and personnel, space is required for maintenance and equipment repair, glassware, gases, and reagents. If time-integrated air sampling is conducted during the project, the center can be designed for sample preparation, sample recovery, sample analysis, system audit and sample storage needs.

Given the multiple uses of the Center, it may be important that the Center be spacious, conveniently organized, and compartmentalized to allow for isolation of sensitive instrumentation. Design of the Center should be flexible to accommodate multiple configurations of equipment and personnel. Most importantly, design of the Center must take into account extremes in operating conditions (weather, electrical and communications load, staffing, etc.) that will no doubt be encountered during certain periods of system operations and site activities, especially for the effects of on-site, heavy equipment.

4-2. Analytical Center System Components

The Analytical Center is characterized by several functional components.

- Structural requirements.

- Location, accessibility, and security needs.

- Utility requirements.
  —Instrument/computer/communications service
  —Environmental controls

- Instrumentation, equipment and furniture needs.
  —Laboratory
  —Office
  —Sample management

- Safety facilities.

These components are described in the following sections and identified in Figure 4-1 as a suggested layout in the Analytical Center.

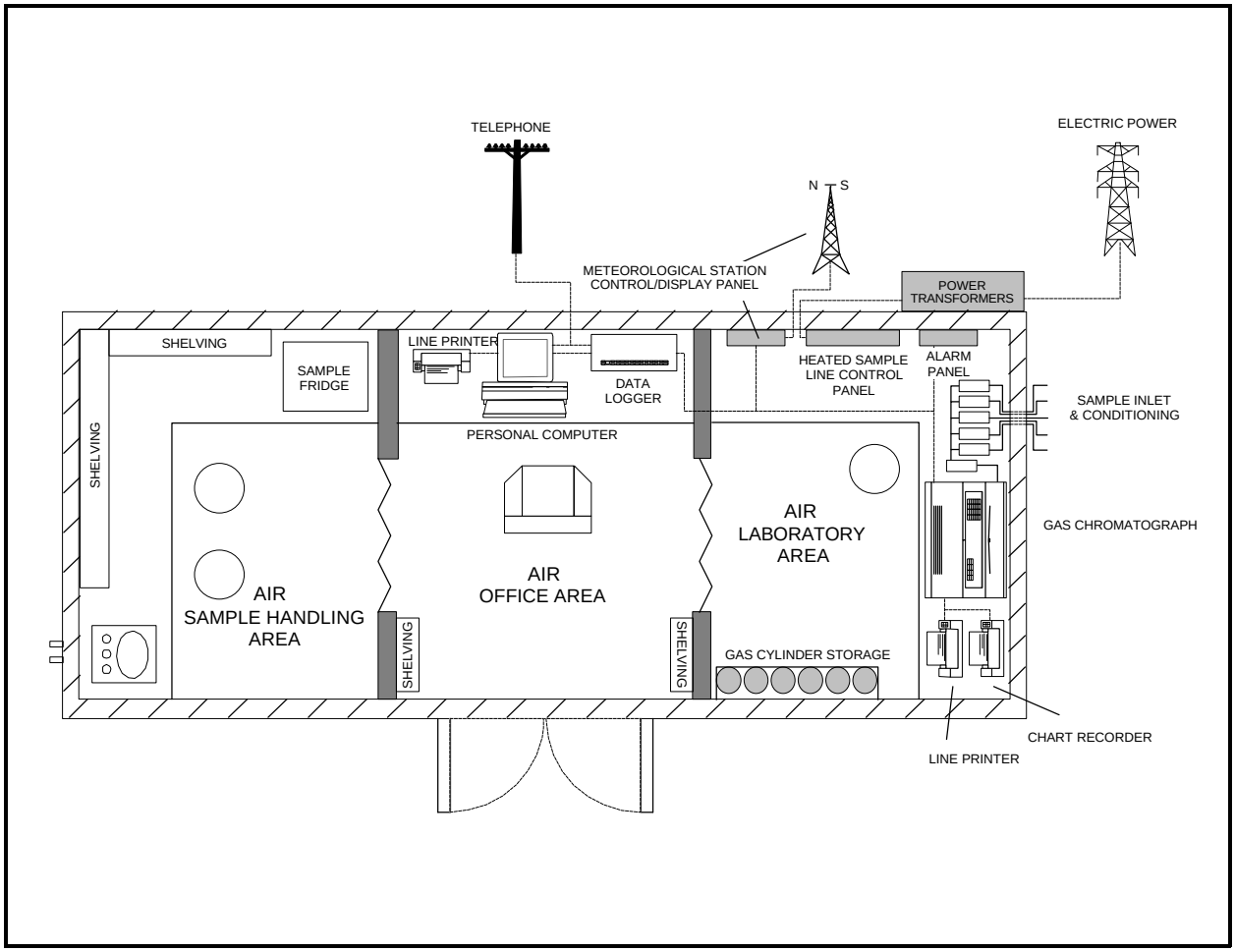


Figure 4-1. Example Analytical Center system components

a. Structural requirements. In most cases, the Analytical Center will be either a mobile or otherwise temporary structure. Many excellent prefabricated utility buildings and trailers are commercially available and can be easily modified for use. If mobile, the structure must be road safe and legal and properly weighted and balanced when fully equipped. When sited, the structure should be anchored to a solid foundation or otherwise secured to minimize vibration. The bare structure may require an area of 200 square feet or greater of space. High traffic areas, sample handling areas, and equipment storage areas should be partitioned from the analytical instrumentation to help maintain a controlled operating environment. Alternatively, it may be more

cost effective to use a second structure that requires a less stringent environment for sample handling and equipment storage.

Common building materials may be used in construction, though volatile materials such as adhesives and foam insulation should be avoided for obvious reasons. A functional window or portal should be located in each wall of the structure for entry of sample lines, wiring, communications lines, etc. The main entry and door should be no less than 36 inches wide to allow access of oversized equipment. The structure should be properly weatherized, insulated, and sealed from dust and drafts. Since cleanliness will be a constant battle, all interior surfaces such as walls, floors, and counter-tops should be smooth and easy to wipe down. Floors should be covered with heavy-weight, seamless linoleum. Tracking of dust and dirt into structures may be further minimized by attaching a small porch at the entry way. Figure 4-2 depicts an Analytical Center at a typical HTRW site.

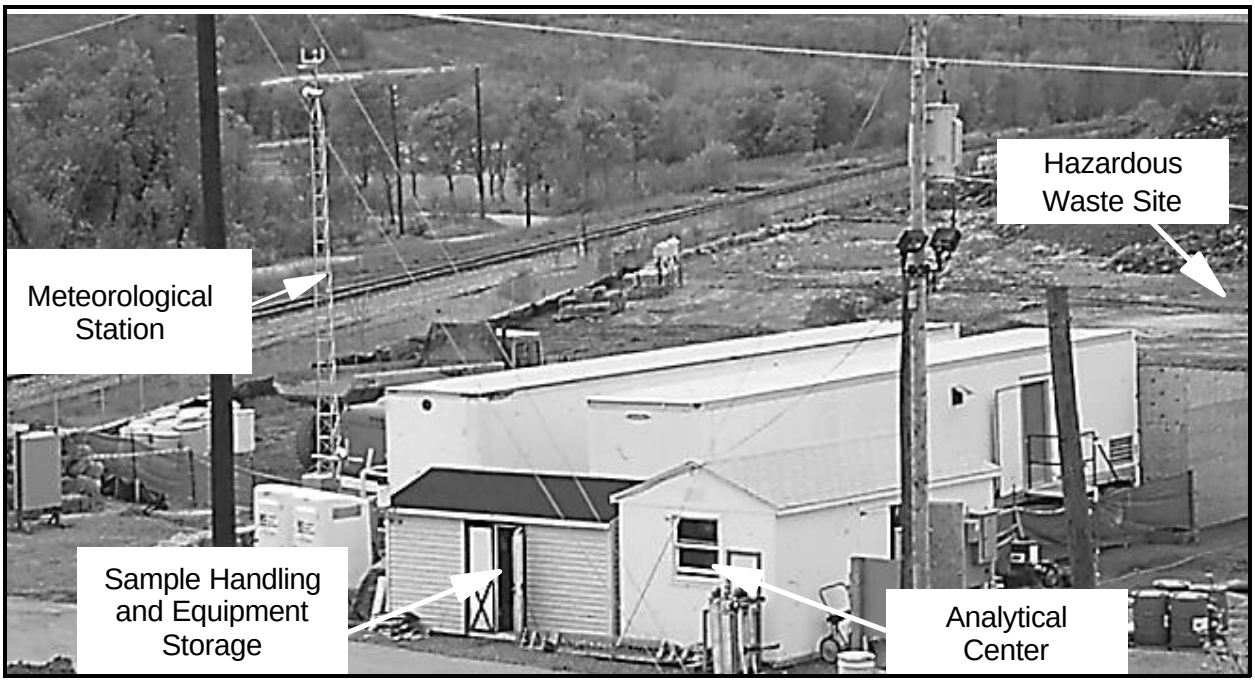


Figure 4-2. Example of a typical Analytical Center at a HTRW.

b. Location, accessibility, and security needs. The Analytical Center should be located in a convenient, easily accessible place, as close to the perimeter air sampling stations as possible. Close proximity to sampling stations will minimize the cost of and exposure to sample lines and electrical wiring. However, the advantage of proximity is offset by the need to locate the Center outside the anticipated exclusion zone and within the secure perimeter of the site. For some applications, it may be feasible to locate the analytical center on adjacent properties to minimize site activity effects.

c. Utilities. The Analytical Center will require utility services to meet the demanding specifications of the monitoring instrumentation and other equipment. These include:

- Electrical power source(s) - a variety of types of service with different amperages and phases will be necessary to accommodate multiple instrument and equipment needs under extreme operating conditions. A well-regulated constant voltage source is essential.

- Telecommunications line(s) - adequate for phone, fax, and modem to support simultaneous access to data storage system(s) and personnel.

- Gas generation/storage - adequate amount and selection of laboratory grade gases for routine instrument operation and calibration. Room temperature storage is essential.

- Water supply/wastewater disposal or storage - optional.

Configurations for these services are suggested in Figure 4-1.

Environmental conditions within the Analytical Center must be maintained to ensure maximum performance of instrumentation as well as personnel comfort. The Center should be equipped with high-capacity, electric heating, ventilation, and cooling equipment. The following are critical elements:

- Temperature - maintained at ~70 ± 5°F using electric base board heater(s)s and electric air conditioner(s) (oversized by 50 percent to compensate for equipment).

- Humidity - maintained at ~40 ± 10 percent RH using air conditioner(s).

- Dust control - maintained with high capacity electrostatic precipitator(s) or other air purifier(s).

- Lighting - incandescent or fluorescent lighting appropriate for use requirements.

- Static electricity control - use of wrist static guards during repairs of electrical components in the Analytical Center.

d. Instrumentation, equipment, and furniture. Equipment and instrumentation employed in the Analytical Center will vary depending on the specific nature of the monitoring program. In general, the following may be items that may be essential to the Analytical Center:

- In the air laboratory (see Figure 4-3):

  —auxiliary real-time monitoring system
  —electrical control panel for heated sample line network
  —sample conditioning system including in-line particulate filters, dryers carrier gas cylinders and regulators with mounting fixtures, and auxiliary air compressor
  —microprocessor controlled sample inlet manifold
  —microprocessor controlled gas analyzer/gas chromatograph
  —calibration gas cylinders and regulators with mounting fixtures

—chart recorder
—line printer
—electrical control panel and data display for meteorological station
—electronic data logger
—audible/visible alarm system w/ telephone pager
—bench space for equipment
—cabinetry for storage of spare parts and tools

- In the air office:

—personal computer with appropriate software for data logger interface, data transfer, word processing,
spreadsheets, and graphics
—line printer
—telephone(s)
—fax
—modem
—bench and/or desk space
—cabinetry for storage of supplies
—secure file storage
—storage for lab notebooks, equipment logs, equipment manuals, reference texts, etc.

- In the air sample management area:

—bench and/or desk space for sample handling
—cabinetry for storage of supplies
—solvent storage cabinet
—refrigerator
—dry ice storage
—sink or wash basin
—waste disposal containers
—secure storage for sample logs, Chain of Custody (COC) forms, shipping records, etc.
—storage for shipping coolers

The several partitioned spaces of the Analytical Center may be built out of or furnished with bench space, desk tops, shelving, and cabinetry appropriate for the above described uses. A suggested layout for these items is provided as Figure 4-1.

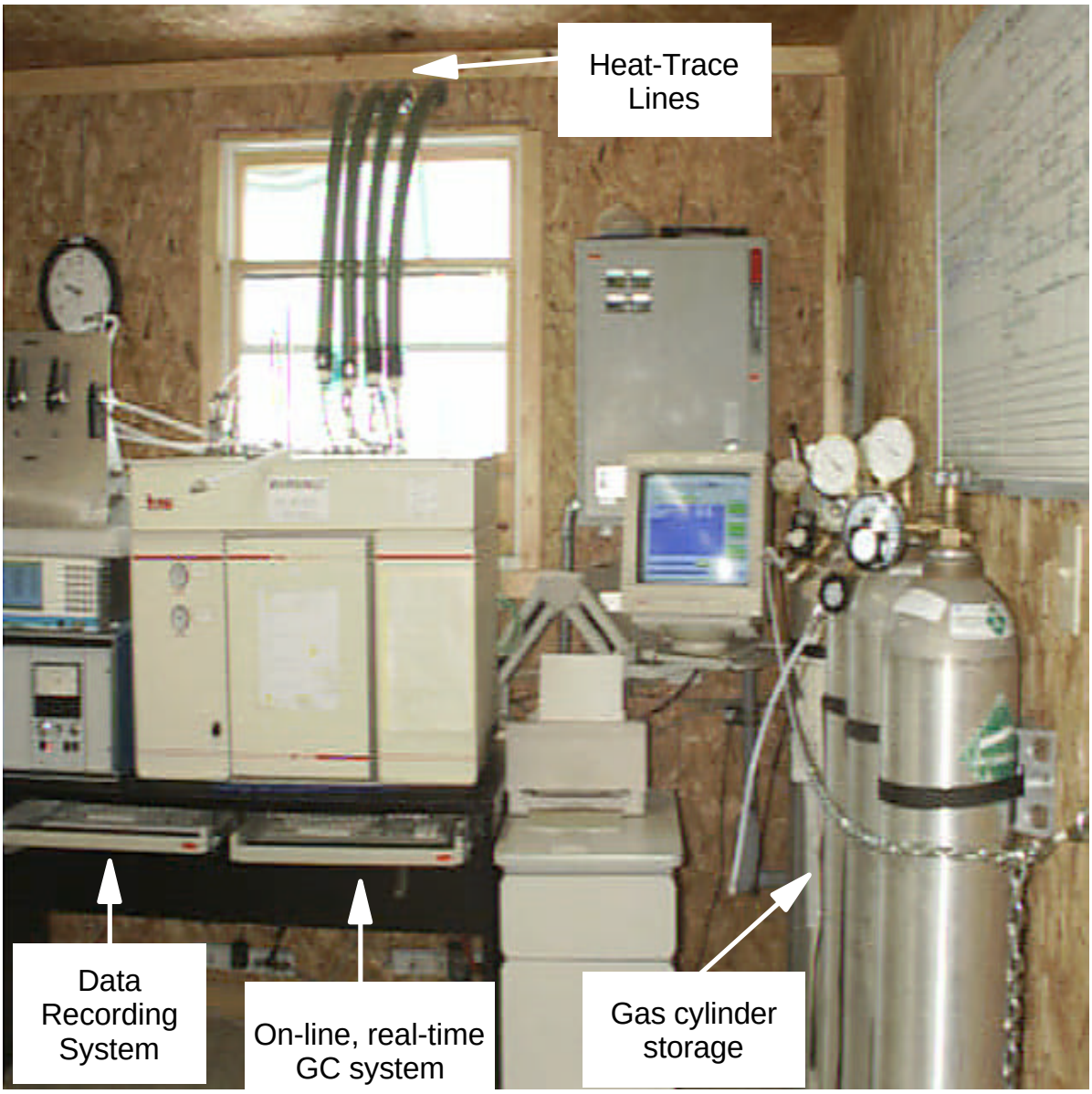


Figure 4-3. Inside of Analytical Center at a HTRW site as part of a FFMS

e. Safety facilities. The Analytical Center should be equipped with safety equipment in accordance with the Site Health and Safety Plan. At a minimum, the Center should have standard laboratory safety gear, including chemical fire extinguishers, an eye wash station, spare safety glasses, and a first aid kit. In addition, an evacuation procedure, emergency contacts, and map directions to hospital should be clearly displayed.

f. Operation and maintenance of analytical center. For many types of site activities, such as RA, the need to operate 24 hours per day has become a normal operating practice; therefore, the real-time analytical system must be able to continuously operate around the clock. This requirement means additional stress on personnel and equipment comprising the Analytical Center as part of the FFMS program. To minimize expenses and optimize productivity, several program objectives need to be identified and addressed as part of the Analytical Center SOP. Some applications may only have to coincide with site activity intervals. In such cases, the system operations may be discontinuous and require additional start-up procedures.

- For projects requiring collection of accurate and reliable data over the 24-hour period, personnel need to review monitoring data on an 8-hour schedule to minimize unacceptable data from the real-time monitoring system. Table 4-1 presents an 8-hour schedule for the Analytical Center operator in evaluation of the performance of the installed real-time monitors. Activities include observation and challenges to the analytical system.

- Other observations need to be performed associated with the support equipment in the Analytical Center to ensure continuous operation over a 24-hour period. To assist the system operator, Table 4-2 documents a typical Analytical Center checklist for continuous operations. This checklist requires the operator to observe settings associated with gas cylinders, the real-time analytical system, the meteorological system, and the data recording system

.

- Finally, for continuous operation, the Analytical Center operator needs a preventive maintenance program to follow to ensure continuous operation of the systems. In addition, guidelines need to be established to address the malfunction of various components and what corrective action needs to be initiated to bring the program back within compliance. Table 4-3 provides an example of a preventive maintenance program for continuous operation of a real-time GC system and support equipment.

- All such activities must be included in a Daily Chemical Quality Control Report (DCQCR) or equivalent record.

Table 4-1
Example Analytical Center Staffing/Schedule For Continuous Operation

Personnel	Time	Operator Onsite Time	Activities
Station Operator	Start of Continuous Operation (0700 hours)	0700-1100	• Complete Analytical Center checklist • Perform calibration -- Internal -- Single component gas -- Multi-component gas • Verify alarm system operation
Station Operator	8-hour Shift Report (1500 hours)	1400-1600	• Complete Analytical Center checklist • Verify proper performance of 8-hr internal calibration check • Verify alarm system operation
Station Operator	8-hour Shift Report (2400 hours)	2300-0100	• Complete Analytical Center checklist • Verify proper performance of 8-hr internal calibration check • Perform single component gas calibration • Verify alarm system operation
Station Operator	8-hour Shift Report (0700 hours)	0100-0700	• Complete Analytical Center checklist • Verify proper performance of 8-hr internal calibration check • Perform calibration -- Single component gas -- Multi-component gas • Verify alarm system operation

4-3. Analytical Systems and Options

a. Non-methane organic compound monitoring. The primary motivation for conducting perimeter ambient air monitoring at a HTRW site are to (1) meet regulatory compliance requirements, (2) respond to emergency situations (chemical spills, inadvertent releases, and fires) and nuisance complaints, (3) verify to absence of off-site migration of contaminants, (4) satisfy APA requirements and data user groups, and (5) maintain system performance. Each of these areas has distinct requirements for ambient air monitoring, which are important to recognize. While each area may have distinct requirements, the impetus for monitoring programs is the risk to human health associated with exposure to the hazardous emissions. Consequently, most FFMS programs require monitoring at trigger levels to protect public health and welfare. Recent regulations have advocated an NMOC monitoring program as the first perimeter alarm level.

On April 30, 1986, the EPA promulgated Appendix E of 40 CFR 50.10, entitled *Reference Method for the Determination of Hydrocarbons Corrected for Methane*. The objective of this NAAQS was to protect the health and welfare of the individuals living in the U.S. The standard requires monitoring for NMOC using commercially available instruments that meet design and performance specifications. Specifically, any ambient

Table 4-2
Example Analytical Center Checklist For Continuous Operation

Start of Continuous Operations (0700 Hours)

I. Tank Pressures Setpoint	Tank	Outlet
G Carrier gas 60 psi	___ psi	___ psi
G Nominal 1 ppm toluene psi	___ psi	___ psi
G Nominal 1,1,1 ppm toluene, tetrachloroethane, Chlorobenzene OFF	___ psi	___ psi
G Nominal 5,5,5 ppm toluene, tetrachloroethene, Chlorobenzene OFF	___ psi	___ psi
G Nominal 10,10,10 ppm toluene, tetrachloroethene, Chlorobenzene OFF	___ psi	___ psi
G auxiliary air (compressor) 60-65 psi	NA	___ psi

II. Real-Time Gas Chromatographic System

G Initiate internal calibration with nominal 1 ppm toluene standard and compare values:

RAM Voltage	Analytical Voltage	Retention Time
_____ V (present)	_____ V (present)	_____ sec (present)
_____ V (previous)	_____ V (previous)	_____ sec (previous)
		previous date/time _____
Within specs? (Y/N) _____	_____	_____

G Initiate nominal 1 ppm toluene calibration check through a selected port. Record concentration.

Gas concentration _____ Monitor response _____ % Error _____ Specification ___%
Within specs? (Y/N) _____

G Initiate nominal 5-5-5 ppm calibration check through a selected port. Record concentrations and retention times.

	Concentration		Within spec.	Retention time (min
	Cal gas	Inst. Resp.	% Error (Y/N)	
Toluene	_____	_____	_____	_____
Tetrachloroethene	_____	_____	_____	_____
Chlorobenzene	_____	_____	_____	_____

G Carrier gas pressure	___ (psi)	14 Set point (psi)
G Auxiliary air pressure	___ (psi)	60-65 Set point (psi)
G Oven temperature	___ (degrees)	70 Set point (degrees)

Table 4-2 (Continued)

II. Data System and Meteorological Monitoring

G	Wind speed	____m/s	**G**	NMOC (East)	____ppm
G	Wind direction	____degrees	**G**	NMOC (South)	____ppm
G	Barometric pressure	____mbars	**G**	NMOC (West)	____ppm
G	Temperature low	____degrees	**G**	NMOC (North)	____ppm
G	Solar radiation	____Langley			
G	Relative humidity	____%			
G	Precipitation	____% H_2O			

IV. Heat-Trace Lines

G Line Temperatures (°F)

Line#1_____ Line#2_____ Specification 212°F ± 25°F
Line#3_____ Line#4_____

V. Alarms

G All alarms enabled.
G External alarm enabled, tested.
G All high threshold levels set to the perimeter action level with low levels set to 0.01 less than the high level.

VI. Printer operations

G Verify the printer is receiving real-time data. Examine the print times for inconsistencies.
G Ensure that the printer has sufficient paper, add as necessary.
G Examine the print quality, replace ink cartridge as necessary.

8-Hour Shift Evaluation (1500 and 2400 Hours)

I. Tank Pressures	Tank	Outlet	Setpoint
G Carrier gas	___ psi	___ psi	60 psi
G Nominal 1 ppm toluene	___ psi	___ psi	4 psi
G Nominal 1,1,1 ppm toluene, tetrachloroethene, Chlorobenzene	___ psi	___ psi	OFF
G Nominal 5,5,5 ppm toluene, tetrachloroethene, Chlorobenzene	___ psi	___ psi	OFF
G Nominal 10,10,10 ppm toluene, tetrachloroethene, Chlorobenzene	___ psi	___ psi	OFF
G auxiliary air (compressor)	NA	___ psi	60-65 psi

Table 4-2 (Continued)

II. Gas Chromatographic System

G Record internal calibration results from the nominal 1 ppm toluene standard and compare values:

RAM Voltage	Analytical Voltage	Retention Time
_____ V (present)	_____ V (present)	_____ sec (present)
_____ V (previous)	_____ V (previous)	_____ sec (previous)
		previous date/time _____
Within specs? (Y/N) _____	_____	_____

G Initiate nominal 1 ppm toluene calibration check through a selected port. Record concentration.

Gas concentration _____ Monitor response _____ % Error _____ Specification __%
Within specs? (Y/N) _____

G Carrier gas pressure ___ (psi) 14 Set point (psi)
G Auxiliary air pressure ___ (psi) 60-65 Set point (psi)
G Oven temperature ___ (degrees) 70 Set point (degrees)

III. Meteorological Monitoring

G	Wind speed	____m/s	**G**	NMOC (East)	____ppm
G	Wind direction	____degrees	**G**	NMOC (South)	____ppm
G	Barometric pressure	____mbars	**G**	NMOC (West)	____ppm
G	Temperature low	____degrees	**G**	NMOC (North)	____ppm
G	Solar radiation	____Langley			
G	Relative humidity	____%			
G	Precipitation	____inch H_2O			

IV. Heat-Trace Lines

G Line Temperatures (°F)
Line#1_____ Line#2_____
Line#3_____ Line#4_____

V. Alarms

G All alarms enabled.
G External alarm enabled, tested.
G All high threshold levels set to the perimeter action level with low levels set to 0.01 less than the high level.

Table 4-2 (Continued)

VI. Printer operations

G Verify the printer is receiving real-time data. Examine the print times for inconsistencies.
G Ensure that the printer has sufficient paper, add as necessary.
G Examine the print quality, replace ink cartridge as necessary.

Weekly Evaluation

I. Gas Chromatographic System

			Last check valve
Q	Pre-column vent flow	____(cc/min)	_____ Set point (cc/min)
G	Detector vent flow	____(cc/min)	_____ Set point (cc/min)
G	Sample pump vent flow	____(cc/min)	_____ Set point (cc/min)
G	Fifth port flow	____(L/min)	_____ Set point (L/min)

II. Heat-Trace Line

G Weekly flow check at probe tip

	Flow (L/min)	Date last performed
Station #1	_____	_____
Station #2	_____	_____
Station #3	_____	_____
Station #4	_____	_____

G Chemical audit at probe tip

		[TOL]	Valve	[TCE]	% Error	[CLB]		Date last performed
Station #1	_____	_____	_____	_____	_____	_____	_____	_____
Station #2	_____	_____	_____	_____	_____	_____	_____	_____
Station #3	_____	_____	_____	_____	_____	_____	_____	_____
Station #4	_____	_____	_____	_____	_____	_____	_____	_____

[TOL] = recovery of toluene in ppm
[TCE] = recovery of tetrachloroethene in ppm
[CLB] = recovery of Chlorobenzene in ppm

III. Meteorological System

G Check battery and line voltage
Line:_____volts 120 V setpoint
Battery:_____volts 13 V setpoint

Table 4-2 (Continued)

Monthly Evaluation

I. Contingency Gas Chromatographic Speciated System

!	**Contingency GC Settings**	Actual	Setpoint
G	Carrier Pressure micrometer setting	_____	225
G	Oven Temperature	_____	45
G	Sample toggle switch	_____	load
G	Gain Setting (right end of instrument)	_____	high

G Software settings. Through the channel option of the controls menu, verify the following Channel one settings:

Temper	TEM
Events	EVT
Compon	CPT
Postrun	save file and auto-inc are enabled

G Contingency GC 3 component challenge. Initiate a 1-1-1 ppm evaluation of the GC and record the values.

Compound	Theoretical concentration	Concentration recovered	% Error	Within spec. (___%)
Toluene	_____	_____	_____	_____
Tetrachloroethene	_____	_____	_____	_____
Chlorobenzene	_____	_____	_____	_____

II. NMOC System

G Meter reading _____ ppm NMOC
G Scale range _____
G Fine scan potentiometer setting _____
G Lamp light position _____
G Power switch _____
G 201 calibration. Initiate 1 ppm toluene only span check by flowing gas from a Tedlar® bag. Record value and note results:

Gas cylinder value	_____ ppm
201 response	_____ ppm
percent error	_____ %
Within ± __%	_____ (yes/no)

Table 4-3
Example of Analytical Center Preventive Maintenance Program For Continuous Operation

Parameter	Sampling method	Sampling system	Component	Symptoms	Activity
I. Volatile Organics	Real-time sample collected through sequential heat-trace sample lines and analyzed by GC/PID	Heat trace line	In-line filter	• Plugging • Low calibration gas response	• Replace with new filter • Replace with new filter
			Line temperature	• Low temperature	• Check main fuses and replace • Audit line with calibration gases • Replace line segment
			Line plugging	• No flow	• Check plugging at GC manifold • Check flow at inlet/J-Box • Replace line segment
		Gas Chromatographic System	Manifold pump	• No flow	• Check pump diaphragm • Replace with spare pump
			Sample pump	• No flow	• Check vacuum and pressure • Check pump diaphragm • Replace with spare pump
			Perma-pure dryer	• Baseline drift on chromatography	• Heat inlet and purge
			In-line filter	• No flow	• Remove, clean in alcohol, dry • Replace with spare filter
			GC column	• Poor chromatography, RT and voltage out-of-specification • Temperature	• Bake out according to maintenance procedures • Replace with spare column • Check oven flow/thermocouple • Check electronic oven board • Replace
			Detector lamp (PID)	• Poor chromatography	• Clean lamp with alcohol • Check connections and light • Replace with spare lamp
		RAM System	NMOC	• Inoperative	• Operator uses portable GC probe to record NMOC at outlet of manifold • Mobilize NMOC monitor on outlet of manifold within 4 hours

TABLE 4-3. (Continued)

Parameter	Sampling method	Sampling system	Component	Symptoms	Activity
II. Meteorological wind speed, wind direction, and temperature	Time-integrated through various instrument specific for meteorological parameters	Meteorological instruments	• Wind direction	• Inoperative	• Mobilize portable meteorological system within 4 hours • Contact NWS at local airport
			• Wind speed	• Inoperative	• Mobilize portable meteorological system within 4 hours • Contact NWS at local airport
			• Temperature	• Inoperative	• Check thermocouple • Mobilize portable meteorological system within 4 hours • Contact NWS at local airport
III. Data Retrieving and Logging Systems	Real-time data retrieving and logging from real-time gas chromatographic and meteorological systems	Data logger	• System output	• Inoperative	• Follow system malfunction guidelines found in SOP • Replace with spare data logger
		Jet Printer	• System output	• Inoperative	• Follow system malfunction guidelines • Replace with strip chart recorder • Replace with spare jet printer

air monitoring can be used if it can pass the following performance specifications:

- Range (minimum) . . . . . 0-5 ppm
- Minimum detectable sensitivity . . . . . 0.1 ppm
- Zero/Span drift (maximum) . . . . . 10%/24 hours
- Precision (minimum) 1%
- Linearity (maximum) . . . . . 1% of full scale
- Operating humidity range 10-100%

While the regulation was later rescinded by EPA, commercial manufacturers made available three basic approaches for monitoring NMOC on a real-time basis. Techniques for monitoring total NMOCs are divided into three detection principles: gas chromatography, non-dispersive infrared, and ionization techniques.

In the GC technique, ambient air is extracted on a continuous basis directly into an FID where all hydrocarbons respond and produce a signal to give a total hydrocarbon (THC) content. To get an NMOC signal, an aliquot of the same air sample is introduced into a stripper column that removes water, carbon dioxide and hydrocarbons other than methane. Methane and carbon monoxide are passed quantitatively to a gas chromatographic column where they are separated. The methane is eluted first and then passed unchanged through a catalytic reduction tube into the FID. The carbon monoxide is eluted into a catalytic reduction tube, where it is reduced to methane before passing through the FID. The NMOC is calculated by subtracting the methane value from the total hydrocarbon value.

Non-dispersive infrared (NDIR) instruments operate on the principle of light absorption characteristics of certain gases. These instruments are usually subject to interferences because other gases such as water vapor and carbon dioxide may also absorb light at the same wavelength as a compound of interest. For the detection of NMOC, a particular wavelength in the infrared part of the electromagnetic spectrum is selected to represent all hydrocarbons, excluding methane. The ambient air sample enters the monitor, and organics absorb the infrared light specific for that part of the electromagnetic spectrum. A comparison is made between a reference cell containing no organics and a sample cell containing organics, which reduces the light energy reaching the detector. The difference in absorbance is directly related to concentration according to Beer's Law.

Finally, PID using UV light (instead of a flame) measures NMOC by ionizing the organics. Similar to the NDIR technique, the detector senses UV light in a particular region of the electromagnetic spectrum that represents major groups of organic compounds. This technique, however, requires the proper selection of the energy lamp used to excite the compounds. The detector senses energy given off from the excited organics and relates it to a concentration. As an example, several commercially available monitors are based upon the PID principle and are uniquely applicable to monitoring NMOC as the first level of alert around an HTRW. In operation, an ambient air sample is extracted through a multi-port valve system to a sample loop (1 mL). After several seconds, the sample loop is isolated from the gas stream, brought to atmospheric pressure, and injected past a PID, which excites the organic compounds as NMOC constituents. Because methane is not detected by the PID, the excited organics detected by the detector represents the total NMOC constituents in the sample. The monitor consequently serves as a real-time NMOC system.

The majority of the commercially available NMOC monitors are based upon the above monitoring techniques. The ambient NMOC monitors can be used as the first level of alarm for a perimeter air monitoring system at an HTRW site. Appendix E of this document identifies the manufacturers of commercially available NMOC monitors.

b. Gas chromatography. For specific identification, GC is by far the most widely employed technique in separating HAPs in ambient air monitoring at HTRW sites. The sensitivity, specificity, and versatility of any GC system, coupled with the relatively volatile nature of most compounds make it a very attractive technique.

Basically, GC is a separation technique wherein components of a sample are separated by differential distribution between a gaseous mobile phase (usually helium, nitrogen, or hydrogen carrier gas) and a solid or liquid held on a stationary phase. In operation, the sample is injected into the carrier gas as a sharp plug, and individual components are detected as they elute from the column at characteristic "retention times" after injection. Both column temperature and carrier gas flow must be carefully controlled to obtain uniform response and retention time characteristics. The technique is similar to the widely practiced liquid-liquid partition column chromatography except that the mobile liquid phase is replaced by a moving gas phase. They are:

- Carrier gas with pressure regulator and flow meters.
- Sample injection system.
- Separation column.
- Detector.
- Data processor unit.

Gas chromatographs are highly adaptable since many variables can be involved in the selection and operation of an instrument. Column lengths, column packing materials, operating temperatures and flow rates, and sample handling equipment can all be manipulated to provide the desired results. Instruments are available with multiple columns, multiple detectors, and multiple sample handling capabilities such that several classes of compounds can be detected rapidly and simultaneously. Following is a brief discussion of the major components of a GC system.

(1) Carrier Gas. A high pressure gas cylinder serves as the source of the carrier gas for the GC system. Commonly used gases are hydrogen, helium, and nitrogen. The carrier gas should be:

- Inert to avoid interaction with the sample or solvent.
- Able to minimize gaseous diffusion.
- Readily available and pure.
- Inexpensive.
- Suitable for detector use.

The basic function of the carrier gas is to transport the sample from the injection port through the column to the detector without interfering with the analytical technique.

(2) Injection Port. The injection port, or sample load, must be able to allow for the introduction of the sample into the system without fractionation, condensation or adsorption in other components of the system. Typically, GC systems use sample loops and are heated to insure that the integrity of the sample does not change.

(3) Chromatographic Column. Once the gas is introduced into the carrier gas stream, it is moved to the chromatographic column where separation occurs. The column is composed of a liquid phase on a solid adsorbent packed in a tube or coated on a tubular glass column.

The retention of the pollutant on the column depends upon its interaction with the solid support and liquid phase of the packing. As the carrier gas moves the pollutant through the column, the more easily adsorbed compound will be retained first while others flush through. This separation depends upon:

- Solvent properties of the support.
- Column temperature.
- Adsorbent-gas phase interaction.
- Other factors.

An important parameter to consider is response time. A column should be chosen that elutes the compounds of interest first and rather quickly. A shorter column would be preferable over a longer one to decrease response time. In commercially available monitors, column lengths vary from inches to several meters. Shorter columns do not separate compounds as efficiently or as completely as a longer column of the same material. Several short columns of different materials could be arranged to give rapid detection of several compound classes. Back flushing the columns after a designated time can be automated and prevents unwanted compounds from reaching the detectors.

Today, GC system use two different types of columns. The conventional type is called a "packed column" and consists of a solid support coated with a liquid stationary phase (gas/liquid chromatograph) or simply a solid adsorbent (gas/solid chromatography). The second type of column is a wall-coated open tubular (WCOT) or capillary column and has been widely adopted for environmental analysis packed column GC. The capillary column consists of a liquid stationary phase coated or bonded to specially treated glass or fused silica tubing. Fused silica tubing is most commonly used because of its physical durability and superior inertness. Bonded (or cross-linked) columns are used in preference to coated columns because of the greater operating temperatures that can be obtained. A significant advancement in column technology is the development of wide-bore capillary columns. These columns can be loaded at rates equivalent to packed columns, yet offer the resolution available with capillary columns.

While the use of packed columns has decreased in recent years, these columns are still very effective for many analyses. The very low boiling compounds, such as methane, chloromethane, ethylene, and others are difficult to resolve using capillary column techniques, unless cooling the compounds to subambient temperatures is possible. Packed columns using carbon molecular sieves are very effective for performing this type of analysis. Also, the stationary phase selection available on packed columns far exceeds that for capillaries.

(4) Data Handling System. The data handling system is the last component of the organic real-time monitoring system. Data handling systems can perform many tasks. Basically, the system receives the input

signal from the GC system and converts that signal to concentration. The data handling system can also provide:

- Instantaneous/averaged printout of pollutant concentration.
- Daily zero/span checks with appropriate adjustments.
- Quality control check.
- Signal warning/alert for high or out-of-control situations.
- Maintenance and input notation.

c. Gas chromatographic detectors. Once the analytes of interest have been separated by the GC system, they must be detected. The GC detection system determines, to a large extent, the specificity and sensitivity of the analysis. Consequently, one should carefully review the data quality objectives of the program when selecting a detector to be coupled with the GC system.
The primary detection types in use today are:

- FID.
- Electron Capture Detector (ECD).
- PID.
- Flame Photometric Detector (FPD).
- Mass Selective Detector (MSD).
- FTIR Detector.
- Hall Detector.
- NPD.

Table 4-4 provides an overview of the characteristics of these available detection systems. The principles of operation for many of these detectors are briefly described in this section.

(1) Flame Ionization Detector. By far the most widely used detector for a real-time, on-line FFMS is the FID. In an FID, the gas sample is introduced into a hydrogen/air flame, where the organic compounds are pyrolyzed, forming ionic intermediates. The ionic intermediates products migrate to a detector plate that is appropriately charged. The migration provides an electric current which is measured by a detector. The electronic current produced is proportional to the concentration of the species. By installing a chromatographic column preceding the detector to separate organic species, the detector can be used to detect both "total non-methane hydrocarbons" and speciated organics.

Straight chain hydrocarbons produce the greatest FID response. An FID responds differently to different compound classes. Equal amounts of hydrocarbon, esters and ethers, do not produce equal FID responses.

The sensitivity of the FID is also dependent on the relative flow rates of carrier gas, hydrogen, and air and upon electrode and linear jet geometry. However, the FID has the widest linear range of any chromatographic detector in common use, on the order of 10^{-7}, and is sensitive to as little as 10^{-11} g of alkanes. A final consideration is that the FID does not respond to water, nitrogen, nitrogen dioxide and other gases which are common to an air sample.

Several commercially available manufacturers incorporate FIDs as the detector for both total hydrocarbons and speciated organics. In addition, some of these GC systems have combined the FID and other detectors to provide greater qualitative information associated with the gas steam, as well as better sensitivity for selected groups of compounds.

Advantages of these combinations include:

- Linear response over 6 decades.
- Insensitive to air, water, and inorganic gases.
- Sensitive to most organic compounds.
- Relatively simple and inexpensive.

Disadvantages of the GC/FID combination include:

- High degree of particulate removal required.
- Semi-real-time analysis.
- Requires pure hydrogen, air and inert carrier gases.
- Detector susceptible to corrosion by HCl.

Particulate matter must be removed to progressively lower levels as the sensitivity of the FID is pushed higher. Particulate matter causes a noisy baseline that could overshadow a response to an organic compound. Some laboratory GC/FID instruments require 1 hour to complete the total analyses of one sample. Recent advances in high speed microparticulate packed columns has provided response times of 30 seconds where several minutes would normally be required. A continuous monitoring GC/FID has been manufactured to provide response times on the order of 1 minute; however, separation efficiency and sensitivity may decrease as the response time is decreased. Response times of less than 3 minutes would allow separation and identification of most hazardous compounds expected to be present if two or more columns were utilized.

(2) Electron Capture Detector. The ECD technique involves exposing the gas sample to a source of electrons (usually from a Ni^{63} foil). The intensity of the electron beam arriving at a collection electrode is monitored. In essence, the ECD measures a decrease of electrical signal rather than a total electrical current. When an electron-capturing species (e.g., nitrated or halogenated organic compound) passes through the cell, the intensity of the electron beam decreases, giving rise to a signal. The carrier gas molecules are excited by a radioactive source

Table 4-4
Example of Commonly Used GC Detectors

Detector	Compounds Detected	Advantages	Limitations
Flame Ionization (FID)	Organics	Rugged and stable over extended period of time.	Not as sensitive as many other detectors. Variable response to compounds
Photoionization (PID)	Most organics except methane	Response selectivity can be varied by choice of lamp energy	Response varies from compound to compound. Less rugged than FID.
Electron Capture (ECD)	Polyhalogenated and nitro compounds	Highly sensitive and selective.	Subject to contamination. Response varies widely from compound to compound. Response drifts during temperature programming. Oxygen in air may cause analytical difficulties when direct injection is used.
Alkali Flame (NPD or AFD)	Nitrogen and phosphorus compounds	Highly sensitive and selective.	Subject to contamination. Response varies more from day to day than for FID or ECD.
Fourier Transform Infrared Spectroscopy (FTIR)	Most organics	May be highly sensitive, using long path length cells. Highly selective	Primarily a laboratory instrument. Very expensive. Water Interferences.
Flame Photometric Detector (FPD)	Sulfur or phosphorus compounds (separately)	Highly selective	Response varies from day to day. Not as sensitive as NPD for phosphorus compounds.
Hall Electrolytic Conductivity (HECD)	Halogen, sulfur, or nitrogen compounds (separately)	Highly selective. Response relatively constant from compound to compound. Stable base line during temperature programming.	Only halogen mode has been employed extensively. Requires considerable operator attention. Not as sensitive as ECD for Polyhalogenated compounds (e.g., PCB's).
Thermal Energy Analyzer (TEA)	Nitrosamines	Highly sensitive and selective.	Very expensive (~$35K).
Mass Selective Detector (MSD)	Most organics and volatile inorganics	Response is very selective and selectable for specific compounds	Very expensive (~$40K). May only detect a limited number of compounds per sample. Requires a more highly trained operator and more attention. Not usually as sensitive as FID or ECD.
Chemiluminescence Detector (CLD)	Nitrogen compounds	Highly selective and sensitive	Recently developed. Limited data on applications.

emitting Beta (to produce a steady background current under fixed applied voltage, as illustrated by the following equations:

$$\text{Radioactive} \longrightarrow \beta^- \text{ Emissions}$$
$$\beta^- + N_2 \longrightarrow 2e^- + N_2^+$$
$$2e^- + \text{Electronegative molecules} \longrightarrow \text{Negative ions}$$

The emitted high energy electrons interact with the carrier gas, which in turn interacts with the sample constituents. However, a problem can occur when the ionized sample molecules react with other sample constituents to produce an electron, which confuses the detector response. To prevent this response, a small amount of methane is added to the carrier gas (argon) to deactivate further reaction by excited molecules.

The ECD technique is highly sensitive and selective for compounds containing electron withdrawing groups, such as a halogen or nitro function group. Unfortunately, the ECD response varies widely from compound to compound, and therefore each analyte requires specific calibration to obtain quantitative data. Table 4-5 lists the relative ECD response factors for various organic compound classes. In addition, the ECD is sensitive to temperature variations, with baseline drifts of 50 percent for a temperature change in the room of only 2°C. One must use special precautions when operating the ECD. They are:

- Ultra-pure, dry N_2 or A_r and 5 percent CH_4 to minimize contamination.
- Leak-tight gas system to reduce background noise.
- Clear gas system.
- Special precaution with operation of a Ni^{63} source.

A gas chromatograph equipped with an ECD has been successfully used in ambient air monitoring applications where sensitivities of low part per trillion for chlorofluorocarbons have been demonstrated over the long term. The Ni^{63} ECD is preferred over the tritium ECD for long-term stability and greater precision. This highly sensitive detector is suitable for trace level determination of a variety of hazardous organic species such as chlorinated aliphatic and chlorinated aromatic solvents and PCBs. In combination with an FID, a dual range instrument that is sensitive to 12 decades of concentration of organics would result. This dual detector instrument would be ideally suited to continuous monitoring applications where large swings in concentration of organics are expected. The sensitivity of the ECD requires longer restabilization times between large upsets, whereas the FID recovers more quickly.

In principle, the ECD could serve as a stand-alone detector similar to the FID and PID. However, in practice, the detector is sensitive to organic gases and other airborne components, and, hence, can only be used in a controlled gas stream (i.e., as a GC detector with a purified nitrogen or argon/methane carrier gas). In

summary, the ECD is highly sensitive, not very linear, and very sensitive to surrounding conditions, therefore probably not well suited to the rigorous demands of an on-line GC system.

Table 4-5
Electron Capture Detector Relative Response Factors (Benzene = 1)

Factor	Compound or class
<1	Aliphatic hydrocarbons
1-10	Aromatic hydrocarbons Alcohols, ketones, ethers Monofluoro compounds
10-100	amines, esters, aldehydes, nitriles Monochloro compounds Trifluoro compounds
$100\text{-}10^3$	Dichloro aliphatic compounds (some) Stilbenes Oxalates
$10^3\text{-}10^4$	Dichloro aliphatic compounds (some) Monobromo compounds Hexafluoro compounds
$10^4\text{-}10^6$	Dichloro aromatic compounds Mononitro compounds
10^9	Monoido compounds Dibromo compounds Trichloro (or greater) compounds

Source: American Laboratory, electron Capture Detectors and Their Applications to Toxicology.

(3) Photoionization Detector. The PID is similar in principle to an FID and ECD except that an energy source in the UV/Visible wavelength region is used. The PID involves subjecting the gas phase compounds to a high-intensity beam of UV radiation of a particular energy. Absorption of the radiation by a gas molecule leads to formation of a positive ion and free electrons, provided the ionization potential for the compound is less than the radiation energy of the lamp, as illustrated by the following equation:

$$R + h\mu \rightarrow R^+ + e^-$$

The ions are collected at an electrode, and the resultant current is monitored. The current is proportional to the analyte concentration in the gas steam.

Since the ionization potential of a particular compound must be less than the radiation energy, compounds having high ionizational potentials will be less easily detected than those of lower ionizational potential. Consequently, the choice of lamp energy will have a profound effect on the detector specificity. This aspect of PID detection is attractive from the viewpoint that using a higher energy lamp will provide a relatively nonselective, highly sensitive detector. A lower energy lamp, however, will yield a selective detector that can detect certain readily ionized compounds (e.g., aromatic hydrocarbons) but will not detect aliphatic hydrocarbons. Consequently, aromatics can be selectively detected in the presence of halogenated alkanes, using a low-energy lamp (e.g., 9.5 eV), whereas both compound classes can be detected with an 11 eV lamp. One of the most important advantages of the PID is that methane is not detected using any of the commercially available lamps and, hence, does not interfere with the analytical system when operated in the "total NMOC" mode. Table 4-6 identifies the photoionization potential of various compounds detected with various PID lamps.

The sensitivity of PID is considerably better than FID in most cases (10 ppb or better). In particular, the PID operates without combustible gases, which minimizes potential safety problems. Table 4-7 outlines different sensitivities the PID has to organic compounds relative to benzene (benzene = 1).

Several manufacturers produce GC/PID systems, which can serve as either a stand alone system or as supporting field portable system. These devices have advantages similar to the GC/FID systems in that qualitative as well as quantitative data are obtained. However, while the PID system is generally more sensitive than FID, the PID system does not give uniform responses from compound to compound. Hence, the system must be calibrated for each specific analyte to yield quantitative data.

Table 4-6
Photoionization Potential Of Several Organic Compounds

Compound	Ionization potential, eV	Compound	Ionization potential, eV
Benzene	9.25	Formaldehyde	10.87
Chlorobenzene	9.42	Vinyl chloride	9.95
o-Xylene	8.56	Ethylene oxide	10.56
m-Xylene	8.56	Acrylonitrile	10.91
p-Xylene	8.44	Allyl chloride	10.04
p-Dichlorobenzene	8.95	Chloroprene	8.80
Nitrobenzene	9.92	1,4-Dioxane	9.13
Phenol	8.50	Hexachlorocyclopentadiene	NA
o-Cresol	8.93	Methyl bromide	10.53
m-Cresol	8.98	Acetaldeyde	10.21
p-Cresol	8.97	Propylene oxide	10.22
Carbon tetrachloride	11.45	Vinylidene chloride	10.16
Chloroform	11.42	Acrolein	10.10
Methylene chloride	13.35	N-Nitrosomorpholine	NA
Methyl chloroform	11.30	Epichlorohydrin	NA
Ethylene dichloride	11.12	Maleic anhydride	9.90
Ethylene dibromide	10.44	Phosgene	11.77
Benzyl chloride	10.60	PAHs	<9
Perchloroethylene	9.32	PCBs	<8.3
Trichloroethylene	9.45	PCDDs	NA
		PCDFs	NA

NA = not applicable.

Table 4-7
Sensitivity Of Organic Compounds Relative To Benzene On A Molar Basis (Benzene = 1.0) for the PID

Sensitivity	Compound Class
<1	n-alkanes, branched/cyclic alkanes, alkenes, ketones, alkehydes, alcohols, esters
1-2	aromatic hydrocarbons, chlorobenzenes, chlorophenols, phthalates
2-3	PAHs, PCBs

A GC/PID is presently the most resistant to corrosion of the chromatographic methods. The PID is a nondestructive detector that can be purchased with Teflon®-coated internals with no decrease in sensitivity. Advantages of the PID include 10 times greater sensitivity than the FID to certain compounds, a linear range of 10^7 (10X greater than FID), and a nondestructive nature. Disadvantages include lower selectivity (inorganic compounds are also detected), drastic reductions in sensitivity due to coatings on the lamp windows, and the need for interchanging several lamps of various energies of identification of compounds. PIDs have been placed in series with FIDs as an available laboratory instrument for continuous monitoring applications. Calculating the response of the PID to that of the FID is a tool which offers further compound characterization not available with the individual detectors.

(4) Flame Photometric Detection. The FPD uses a hydrogen/air flame to decompose the compound and excite certain elements. The light emitted by certain elements (e.g., sulfur and phosphorus) is monitored by a photomultiplier tube. The element to be monitored is selected by placing an appropriate optical filter in front of the photomultiplier tube to allow only light of the particular wavelength to be detected. While several

elements could be monitored by this approach, only sulfur and phosphorus compounds (separately) are generally analyzed.

The FPD is used as a total sulfur or phosphorus detector in a stand-alone system similar to the FID for total hydrocarbons. The use of the GC/FPD is advantageous for monitoring sulfur or phosphorus-containing organics.

(5) Mass Selective Detector. A MSD determines the chemical composition of a sample by measuring the molecular weights of the molecules or molecular fragments. This determination is accomplished by converting a small quantity of a sample gas into electrically charged ions, separating the ions of differing mass-to-charge (m/e) ratios by the action of magnetic and/or electrostatic force fields, and then measuring the levels of the resulting output signals.

Mass spectrometers employ several operating components, including (1) a sample inlet system for introducing a small quantity of the substance to be analyzed into the instrument; (2) an ion source to ionize a portion of the sample; (3) a mass analyzer that separates or resolves the ions according to their mass-to-charge ratios; (4) an ion current detector that detects and amplifies the resolved ion current signals; (5) a vacuum pump to maintain a low pressure within the mass spectrometer; and (6) data processing system. These components are combined with electronics that control their functions and process the output data.

Mass spectrometers are inherently fast, sensitive, and capable of detecting wide concentration ranges because they analyze the sample in the gas phase and can detect single ions and moderate ion currents representing a wide molecular concentration range. The MS is quantitative and linear since its output is directly proportional to the concentration of the species in the sample. It is reliable and maintenance free because it is an electronically-based instrument rather than chemically based as are many single sensors. Mass spectrometers are very stable. Relative compound-to-compound sensitivities can be precisely controlled, while common-mode sensitivity variations are compensated by normalizing the outputs against measured values of known air constituents. Finally, the mass spectrometer has maximum flexibility because its broad capabilities can be selectively used under programmable microprocessor control.

A mass spectrometer identifies the chemical composition of a sample by measuring the molecular weights of its molecules or molecular fragments. The analysis (1) causes the sample to become electrically charged ions; (2) separates those ions by differing mass-to-charge ratios by magnetic/electrostatic force fields; and (3) detects those separated ions through electron multipliers.

When the mass spectrometer's magnetic field is scanned, the output appears as a series of peaks called a mass spectrum. Each peak corresponds to the ion's current intensity at a particular mass-to-charge ratio. Each chemical compound has its own unique mass spectrum (or fingerprint) caused by the statistically repeatable fragmentation of its molecules during the electron-bombardment process that creates ions. For example, Nitrogen, N_2, has a molecular weight of 28 atomic mass units (amu). When ionized under electron bombardment, it forms ions at m/e 28 from N_2^+ and at m/e 14 from N^+ (due to fragmentation) and N_2^{++} (due to double ionization). Other diatomic and triatomic molecules have correspondingly simple mass spectra and can be detected and identified based on the measurement of one or two mass peaks.

Larger molecules with more atoms have more complex mass spectra due to the greater number of different fragment ions that are formed. For example, xylene, C_8H_{10}, has a number of peaks in its mass spectrum corresponding to various ways the molecule can fragment. The information contained in the mass spectrum of xylene, in terms of the m/e values present and their intensity ratios, is sufficient to distinguish it uniquely

among all of the other compounds. The number of mass peaks required to make a compound identification depends upon the characteristics and complexity of the sample mixture.

The GC/MS techniques are particularly suited for analysis of organics using a concentration step. This technique has been used to identify organic ambient air contaminants. The concentration step involves passing the air sample through an absorber column that traps the organic material followed by thermal or solvent desorption of that material in the GC. This technique is continuous and overall response times of a GC/MS are typically greater than 3 minutes. At present, no GC/MS instrumentation is in routine use as a continuous monitor. Double mass spectrometry (MS/MS) and laser multiphoton ionization mass spectrometry have been identified as potential on-line or real-time instruments for the identification of polycyclic aromatic hydrocarbons. These instruments do not use the GC for separation of components and therefore do not involve the same delays in response time.

A disadvantage of GC/MS and MS/MS techniques is the complexity and cost of the instrumentation. Investments costing more than $75,000 are usually required. The mass spectra produced is complex and close to real time results can only be provided through a computer with extensive library searching capabilities. The MS can scan for certain compounds within seconds; however, full spectrum scans usually take greater than 3 minutes. These disadvantages should be weighed against the high sensitivity and resolution capabilities of the GC/MS system. Portable field GC/MS have become available which should be considered for FFMS application.

(6) Fourier Transform Infrared Spectroscopy (FTIR). In recent years, real-time optical monitoring has been developed which utilizes infrared detection of contaminant concentrations at HTRW sites. Obvious advantages to using optical monitoring are:

- Spectral data storage capability for identification and later evaluation.
- Semi-real-time assessment of temporal and spacial profile of HAPs from the site.
- Reasonable cost per analyte based on number of HAPs identified per sample.
- Offers both survey screening and quantitation application at HTRW sites.

Optical sensing is effective for measuring a variety of gases and volatile vapors that have absorption features in the infrared or ultra-violet spectrum.

An optical emission FTIR spectrometer can be operated in three different modes. They are:

- Closed cell mode consists of a source and detector, along with a 10-m to 30-m folded path gas cell. The sample is extracted from the ambient air and drawn into the instrument gas cell. This mode would be most applicable to HTRW, real-time detection systems providing multiple compound quantification for stable compounds.
- FTIR can also utilize an open cell mode with an external source and detector. The sample is the source emissions or ambient atmosphere along a line-of-sight between the source and detector. The current pathlength is limited to about 1,000 m but can be extended to 3 km with the addition of an auxiliary telescope. This is the most useful mode of operation for FFMS and area source emission verification.

The beam can also be aimed through test ports in incinerator stacks for source measurements as part of the remediation program.

- Emission mode is used with hot sources, such as incinerator stack plumes, where the detector is aimed at the hot vapor, which serves as its own IR source. Opaque sources, such as a smoke plume, are also readable for identification, although quantification is more difficult. Spectra show both emissions peaks due to the composition of the source itself, as well as absorption peaks from the ambient air long the path from source to detector.

The basic components of an FTIR system includes a transmitter, receiver, and electronic system. In operation, IR light projected across a cell or an open area, returned utilizing a retro reflector to the optical detection system. The heart of the optical detection system is the Michelson-type interferometer.

In this type of interferometer, a radiation is split into two paths, one going through the sample coil containing the analytical gas and the other beam going through the moving mirror, then recombined with the original path after a path difference has been introduced and an interferogram produced. Light from the sample cell can be considered to be information encoded in a light-density versus time domain. From this interferogram, a Fourier transformation is performed by computer to transform the time domain data to the wavelength domain.

Computerized data processing is also required to provide the computational power to the system to provide real-time spectra, spectrum matching, and identification and quantification of the HAPs at the HTRW site.

Interferograms of more than 300 chemicals have been identified and can be stored in the computer system as reference spectra. The established precision and accuracy is 10 percent. The accuracy of the instrument is HAPs specific. The value of 10 percent represents a reasonable upper bound for the range that is achieveable for different HAPs assuming that they are present at concentrations above the noise level. The FTIR technology is limited to IR active compounds and suffers from water interferences

(7) Dual Detectors. Combining the high sensitivity of the FID detector to easily pyrolized, low boiling organic compounds with the high sensitivity of ECD detectors to higher boiling aromatics, etc., is one method for more complete quantification of HAPs emissions from HTRW sites. One instrument could be chosen with two columns, each specified to enhance the separation of and response time associated with the appropriate organic compounds. One or both detector(s) could be used at a given time. The non destructive nature of the PID detector allows its use in series with other GC detectors. The PID/FID, PID/ECD and PID/NPD combinations have all been used for specific applications. A typical PID/FID application is the identification of hydrocarbon classes. The PID response increases with increasing degrees of unsaturation and the FID response is mostly unaffected by double bonds. In comparison, the reactive response of these two detectors, alkanes, olefins, and aromatic compound classes can be identified in complex sample matrices.

In summary, the selection of the appropriate detector depends upon the analyte of concern, the level at which it must be detected, and the responsiveness of the system to the environment in which the analyte is a part. Table 4-8 summarizes the characteristics of the various detectors in combination with GC systems, while Figure 4-4 compares detection limits of the detectors discussed. Table 4-9 identifies useful detector combinations in HAPs monitoring and detection, while Table 4-10 provides guidelines, advantages, and limitations associated with useful GC detector combinations.

d. Combination NMOC/speciated gas chromatographic system. In recent years, regulatory agencies responsible for monitoring emissions from HTRW sites have required the monitoring of both NMOC and

speciated organic compounds as part of the FFMS program to meet the data quality objectives of the remediation air program. An example approach could require that an NMOC trigger level be established at the perimeter of the HTRW site to which additional speciated organic monitoring is to occur if the trigger level is exceeded. The perimeter monitoring would include:

- NMOC perimeter trigger level. As an example, an average NMOC concentration level of greater than 1 ppm would trigger organic speciation compound identification by the analytical system, as illustrated in Figure 4-5.

- Speciated compound identification. If the NMOC is determined to be greater than 1 ppm, the analytical system immediately speciates the air sample to determine if the agreed upon PALs has been exceeded, as illustrated in Figure 4-6.

- Net concentration. If the PAL is exceeded, the data system that determines the net concentration by subtracting the upwind station concentration for that analyte from the downwind station concentration to determine the influence of HTRW site on the community, as illustrated in Figure 4-7.

HTRW projects may require the monitoring of NMOC and speciated VOCs by incorporating monitoring system using sample transport lines to collect samples from different locations around the perimeter of the HTRW site.

Real-time perimeter air monitoring system for evaluating NMOC and speciated organics by GC equipped with two photoionization detectors could be constructed or purchased to analyze multi-sampling probes extending to various points on the site perimeter. Such a system could provide both an automated NMOC mode and a speciated VOC mode. The system provides for automatic and real-time monitoring of NMOC and speciated VOCs in the low ppb to percent range.

This example system involves a photoionization detector in the analytical center with a microprocessor control, which allows it to operate in the "real-time mode." The unit rapidly scans several sampling points around the perimeter of the HTRW site in the "Rapid Analytical Mode (RAM)" for NMOC, without methane interference, and then automatically switches to a chromatographic mode when the "RAM" mode indicates the presence of unacceptable levels of NMOC, as illustrated in Figure 4-8.

The basic components of the analytical system include:

- Multipoint sequencer.

- "RAM" NMOC concentration mode.

- Analytical GC speciated VOC mode.

- Dual NMOC/VOC alarm levels.

- Data processing of NMOC/speciated VOC concentrations.

Multiple heat-trace sample lines extract ambient air from around the HTRW site and transports the air sample to the real-time, on-line GC system with multipoint sequencer located in the Analytical Center.

The multipoint sequencer consists of numerous solenoid valves controlled by the microprocessor so that one sample at a time is switched to the sampling manifold while all others are vented to the exhaust pump. This design allows the sample to flow continuously through the heated sampling lines; therefore, a fresh sample is always available for analysis. The valve compartment contains separate handling and autocalibration components together with the manifold sampling pump, carrier gas controls, and a 10-port sampling valve.

Table 4-8
Example Characteristics Of Various Common Detectors Used as Part of FFMSs at HTRW Sites

	Detector		
Category	**ECD**	**FID**	**PID**
Minimum quantity	10^{-14} g/sec	10^{-11} to 10^{-12} g/sec (~0.50 ppb)	10^{-12} g
Response	Extremely selective electronegative compounds	Selective only organics	Selective response (change UV source)
Linearity	1 to 10^5	1 to 10^5	1 to 10^6
Stability	Fair	Excellent	Fair
Carrier gas	He or H_2	Nitrogen/Helium	Nitrogen/Helium
Temperature limit	325°C	400°C	300°C

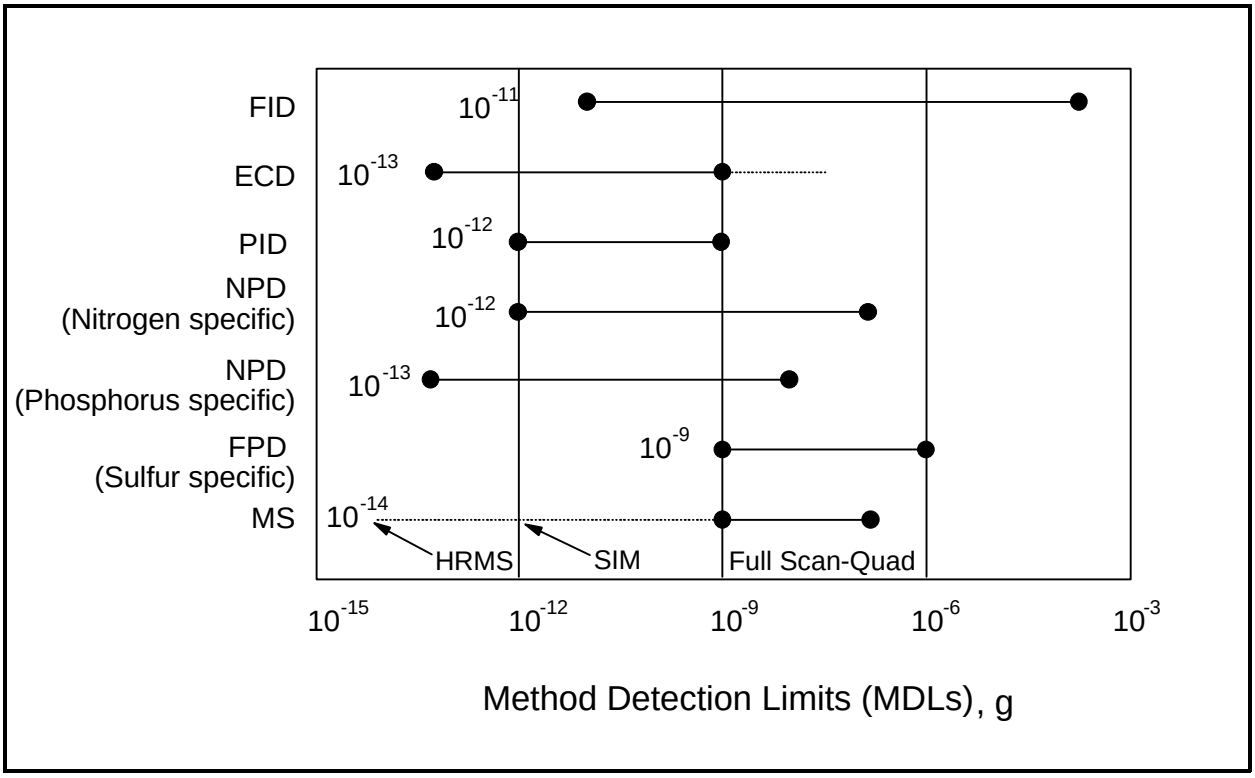


Figure 4-4. GC detector comparison associated with method detection limits

Table 4-9
Examples of Useful GC Detector Combinations

Detector Combination	Application
ECD-PID (Series)	Volatile aromatics and chlorinated solvents
PID-FID (Series)	Aromatic hydrocarbons
ECD-FID (Series)	Chlorinated hydrocarbons
NPD-FID (Parallel)	Nitrogen or phosphorous compounds
FPD-FID (Parallel)	Sulfur compounds
PID-NPD (Series)	Amines
MS-FID (Parallel)	Aromatic and halogenated volatile compounds
ECD-FID (Parallel)	Aromatic and halogenated volatile compounds
ECD-PID-FID (Parallel)	Aromatic and halogenated volatile compounds

Table 4-10
Example of Common GC Detectors, Detection Limits, And Advantages/limitations

Detector	Compounds Detected	Advantages	Limitations	Detection Limits (ng/m^3)
Flame Ionization (FID)	Non-halogenated organics; PAHs	Response is relative constant from one compound to another	Not as sensitive as many of the other detectors	5-100
Photoionization (PID)	Most organics except methane; aromatic organics	Response selectively can be varied by choice of lamp energy	Response varies from compound to compound. Less rugged than FID	25-100
Electron Capture (ECD)	Polyhalogenated and nitrogenated organics	Highly sensitive and selective Response drifts during temperature programming	Subject to contamination. Response varies widely from compound to compound.	5-100
Flame photometric Detector (FPD)	Sulfur or phosphorus compounds (separately)	Highly selective	Response varies from day to day. Not as sensitive as NPD for phosphorus compounds	5-500

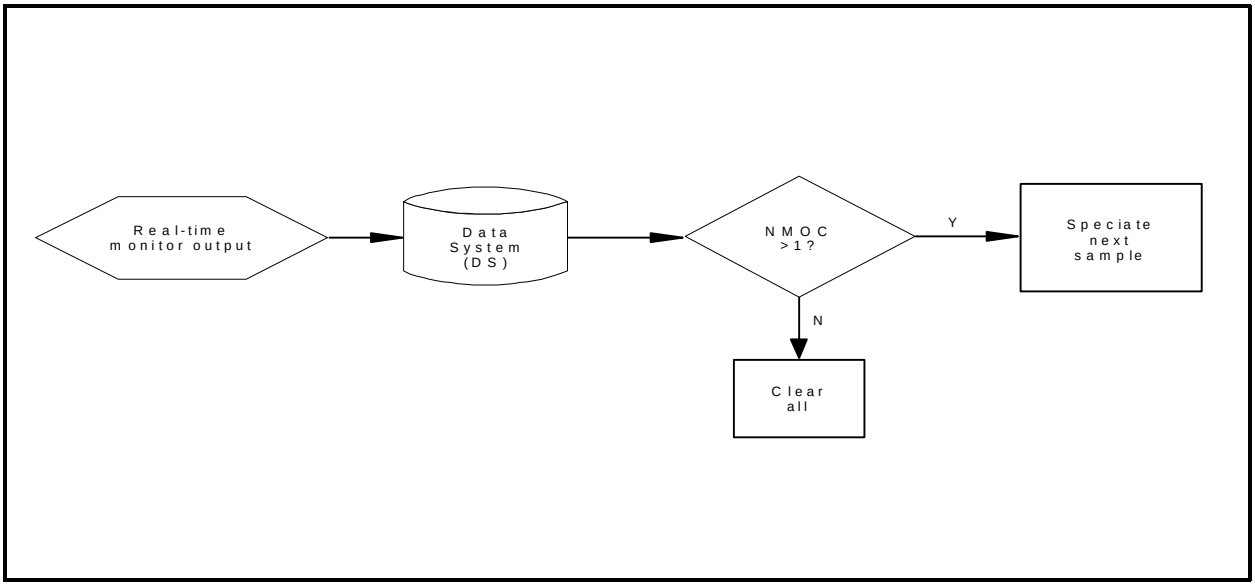


Figure 4-5. Example of schematic for NMOC decision mode.

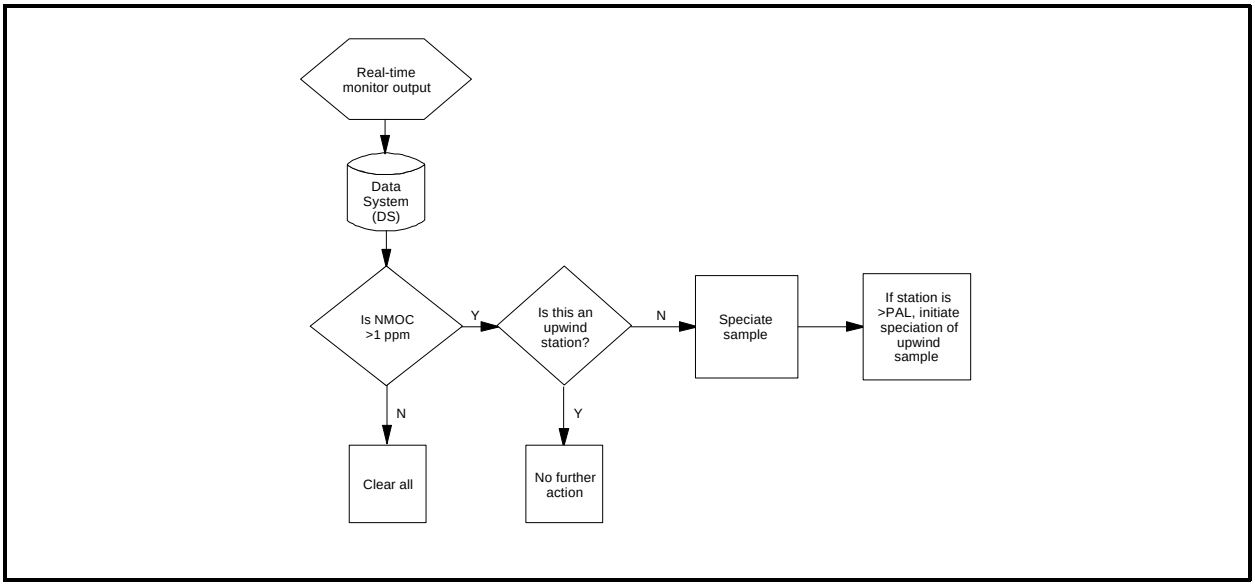


Figure 4-6. Example of schematic for speciated decision mode

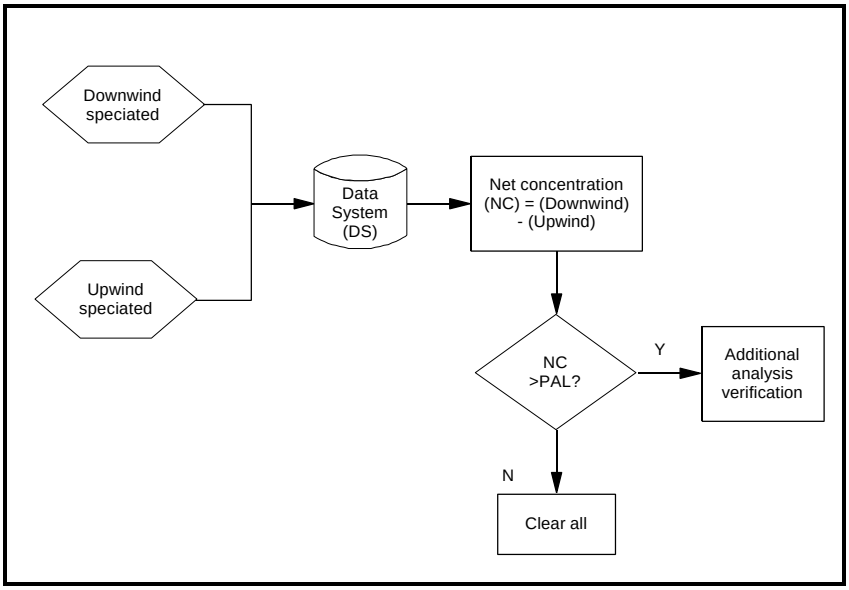


Figure 4-7. Schematic of net concentration decision mode

In operation, ambient air is pulled, from sample inlet locations into the inlet of the sample transfer lines at each of the HTRW perimeter locations, passed through an in-line heated filter to remove particles, then passed on through to the real-time, on-line GC system in the Analytical Center. The multi-point sequencer rotates in the GC system manifold from each of the perimeter sampling points. The process is controlled by a micro-processor, allowing one ambient air sample at a time to be switched to the sample loop while all others are vented, thus providing a "fresh" sample to the analyzer during a sample event. The ambient air sample enters the system to a sample loop, as illustrated in Figure 4-9. After a predetermined period, the sample loop is isolated from the sample gas stream, purged with nitrogen gas where the VOCs are directed to the first PID, by-passing the GC column. In this "RAM" mode, the column is bypassed and the sample is directed to the first PID. The "RAM" mode provides total NMOC concentration in the gas stream. The whole system is under microprocessor control and the switch from "RAM" to chromatographic speciated analysis is initiated when the "RAM" average NMOC measurement exceeds 1 ppm. When the NMOC average value is >1 ppm, a speciated analysis is performed on the extracted ambient air sample. In the "analytical mode," the analyzer performs a gas chromatographic separation of VOC components in the sample. As the nitrogen gas stream containing the extracted VOCs passes through the capillary GC column, the contaminants interact with the inner coated walls on the capillary column, thus enabling separation. As the individual contaminants exit the GC column, their presence are detected by a second PID. The response of the detector is directly proportional to the concentration of analyte in the nitrogen gas stream. Analytical identification is determined by performing multipoint calibration of the system, using retention time as the identification technique. Due to detection limitations and number of target compounds, real-time on-line monitoring allows only for a definitive list of VOCs (up to 15 compounds) to be monitored at any one sample point..

e. Manufacturers of monitoring systems. This section discusses the various aspects of monitoring systems applicable to HTRW sites for characterizing NMOC and speciated organics emissions. Appendix F provides a listing of numerous manufacturers of these systems as a system design starting point.

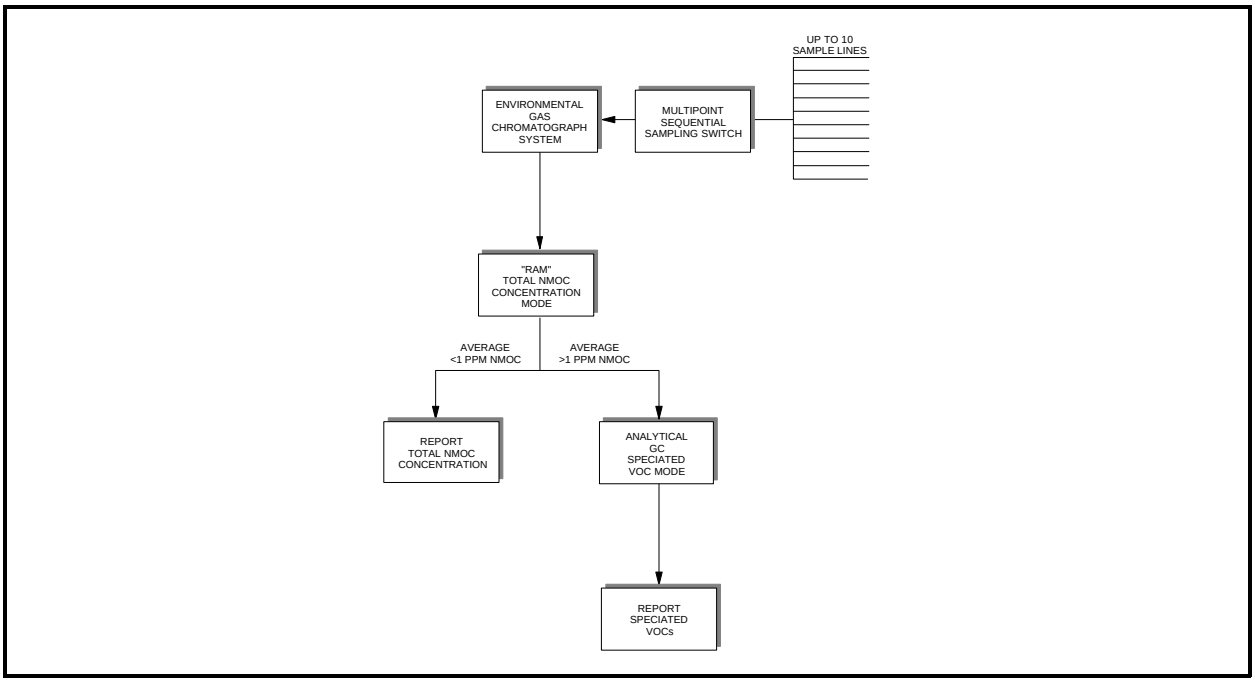


Figure 4-8. Schematic of real-time gas chromatograph system with NMOC "RAM" and speciation VOC modes (functions)

4-4. Supporting Measuring Methods

a. Introduction. As specified in CERCLA and SARA regulations, the EPA has the responsibility for assessing and characterizing all contaminant migration pathways from waste to the environment and the resulting environmental impacts. Specifically, the regulations specify that "all potential migration pathways for contaminants" be characterized and quantified. In addition, all emissions from HTRW site during remediation must be within compliance with Federal and State ARAR and other nonbinding criteria "to-be-considered (TBC)" emission limits. These requirements include not only local, State, or community standards, but also the NAAQS. Over the last 25 years, EPA has developed national standards for seven criteria pollutants. The seven primary criteria pollutants are SO_2, NO_x, O_3, CO, TSP matter as PM_{10}, Pb, and NO_2. The NMOC was promulgated, then rescinded (however, the NMOC is still used). Table 4-11 identifies the criteria pollutants, the averaging time for those pollutants, the associated standards for each of the pollutants, and the Reference Measurement Method (RMM) to be used to quantitate them. Monitoring at HTRW sites may require the application of EPA's RMMs to demonstrate compliance or to be operated collocated with the real-time on-line FFMS. In ambient air monitoring for criteria pollutants, there are two sampling and analytical designated methodologies:

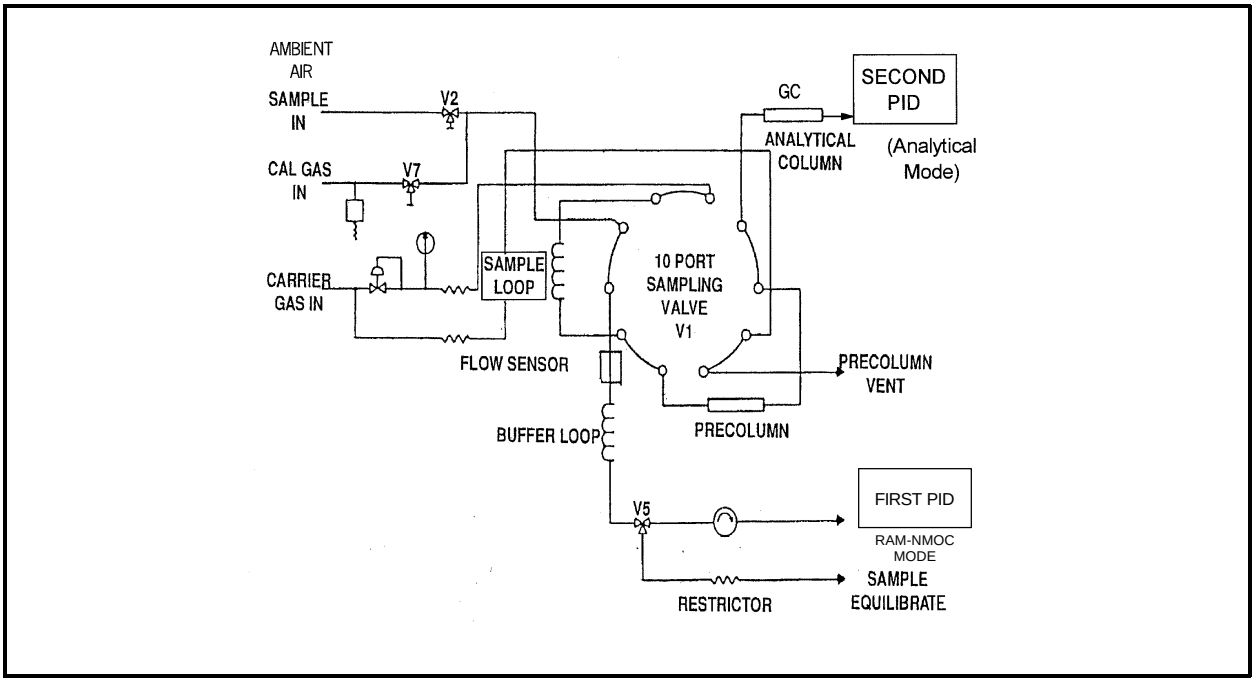


Figure 4-9. Example of a commercially available multi-port NMOC/analytical gas chromatographic system for HTRW applications

- Reference Measurement Method. One specific method of analysis for a particular pollutant that has been promulgated by EPA for criteria pollutant measurement.

- Equivalent or Reference Method. A method that has been found experimentally accurate enough by EPA to match analysis specifications given for the reference methods (range, precision, and sensitivity) or have been made available through EPA guidance documents. In terms of methods which can be used to support a FFMS, either promulgated or guidance methods can be reference methods. These methods can also be used as contingency or off-site methods.

These methods (reference and equivalent) were chosen by the EPA after a comprehensive review of available methodologies for measuring the criteria pollutants. Although, perhaps not representative of "state-of-the-art" techniques, these methods have been carefully evaluated and errors and/or interferences quantified where possible. They also represent the methods required or accepted by EPA for use at most HTRW remedial active sites. In most situations, air methods that have been made available as guidance methods are accepted as a reference method for some HTRW applications.

Table 4-11
Criteria Pollutants and Their Reference Methods

Pollutant	Averaging time	Primary standards[b,c]	Secondary standards[d]	Reference measurement method[e]
Sulfur dioxide (SO_2)	Annual arithmetic mean	80 µg/m^3 (0.03 ppm)		Pararosaniline method
	24 hr	365 µg/m^3 (0.14 ppm)		
	3 hr	--	1,300 µg/m^3	
Suspended particulate matter (SPM) As PM_{10}	Annual geometric mean	50 µg/m^3		High volume sampling method
	24 hr	150 µg/m^3		
Carbon monoxide (CO)	8 hr	10 mg/m^3 (9 ppm)	Same as primary standard	Nondispersive infrared spectroscopy
	1 hr	40 µg/m^3 (35 ppm)		
Ozone (0_3)	1 hr	0.12 ppm	Same as primary standard	Gas-phase chemiluminescent method with ethylene
Hydrocarbons (corrected for methane) [rescinded]	3 hr (6 to 9 a.m.)	160 µg/m^3 (0.24 ppm)	Same as primary standard	Flame ionization detection using gas chromatography
Nitrogen dioxide (NO_2)	Annual arithmetic mean	100 µg/m^3 (0.05 ppm)	Same as primary standard	Gas-phase chemiluminescence with ozone
	1 hr	0.25 ppm		
Lead (Pb)	Calendar quarter	1.5 µg/m^3	Same as primary standard	High volume sampling, atomic absorption analysis

a Environmental Protection Agency, *Federal Register* 40 CFR 50 p. 4-6 (July 1, 1979).
b National standards other than those based on annual arithmetic means, annual geometric means, or quarterly arithmetic means are not to be exceeded more than once per year.
c National Primary Standards: The levels of air quality necessary, with an adequate margin of safety, to protect the public health.
d National Secondary Standards: The levels of air quality necessary to protect the public welfare from any known or anticipated adverse effects of a pollutant.
e Reference method as described by EPA. An "equivalent method" means any method of sampling and analysis which can be determined to have a "consistent relationship to the reference method."

An RMM may be either manual or automated. If manual, it is a detailed chemical procedure specifying all important parameters. If automated, it consists of a measurement principle (MP) and a calibration principle (CP). Thus for an automated method, any instrument using the measurement principle (designated by the EPA) is a separate reference method. Among the gases, SO_2 is the only manual Reference Method. Nitrogen dioxide, O_3, CO, and hydrocarbon (HC) use automated methods and thus follow a particular measurement principle; there are several reference methods for each.

The Federal Reference Methods (i.e., the complete description of the procedure for manual methods and the detailing of the MP and CP for automated Method) are contained in the Appendices to 40 CFR 50.

b. EPA compendium methods. Historically, VOCs are not addressed as criteria pollutants, and thus do not have associated reference or equivalent sampling and analytical methodology. The monitoring and analytical techniques of VOCs were based on professional judgments rather than adherence to any documented uniform guidelines. As a result, there was little consistency among the sampling and analysis procedures and the intended uses of the data. The absence of standardized procedures left many deficiencies in air monitoring programs and raised serious concerns about the comparability of the data.

The EPA has developed two ambient air compendia to address these deficiencies. They are:

- *Compendium of Methods for Determination of Toxic Organic Compounds in Ambient Air.*
- *Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air.*

The Compendia have been prepared to provide Regional, State, and local environmental regulatory agencies, as well as other interested parties, with methods that can be used as RRMs. These guidance methods are generally used for determination of selected HAPs at HTRW sites. The Organic Compendium contains 17 methods, as illustrated in Figure 4-10 while the Inorganic Compendium contains five methods, as illustrated in Figure 4-11.

While the Compendium methods are guidance methods they are frequently utilized as RMM for HTRW projects The majority of the methods address monitoring for classes of compounds, i.e., volatile and semi-volatile organics, inorganic compounds, while other methods address specific HAPs. Table 4-12 outlines a brief description and applicability for each of the Organic and Inorganic Compendium methods.

(1) *EPA Organic Compendium*.

(a) *Organic Compendium Method TO-1: Volatile Organic Compounds (80° to 200°C)*. Volatile organic compounds are emitted into the atmosphere from a variety of activities at an HTRW site. Many of these compounds are toxic; hence knowledge of the levels of such materials in the ambient atmosphere is required to determine human health impacts. Conventional air monitoring methods (e.g., for workspace monitoring) have relied on carbon adsorption approaches with subsequent solvent desorption. Such techniques allow subsequent injection of only a small portion, typically 1 to 5 percent of the sample onto the GC system. However, typical ambient air concentrations of these compounds require a more sensitive approach. The thermal desorption process, wherein the entire sample is introduced into the analytical (GC/MS) system, fulfills this need for enhanced sensitivity.

Organic Compendium Method TO-1, which may be replaced with TO-17, describes a generalized protocol for the collection and determination of certain VOCs that can be captured on Tenax® GC [poly(2,6-diphenyl phenylene oxide)] and determined by thermal desorption GC/MS techniques, as illustrated in Figure 4-12. The method is applicable to nonpolar organics having boiling points in the range of approximately 80° to 200°C.

Sampling involves drawing ambient air through a cartridge containing ~1 to 2 grams of Tenax®. Certain VOCs are trapped on the resin while highly volatile organic compounds and most inorganic atmospheric constituents

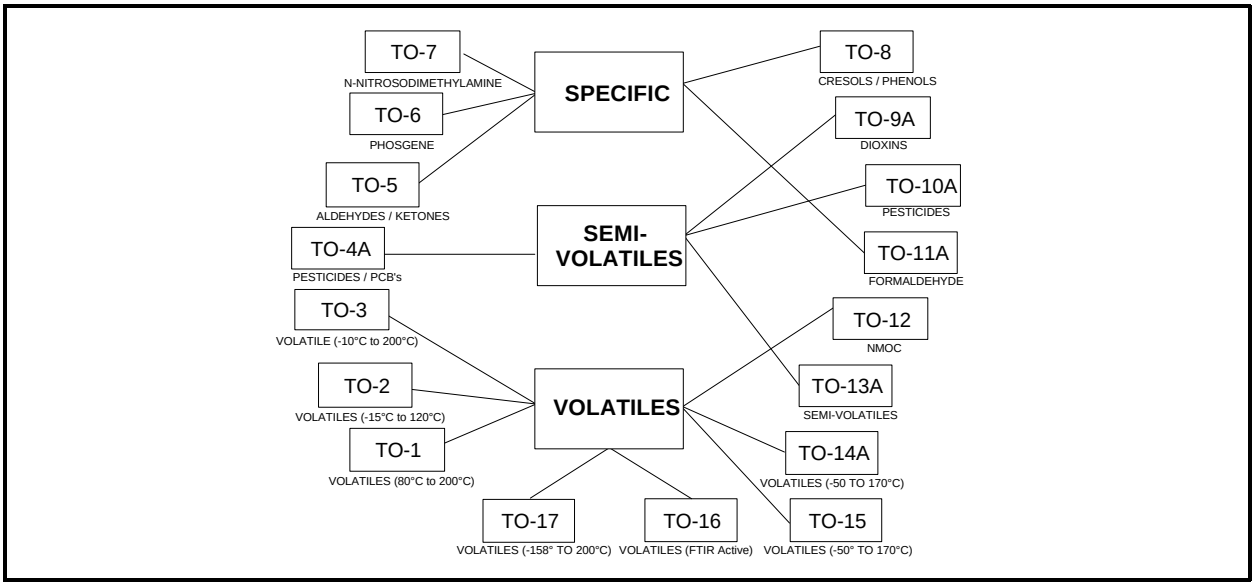


Figure 4-10. Compendium of organic methods for sampling and analysis of HAPs at HTRW sites

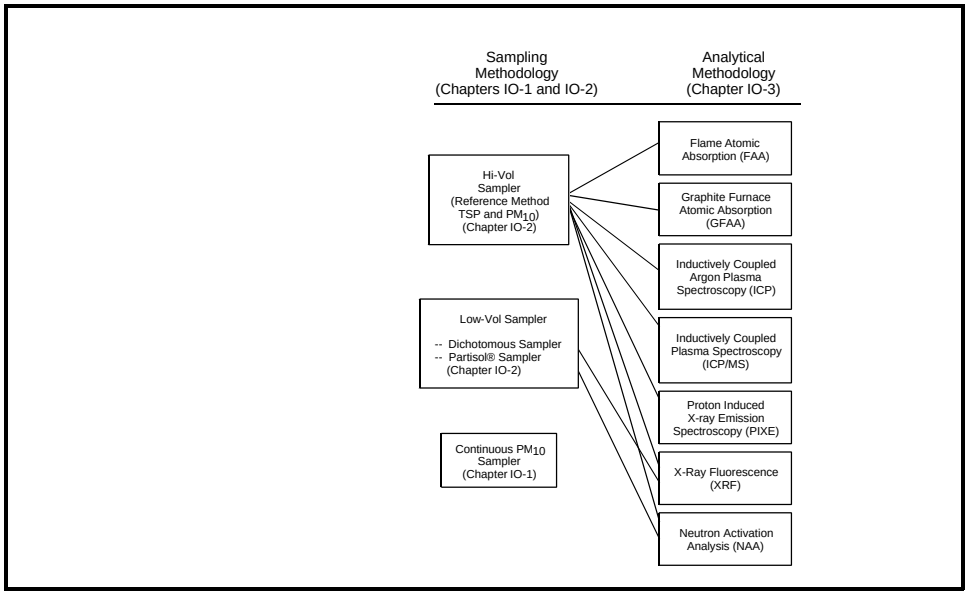


Figure 4-11. Compendium of inorganic methods for sampling and analysis of HAPs at HTRW sites

Table 4-12
Brief Method Description and Applicability for Organic and Inorganic Compendia

Organic Compendium		
Method No.	**Description**	**Types of compounds determined**
TO-1	Tenax GC adsorption and GC/MS analysis	Volatile, nonpolar organics (e.g., aromatic hydrocarbons, chlorinated hydrocarbons) having boiling points in the range of 80° to 200°C
TO-2	Carbon molecular sieve adsorption and GC/MS analysis	Highly volatile, nonpolar organics (e.g., vinyl chloride, vinylidene chloride, benzene, toluene) having boiling points in the range of -15° to +120°C
TO-3	Cryogenic trapping and GC/FID or ECD analysis	Volatile, nonpolar organics having boiling points in the range of -10° to +200°C
TO-4A	High volume PUF sampling and GC/MS analysis	Organochlorine pesticides
TO-5	Dinitrophenylhydrazine liquid impinger sampling and HPL/UV analysis	Aldehydes and ketones
TO-6	High performance liquid chromatography (HPLC)	Phosgene
TO-7	Thermosorb/N adsorption	N-nitrosodimethylamine
TO-8	Sodium hydroxide liquid impinger with high performance liquid chromatography	Cresol/phenol
TO-9A	High volume PUF sampling with high resolution gas chromato-graphy/high resolution mass spectrometry (HRGC/HRMS)	Polyhalogenated Dioxin/Furans
TO-10	Low volume polyurethane foam (PUF) sampling with gas chromatography/ electron capture detector (GC/ECD)	Pesticides
TO-11A	Adsorbent cartridge followed by high performance liquid chromatography (HPLC) detection	Formaldehyde
TO-12	Cryogenic preconcentration and direct flame ionization detection (FID)	Non-methane organic compounds (NMOC)
TO-13A	PUF or PUF/XAD-2 adsorption with GC/MS detection	Polynuclear aromatic hydrocarbons (PAHs)
TO-14A	SUMMA® passivated canister sampling with GC/MS detection	Non-polar volatile organic compounds
TO-15	SUMMA® passivated canister sampling with GC coupled to a MS or ion trap	Polar and nonpolar volatile organic compounds
TO-16	Real-time monitoring by fourier transform infrared spectroscopy (FTIR)	Volatile organic compounds
TO-17	Real-time or solid adsorbent sampling followed by GC/MS (or alternate) detection	Volatile organic compounds

Table 4-12 (continued)

Inorganic Compendium		
Method No.	**Description**	**Types of compounds determined**
Chapter 1		
IO-1.1	Graseby PM_{10} Beta Attenuation	SPM at the 10µ cut size
IO-1.2	Thermo PM_{10} Beta Attenuation	SPM at the 10µ cut size
IO-1.3	R&P PM_{10} TEOM® Sampler	SPM at the 10µ cut size
Chapter 2		
IO-2.1	High-volume sampler	Total SPM
IO-2.2	Dichotomous sampler	SPM at the 10µ and 2.5µ cut size
IO-2.3	R&P Partisol® sampler	SPM at the 10µ cut size
IO-2.4	Air volume calculation	Calculate standard air volume
Chapter 3		
IO-3.1	Filter selection, preparation, and extraction	Filter management
IO-3.2	Analysis of filter by atomic absorption (AA)	Analysis for metals
IO-3.3	Analysis of filter by X-ray fluorescence (XRF)	Analysis for metals
IO-3.4	Analysis of filter by Inductively Coupled Plasma (ICP) spectroscopy	Analysis for metals
IO-3.5	Analysis of filter by ICP/MS	Analysis for metals
IO-3.6	Analysis of filter by Protein Induced X-Ray emission Spectroscopy (PIXE)	Analysis for metals
IO-3.7	Analysis of filter by Neutron Activation Analysis (NAA)	Analysis for metals
Chapter 4		
IO-4.1	Measurement of atmospheric strong acidity using annular denuder	Analysis for SPM pH
IO-4.2	Measurement of atmospheric reactive gases and fine particles using annular denuder	Analysis for sulfates, nitrates, PM_{10}, pH, etc.
Chapter 5		
IO-5.1	Measurement of atmospheric mercury concentration	Analysis for mercury

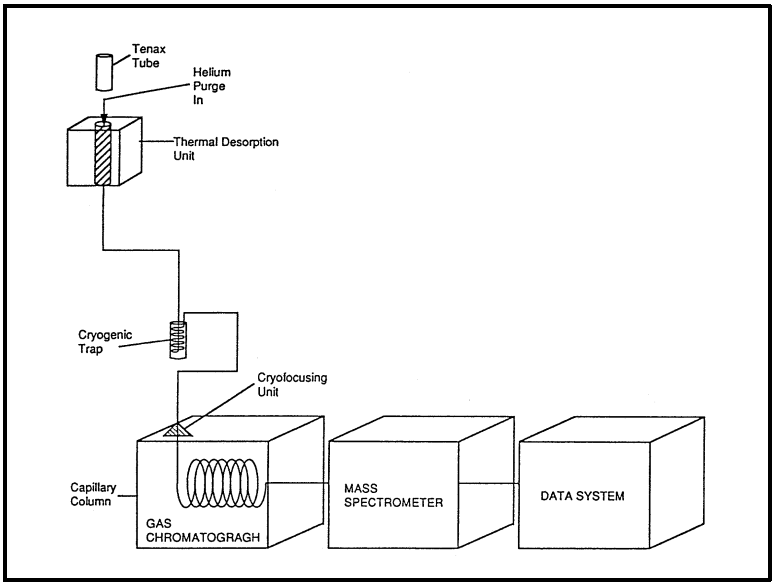


Figure 4-12. Compendium Method TO-1 Analytical Scheme

pass through the cartridge. The cartridge is then transferred to the laboratory and analyzed. For analysis, the cartridge is placed in a heated chamber and purged with an inert gas. The inert gas transfers the VOCs from the cartridge onto a cold trap and subsequently onto the front of the GC column, which is held at low temperature (e.g., -70°C).

Method TO-1 has numerous interferences including Tenax® contamination, compound breakthrough during collection on Tenax®, and artifact formation on the adsorbent during sampling. The analysis procedure also involves a "one-chance" analysis and leaves no reanalysis options when method QC failures.

(b) *Organic Compendium Method TO-2: Volatile Organic Compounds (-15° to +120°C)*. Compendium Method TO-2 is similar to Method TO-1 except the adsorbent is a carbon molecular sieve (CMS) rather than Tenax®. This sieve allows some of the more volatile organics, i.e., vinyl chloride, to be captured and analyzed.

Method TO-2, which may also be replaced with TO-17, is suitable for the determination of certain nonpolar VOCs having boiling points in the range of -15° to 120°C. The analytical detection limit varies with the analyte. Detection limits of 0.01 to 1 ppbv are achievable using a 20-liter sample.

Sampling involves drawing ambient air through a cartridge containing ~0.4 g of a CMS adsorbent. Volatile organic compounds are captured on the adsorbent while major inorganic atmospheric constituents pass through (or are only partially retained). Prior to the actual laboratory analysis the cartridge is purged with 2 to 3 liters of pure, dry air (in the same direction as sample flow) to remove adsorbed moisture.

Similar to Compendium Method TO-1, the cartridge is heated to 350° to 400°C, under helium purge, and the desorbed organic compounds are collected in a specially designed cryogenic trap. The collected organics are then flash evaporated onto a capillary column GC/MS system (held at -70°C). The individual components are identified and quantified during a temperature programmed chromatographic run, as illustrated in Figure 4-12.

Similar to Method TO-1, contamination of the CMS, sampling compound breakthrough, and antifact formation are potential weaknesses of the TO-2 methodology and also is limited to a single analysis.

(c) *Organic Compendium Method TO-3: Volatile Organic Compounds (-10° to 200°C)*. Compendium Method TO-3 involves the collection of VOCs having boiling points in the range of -10° to 200°C in a

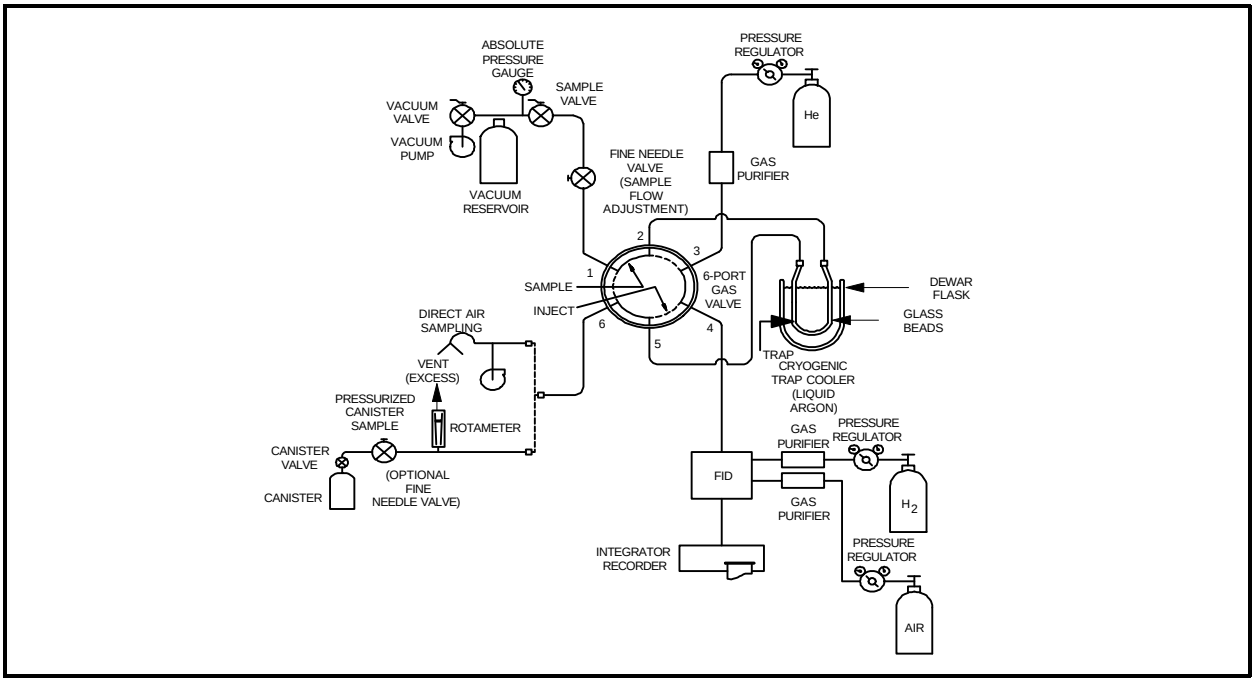


Figure 4-13. Compendium Method TO-3 Sampling and Analytical Methodology

cryogenic trap constructed of copper tubing packed with glass beads, as illustrated in Figure 4-13. The collection trap is submerged in either liquid oxygen or argon. Liquid argon is highly recommended because of the safety hazard associated with liquid oxygen. With the sampling valve in the fill position, an air sample is admitted into the trap by a volume measuring apparatus. In the meantime, a GC column oven is cooled to a subambient temperature (-50°C) for sample analysis. Once sample collection is completed, the value is switched so that the carrier gas sweeps the contents of the trap onto the head of the cooled GC column. Simultaneously, the liquid cryogen is removed, and the trap is heated to assist the sample transfer process. The GC column is temperature programmed, and the component peaks eluting from the columns are identified and quantified using flame ionization and/or electron capture detection. Alternate detectors (e.g., photoionization) can be used as appropriate. An automated system incorporating these various operations as well as the data processing function has been described in the literature. Due to the complexity of ambient air samples, high resolution (capillary column) GC techniques are recommended. However, when highly selective detectors (such as the electron capture detector) are employed, packed column technology without cryogenic temperature programming can be effectively used in some cases.

(d) *Organic Compendium Method TO-9A: Dioxins/Furans*. Compendium Method TO-9A is used for the determination of polyhalogenated dibenzo-p-dioxins and dibenzofurans (PHDDs/PHDFs) in ambient air. This includes polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDDs/PCDFs), and bromo/chloro dibenzo-p-dioxins and bromo/ chloro dibenzofurans (BCDDs/BCDFs).

As illustrated in Figure 4-14, ambient air is drawn at a flow rate about 200 to 280 L/min into a high volume sampler, which includes a quartz fiber filter and cleaned and quality assured polyurethane foam (PUF) backup adsorbent cartridge. Figure 4-15 depicts a typical TO-9A adsorbent cartridge. Sampling is normally performed for 24-hours. During sampling, the dioxin/furans are retained on the adsorbent cartridge. After sampling, the filter and PUF are placed in an ice chest and shipped to the laboratory at ambient temperatures where they are analyzed for specific analytes using high resolution GC/high resolution MS (HRGC/HRMS).

The sampling system consists of a vacuum pump capable of drawing an airflow of about 200 to 280 L/min, a dual sampling module, a flow venturi, an elapsed time indicator, a 7-day timer, and an anodized aluminum shelter.

Prior to analysis, the filter and PUF are combined and spiked with surrogate compounds and Soxhlet extracted with benzene or toluene for 16 hours. The resulting extract is then subjected to an acid/base cleanup procedure followed by cleanup procedures on micro columns of silica gel, alumina, and carbon. The extract is spiked again to determine method efficiencies achieved from previous spikes and then concentrated for HRGC/HRMS analysis.

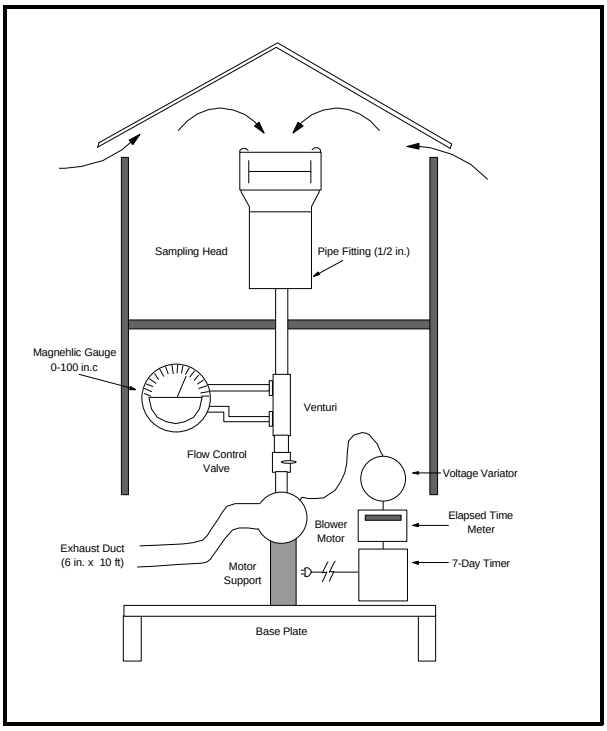


Figure 4-14. Compendium Method TO-9A Sampler for Dioxins/Furans

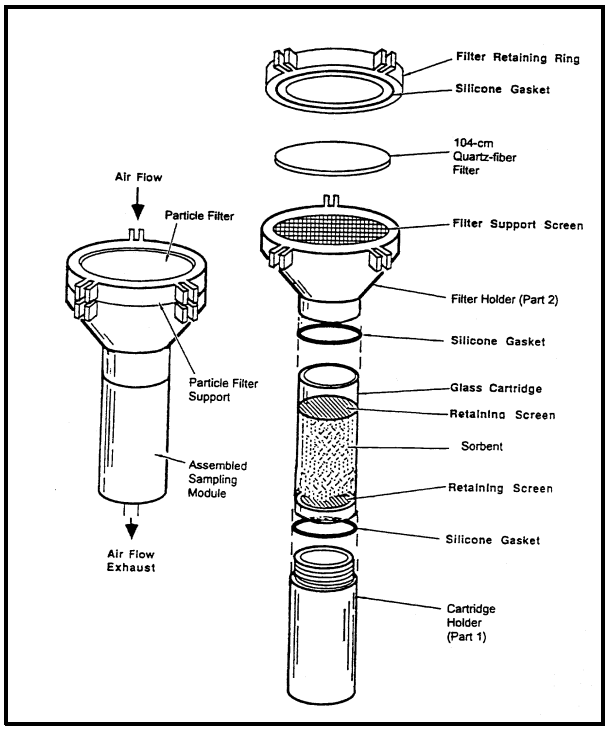


Figure 4-15. Example of TO-9A adsorbent cartridge used for capturing dioxins/furans

Analysis is performed using HRGC/HRMS operated in the select ion monitoring (SIM) mode using a 30-m SE54 or 60-m SP-2231 fused silica capillary column. This analysis determines the sampler efficiency, method efficiency, and the concentrations achieved for the PHDDs/PHDFs. The analytical results and volume of air sampled are used to calculate the concentrations of other compounds.

The major components of the analytical system are the HRGC/HRMS with data system and the Soxhlet extraction system. The HRGC should be equipped for temperature programming, and the injection port should be designed for capillary columns. The HRMS system should be operated in the electron impact ionization mode, and the static resolving power of the instrument should be maintained at 10,000 (10 percent valley definition). The system should be operated in the SIM mode with a total cycle time of 1 second or less. The same set of ions should be used for both calibration and sample analysis. The HRGC/HRMS must be equipped with a data system to provide for instrument control and data acquisition, processing, and storage.

(e) *Organic Compendium Method TO-12: Nonmethane Organic Compounds (NMOC)*. As discussed earlier, regulatory agencies have required perimeter air monitoring programs at HTRW sites to monitor NMOC as a first level indicator of emission with subsequent analysis for speciated VOCs if the NMOC value at the perimeter exceeds a predetermined threshold value. Compendium Method TO-12 is a technique for monitoring NMOC either on a real-time basis or by utilizing time-integrated technique. This method involves a simple cryogenic preconcentration procedure with subsequent direct FID sample analysis, similar to Compendium Method TO-3. The method is sensitive and provides accurate measurements of ambient NMOC concentrations where speciated data are not required.

Method TO-3 involves the collection of VOCs in a trap cooled to -160°C and analyzed by GC/FID for compound speciation, while Method TO-12 combines the same type of cryogenic concentration technique but using a simple GC/FID for a total NMOC determination, without the GC columns and complex procedures necessary to achieve species separation (as illustrated in Figure 4-13).

Compendium Method TO-12 can be used either for direct, in situ ambient measurements or (more commonly) for analysis of integrated samples collected in specially treated stainless steel or silanized canisters. The use of sample canisters allows for the collection of integrated air samples over an extended time period by unattended, automated samplers providing a TWA sample result.

In the integrated mode, an ambient air sample is extracted into a pre-evacuated treated stainless steel canister, either through the utility of a metal bellows pump, as illustrated in Figure 4-16 or by using the initial vacuum as a means of sample extraction.

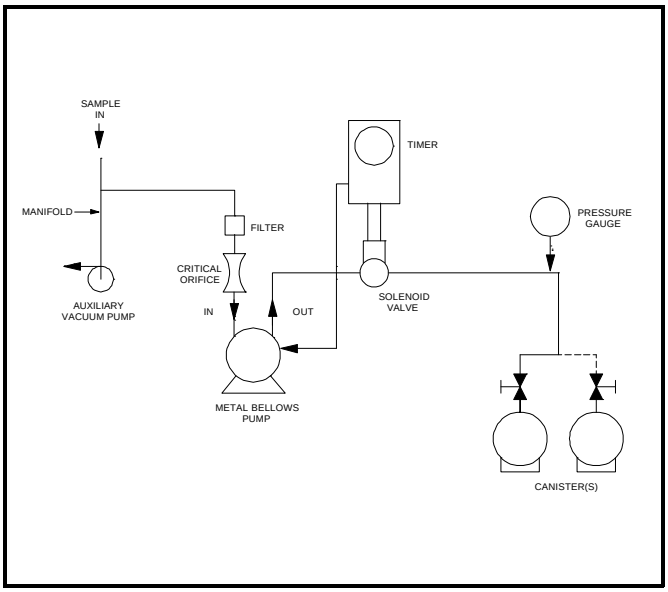


Figure 4-16. Compendium Method TO-14A sampling system using pressurized treated stainless steel canister(s)

In the in situ mode, a whole air sample is extracted directly from the ambient air and delivered to the analytical system for analysis on-site.

As illustrated in Figure 4-13, the analysis requires drawing a fixed-volume portion of the sample air, either from the canister or in situ, at a low flow rate through a glass-bead filled trap that is cooled to approximately -186°C with liquid argon.

The cryogenic trap simultaneously collects and concentrates the NMOC (either via condensation or adsorption) while allowing the methane, oxygen, etc., to pass through the trap without retention. The system is dynamically calibrated so that the volume of sample passing through the trap does not have to be quantitatively measured, but must be precisely repeatable between the calibration and the analytical phases. After the fixed-volume air sample has been drawn through the trap, a helium carrier gas flow is diverted to pass through the trap, in the opposite direction to the sample flow, and into an FID. When the residual air and methane have been flushed from the trap and the FID baseline restabilized, the cryogen is removed and the temperature of the trap is raised to approximately 90°C.

The NMOC compounds previously collected in the trap revolatilize due to the increase in temperature and are carried into the FID, resulting in a response peak or peaks from the FID. The area of the peak or peaks is integrated, and the integrated value is translated to concentration units via a previously-obtained calibration curve relating integrated peak areas with known concentrations of propane.

By convention, concentrations of NMOC are reported in units of parts per million carbon (ppmC), which, for a specific compound, is the concentration in units of part per million by volume (ppm_v) multiplied by the number of carbon atoms in the compound.

(f) *Organic Compendium Method TO-13A: Semi-Volatiles*. Organic Compendium Method TO-13A is used for the determination of benzo(a)pyrene [B(a)P] and other PAHs in ambient air. The 16 compounds which have been quantitatively analyzed by GC/FID and GC/MS using this method are:

Acenaphthene
Acenaphthylene
Anthracene
Benz(a)anthracene
Benzo(a)pyrene
Benzo(e)pyrene
Benzo(g,h,i)perylene
Benzo(k)fluoranthene

Chrysene
Dibenz(a,h)anthracene
Fluoranthene
Fluorene
Indeno(1,2,3-cd)pyrene
Naphthalene
Phenanthrene
Pyrene

In operation, ambient air is drawn at a flow rate of about 200 to 280 L/min into a high-volume sampler equipped with a quartz fiber filter and backup PUF or organic resin adsorbent cartridge (see Figure 4-15).

The sampling system (see Figure 4-14) is similar to Compendium Method TO-9A and consists of a vacuum pump capable of drawing an airflow of about 200 to 280 L/minute, dual sampling module, flow venturi, elapsed time indicator, 7-day skip timer, and an anodized aluminum shelter. The semivolatiles in the ambient air are retained on the filter or backup adsorbent cartridge.

The sampling period is about 4 to 24 hours, depending on the expected ambient pollutant concentration. After sampling, the samples are stored in an ice chest at 20°C until receipt at the analytical laboratory, at which time they are stored refrigerated at 4°C. The filter and cartridge are analyzed for PAHs using GC/MS, GC/FID, or high performance liquid chromatography (HPLC) with UV (to determine naphthalene, acenaphthylene, and acenaphthene) or fluorescence detectors (to determine the remaining PAHs). Sample holding time should not exceed 20 days.

The choice of PUF or XAD-2 resin as the filter backup adsorber depends on the target compounds of interest. XAD-2 is reported to have a higher collection efficiency for the more volatile PAHs (naphthalene, acenaphthylene, and acenaphthene) than PUF as well as a higher retention efficiency for both volatile and reactive PAHs. On the other hand, PUF adsorbers are easier to handle in the field and have been successfully used for collecting organochlorine pesticides and PCBs.

Some limitations of the method are that the collection efficiency from other compounds not listed in the method or identified elsewhere in the literature must be determined by the user. In addition, problems with baseline noise, baseline drift, peak resolution, and changes in sensitivity may occur in HPLC analysis. Also, heat, ozone, NO_2, and UV light may cause sample degradation. These problems should be addressed in the user prepared project specific SOP.

(g) *Organic Compendium Method TO-14A: Volatile Organic Compounds (-15° to 170°C)*. Organic Compendium Method TO-14A is used for the determination of VOCs in ambient air at HTRW sites.

Ambient air samples are collected using treated passivated stainless steel or silanized canisters; VOCs are subsequently separated by GC and measured by mass-selective detector or multidetector techniques.The 40 organic compounds that have been successfully collected in pressurized canisters by this method are:

Freon 12 (Dichlorodifluoromethane)
Methyl chloride (Chloromethane)

Freon 114 (1,2-Dichloro-1,1,2,2-tetrafluoroethane)
Vinyl chloride (Chloroethylene)
Methyl bromide (Bromomethane)
Ethyl chloride (Chloroethane)
Freon 11 (Trichlorofluoromethane)
Vinylidene chloride (1,1,-Dichloroethene)
Dichloromethane (Methylene chloride)
Freon 113 (1,1,2-Trichloro-1,2,2-trifluoroethane)
1,1-Dichloroethane (Ethylidene chloride)
cis-1,2-Dichloroethylene
Chloroform (Trichloromethane)
1,2-Dichloroethane (Ethylene dichloride)
Methyl chloroform (1,1,1-Trichloroethane)
Benzene (Cyclohexatriene)
Carbon tetrachloride (Tetrachloromethane)
1,2-Dichloropropane (Propylene dichloride)
Trichloroethylene (Trichloroethene)
cis-1,3-Dichloropropene (cis-1,3-dichloropropylene)
1,1,2-Trichloroethane (Vinyl trichloride)
Toluene (Methyl benzene)
trans-1,3-Dichlorpropene (trans-1,3-Dichloro propylene)
1,2-Dibromomethane (Ethylene dibromide)
Tetrachloroethylene (Perchloroethylene)
Chlorobenzene (Phenyl chloride)
Ethylbenzene
m-Xylene (1,3-Dimethylbenzene)
p-Xylene (1,4-Dimethylxylene)
Styrene (Vinyl benzene)
1,1,2,2-Tetrachloroethane
o-Xylene (1,2-Dimethylbenzene)
1,3,5-Trimethylbenzene (Mesitylene)
1,2,4-Trimethylbenzene (Pseudocumene)
m-Dichlorobenzene (1,3-Dichlorobenzene)
Benzyl chloride (α-Chlorotoluene)
o-Dichlorobenzene (1,2-dichlorobenzene)
p-Dichlorobenzene (1,4-dichlorobenzene)
Hexachlorobutadiene (1,1,2,3,4,4-Hexachloro-1,3- butadiene)

Compendium Method TO-14A represents two sampling procedures, depending on the type of sample collected: sub-atmospheric pressure sampling and pressurized canister sampling. Subatmospheric pressure sampling is used to take grab samples (duration 10 to 30 seconds) or time-integrated sample (duration 12 to 24 hours). The integrated samples are taken through a flow-restrictive inlet (i.e., mass flow controller) as illustrated in Figure 4-16. The canister is evaluated to 0.05 mm Hg; when opened to the atmosphere, the differential pressure causes the sample to flow into the canister. Pressurized sampling is used when longer-term integrated samples or higher volume samples are required. A pump and flow control device is used to achieve a final canister pressure of 103 to 206 kPa (15 to 30 psig). A metal bellows-type pump draws in air from the sampling manifold to fill and pressure the canister.

Subatmospheric pressure and pressurized canister sampling systems are commercially available and have been used as part of EPA's Toxic Air Monitoring Stations (TAMS), Urban Air Toxic Pollutant program (UATP), and the non-methane organic compound (NMOC) sampling and analysis program.

After the air sample is collected, the canister valve is closed, an identification tag is attached to the canister, and the canister is transported to a predetermined laboratory for analysis. Upon receipt at the laboratory, the canister tag data is recorded and the canister is attached to the analytical system. During analysis, water vapor is reduced in the gas stream by a Nafion® dryer (if applicable), and the VOCs are then concentrated by collection in a cryogenically-cooled trap, as illustrated in Figure 4-17.

The cryogen is then removed and the temperature of the trap is raised. The VOCs originally collected in the trap are revolatilized, separated on a GC column, then detected by one or more detectors for identification and

quantitation. The analytical strategy for Method TO-14A involves using a high-resolution GC coupled to one or more appropriate GC detectors As described in Paragraph 4.3, GC detectors can be divided into two groups: specific and nonspecific detectors. The nonspecific detectors include, but are not limited to, the NPD, the FID, the ECD, and the PID. The specific detectors include the MS operating in either the SIM mode or the SCAN mode, or the ion trap detector.

(h) *Organic Compendium Method TO-15: Volatile Organic Compounds (-75°to 120°C)*. Compendium Method TO-15 is distinguished from the TO-14A method in that it (1) addresses a more extensive set of compounds (the VOCs mentioned in Title III of the CAAA of 1990, which includes many VOCs that cannot be addressed by the TO-14 method), (2) uses GC/MS techniques as the only means to identify and quantitate target compounds; (3) establishes method performance criteria for acceptance of data, allowing the use of alternate but equivalent methods; and (4) includes variations in canister construction materials.

Compendium Method TO-15 sampling is identical to Method TO-14A. After sampling, the canister is returned to the laboratory for analysis. Compendium Method TO-15 uses the dry purge of solid adsorbents as a water management technique; a known volume of sample is directed from the canister and through a concentration trap. Prior to analysis, co-collected water vapor is reduced by dry purging the concentration trap without the loss of target compounds. After the drying and concentration steps are completed, the VOCs are thermally desorbed, entrained in a carrier gas stream, and carried onto a GC column for separation. As an alternative to the dry purge

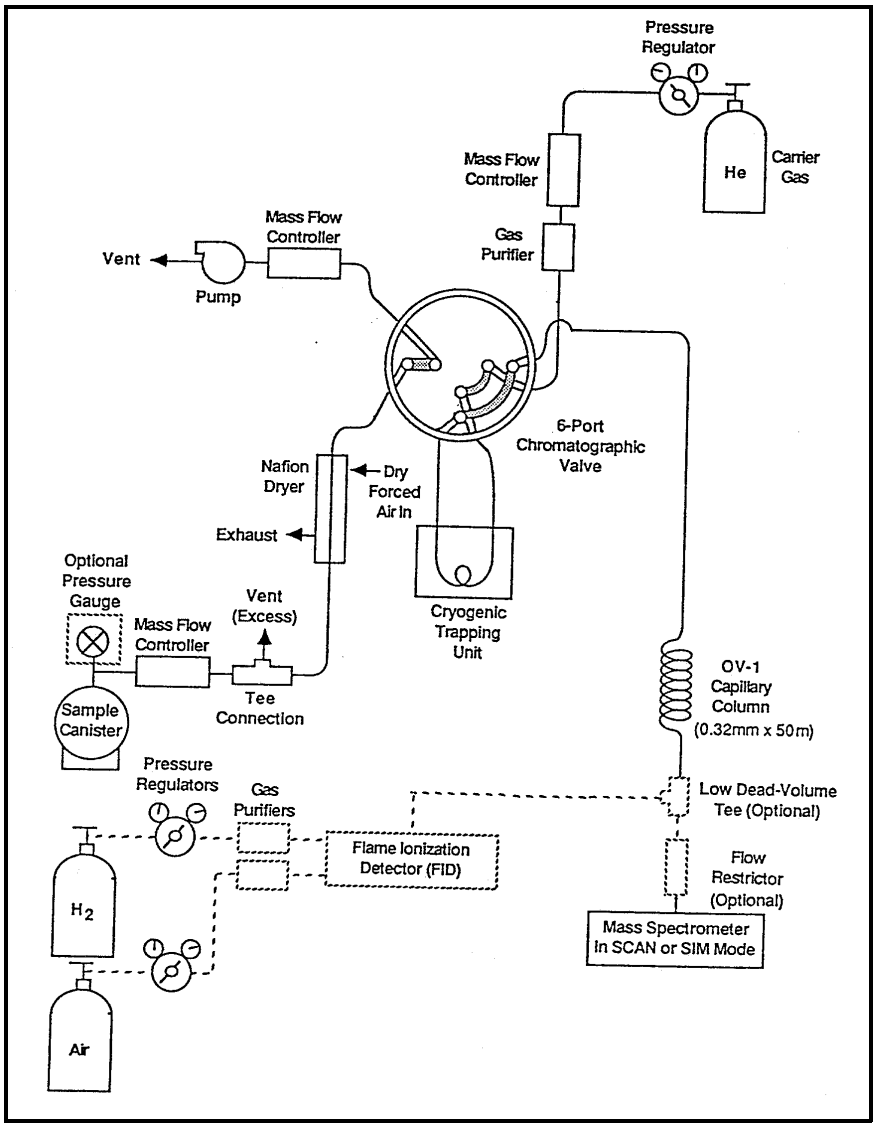


Figure 4-17. Compendium Method TO-14A analytical scheme

water management technique, the amount of water vapor in the sample can be reduced below any threshold for affecting the proper operation of the system by reducing the sample size. For example, a small sample can be concentrated on a cold trap and released directly to the GC column. The reduction in sample volume may require an enhancement of detector sensitivity. Other water management approaches are also acceptable as long as the approaches do not eliminate compounds on the target list.

The analytical strategy for Method TO-15 involves using a high resolution GC coupled to a mass spectrometer. If the mass spectrometer is a linear quadruple system, it is operated either by continuously scanning a wide range of mass to charge ratios (SCAN mode) or by monitoring selected ions indicative of a target list of compounds (SIM mode). If the mass spectrometer is based on a standard ion trap design, only a scanning mode is possible. Mass spectra for individual peaks in the total ion chromatogram are examined with respect to the fragmentation pattern corresponding to various VOCs and including the intensity of primary and secondary ions. The fragmentation pattern is compared with stored spectra taken under similar conditions to identify the compound. For any given compound, the intensity of the primary fragment is compared with the system response to the primary fragment for known amounts of the compound to establish the compound concentration that exists in the sample.

(i) *Organic Compendium Method TO-16: Volatile Organic Compounds (-15° to 170°C)*. Compendium Method TO-16 involves the use of FTIR for monitoring emissions from an HTRW sites. In operation, an IR source is set at one end of the site with a receiver at the other end of the site. The sample is the source emissions or ambient atmosphere along a line-of-sight between the source and detector. The current pathlength is limited to about 1,000 m but can be extended to 3 km with the addition of an auxiliary telescope. This design is the most useful mode of operation for fenceline monitoring and area source emission verification. There are several obvious advantages to using optical monitoring over conventional point sampling. They are:

- Spectra stored for later identification.
- Use as a survey screening tool.
- Real-time assessment of temporal and spacial profile of volatile organics from the site.
- Reasonable cost per analyte.
- Usability with a tracer release for dispersion modeling.

Optical sensing is effective for measuring a variety of inorganic gases and volatile organic gases that have absorption features in the infrared or ultra-violet spectrum.

The basic components of an extractive FTIR system include a transmitter, receiver, and electronic system. In operation, IR light projected across an open area and returned using a retro reflector to the optical detection system. The heart of the optical detection system is the Michelson-type interferometer.

(j) *Organic Compendium Method TO-17: Volatile Organic Compounds (-25° to 170°C)*. Compendium Method TO-17 is similar to Compendium Method TO-1 and TO-2 but allows for use of adsorbents other than Tenax®. Method TO-17 describes a procedure for the sampling and analysis of VOCs in ambient air at sub-ppb, ppb and ppm levels. The method is based on pumping a volume of air through a sorbent tube to collect and concentrate VOC pollutants. The VOCs are subsequently analyzed using a fully automated thermal desorption-capillary GC procedure:

- Stage 1: Sample transferred to preconcentrator step.
- Stage 2: Dry purge sorbent tube with ~200 mL pure inert gas before analysis, if required.
- Stage 3: Thermal desorption of the sorbent tube (primary desorption).
- Stage 4: Separation by high resolution capillary GC.
- Stage 5: Measurement by MS or conventional GC detectors.

The method is applicable to all vapor-phase organic air pollutants that meet the following criteria:

- Volatility range n-C3 to n-C20.

- Compatible with standard GC analysis.

(2) *EPA Inorganic Compendium.*

(a) *Inorganic Compendium Chapter IO-1: Continuous Measurement of PM_{10} in Ambient Air*. Inorganic Compendium Chapter IO-1 contains EPA equivalent instrumental methods for PM_{10} that give a continuous measurement of ambient PM_{10} concentration. The method addresses two different measurement principles that have received EPA's approval as equivalent methods: the beta attenuation monitor (BAM) uses beta radiation, and the tapering element oscillating microbalance (TEOM®) uses an oscillating pendulum as the measurement technology. Those methods that compose Chapter IO-1 of the Inorganic Compendium are:

- Inorganic Compendium Method IO-1.1: Continuous Monitoring of Ambient PM_{10} Concentration Using the Graseby PM_{10} Beta Attenuation Monitor.

- Inorganic Compendium Method IO-1.2: Determination of PM_{10} in Ambient Air Using the Thermo Beta Gauge Automated Particle Sampler.

- Inorganic Compendium Method IO-1.3: Determination of PM_{10} in Ambient Air Using the R&P Continuous TEOM® Particulate Sampler.

Unlike the reference methods, the equivalent methods allow concentration to be tracked in near real-time. This feature is useful when parameters such as the diurnal variation in concentration or the change in concentration associated with certain activities on the HTRW site are of interest.

Compendium Method IO-1.1 utilizes the Graseby beta gauge monitor, which directly measures particulate mass at concentrations of 0.005 to 20 milligrams per cubic meter (mg/m^3) on a real-time basis using the beta attenuation technique. This instrument provides half-hourly and daily averages and affords the potential for limited subsequent chemical analysis of the particulate samples. With certain specifications, the Andersen instrument has been designated as an equivalent method for determining 24-hour average PM_{10} concentration in ambient air by the EPA under Designation No. EQPM-0990-076, effective September 18, 1990. The monitor described in detail in Method IO-1.1 presents the configuration and operation of the instrument as an equivalent method for PM_{10}.

The Graseby beta instrument operates by drawing ambient air through a PM_{10} inlet head at a flow rate volume of 16.7 liters per minute. The air containing PM_{10} enters the instrument where it is pulled through the glass fiber filter tape, and the particles are deposited on the tape. Low level beta radiation is emitted from a stainless steel capsule, containing Krypton-85 gas, towards the filter tape containing deposited PM_{10}. The particle matter on the tape reduces the intensity of the beta radiation reaching the measuring chamber on the opposite side of the tape. To compensate for the effect of the filter tape on the reduction of the level of beta radiation, the source directs a second beam of beta particles through a "foil" that mimics clean filter tape to a second measuring chamber (compensation chamber). No airflow is directed to the compensation foil so the effect of the foil on the beta radiation intensity remains constant. The instrument compares the measurement of the

compensation foil to the measurement of the filter tape with deposited PM_{10} to determine the mass of the particulate matter. Because changes in temperatures, pressure, or humidity can affect PM_{10} measurement of the filter tape, the measurements made through the compensation foil are impacted to the same degree. The foil measurements provide baseline data to compensate for these meteorological effects. This monitor is less sensitive to temperature, pressure, and humidity fluctuations than some other types of continuous particle monitors because of the compensation foil measurements that provide baseline data. Because the measuring mechanism lacks moving parts, the instrument is not as sensitive to vibrational effects as other types of continuous particulate monitors.

The Graseby monitor has certain limitations or interferences. In high-humidity or rainy climates, water may collect on the filter tape and cause artificially high mass readings. In these same climates, where the instrument is housed in an air-conditioned environment, the ambient air inlet tube should be insulated to avoid condensation or the inlet tube heater used to ensure that any water drawn into the unit is vaporized. For the specific beta particle source used in this instrument, any replacement or maintenance work on the source may only be performed by trained personnel with radiological authorization.

Compendium Method IO-1.2 uses the Thermo beta gauge monitor, which operates under the same basic principles as the Graseby monitor, but with some differences. This instrument was designated as an equivalent method for PM_{10} by the EPA under Designation No. EQPM-0391-081, effective March 5, 1991. The Thermo monitor can measure ambient mass concentration with a resolution of about 3 micrograms per cubic meter ($\mu g/m^3$) for a 1-hour sampling period. A constant volumetric flow rate for the PM_{10} inlet of 18.9 L/min is used compared to the 16.67 L/min for the Graseby unit. A major difference between the two monitors is the beta source. The Thermo monitor uses a carbon-14 beta source compared to Krypton-85 gas for the other monitor. The carbon-14 source does not require a license by the Nuclear Regulatory Commission, whereas the Krypton-85 does.

Different from the β-gauges, the Inorganic Compendium Method IO-1.3 uses the Rupprecht and Pataschnick (R&P) Continuous PM_{10} Monitor, which is based upon a tapering element oscillating microbalance (TEOM®) as a filter-based measurement system to continuously measure particulate mass at concentrations between 5 $\mu g/m^3$ and several grams per cubic meter (g/m^3) on a real-time mass monitoring basis. The instrument calculates mass rate, mass concentration, and total mass accumulation on exchangeable filter cartridges that are designed to allow for future chemical and physical analysis. In addition, this instrument provides for hourly and daily averages. This system operates on the principal that particles are continuously collected on a filter cartridge mounted on the tip of a tapered hollow glass element. The element oscillates in an applied electric field. With this monitor, particle-laden air enters through an air inlet and then passes to the sensor unit containing the patented microbalance system. The inlet system may or may not be equipped with an optional sampling head to preseparate particles at either a 2.5 or 10 μm diameter. The R&P PM_{10} inlet is designed to allow only particulate matter $\leq$10 μm in diameter to remain suspended in the sample air stream as long as the flow rate of the system is maintained at 16.67 L/min. The monitor can be operated as a TSP monitor or as a PM_{10} monitor.

In operation, the sample stream passes into the microbalance system, which consists of a filter cartridge and oscillating hollow tube, where the stream is heated to a predetermined temperature. The filter cartridge is a half-inch diameter thin aluminum base (foil-like) assembly. A water resistant plastic cone, which fits onto the

oscillating element, is attached to the aluminum base. An automatic flow controller pulls the sample stream through the monitor at flow rates between 0.5 and 5 L/min. The wider end of the hollow element is fixed to a platform and is vibrated at its natural frequency. The oscillation frequency of glass element is maintained based on the feedback signal from an optical sensor.

As mass accumulates on the filter cartridge, the resonant frequency of the element decreases, resulting in a direct measurement of inertial mass. Based upon the direct relationship between mass and frequency, the monitor's microcomputer calculates the total mass accumulation on the filter, and the mass rate and mass concentration in real-time.

The TEOM® monitor is very sensitive to mass concentration changes and can provide precise measurements for sampling durations of 1 hour or less. To achieve this level of precision, the hollow glass element must be maintained at a constant temperature to minimize the effects of thermal variations. Because the instrument's primary operating mechanism is the microbalance system, the instrument should be isolated from mechanical noise and vibrations as much as possible. The operating temperature of the element can be lowered to minimize the potential particle loss bias for more volatile compounds but must be maintained above the maximum ambient temperature encountered during the field sampling.

(b) *Inorganic Compendium Chapter IO-2: Time-Integrated Measurements of Suspended Particulate Matter (SPM) in Ambient Air*. Inorganic Compendium Chapter IO-2 contains both reference and equivalent time-intergrated methods for monitoring total SPM, PM_{10} and $PM_{2.5}$ concentration. These methods that compose Chapter IO-2 are:

- Method IO-2.1: Sampling of Ambient Air for Suspended Particulate Matter (SPM) Using High Volume (HV) Sampler.
- Method IO-2.2: Sampling for Suspended Particulate Matter in Ambient Air Using a Dichotomous Sampler.
- Method IO-2.3: Sampling of Ambient Air for Suspended Particulate Matter Using Low Volume Partisol® Sampler.

Inorganic Compendium Method IO-2.1, Suspended Particulate Matter (SPM) Monitoring Using High Volume (HV) Sampler, is the EPA reference method for TSP and is codified at 40 CFR 50, Appendix B. This method uses a high-volume sampler (hi-vol) to collect particles with aerodynamic diameters of approximately 100 μm or less. The hi-vol samples 40 to 60 ft^3/min of air with the sampling rate held constant over the sampling period. The hi-vol's design causes the TSP to be deposited uniformly across the surface of the filter. The TSP hi-vol can be used to determine the average ambient TSP concentration over the sampling period, and the collected material can subsequently be analyzed to determine the identity and quantity of inorganic metals present in the TSP.

Modifications to the inlet of the sampler used in Compendium Method IO-2.1 allows the measurement of PM_{10}. The PM_{10} hi-vol is identical to the TSP hi-vol except that it is equipped with an inlet that directs only PM_{10} particulate matter to the filter.

The Federal reference method for PM_{10} measurements is based on particulate selection by inertial separation followed by filtration and gravimetric determination of the PM_{10} mass on the filter substrate. The referenced method for PM_{10} is codified at 40 CFR 50, Appendix J. The standard for this method specifies the features for a reference PM_{10} measurement method. These features are summarized as follows:

- The sampling inlet has a cut-point of 10 $\pm$0.5 μm aerodynamic diameter, as determined in a wind tunnel using liquid particles of specified diameter at specific wind speeds.

- Flow-rate remains stable over a 24-hour period, independent of filter loading, within $\pm$5 percent of the initial average flow reading and within $\pm$10 percent of the initial flow rate for instantaneous flow measurements.

- Measurement precision for a 24-hour period should be within $\pm$5 $\mu g/m^3$ for concentrations less than 80 $\mu g/m^3$ or $\pm$7 $\mu g/m^3$ of measured PM_{10} for concentrations greater than 80 $\mu g/m^3$.

- For a nominal air volume sampled over a 24-hour period, the filter media should collect more than 99 percent of a 0.3 μm particles and have an alkalinity of <25 microequivalents per gram and a net equivalent weight gain or loss of not more than 5 $\mu g/m^3$.
- Prior to weighing, the filter should be equilibrated at constant temperature ($\pm$3 percent) between 15° and 30°C and constant relative humidity ($\pm$5 percent) between 20 and 45 percent.

Inorganic Compendium Method IO-2.2, Dichotomous Sampler for Monitoring PM_{10} and $PM_{2.5}$, is a method for determining of inhalable particles with diameters of less than 10 micrometers.

A dichotomous sampler is used to separate the particles by size, into coarse particles (2.5-10 μm) and fine particles (less than 2.5 μm). A ring-mounted 37-millimeter Teflon® filter is used to collect particles.

In operation, the particles enter the sampler inlet at a flow rate of 17.6 L/min where they are separated into fine (less than 2.5 μm) and coarse (2.5-10 μm) fractions by a virtual impactor. Constant air flow through the system is maintained by a mass flow controller. The sampling duration usually varies from 12 to 24 hours depending upon experimental design and amount of ambient air particulate present. The particles are collected on 37 mm diameter Teflon® filters. Filters are analyzed for specific trace metals by X-ray fluorescence (XRF) spectrometry.
Inorganic Compendium Method IO-2.3, Partisol Samplers, is a microprocessor-controlled manual sampler with a unique set of features that make it a suitable platform for the measurement of particulate concentration, acid aerosol, and other constituents found in the atmosphere. When equipped with a PM_{10} inlet and operated in its most basic mode, the hardware performs the same function as traditional high-volume PM_{10} samplers. For some apportionment or traffic studies, the device can be set up to sample by wind velocity and/or direction, or by time of day.

In operation, ambient air is drawn through a low flow (16.7 L/min) PM_{10} or $PM_{2.5}$ inlet where particle size selection takes place. The particulate-laden air is then directed through a collection filter composed of either quartz, Teflon®-coated glass, or Teflon®, where the particulate matter is collected. A mass flow control system maintains the sample flow through the system at the prescribed volumetric flow using information from sensors

that measure the ambient temperature (°C) and ambient pressure (atmospheres). A piston pump provides the vacuum necessary to draw the sample stream through the inlet, filter, and mass flow controller. A microelectronics system provides the user with menu-driven programming and diagnostic and data storage capabilities.

The sample filter is conditioned and weighed both before and after sample collection to determine the amount of mass collected during the sampling period, which is 24 hours for EPA reporting purposes. As is the case with all filter-based manual samplers, proper filter handling is an important element in the computation of valid mass concentration results.

As a general rule, a PM_{10} sampler is used, except for the following two cases, at HTRW sites: (1) when deposition (particularly for larger particles) is of concern because of the potential for ingestion through contact with surfaces (i.e., lead ingestion); or (2) when toxic compounds (usually metals) may be present in the larger size particles. Usually this occurs when the source of the particulate matter is from grinding or erosion of soil or ore. If more detailed information on both inhalation and ingestion as routes of exposure is required, both TSP and PM_{10} sampling may be needed.

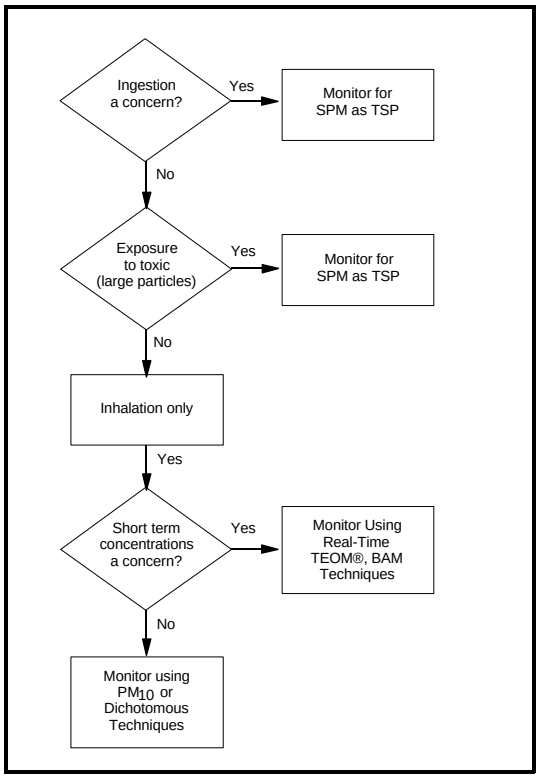


Figure 4-18. Example of a PM_{10} Sampling Decision Tree for HTRW sites.

In deciding between integrated (PM_{10} and dichotomous) and near real-time samplers (BAM and TEOM®) for PM_{10}, the following points should be considered. Generally, integrated sampling is preferred for the compounds of concern. Near real-time samplers are used if short-term variations in SPM are of interest. The information from the BAM and TEOM® would be used to estimate short-term concentration levels of certain SPM constituents with certain assumptions about time variation in composition of SPM. At this point, analysis of samples from BAM and TEOM® is experimental and needs to be further developed.

If only SPM is of interest, the PM_{10} hi-vol sampler with size selective inlet and quartz fiber filter is generally used because it allows for the collection of a large volume of air sample. However, analysis for some particulate compounds may not be as sensitive on quartz fiber filters. In that case, the dichotomous sampler would be used. Separation of fine particles from coarse particles is also possible with the dichotomous sampler, making it preferable when doing a more refined risk assessment.

In deciding between the BAM and TEOM® sampler, factors such as cost, need for a climate-controlled shelter, etc., must be considered. Figure 4-18 presents a PM_{10} sampling decision tree, which can be used for HTRW sites involving

the perimeter air monitoring program. Table 4-13 discusses the advantages/disadvantages associated with sampling methods discussed above.

(c) *Inorganic Compendium Chapter IO-2.3: Chemical Species Analysis of SPM on Filters*. Inorganic Compendium Method IO-2.3 includes five options for quantitative analysis of particles collected on filter materials as discussed in Inorganic Compendium Chapters IO-1 and IO-2. They are:

- Atomatic absorption (AA) spectroscopy (Compendium Method IO-3.2).
- XRF spectroscopy (Compendium Method IO-3.3).
- Inductively coupled plasma (ICP) atomic emission spectroscopy (Compendium Method IO-3.4).
- Inductively coupled plasma/mass spectroscopy (ICP/MS) (Compendium Method IO-3.5).
- Proton induced X-ray emission (PIXE) spectroscopy (Compendium Method IO-3.6).
- Neutron activation analysis (NAA) (Compendium Method IO-3.4).

Several factors influence the selection of an analysis option. These include cost, the elements for which the analytical method can be used, the number of samples and number of elements to be determined per sample, and sensitivity for the elements of interest. Table 4-14 illustrates the comparison of the analytical techniques with their associated weaknesses and strengths.

In XRF analysis, the sample is irradiated with one or more X-ray beams, and the elements in the sample emit X-rays at characteristic wavelengths. The wavelengths detected indicate which elements are present, and the quantity of each element is determined from the intensity of the X-rays at each characteristic wavelength. XRF analysis can be used for all elements with atomic weights from 11 (sodium) to 92 (uranium), and multiple elements can be determined simultaneously. This analysis technique is nondestructive and requires minimal sample preparation--the filter is inserted directly into the instrument for analysis. This technology is relatively inexpensive, but the detection limit is higher than other analysis techniques. Typically, analytical costs are about $100 per sample. Analysis by XRF typically involves the collection of PM by dichotomous sampler, although a PM_{10} hi-vol sampler with quartz fiber filter or cellulose filter can also be used.

In ICP analysis, the sample is excited using an argon plasma “torch.” When the excited atoms return to their normal state, each element emits a characteristic wavelength of light. The wavelengths detected and their intensity indicate how much of which elements are present. Up to 48 elements can be determined simultaneously. As with FAA and GFAA, the PM sample must be extracted and digested for ICP analysis, and the material introduced into the instrument is destroyed during analysis. An ICP instrument is more costly than FAA or GFAA instruments. The detection limit for GFAA is better than that for ICP for most elements. Analysis by ICP typically involves collection of PM by a hi-vol sampler.

Two atomic absorption (AA) analysis options are included in Inorganic Compendium Chapter IO-3: FAA and GFAA. The measurement principle is the same; the two options differ in how the sample is introduced into the instrument. Both types of atomic absorption spectroscopy involve irradiating the sample with light of a single wavelength and measuring how much of the input light is absorbed. Each element absorbs light at a characteristic wavelength; therefore, analysis for each element requires a different light source and only one element can be determined at a time. Analysis by AA typically involves collection of PM by a hi-vol sampler.

Table 4-13.
Advantages/Disadvantages Associated with Sampling Methods Presented in Inorganic Compendium Method IO-1

Sampling method	Advantages	Disadvantages
Hi-Vol Sampler (Reference Method)	•Collects TSP/PM_{10} uniformly across the surface of filter •Can be used to determine average TSP/PM_{10} concentration over the sampling period •Allows analysis of filter for metals •Because of higher flow rate, collects more material so lower ambient concentration of inorganic material can be detected •Simple to operate	•Requires 110V, 20-amp electrical service •Sampler is large and bulky and is not easily moved
Dichotomous Sampler (Reference Method)	•Capable of collecting size-fractionated PM •Operates at low flow rates, allowing for use of filter media which would clog quickly at high flow rates •Fairly low power requirements - could be adapted for remote use •Small, easy to handle	•Fairly complicated to operate •Small sample volume, which makes chemical analysis of collected PM difficult
BAM (Equivalent Method)	•Allows for real-time measurement of particulate concentrations (PM-10) •Reduces need for frequent filter changes because it uses a filter strip on which chemical analyses can be performed •Primary operating mechanism lacks moving parts, and is therefore not sensitive to vibrations that might adversely affect the accuracy of other continuous monitors •Less sensitive to temperature, pressure, and humidity fluctuations than other continuous monitors	•Cannot be used to differentiate or quantitate heavy metals and other PM of concern
TEOM® (Equivalent Method)	•Allows for real-time measurement of particulate concentrations	•Cannot be used to differentiate or quantitate heavy metals and other PM of concern •Sensitive to noise, temperature fluctuations

Table 4-14
Advantages/Disadvantages Associated with Analytical Options Discussed in Inorganic Compendium Chapter IO-3

	ADVANTAGE	DISADVANTAGE
FAA	• easy to use • extensive applications • low detection limits	• higher concentration • sample dissolution required • one (1) element at a time
GFAA	• well documented applications • lower detection limits than Flame AA	• limited working range sample • low sample throughput • one element at a time • more operator skill
ICP	• multi-element • high sample throughput • well documented applications • intermediate operator skill • linear range over 5 orders of magnitude	• more expensive (~120K) • sample dissolution is required • other elements can interfere
ICP / MS	• multi-elements • low concentrations • isotopic analysis • intermediate operator skills	• most expensive (~250K) • limited documented applications
PIXE	• multielement • non-destructive • minimal sample preparation	• standard/sample must match closely (matrix) • matrix offsets and background impurities may be a problem
XRF	• multielement • non-destructive • minimal sample preparation	• standard/sample must match closely (matrix) • matrix offsets and background impurities may be a problem
NAA	• multielement • non-destructive • minimal sample preparation • % to ppb range • high sample throughput • well documented applications	• some elemental interferences • standard sample matrix corrections • required access to research nuclear reactor

In FAA, the sample is atomized and introduced into the optical beam using a flame, typically air/acetylene or nitrous oxide/acetylene. In GFAA, a graphite furnace electrometer atomizer is used. These analytical techniques are destructive and require that the sample be extracted or digested in order to introduce it into the system in solution. GFAA instrumentation is the more expensive of the two. Typically, analytical costs are about $225 per sample. The detection limit for FAA is lower than for XRF; the detection limit for GFAA is typically about two orders of magnitude better than FAA.

Analysis by ICP/MS uses argon plasma torch to generate elemental ions for separation and identification by mass spectrometry. This analysis technique allows for greater than 60 elements to be determined simultaneously, and even the isotopes of elements can be determined. For ICP/MS analysis, the PM sample must be extracted or digested, and the analysis is destructive. ICP/MS analysis is the most expensive of those included in this method, but has the greatest sensitivity (lowest detection limit).

PIXE analysis is very similar to XRF analysis in that the sample is irradiated by a high energy source, in this case high energy protons, to remove inner shell electrons. Fluorescent X-ray photons are detected using the same detection methods as XRF. Analysis by PIXE also typically involves collecting SPM by dichotomous sampler.

Some of the analytical techniques listed above are typically used only with particular sampling methods. Figure 4-19 illustrates the relationships between sampling technologies and compatible analytical techniques. Furthermore, the type of filter medium used to capture the sample is a factor in the choice of analytical technique and vice-versa.

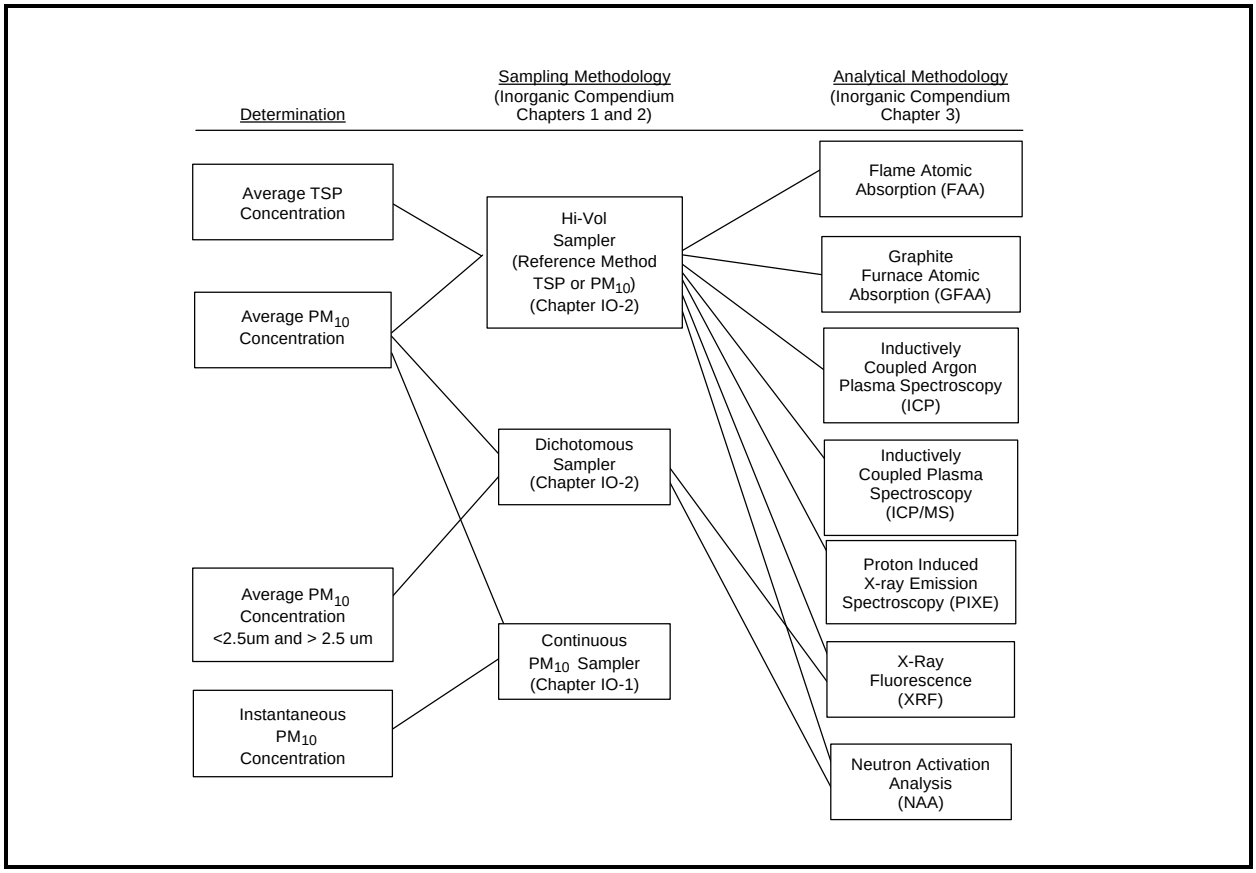


Figure 4-19. Relationship between sampling technologies and analytical techniques discussed in EPA's Inorganic Compendium.

Most importantly, the choice of analytical method will depend on the inorganic compounds of interest and the detection limits desired. Figure 4-20 provides a relative comparison of the ranges of detection limits that are typically for the various techniques. Table 4-15 provides a more detailed summary of the species measured and the respective minimum detection limits.

While factors such as element specificity and sensitivity are critically important, considerations such as cost and throughput (the number of samples and number of elements to be determined per sample) are also very important. Figure 4-21 provides a comparison of the various available analytical options discussed in Inorganic Compendium Method IO-3.

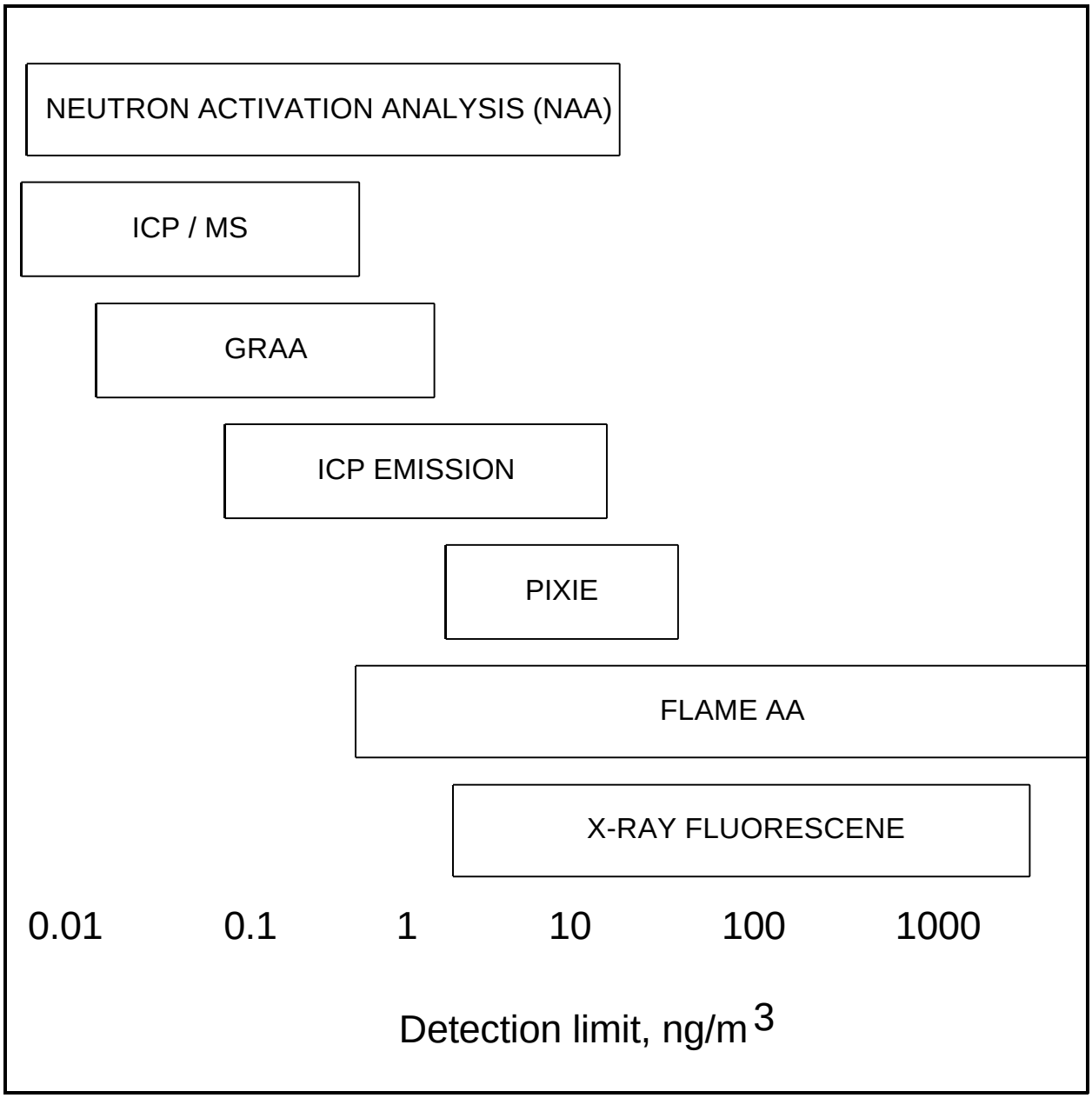


Figure 4-20. Typical detection limits for Inorganic Compendium Chapter IO-3 analytical options

Table 4-15
Minimum Detection Limits (ng/m^3) of Ambient Air Samples For Different Inorganic Compendium Chapter IO-3 Analytical Methods[a]

	Analytical Technique						
Species	**NAA**	**XRF**	**PIXE**	**AAS**	**GFAA**	**ICP**	**ICP/MS**
Ag	0.12	6	NA	4	0.005	1	1.01
Al	24	5	12	30	0.01	20	1.01
As	0.2	0.8	1	100	0.2	50	1.10
Au	NA	2	NA	21	0.1	2.1	NA
Ba	6	25	NA	8	0.04	0.05	NA
Be	NA	NA	NA	2	0.05	0.06	0.02
Br	0.4	0.5	1	NA	NA	NA	NA
Ca	94	2	4	1	0.05	0.04	NA
Cd	4	6	NA	1	0.003	0.4	0.02
Ce	0.06	NA	NA	NA	NA	52	NA
Cl	5	5	8	NA	NA	NA	NA
Co	0.02	0.4	NA	6	0.02	1	0.01
Cr	0.2	1	2	2	0.01	2	0.01
Cs	0.03	NA	NA	NA	NA	NA	NA
Cu	30	0.5	1	4	0.02	0.3	0.01
Eu	0.006	NA	NA	21	NA	0.08	NA
Fe	4	0.7	3	4	0.02	0.5	0.01
Ga	0.5	0.9	1	52	NA	42	NA
Hf	0.01	NA	NA	2,000	NA	16	NA
Hg	NA	1	NA	500	21	26	NA
I	1	NA	NA	NA	NA	NA	NA
In	0.006	6	NA	31	NA	63	NA
K	24	3	5	2	0.02	NA	NA
La	0.05	30	NA	2,000	NA	10	NA
Mg	300	NA	20	0.3	0.004	0.02	0.02
Mn	0.12	0.8	2	1	0.01	0.1	0.02
Mo	NA	1	5	31	0.02	5	0.02
Na	2	NA	60	0.2	<0.05	NA	NA
Ni	NA	0.4	1	5	0.1	2	0.02
P	NA	3	8	100,000	40	50	NA
Pb	NA	1	3	10	0.05	10	0.01
Pd	NA	5	NA	10	NA	42	NA
Rb	6	0.5	2	NA	NA	NA	NA
S	6,000	2	8	NA	NA	10	NA
Sb	0.06	9	NA	31	0.2	31	0.01
Sc	0.001	NA	NA	50	NA	0.06	NA
Se	0.06	0.6	1	100	0.5	25	1.10
Si	NA	3	9	85	0.1	3	NA
Sm	0.01	NA	NA	2,000	NA	52	NA
Sn	NA	8	NA	31	0.2	21	0.01
Sr	18	0.5	2	4	0.2	0.03	NA
Ta	0.02	NA	NA	2,000	NA	26	NA
Th	0.01	NA	NA	NA	NA	63	NA
Ti	65	2	3	95	NA	0.3	0.01
Tl	NA	1	NA	21	0.1	42	0.01
U	NA	1	NA	25,000	NA	21	0.01
V	0.6	1	3	52	0.2	0.7	0.01
W	0.2	NA	NA	1,000	NA	31	0.01
Y	NA	0.6	NA	300	NA	0.1	0.01
Zn	3	0.5	1	1	0.001	1	0.01
Zr	NA	0.8	3	1,000	NA	0.6	

Table 4-15 (continued)

	Analytical Technique						
Species	**NAA**	**XRF**	**PIXE**	**AAS**	**GFAA**	**ICP**	**ICP/MS**
Cl	NA	NA	NA	NA	NA	NA	NA
NH_4	NA	NA	NA	NA	NA	NA	NA
NO_3	NA	NA	NA	NA	NA	NA	NA
SO_4	NA	NA	NA	NA	NA	NA	NA
Elemental Carbon	NA	NA	NA	NA	NA	NA	NA
Organic Carbon	NA	NA	NA	NA	NA	NA	NA

[a] Minimum detection limit is three times the standard deviation of the blank for a filter of 1 mg/cm^2 areal density.

ICP = Inductively Coupled Plasma Emission Spectroscopy.
AAS = Flame Atomic Absorption Spectrophotometry.
PIXE = Proton Induced X-ray Emissions.
XRF = X-ray Fluorescence.
NAA = Instrumental Neutron Activation Analysis.
GFAA = Graphite Furnace Atomic Absorption Spectroplometry
ICP/MS = Inductively Coupled Plasma Emission/Mass Spectroscopy.

Unfortunately, no one analytical methods can address all data quality objectives for a particular ambient air monitoring program. Each method has its own attributes, specifies, advantages, and disadvantages, as previously discussed. However, Inorganic Compendium Chapter IO-3 attempts to bring together into one chapter the various analytical option, in a step-by-step methodology, to facilitate accurate and reliable data for SPM and metal concentration in the ambient air.

4-5. System Alarm Configuration

Because personnel are not always available to review data as it is generated by an air monitoring network, a system alarm is necessary to alert on-site staff to periods when their oversight is necessary. Such an alarm system must monitor instrumentation to determine when emissions of targeted compounds exceed action levels or when system upsets occur that could prevent the monitoring system from detecting upsets. The alarm system must then be capable of alerting on-site staff of these conditions. The following paragraphs discuss some specific considerations pertinent to the design of an alarm system. These considerations include the components of an alarm system, conditions that should be considered as triggers, and suggested methods of notification.

There are three components to an air monitoring alarm system. They are the air monitoring instrument, a trigger circuit, and a notification system.

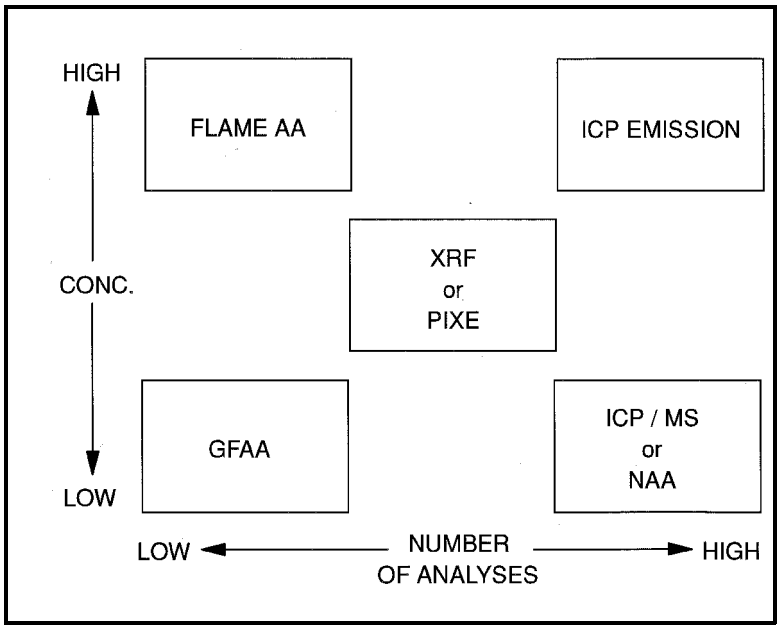


Figure 4-21. Throughput of analytical options in Chapter IO3

Most real-time air monitors have all three of these components integral to the instrument in the form of audible alarms. These alarms could be configured to alert personnel within the Analytical Center to excessive concentrations or instrument upsets. However, these alarms are typically not able to alert staff outside of the Analytical Center.

In the event that the selected air monitoring instrument is not equipped with an alarm feature, a computer with an analog to digital data card, a commercially available data logger, or a custom circuit can be used as a trigger for the alarm system.

A commercially available home security usually provides the most reliable and cost effective alert mechanism. These systems are available with time-proven smoke alarms, auto-dialers, weather-protected alarms, and backup power supplies. Other components are easily adapted as needed.

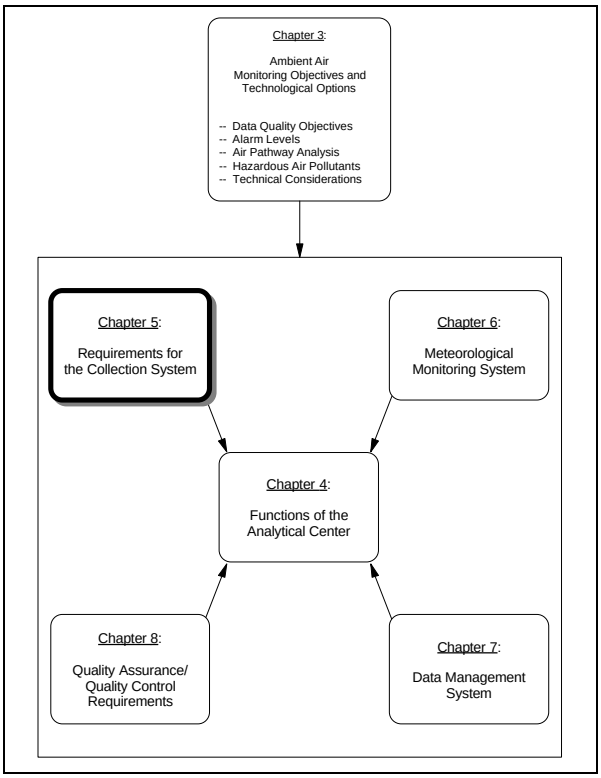
To be effective, the alarm system must be designed to monitor real-time air sampling instrumentation for exceedences of all project specific action levels. If backup monitors are available for use during failures of the primary real time monitoring system, these instruments must also be monitored by the alarm system. In addition, the alarm system should be designed to alert on-site staff to conditions that could adversely affect the operation of monitors or the alarm system itself. Some of these potential process upsets might include line voltage spikes or power outages, high wind speeds, or aberrations of critical instrumentation parameters (e.g., high or low over temperature, low flow rates, etc.).

The alarm system must be capable of notifying on-site staff, regardless of their location, whenever the air monitoring network is required to operate. If a staff member is always in the building or buildings in which the real-time air monitoring instrumentation is operating, then the alarm must be loud enough to be heard throughout the building, regardless of distracting activity. If a staff member will always be on the property but not necessarily in the same building(s) as the instrumentation monitors, during periods when the monitors are required to operate, an outdoor audible alarm system can be established in addition to the building alarm(s). If there will not always be a staff member on site during periods when the alarm system is required to operate, a remote notification system must be established. This system might include an

alarm to alert a guard, other on-site personnel, or a commercial security company by utilizing a auto-dialer to telephone or page air monitoring staff, or a frequency modulated (FM) transmitter.

SUMMARY OF REQUIREMENTS FOR THE COLLECTION SYSTEM

The collection system refers to the process by which a representative system is collected from the point of extraction, transferred to the analytical system, and analyzed. The sample must be handled in a manner that preserves its original physical form and chemical composition. Any contaminants in the sample must be removed prior to analysis.



SECTION I: INTRODUCTION
- Goal of the Collection System
- Collection System Overview

SECTION II: SYSTEM DESIGN, STRUCTURE, AND COMPONENTS

SECTION III: SAMPLING SYSTEM INLET PARTICULATE CONTROL
- Introduction
- Filter Selection
- Inlet Placement/Probe Height

SECTION IV: SAMPLE TRANSPORT REQUIREMENTS
- Sample Transfer Line
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- Sample Pumps

SECTION V: SAMPLE CONDITIONING SYSTEM
- Condensation
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SECTION VI: ROUTINE MAINTENANCE AND CORRECTIVE ACTION REQUIREMENTS
- Routine Maintenance
- Corrective Action Requirements

SECTION VII: TIME-INTEGRATED AND REAL-TIME PM_{10} MONITORING REQUIREMENTS FOR COLLECTION SYSTEM
- Description of Sampling Systems
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SECTION VIII: AUDITING OF COLLECTION SYSTEM

The goal of the collection system is to extract a sample that is representative of the ambient air at the site. Chapter 5 discusses the components and requirements of this system that are necessary to ensure sample integrity.

Panel 5-1. Overview of the Requirements for the Collection System.

5-1. Introduction

The goal of any perimeter air monitoring system at an HTRW site is to collect a representative sample from the point of extraction, transfer that sample to the analytical system, and determine the concentration of the analytes of concern without compromising sample integrity. The extracted sample should represent a subset of the ambient air at the HTRW site and be collected and handled in a manner that preserves its original physical form and chemical composition and that prevents changes in the concentration of the analytes from outside contamination. If other species are present in the sample gas that interfere, they must be removed prior to analysis. This removal may involve filtering or scrubbing the gas sample before delivering it to the analyzer compartment in the Analytical Center. It should be remembered during the FFMS system design that depending on the site environment, components of interest and collection system characteristics, it may not be necessary to heat the sample transport lines.

5-2. System Design, Structure, and Components

The extraction of a representative sample from a point and its transport to the analyzer in the Analytical Center as part of a volatile FFMS at a HTRW site must involve three major subsystems to ensure the integrity of the sample. The three subsystems, as identified in Table 5-1 and illustrated in Figure 5-1, are sample inlet, sample transport, and sample conditioning.

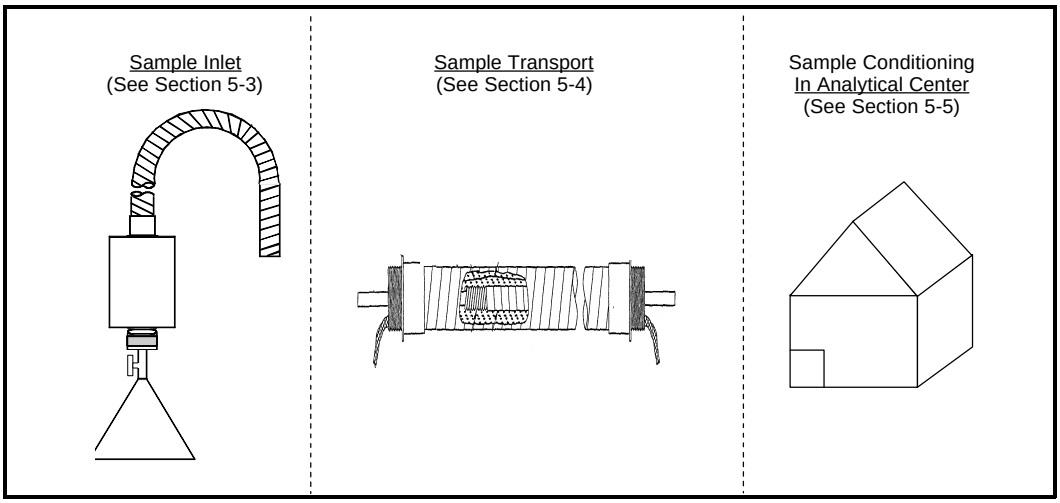


Figure 5-1. Example components of the sample collection system for FFMS

Table 5-1
Example of Subsystems of the Collection system of a Real-time VOC FFMS

Sample Inlet	Sample Transport	Sample Conditioning
-Probe	-Heated Transfer Lines	-Moisture Removal
-Primary Coarse Particulate Filter	-Sample Pumps	-Secondary Fine Particulate Filter
-Audit Gas Connection	-J-Boxes for Joining Heat Trace Line Segments	-Calibration Gas System Injection
-Flow Measurement Connection		-Flow Measurement Control Device

- **Sample inlet**--The purpose of the sample inlet system is to extract a representative sample from the ambient air, minimize the influence of moisture, and remove coarse particulate matter from the gas stream to prevent contamination of downstream components. Figure 5-2 illustrates a typical inlet configuration.

- **Sample transport**--A sample transport system provides the ability to pass the ambient gas sample from the point of extraction to the conditioning system through temperature controlled samples lines. The sample transport components are the heat-trace lines, J-boxes, and pumping system. Figure 5-3 illustrates heat-trace sample lines as part of the extractive system.

- **Sample conditioning**--the objective of the sample conditioning system is to condition the sample stream by removing secondary fine particles and moisture prior to entering the analytical system in the Analytical Center.

Figure 5-2. Typical inlet configuration of a perimeter volatile organic sampling system

5-3. Sampling System Inlet Particulate Control

a. Introduction. It is imperative that with any ambient real-time FFMS for volatile organics some attention be given to particulate control prior to sample analysis. Most extractive gas analyzers and organic species analyzers require the removal of particulate matter.

Particulate matter can interfere with the sample concentration and analysis, thus jeopardizing the validity of the gas concentration acquired. The removal of particulate matter in a fixed-fenceline extractive system is performed in two stages. First, the coarse particles are removed at the probe inlet to minimize clogging of sample lines. Second, a fine filter is employed at the end of the sample line, usually at the analyzer inlet in the Analytical Center, to remove fine particles (down to 1 micron) so data is not compromised. The types of filter bodies and filter elements are based upon requirements for the particle size, stream loading factors, and the nature of the analyte gases to be analyzed. The objective of this section is to discuss the types of particulate control devices available and their application to ambient air monitoring at hazardous waste sites

b. Filter selection

(1) Coarse filtration. The objective of the coarse filter is to remove, at the front of the extractive system, large particles of 10 microns or greater. Three mechanisms applicable for removing large particles from a gas stream. They are:

- Passive filtration.
- Inertial separation.
- Inertial filtration.

In passive filtration, the particles are removed by impacting (filtering) on a surface area. The surface area can either be a flat porous material design or a cylindrical configuration design. In the flat porous material design, air is pulled through the filter device, removing the particles of concern. The problem with this approach is that the filter material can become moist from atmospheric water aerosols and can interact with the analytes of concern, resulting in reduction or even elimination of the analytes of concern from the sample gas.

Figure 5-3. Example of heat-trace line layed above ground as part of perimeter volatile organic sampling system

Experience has shown that the cylindrical configuration is most applicable for extractive FFMSs. In this configuration, a sintered metal filter of large surface area, typically constructed of sintered 316 stainless steel, is placed at the inlet of the heated sample probe, as illustrated in Figures 5-4 and 5-5. Sintered filters normally remove all particles that are larger than 10 to 50 micrometers. Other types of material used in sintered filters are glass, ceramic, quartz, Carpenter 20 steel, and Hastelloy C steel. As illustrated in Figure 5-5, the porous medium is proceeded by a funnel to prevent excessive moisture from entering the extractive system and is embedded in a heated compartment to prevent moisture from plugging the porous material. This configuration allows minimum interference from particles building up on the sintered filter and from moisture interference. These filters should be maintained at or above the ambient temperature during sampling. As diagrammed in Figure 5-6 and pictured in Figure 5-7, the complete inlet system consists of an inlet funnel and a heated compartment containing a sintered stainless steel filter connected to the heated transfer line.

Figure 5-4. Example of sintered stainless steel inlet filter as part of a perimeter VOC FFMS

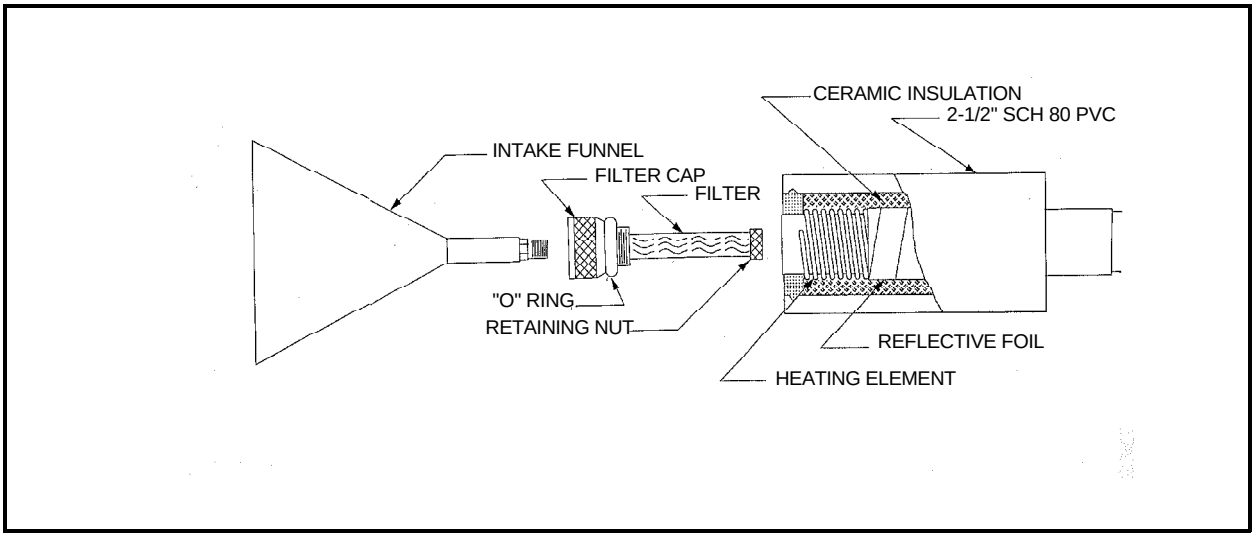


Figure 5-5. Example of probe inlet design with intake funnel and heated sintered stainless steel filter for particulate matter control

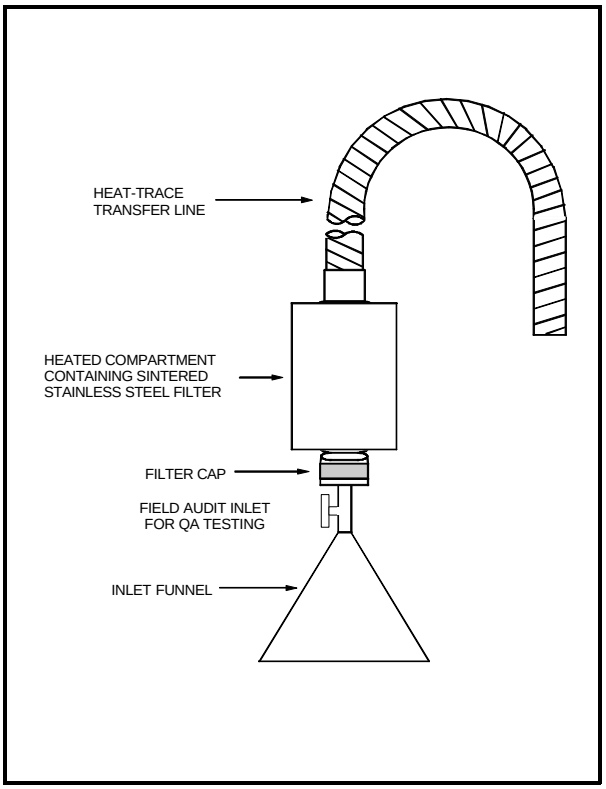


Figure 5-6. Composite of a FFMS inlet design for extracting samples for VOC analysis

Figure 5-7. Example of field application of an inlet configuration for an extractive perimeter VOC FFMS

Large particles can also be removed by inertial separation. This type of coarse particulate removal can be accomplished by using a flow-through cyclone on the inlet of the sampling line. In the cyclone, the sample gas is introduced tangentially and exhausted through the bottom of the apparatus. The cyclonic flow causes the particles to be thrown against the walls of the device. The particulate-free gas stream is exhausted from the vortex inside the cyclone. Cyclones have a distinct particle cut size depending on the geometry, flow rate, and gas viscosity. The application of a cyclone as a coarse particle remover would be most applicable under ambient conditions of high particulate loading and in the presence of water droplets because cyclones do not plug easily and can be cleaned easily. The major drawback to the application of a cyclone in an ambient air monitoring program is that the cyclone is not readily heated, thus providing conditions where the sample gas is in contact with moisture droplets, allowing some form of scrubbing of target analytes to occur. The last mechanism for particulate removal is the inertial filtration. As illustrated in Figure 5-8, inertial filtration involves a flow-through tube filter where the sample gas is extracted from the main gas stream at a 90° angle. Within the probe, the high speed sample passes through a tubular (inertial) filter. A small portion of this sample is drawn radially through the porous filter wall at a velocity so low that the inertia of solid and liquid particles will be too high to curve through the wall of the filter. Consequently, the large ratio of axial to radial sample gas velocity in the tube filter prevents large particles from impinging on the filter pore structure. Small particles establish a dynamic membrane on or within the porous wall, and in equilibrium with very low drag forces, effectively prevents transmission of particulate contaminants much smaller than the filter pore size. The turbulent nature of particulate laden gas flowing through the filter tends to keep the filter clean by abrasion. The flow-through tube filter can be mounted either internally or externally to the sample inlet device. This approach has not been actively used at HTRW sites, but may have applicability in the future to the particulate management program for monitoring VOCs.

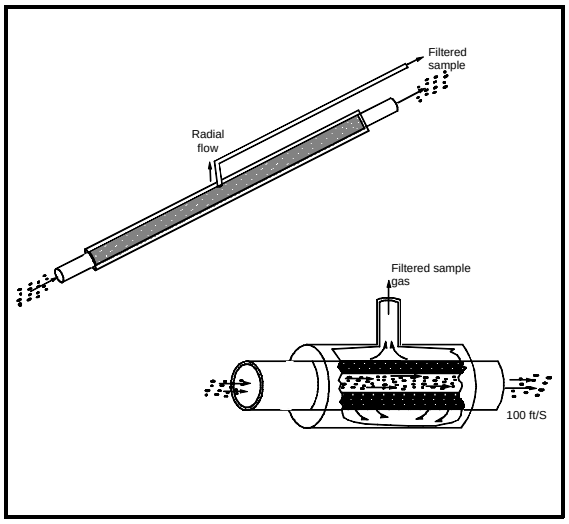


Figure 5-8. Example of an inertial filtration system as a particulate matter control device on an extractive VOC FFMS

(2) Fine filtration. Gases collected for FFMS systems will nearly always require complete removal of all particles larger than 1 micron prior to analysis. To reduce particles to this level, a secondary particulate control device is needed after the primary device. The secondary fine filtration device is usually located at the inlet to the analytical system in the Analytical Center. The fine filtration device needs to be a low-resistance, high-efficiency filter. Fine filters are divided into two categories: surface filters and depth filters. Surface filters remove particles from the gas stream using a porous matrix. These filters can remove particles smaller than the actual filter pore size as a result of particulate cake build-up and electrostatic forces acting to trap smaller particles without excessive resistance. Depth filters collect particulate matter within the bulk of the material. The depth filter may consist of loosely packed fibers or relatively large diameter granules. The spun glass filter or cellulose filter, when maintained, are reliable and efficiently remove particles as small as 0.5 microns. Spun glass, when packed to a density of 0.1 g/cm^3 and a bed depth of at least 2 inches, can act as an inexpensive secondary filter for normal gas flow rates.

c. Inlet placement/probe height. In many cases, constraints on placing sampler inlet probes as part of the FFMS can be encountered because of wind flow obstructions caused by nearby buildings, trees, hills, or other obstacles. Other constraints might be related to security, the accessibility of electrical power, and the proximity to roadways or other pollution sources that might affect the representativeness of the sample for measuring the HTRW site's effect on air quality. Specific guidelines for probe siting for sampling representative conditions are:

- The most desirable height for sampler inlets is near the breathing zone (i.e., about 5 to 6 feet above ground). Practical factors such as high impermeable fences surrounding the HTRW site may sometimes require that sampling inlets be placed slightly higher (at least 1 meter above the top of the fence). As a compromise, the EPA requires the inlet to be between **2 to 15 meters** above ground.

- Inlet probes must be located away from obstacles and buildings so that the distance between the obstacles and the sampler inlet is at least twice the height that the obstacle extends above the probe inlet. **Airflow must be unrestricted in an arc of at least 270°** around the inlet, and the predominant wind direction for the season of greatest pollutant concentration potential must be included in the 270° arc.

- The **inlet probe and nearby roadways** must be sufficiently separated to avoid the effects of dust re-entrainment and vehicular emissions on measured air concentrations.

- The **inlet probe** must **not be impacted** by the location of collocated samplers or other obstacles.

- Stations that include particulate matter sampling systems collocated with the extractive gas inlet probe should not be located in an unpaved area unless there is vegetative ground cover year round so that the effect of locally re-entrained or fugitive dusts will be kept to a minimum.

Figure 5-9 illustrates a properly placed extractive gas inlet probe collocated with RMM time-integrated monitoring systems.

Figure 5-9. Example of properly placed extractive perimeter VOC inlet probe collocated with RMM time-integrated monitoring systems

5-4. Sample Transport Requirements

a. Sample transfer line. The main objective of the sample transfer line is to transport the sample gas from the extractive gas inlet probe assembly to the Analytical Center. In developing a sample transfer line, certain factors must be considered to ensure the transport of a sample from the inlet probe to the analytical system. These factors are:

- Sample integrity.
- Sample flow rate.
- Cost.
- Temperature

The gas sample should be transported from the inlet probe to the rest of the transport system with minimum loss and interaction. There are several mechanisms by which interaction between sample gas and inlet probe can occur. They are:

- Reaction.
- Absorption.
- Adsorption.
- Dilution.

Gas phase reaction in transfer lines can occur by homogeneous gas phase reaction and by heterogenous catalytic reaction. Materials of construction such as Teflon®, stainless steel or glass are generally very poor catalysts and would not be expected to cause reactions. Absorption and adsorption by the walls of the transfer line would eventually reach equilibrium; consequently, the concentration of the constituent stream would not be changed. Studies have indicated that absorption and adsorption are negligible for stainless steel, Teflon®, polypropylene, polyethlyene, and Tygon®.

The choice of proper material of construction is very important. Acceptable construction material must meet these important criteria:

- Material must have sufficient chemical resistance to withstand the corrosive constituents of the sample.
- Material must not exhibit excessive interaction (reaction, absorption, adsorption) with the sample gases.
- Material must be heated if moisture is not removed prior to sample transfer.

Consequently, the integrity of the sample greatly depends upon the material of construction of the transfer lines. For most air monitoring applications, construction materials focus on four types: Teflon® fluorocarbon resins, polyvinylchloride, stainless steels, and borosilicate glass. Each material is discussed below as to their applicability to a real-time volatile organic FFMS.

(1) Teflon® Fluorocarbon Resins. Teflon® resins are chemically inert to almost all industrial chemicals and solvents, which means that they can be in continuous contact with another substance with little detectable chemical reaction taking place. The inertness of Teflon® is due to (1) the very strong interatomic bonds between carbon and fluorine atoms; (2) the shielding of the carbon backbone of the polymer by fluorine atoms; and (3) the very high molecular weight (or long polymer chain length) compared to many other polymers. The two members of the family of Teflon® resin that are most commonly used in real-time FFMS are polytetrafluoroethylene (PTFE) and fluorinated ethylene-propylene copolymer (FEP).

(a) PTFE Teflon® resin is a white to translucent (opaque) solid polymer made by polymerizing the tetrafluoroethylene (C_2F_4) monomer. It is a highly crystalline polymer with high thermostability. Its heat resistance, chemical inertness, electrical insulation properties, and low co-efficient of friction in very wide temperature ranges make PTFE an outstanding plastic. When melted, PTFE does not flow like other

thermoplastics, and it must be shaped initially be techniques similar to powder metallurgy. PTFE shows excellent resistance to corrosive agents and dissolution by solvents, with a maximum continuous service temperature of 260°C (500°F). The PTFE Teflon® is the most common material used in transfer line for volatile organic extractive sampling systems.

(b) FEP Teflon® is a true thermoplastic that can be melted, extruded, and fabricated by conventional methods. FEP has a glossy surface and is transparent in thin sections, eventually becoming translucent as thickness increases. The FEP has a maximum continuous service temperature of 250°C (482°F).

(2) Polyvinylchloride (PVC). Polyvinylchloride is a linear chain compound produced by the polymerization of the vinyl chloride monomer. Rigid vinyl materials are primarily made of high molecular weight vinyl chloride polymers and are unmodified by plasticizers or similar materials; the addition of plasticizers will increase the flexibility of the PVC product. Rigid PVC has sufficient structural strength, impact resistance, and hardness to replace metals in many forms. PVC has relatively good resistance to chemical attack but is subject to degradation by ketones, aldehydes, amines, chlorinated alkanes, and alkenes in the pure solvent form, although the effect aqueous solutions of these solvents have on the integrity of PVC is not exactly known.

Flexible PVC (Tygon®) is quite different than rigid PVC due to the addition of more than 25 percent of various phthalates esters or plasticizers. These plasticizers give the PVC tube its flexibility, but are also the source of cross contamination when the tubing is used as part of a FFMS for organics. Phthalate esters can leach into the sample, where they are commonly detected by the analytical system in the Analytical Center.

(3) Stainless steel. Stainless steel is one of a variety of steels alloyed with enough chromium to resist corrosion, oxidation, or rusting. There are two types of stainless steel that are generally used for FFMSs for organic sampling: Type 304 and Type 316. Both are heavier and more costly than polymers.

- **Type 304.** Type 304 stainless steel is a chromium-nickel steel with general purpose corrosion resistance. It is nonmagnetic in the annealed condition, but slightly magnetic when purchased. Type 304 stainless steel can be formed to most desired shapes with little difficulty.

- **Type 316**. Type 316 stainless steel is a non-hardenable chromium-nickel steel containing molybdenum, with superior corrosion and heat-resisting qualities. Type 316 has improved resistance to sulfur species and sulfuric acid and is commonly used for chemical handling equipment such as heat exchangers, condensers, evaporators, and piping.

While stainless steel can maintain the integrity of the gas sample, it has limited application as a transfer line as part of a FFMS around the perimeter of a HTRW site due to its rigid structure and limited tube lengths.

(4) Borosilicate Glass. Borosilicate glass is a soda-lime glass containing about five percent boric oxide, which lowers the viscosity of the silica without increasing its thermal expansion. Such glasses have a very low expansion coefficient and high softening point (about 593°C), with a continuous use temperature of 482°C. The tensile strength is about 10,000 psi. Pyrex® is a borosilicate glass that is commonly used for field application at HTRW sites.

In summary, Figure 5-10 illustrates a typical transfer line assembly containing sample line, heating elements and insulation.

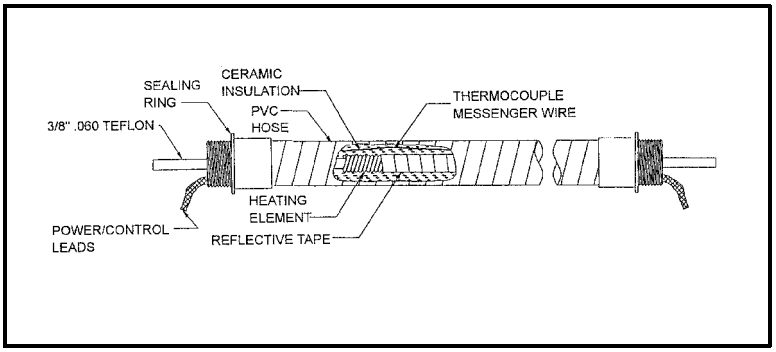


Figure 5-10. Example of a complete heat-trace line assembly containing PTFE Teflon® as part of an extractive VOC FFMS

For most applications, the placement of inlet sample probes as part of a volatile gas monitoring system around a HTRW site may require up to 1,000 feet per sample point extended from the Analytical Center, as illustrated in Figure 5-11:

- Inlet probe 1: 250 ft. from Analytical Center.
- Inlet probe 2: 800 ft. from Analytical Center.
- Inlet probe 3: 950 ft. from

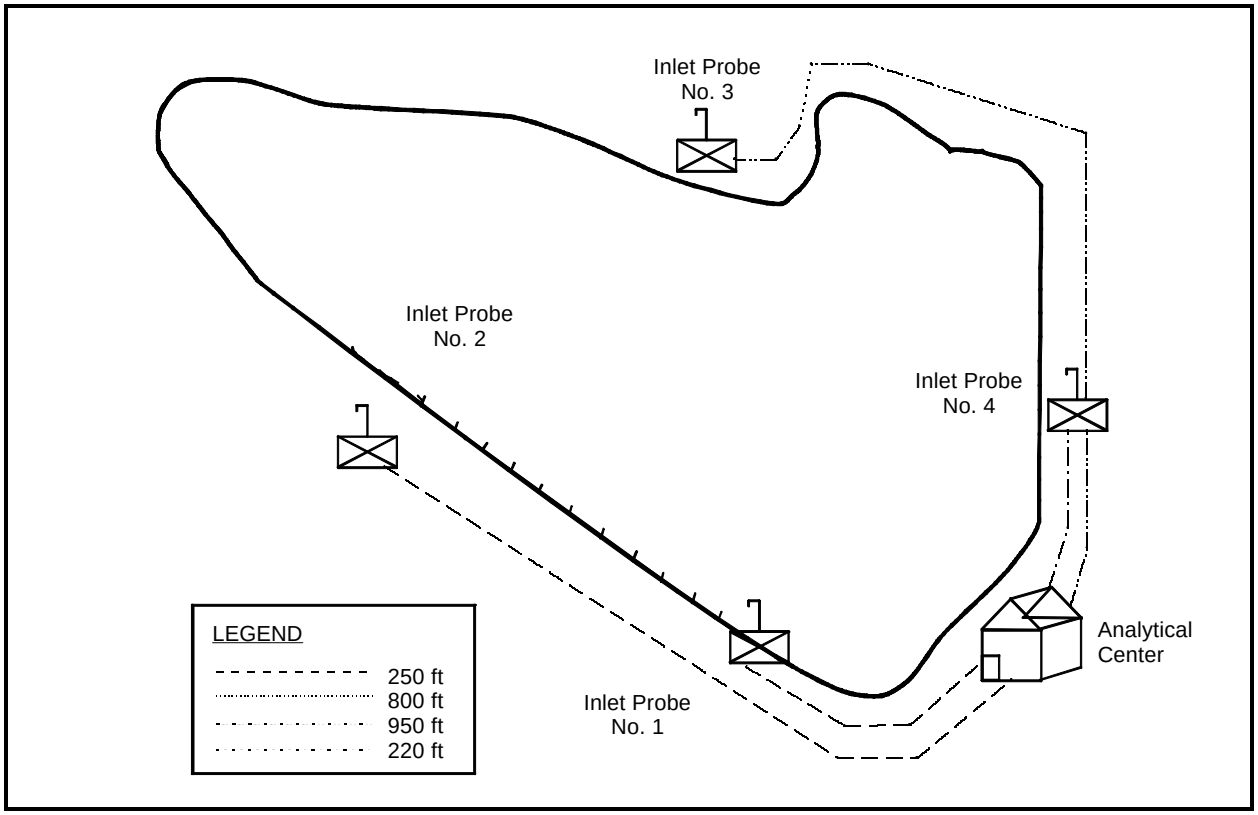


Figure 5-11. Example of up to 1,000 feet per sample point of heat-trace lines extends from Analytical Center to specific inlet probe locations around perimeter of HTRW site

Analytical Center.

- Inlet probe 4:220 ft. from Analytical Center

In developing an extractive FFMS, one has to determine whether heat-trace lines of single length would be applicable or to divide the lines into segments of nominal 200 feet to reach the inlet probe locations. There are several reasons for designing the system using nominal 200-foot segments. They are:

- The ability to provide heat to lines in excess of 500 feet is difficult due to the power requirements in maintaining temperature to a pre-set level.

- If a line fails due to line damage, electrical shorts etc., it is easier to replace a nominal 200-foot length than a 1,000-foot length of line.

- If a segment of line needs to be replaced, it is less costly and easier to work with a nominal 200-foot segment.

Consequently, the inlet probes may be joined with the Analytical Center, using heat-trace lines constructed of nominal 200-foot segments, with junction boxes (J-box), as illustrated in Figure 5-12.

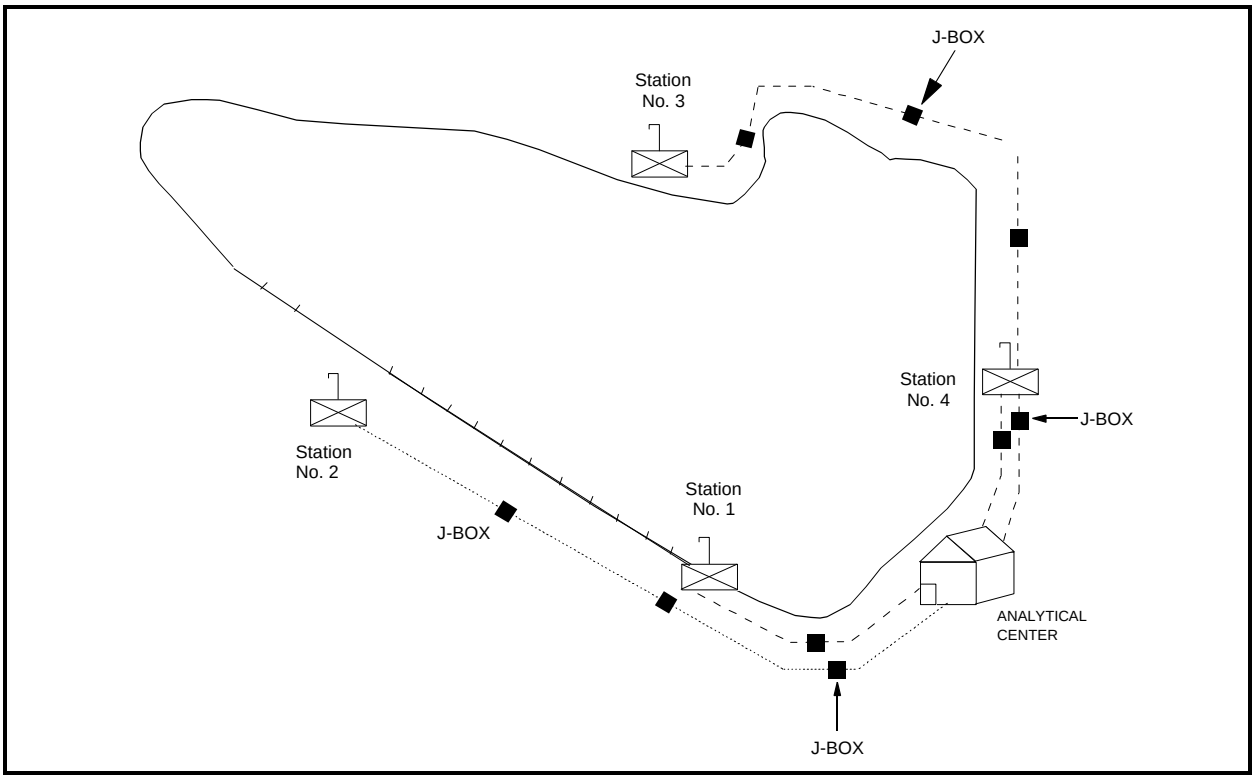


Figure 5-12. Example of nominal 200-foot heat-trace line segments connected to Analytical Center using J-Boxes around perimeter of HTRW site

The components of a typical J-box are illustrated in Figure 5-13. The J-box allows the union of several 200-foot PTFE Teflon® segments using stainless steel fittings. Each of the sample lines is connected to its predecessor via an electrical junction box, as illustrated in Figure 5-14. The lines feed into either side of the enclosure where they are joined with a stainless steel compression fitting. To minimize any cold spots in the J-Box, the heated portion of the sample line actually enters the box to the tube union that is covered with a high-efficiency strip of insulation to minimize heat loss. Terminal blocks to provide power for the adjacent sections are also contained in the enclosure, as well as thermocouple connectors and mounting to monitor each section during regular audits of the system.

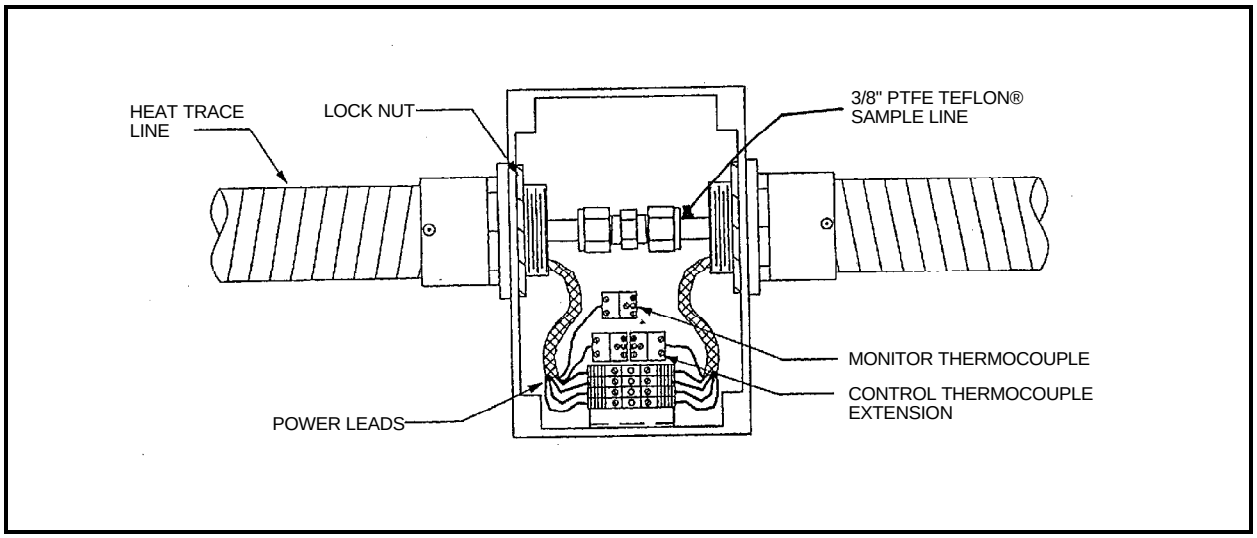


Figure 5-13. Example of components of a typical J-Box used to connect nominal 200 foot lengths of heat-trace lines

All heat-trace lines should be wrapped in a very uniform fashion to ensure a consistent temperature across the entire device. Multiple heating elements are usually cut to a precise resistance and wired in a parallel circuit over the entire unit. Current draw per element is kept relatively low to extend service life. High efficiency insulation applied in a consistent manner also increases temperature stability and product life. In addition, foil is applied over the heating elements to reflect heat back to the sample line core. This design has the effect of increasing the lines' efficiency and temperature stability. The ends of the heated lines should be sealed in a high-temperature epoxy potting compound to protect both the device and its user.

All heat-trace lines should be sleeved in a heavy-duty, flexible vinyl hose suited for direct burial applications. The seals should be rated for outdoor use. Due to the length requirements for the heat-trace lines, they should be designed for 480 VAC, three-phase power, which allows the user to keep the current draw circuit leg down to a manageable level and extends product life and reliability.

Figure 5-14. Actual on-site connection of two heat-trace lines using a J-box as part of a FFMS

Control for the heat-trace sample line are provided by panel mount temperature controllers. Each controller reads the temperature of the line at the beginning of the sample path. That signal is conveyed through the adjoining 200-ft. sections by means of a thermocouple messenger wire. The uniform watt-density along the entire sample line run allows for precise control of the heated sections with minimal temperature variance.

b. Sample flow rate requirements. The sample line must be large enough so that a pump can handle the pressure drop, yet small enough so the response time is not excessive. Flow rates as a function of pressure drop are shown for various line sizes in Figure 5-15.

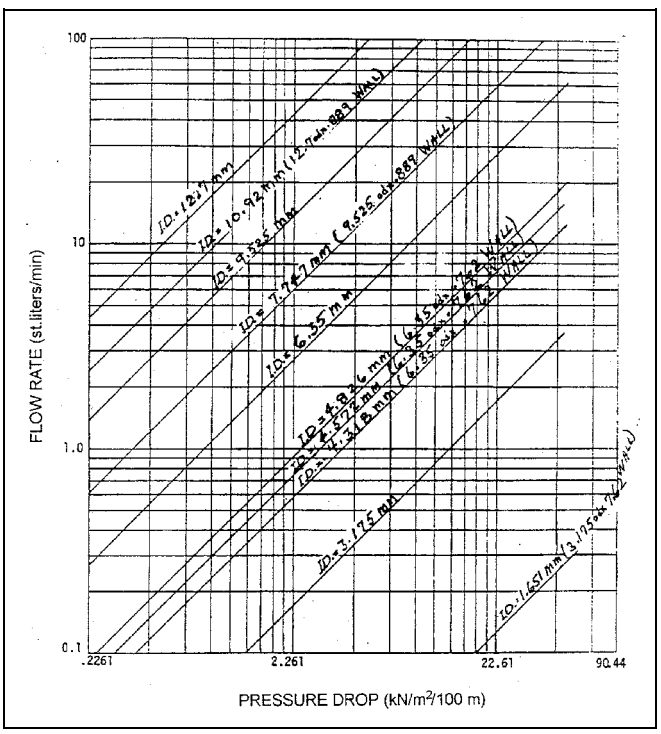


Figure 5-15. Example of flow rates vs. pressure drop for various sample lines sizes

Studies have shown that for a typical flow rate of two liters per minute (ℓ/min), 6.35 mm I.D. tubing will give only a pressure drop of between 1 and 3 mm Hg per 100 ft. of tubing. This reading is not an excessive pressure drop for a real-time volatile FFMS.

The lag time (t) for a sample line volume (V) may be calculated according to the following equation:

$$t = \frac{V}{F}$$

where:

t = Lag time (sec);
V = sample line volume (ft^3); and
F = Flow rate (ft^3/sec).

As an example, for a tube with an I.D. of 6.35 mm and 100 ft. from the sample inlet probe to the Analytical Center, the lag time for a flow rate of 2 1/min is calculated as follows:

- 1st = Convert diameter of tube from mm to ft.:

$$(6.35\ \text{mm})(32.808 \times 10^{-4}\ \text{ft/mm}) = 0.0208\ \text{ft.}$$

- 2nd = Calculate area of tube:

$$A = \pi r^2 = \pi \left(\frac{D}{2}\right)^2 = \frac{\pi D^2}{4} = \frac{\pi\ (0.0208\ \text{ft})^2}{4} = 0.0003398\ \text{ft.}^2$$

- 3rd = Calculate volume of sampling line:

$$V = (A)(L) = (0.0003398\ \text{ft}^2)(100\ \text{ft}) = 0.03398\ \text{ft}^3$$

- 4th = Convert flow rate from L/min to ft^3/sec:

$$(2\ \text{l/min})(5.886\text{x}10^{-4}\ \frac{\text{ft}^3 \cdot \text{min}}{\text{L} \cdot \text{sec}}) = 0.001177\ \text{ft}^3\text{/sec}$$

- 5th = Calculate lag time using volume and flow rate:

$$\frac{V}{F} = \frac{(0.03398\ \text{ft}^3)}{(0.001177\ \text{ft}^3\text{/sec})} = 29.0\ \text{s}$$

Table 5-2
Example of Sampling Line Lag Time For Various Dimensions

	Lag time per (30.48 m) length (seconds)	
Tubing Size (mm)	**1 liter per min**	**2 liter per min**
1.651 (3.175 o.d. x 0.762 wall)	3.9	2
3.175 (3.175 i.d.)	14	7.2
4.318 (6.35 o.d. x 1.016 wall)	27	13
4.572 (6.35 o.d. x 0.889 wall)	30	15
4.826 (6.35 o.d. x 0.762 wall)	33	17
6.35 (6.35 i.d.)	58	29
7.747 (9.525 o.d. x 0.889 wall)	86	43
9.525 (9.525 i.d.)	130	65
10.92 (12.70 o.d. x 0.889 wall)	170	86
12.70 (12.70 o.d.)	230	116

For the above example, the lag time calculation would be 29 seconds for a 100-foot heat-trace lines segment. This lag time is well within the EPA guideline of 15 minutes. Table 5-2 displays lag times for 100 feet of sample line with various inside diameters for flow rates of 1 and 2 standard liters per minute (L/min).

(1) Heating of sample inlet/ transfer line. Ambient air samples usually contain a measurable percent of water that, when cooled, can condense out in the sample line. This characteristic can present a

significant problem in an ambient air program because many organics are soluble in water. In addition, very few analytical systems are insensitive to water vapor. For those systems, the sample gas is maintained above the dew point by heating the sample inlet and filter, transfer line, and pump before the moisture removal system.

When the FFMS components of interest are easily condensed or water soluble, it is necessary to avoid water condensation or removal from the sample. There are two methods for keeping water in the vapor phase in a sample gas stream extracted at a HTRW site: heating and pressure reduction. Heating a gas stream above the dew point will keep water in the vapor phases if the total pressure is near atmospheric. By dropping the pressure of the gas stream, a lower condensation temperature can be realized. Figure 5-16 shows the relationship for temperature required to keep water in the vapor phase as a function of pressure. The application of this method is to heat the gaseous sample above the dewpoint until the pressure can be reduced to a level where condensation will not occur at room temperature. Once the appropriate pressure is achieved, no further heating would be required.

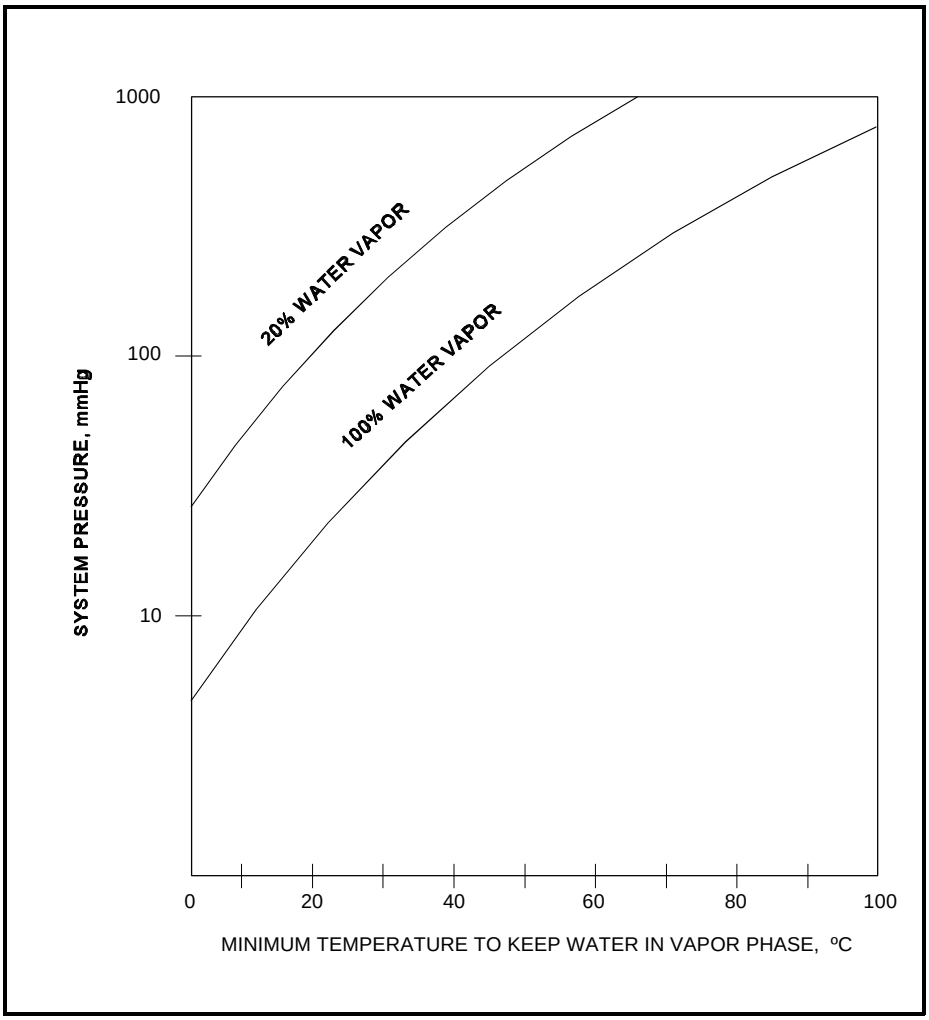


Figure 5-16. Example of temperature vs. system pressure to maintain water in the vapor state

Table 5-3 presents the maximum temperature of various plastic materials. Depending upon the condition and extraction locations, all materials are candidates for transfer material. The less heat resistant plastics (polypropylene and polyethylene) cannot be used as efficiently when heating the sample transfer line to 212°F. For most FFMS sample transfer applications, PTFE Teflon® will be the best candidate as the material of construction for a heated transfer line.

(2) Cost. Costs are very important when considering putting together a real-time FFMS.

Table 5-3
Maximum Continuous Operating Temperatures for Heat Trace Lines Materials of Consruction

Material	Maximum Temp. (°C)
Plastics	
Teflon	250
Viton	150
Polyethylene*	80-125.6
Polypropylene	110
PVC	110
Tygon*	60-82.2
Stainless Steels	
Carpenter 20	871
316 SS	870
304 SS	788
Nickel Alloys	
Hastelloy C-276	1,038
Inconel 625	980
Incoloy 800	760
Incoloy 825	704
Non metallics	
Aluminum silicate	1,540
Quartz glass (fused silica)	900-1,200*
Ceramic	1,094-1,538*
Zirconium oxide	2,204
Pure Element	
Titanium	800-1,000

*Depending on type used.

Table 5-4 illustrates the cost of various heat-trace line materials per 100 feet of construction.

(3) Placement of heat trace lines. Once all variables for the construction and design of the heat-trace lines have been selected, consideration must be given to locating the line around the perimeter of the HTRW site. As illustrated as an example in Figure 5-11, heat-trace lines may have to be extended up to 1,000 feet around the HTRW site. Placement of heat-trace lines may require laying the lines across access points to the interior of the

HTRW site. Passenger vehicles and heavy-duty trucks will need access to the site. Two options are available for placement of heat-trace lines around a HTRW site:

- Aerial placement.
- Burial option.

Aerial placement depends on the availability of support poles (i.e., telephone poles) around the HTRW site. A limitation of this approach is that the lines are heavy and during inclement weather may strain the internal components of the lines due to ice formation. This application has not been routinely used at HTRW sites.

Table 5-4
Example Cost of Various Sample Line Materials Based on 100 ft of 6.35 mm OD Tubing

Material	Wall Thickness	List Price per 30.48 m, $
Heat Traced Teflon®	0.889	2,500
Heat Traced 316 Stainless Steel	1.016	3,250
Carpenter 20 Stainless Steel	0.889 welding	4,500
Heat Traced 304 Stainless Steel	0.889 seamless	3,000
Viton® Heat Trace	1.575	1,450
Tygon® Heat Trace	1.575	1,560
Aluminum	0.889	1,100
Glass	8mm CD x 6mm ID	733
Nylon®	0.762	440
Polypropylene	0.787	431
Polyethylene	1.016	370

The most common option is placing the lines on the ground and burying the lines in areas where access is needed to the site. When the lines are above ground, the lines should be enclosed in a suitable conduit to protect from accidental damage, as illustrated in Figure 5-17. In this illustration, the 4-inch heat-trace line is encapsulated in scheduled 80 PVC conduit/pipe for protection. Other materials of construction (i.e., cast iron, steel etc.) can also be used to protect the lines. The heat-trace lines should then be placed in a shallow trench, as illustrated in Figure 5-18, for further protection.

For those areas where access to the interior of the site is required, the encapsulated heat-trace lines must be buried to protect them from damage from on-site vehicles. These lines should be buried below the "frost line" for that region or at a minimum of 2 feet. After burial, 1-in. thick steel plates should be placed over the area of the buried

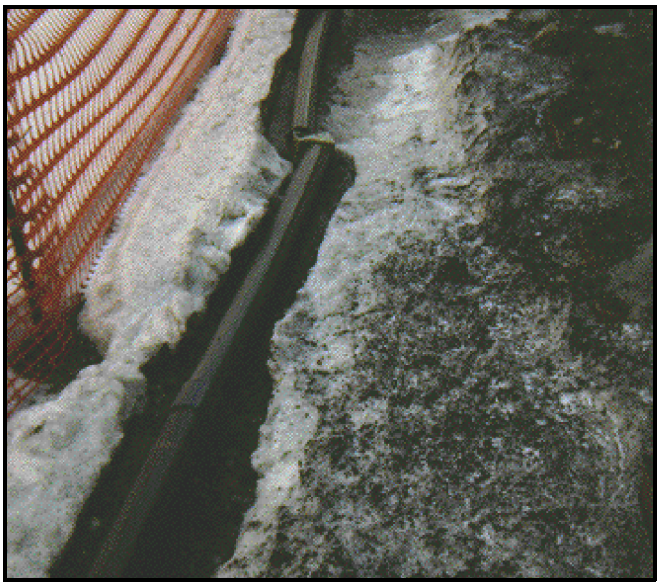


Figure 5-17. Example of encapulated heat-trace line in PVC conduit around the perimeter of a HTRW site

Figure 5-18. Example of encapulated above-surface heat-trace lines entering sub-surface location around the perimeter of a HTRW site

encapsulated heat-trace lines to provide additional protection from heavy truck traffic. These would be the only areas where truck traffic would be allowed to enter or exit from the site. Figure 5-18 illustrates encapsulated surface heat-trace line from entering subsurface location at the entrance of a HTRW site.

c. Sample pumps

The main purpose of a pump in a perimeter air monitoring system is to transfer the gas stream from one location to another. This process may be done either by positioning the pump upstream of the analytical system (positive pressure) or downstream of the analytical system (negative pressure). The pump location will determine the characteristics of that pump.

Pumps can be divided into three broad categories:

- Positive displacement pumps.
- Centrifugal pumps.
- Eductor.

(1) Positive displacement pumps. Positive displacement pumps can be characterized by a linear relationship between the change in capacity (ΔQ) of the pump and the pressure drop (ΔP) across the pump. In essence, as the volumetric flow rate changes, a concurrent and direct change occurs in the pressure drop across the pump, which becomes a constant.

The name positive displacement pump arises from the fact that air is displaced by the movement of the inner components of the pump. The mechanism by which the moving part displaces the air determines the principle of operation. For example, pumps containing fixed casings with movable pistons are called reciprocating pumps, part of the positive displacement classification. Pumps that utilize a

gear or lobe to move air are called rotary pumps. Table 5-5 illustrates the two subdivisions of the positive displacement pump.

The piston pump is characterized by the movement of a piston in a fixed volume. The piston displaces the air occupying the same space on the discharge side. Likewise, the air displaces the piston on the suction side.

Table 5-5
Subdivisions of Positive Displacement Pumps

Principle of Operation	Type of Pump
Reciprocating	piston plunger diaphragm
Rotary (not discussed in this manual)	gear lobe vane screw rotary plunger

The diaphragm pump is by far the most common pump used in perimeter air monitoring sampling systems. The operation is very similar to the piston pump. Once again, air is displaced by movement of a diaphragm, the outer edges of which are bolted to a flange on the pump casing. The diaphragm may be made of metal, Teflon®, or neospore. The most important characteristic of the diaphragm material is its flexibility and resistance to reaction with the air being moved. As the diaphragm moves up, air flows into the pump via a suction valve. As the diaphragm moves down, air is funneled through a discharge valve. Consequently, the gas moves into and out of the pump. Figure 5-19 illustrates the operation of a typical diaphragm pump, the most commonly used pump as part of a HTRW FFMS.

(2) Centrifugal pump. Different from the positive displacement pumps, centrifugal pumps employ centrifugal force to move air. The movement of an impeller rotating in a volute ("snail's shell") casing causes a differential pressure, thus pulling air into the center of the shaft. The air is then picked up by the rotating vanes and accelerated. It is then discharged by way of the discharge nozzle.

(3) Air driven eductor. Air driven eductors are becoming more prevalent as the pump of choice for real-time monitoring systems. Present application of the eductor has been both as the primary or secondary air mover. In the primary configuration, the eductor acts according to the jet principle, as depicted in Figure 5-20.

At the nozzle, the high pressure driving force is converted into a high velocity stream. The passage of the high velocity stream through the suction chamber creates a decreased pressure (vacuum),

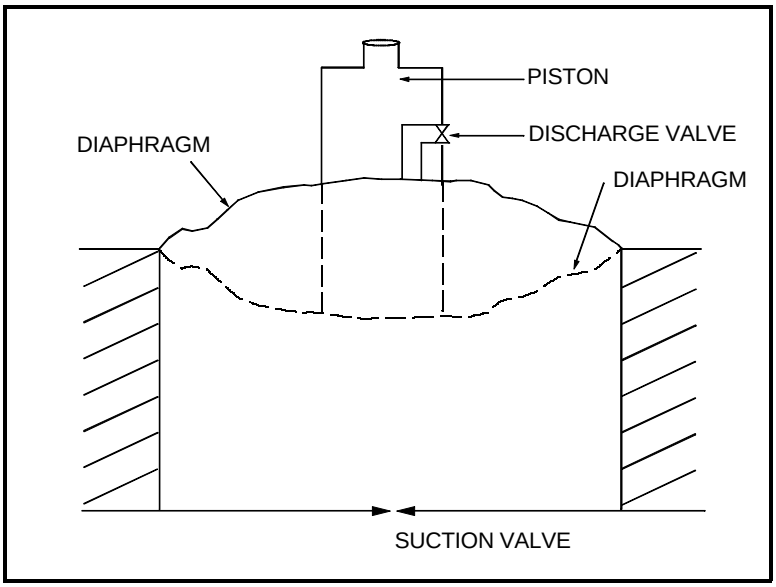


Figure 5-19. Example of the operation of a diaphragm pump used as part of a FFMS at a HTRW site

thus drawing air into the chamber. The incoming air is mixed with the high velocity gas mixture and is ejected against a moderate pressure through a diffuser. In this configuration, the high pressure gas stream pulls the ambient air into the eductor area. A second pump, located downstream of the conditioning system, pulls the needed gas sample off of the air inlet position before the eductor or nozzle.

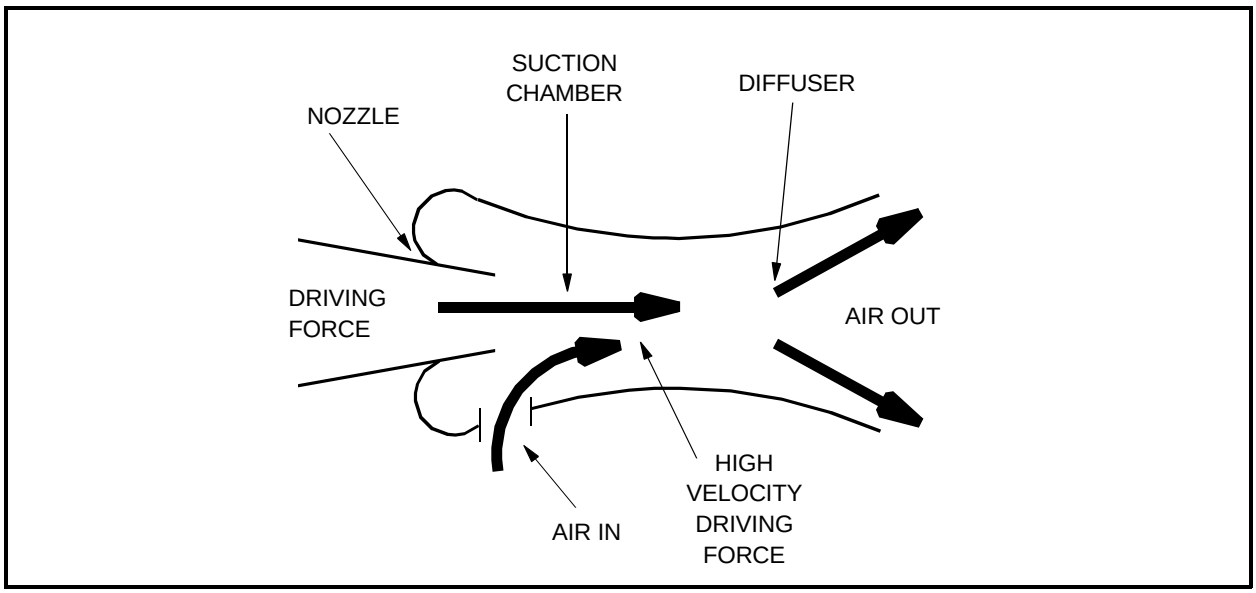


Figure 5-20. Example of an air driven eductor used as part of a FFMS at a HTRW site

As evidenced by the above discussion there are many choices available in selecting a pump. A comparison of some of the advantages and disadvantages of pumps used in HTRW FFMSs are given in Table 5-6.

Table 5-6
Example of Advantages/Disadvantages of Air Moving Systems

Pump type	Advantages	Disadvantages
Piston pump (reciprocating)	1. Can operate at high suction pressure 2. Can be metered	1. Small capacity 2. Seal required between piston and piston chamber 3. Working parts such as check valves and piston rings may cause difficulties 4. Pulsating flow 5. Moderate maintenance
Diaphragm pump (reciprocating)	1. Wide range of capacities 2. No seal required 3. Good in continuous operation	1. Limited materials of construction 2. Operation at limited suction pressures 3. Pulsating flow 4. Periodic diaphragm replacement 5. Moderate maintenance
Centrifugal pump	1. Large Range of capacities 2. No close clearance 3. Can obtain high suction heads by multistages 4. Light maintenance	1. No small capacities 2. Turbulence 3. Operational noise
Eductors	1. No moving parts 2. Limited hardware in contact with gas stream	1. Requires unrestricted flow 2. Plugging in exit port of eductor 3. May require steam to help dislodge particles

5-5. Sample Conditioning System

As with most analytical systems, sample conditioning involving water management is an important component of the extractive system to maintain the integrity of the sample. Most analytical techniques are sensitive to water vapor, interfering with the detection and quantification of the analytes. In addition, condensation within the sample extraction system can compromise the sample by scrubbing out the analyte of concern. Therefore, the design of an extractive system must address the water management issue. There are a variety of techniques available for water management, including:

- Condensation.
- Permeation dryers.
- Dessicant techniques.
- Sample temperature.

a. Condensation. Condensation is the most common form of water management for gas streams containing a large percent of water (i.e., incinerator gases, etc.). In operation, a condenser is used to cool the gas stream below the dew point of water to condense the water at a centralized location. Condensers can be cooled either by circulating fluid outside the condensing surfaces or by circulating air. Refrigerated condensers are most commonly used for cooling sample gas streams. A typical refrigerated condenser contains a primary and

secondary configuration where the moisture level is reduced to less than 3 percent in the primary condenser and less than 1 percent in the secondary condenser. Because the first condenser is less than atmospheric, the efficiency is not as good as the secondary condenser, which is greater than atmospheric. The secondary condenser is more efficient because the increase pressure enhances the condensation process by reducing the vapor pressure of moisture and increasing the residence time in the coil. Sample gas exiting the condenser typically contains moisture levels approaching 0 percent.

While the condenser is the most effective moisture control technique, its major drawback is that the gas stream is in contact with the condensed water, which may lead to sample component loss, especially for polar compounds. Because a liquid is condensed from the gas stream, an automatic drain valve should be incorporated into the system to help eliminate gas adsorption in the condensate.

b. Permeation dryers. Permeation dryers have become increasingly utilized as part of an FFMS moisture handling component. The permeation dryer, which utilizes a non-contact technique, is composed of semi-permeable membrane lines housed in a hollow stainless steel tube, as illustrated in Figure 5-21. The dryer is a bundle of membrane tubes with a common header in a shell and tube configuration. This type of dryer is termed a tube-and-shell type.

In operation, the moist ambient gas stream must enter the dryer at positive pressure through the tube side, as illustrated in Figure 5-21. Counter current to this flow is a low pressure dry purge gas supplied to the shell side of the tube-and-shell. This differential pressure is used along the tubes, which are made of semi-permeable membrane. This unique membrane allows water vapor molecules to permeate through its skin, retaining the gas constituents. The water molecules move from the high pressure gas stream to the low pressure purge gas stream through the semi-permeable tube membranes. The now water-laden purge gas stream is exited out the side of the dryer. The water-free gas stream exits out of the high pressure outlet side of the dryer. The efficiency of the dryer at constant temperature and humidity is based on the amount of tubing in the shell, and permeation drying can be accomplished by heating the inlet to the drier so the entering gas stream is above the dew point of all constituents. In addition, periodic blow-back of the system helps to remove embedded particles in the tube membranes thus increasing the efficiency and life of the water management system.

The gas stream must enter the device above its dew point to allow permeation to occur; liquid water plugs the system, decreasing its efficiency. Likewise, particles can adversly affect the operation of the dryer.

Advantages for using a permeation dryer over a condensation technique are:

- Non-contact technique so less acceptable to condensation.
- Less possibility sample component loss due to condensation.
- No condensate trap required.
- Competitively priced.

Disadvantages for using a permeation dryer are:

- Plugging of the membrane tubes due to particles.
- Required hardware associated with the low pressure dry purge gas inlet.
- Loss of polar components.
- Location limitation of dryer application.

5-6. Routine Maintenance and Corrective Action Requirements

a. Routine maintenance. Quality of monitoring data is directly linked to the performance of the real-time FFMS at an HTRW site. Routine preventative maintenance of instrumentation and equipment is essential to ensure the performance of the real-time system. Maintenance procedures should be developed for any real-time system that are specific to the individual instrument and other equipment components employed. At a minimum, all real-time system equipment, instrumentation, tools, and other items requiring routine maintenance should be serviced in accordance with manufacturer's specifications or recommendations. Typical routine, preventative maintenance activities associated with the various components of a typical collection system are outlined in Table 5-7. Manufacturer's guidelines provided for specific equipment or instrumentation deployed and/or actual field experience with the equipment or instrumentation may dictate additions to the activities listed.

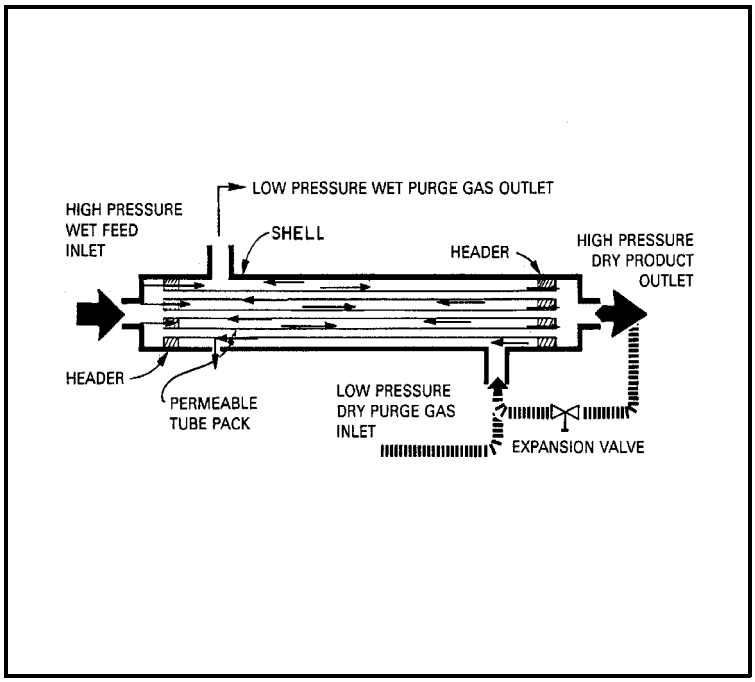


Figure 5-21. Example of a perma-pure dryer used as part of a FFMS at a HTRW site

All routine maintenance activities should be documented on a form such as the example provided as Figure 5-22. Such records must be traceable to the specific equipment item. These records will be subject to audit by project quality assurance personnel. Preventative maintenance and corrective action activities should also be documented in the instrument log book, site log books, and daily reports (i.e., DCQCR).

b. Corrective action requirements. In the event that extractive system operating conditions are identified that adversely affect data quality to any significant degree, the cause(s) should be determined and corrective actions taken to prevent recurrence. These actions may involve maintenance, repairs, or modifications to

instrumentation or equipment and/or modification of operating procedures. Corrective actions may be initiated:

- When predetermined acceptance standards (objectives for precision, accuracy, and completeness) are not attained.
- When data compiled are determined to be faulty.
- When quality assurance requirements have not been achieved.
- As a result of routine preventive maintenance activities.
- As a result of system and performance audit reports.
- As a result of a management assessment.
- As a result of laboratory/inter-laboratory comparison studies.

Table 5-7
Example of Routine Maintenance and Corrective Action for a Sample Collective System

Instrument	Type of performance	Frequency	Specifications
• Analytical system	• Calibration -- Single point *NMOC *Speciated organics	• Daily	• ±10% of RT and peak voltage • Recovery 75-125%
	-- Multi-point	• Weekly	• ±25% audit accuracy
	• Operating flows and oven temp.	• Daily	• ±25% of set-points
• Sample Transfer System (Heat-trace lines)	• Chemical checks of heat-trace lines -- NMOC -- Single point speciated organics	• Weekly	• 60-140% recovery
	• Leak check	• Weekly	• ±2" Hg vacuum for 15 minutes
	• Flow check	• Weekly	• ±10% of initial flow
• Meteorological system	• Wind direction • Wind speed • Temperature (T_1/T_2)	• Quarterly	• Wind direction: 5° • Wind speed: ±0.2 m/s • Temperature: ±0.5°C
• Data acquisition system	• Electronic voltage checks and calculations	• Quarterly	• ±10% of set-points

PERIMETER AIR MONITORING SYSTEM
EQUIPMENT MAINTENANCE/REPAIR REPORT

Instrument/Equipment Item: _____ Date: _____

Description of Problem: _____

Action(s) Taken: _____

Date/Time Item Returned to Service: _____

Initials: _____

Figure 5-22. Example of equipment maintenance/repair report as part of a FFMS program

- When samples and test results cannot be traced with certainty.
- When designated approvals have been circumvented.
- When other operating procedures are determined to be faulty.

Corrective action procedures should be developed as part of the Project Quality Assurance Plan, the Perimeter Air Sampling Plan (PASP), and the various SOPs. In the case of instrumentation and equipment, manufacturer's recommendations should be the starting point for all equipment diagnostics, maintenance, and repairs. Corrective action activities recommended as a result of system or performance audits will be recorded in the relevant audit report. In addition, all corrective action activities should also be documented on a form such as the example provided as Figure 5-23. These records must also be traceable to the specific equipment or procedural item. Corrective action activities should also be documented in the instrument log book and daily reports.

5-7. Time-Integrated and Real-Time PM_{10} Monitoring Requirements for Collection System

PM_{10} monitoring at the perimeter of a HTRW site is often required and can be integrated within the FFMS by locating the PM_{10} monitors next to designated extractive gas inlet probe. From a regulatory standpoint, sampling options for TSP and PM_{10} compliance monitoring collocated with sample inlet probes for FFMS volatile organics fall into two categories as discussed in Chapter 4: reference methods and equivalent methods. Reference methods are those sampling procedures that were initially established by EPA for determining average TSP and PM_{10} concentrations during a fixed time period. Hence, these methods are also termed time-integrated. These are by far the most commonly used TSP and PM_{10} measurement methods. Alternatively, EPA has more recently designated certain continuous reading instruments as equivalent methods for measuring ambient air concentrations of TSP and PM_{10} at or near real-time. Real-time measurements are useful when parameters such as the diurnal variation in concentration or changes in concentration associated with specific site activities of interest. Figure 5-24 illustrates a collocated time-integrated TSP system with sample inlet probe for a FFMS for volatile organics.

a. Description of sampling systems

(1) Reference methods. The reference or time-integrated method for TSP is codified at 40 CFR 50, Appendix B. This method uses a high-volume (hi-vol) sampler to collect particles with aerodynamic diameters of approximately 100 microns (m) or less. The essential features of a typical hi-vol sampler are shown in Figure 5-25. It is a compact unit consisting of a protective housing; a high-speed, high-volume electric blower; a filter holder capable of supporting an 8 by 10-inch filter; and a flow-controller and blower assembly capable of maintaining the air-flow rate through the instrument at 40 to 60 cubic feet per minute (ft^3/min) throughout the sampling period. The hi-vol sampler design causes the TSP to be deposited uniformly across the surface of the fixed filter. The TSP hi-vol can be used to determine the average ambient TSP concentration over the sampling period, and the collected material subsequently can be analyzed to determine the identity and quantity of inorganic metals present in the TSP. As discussed in Chapter 4, the TSP methodology has been included as part of Chapter 2, Method IO-2.1, "Sampling of Ambient Air for Suspended Particulate Matter (SPM) Using High Volume (HV) Sampler" of *EPA's Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air*.

PERIMETER AIR MONITORING SYSTEM
CORRECTIVE ACTION REPORT

Date: _____
Time: _____

Description of Problem: _____

Recommended Corrective Action: _____

Action(s) Taken: _____

Date/Time Action Implemented: _____

Initials: _____

Figure 5-23. Example of a corrective action report as part of a FFMS program

Figure 5-24. Example of application of a RMM for time-integrated TSP monitoring collocated with sample inlet probe for a FFMS for volatile organics around the perimeter of a HTRW site

The reference method for PM_{10} is codified in 40 CFR 50, Appendix J. Two technologies have qualified as meeting the sampling requirements of the reference method for PM_{10}: a hi-vol with a 10 m inlet and a dichotomous sampler. The PM_{10} hi-vol is identical to the TSP hi-vol except that it is equipped with a sampling inlet that directs only particles with aerodynamic diameter of 10 m or less to the filter.

A dichotomous sampler, shown in Figure 5-26, collects only PM_{10}. The sample is further split into fractions above and below 2.5 m at the sample inlet. Both the hi-vol and dichotomous samplers deposit the particulate matter uniformly across the surface of fixed filters. Both can be used to determine average ambient PM_{10} concentration over the sampling period, and the collected material from both subsequently can be analyzed for inorganic metals and other materials present.

Similar to the TSP methodology, Chapter 2, Method IO-2.2, "Sampling for Suspended Particulate Matter in Ambient Air Using a Dichotomous Sampler," has been included as part of *EPA's Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air*.

Both the hi-vol or dichotomous sampler can be equipped with either of two basic types of flow control systems, a mass-flow-control (MFC) system and a volumetric-flow-control (VFC) system. The calibration and standard operating procedures differ considerably between these two types of flow-control systems, and therefore operational procedures are control-system-specific.

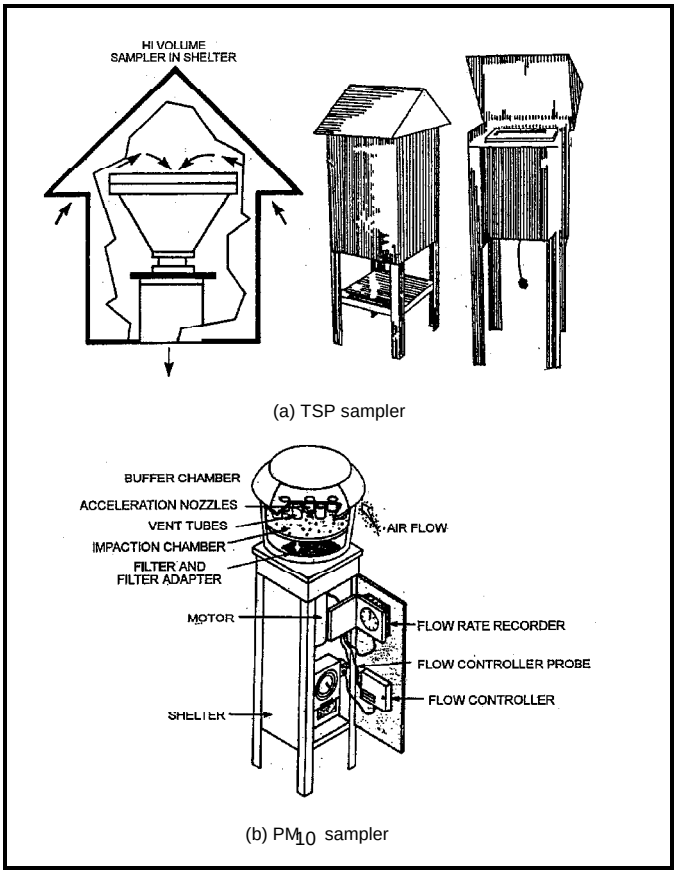


Figure 5-25. Example of (a) TSP sampler and (b) PM_{10} sampler

The flow rate in an MFC system is actively sensed and controlled at a predetermined set point. Air is pulled through the filter into the intake of the blower and subsequently exits the sampler through an exit orifice, which facilitates measurement of the flow with a manometer or pressure recorder. The flow rate is controlled by an electronic mass-flow controller, which uses a flow sensor installed below the filter holder to monitor the mass flow rate and related electronic circuitry to control the speed of the motor accordingly. The controlled flow rate can be changed by an adjustment knob on the flow controller.

A VFC system maintains a constant volumetric flow rate through the inlet, rather than a constant mass flow rate as in the MFC system. In a popular commercial VFC system, a choked-flow venturi is employed such that the air attains sonic velocity in the throat of the device. In this "choked" mode, the flow rate is unaffected by downstream conditions, such as motor speed or exit pressure, and is a predictable function of upstream conditions, such as the ambient pressure and temperature. Thus, the volumetric flow is controlled without any moving parts or electronic components. In this type of flow control system, no means is provided for adjusting the controlled flow rate.

Once the filtration collection technique is selected (i.e., Hi-Vol, Partisol®, PM_{10}), consideration must be given to the type of filter to use in the collection device. Several air sampling filter types are available and the specific filter used depends upon the desired physical and chemical characteristics of the filter and the analytical methods to be used. No single filter medium is appropriate for all desired analyses. Particle sampling filters consist of a tightly woven fiber mat or plastic membrane penetrated by microscopic pores. Several characteristics are important in selecting a filter media, including:

- Particle sampling efficiency.
- Mechanical stability.

- Chemical stability.
- Temperature stability.
- Blank concentrations.
- Flow resistance and loading capacity.
- Cost and availability

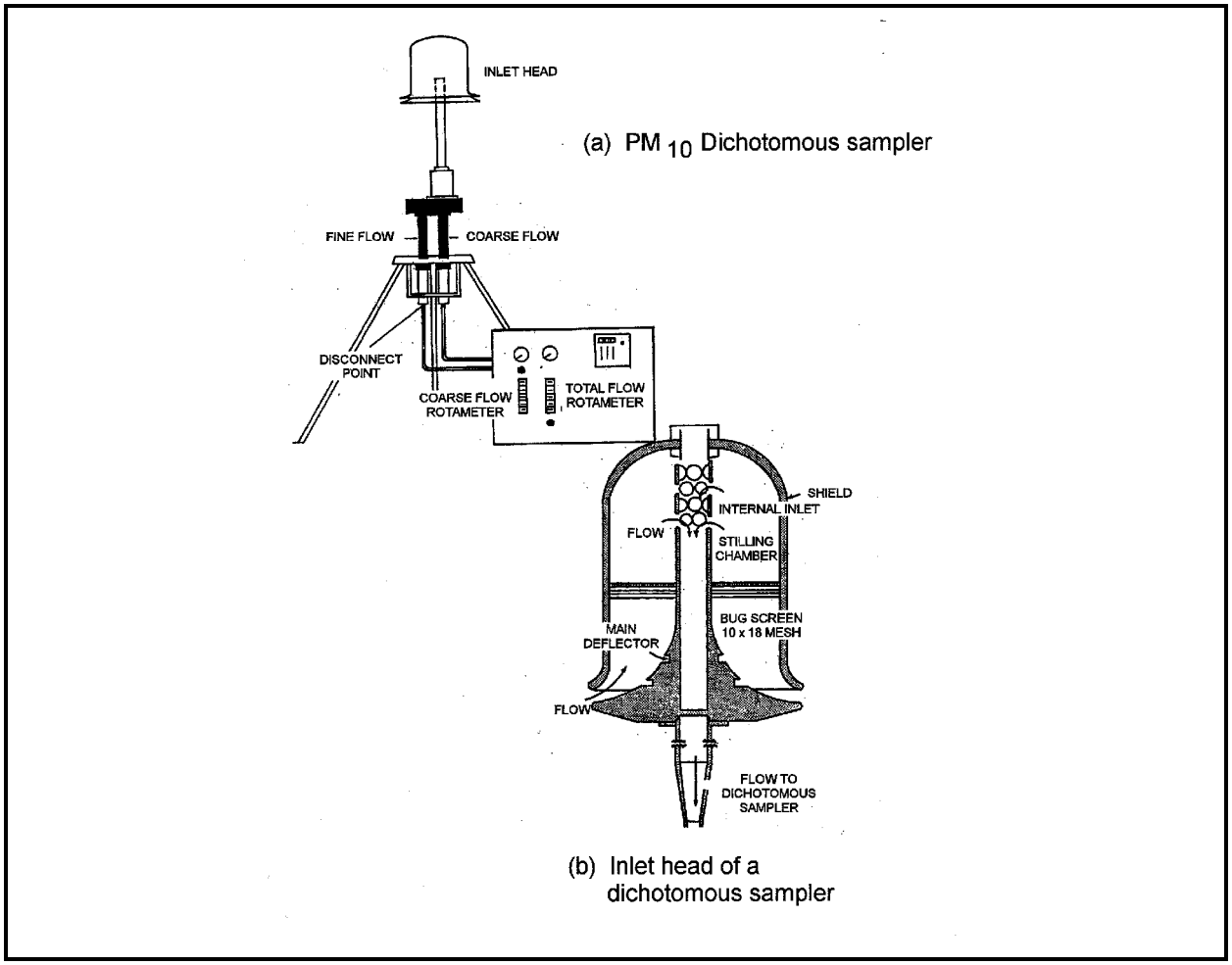


Figure 5-26. Example of PM_{10} dichotomous sampler (a) and inlet head (b)

A comparison of several air sampling filter types is presented in Table 5-8 with the chemical and physical characteristics and the corresponding chemical analytical methods that can be used for analysis of the sample.

Table 5-8
Example of Types of Filter Media for Particulate Sampling

Filter type	Filter sizes (mm)	Characteristics: Chemical	Characteristics: Physical	Analysis Methods
Ringed Teflon membrane	25 37 47	• Low blank levels • Low blank weight • No carbon analysis • Low hygroscopic tendency • Inert to gas adsorption	• White, nearly transparent surface • Minimal diffusion of transmitted light • High flow resistance • High particle collection efficiency • Melts at 60°C • Multiple pore sizes available • Cannot be accurately sectioned	• XRF, PIXE, NAA, AA, ICP/MS, Gravimetry (GRAV.), Optical Adsorption (OA), Ion Chromatography (IC), and Automated Colorimetry (AC)
Teflon membrane--polypropylene backed	47	• Low blank levels • High blank weight • No carbon analysis • Low hygroscopic tendency • Inert to gas adsorption • High background levels for PIXE and XRF	• White opaque surface • Diffuses transmitted light • High flow resistance • High particle collection efficiency • Melts at 60°C	• Grav., PIXE, XRF, NAA, AA, ICP, ICP/MS, IC, AC
Nylon membrane	25 37 47	• Low blank weight • Low hygroscopic tendency • High HNO_3 collection efficiency • Passive adsorption of low levels of NO, NO_2, PAN, and SO_2	• Diffuses transmitted light • High flow resistance • Melts at 60°C • 1 m pore size	• IC, AC
Silver membrane	25 37	• High blank weight • Low hygroscopic tendency • Resistant to chemical attack • Passive adsorption of organic vapors	• Gray-white surface • Diffuses transmitted light • High flow resistance • Melts at 350°C	• Grav., X-ray Diffraction (XRD)
Cellulose esters membrane (cellulose nitrate mixed esters and cellulose acetate)	37 47	• Low blank weight • Highly hygroscopic • Dissolved by several organic solvents • Negligible ash content	• White opaque surface • Surface diffuses transmitted light • High flow resistance • Melts at 70°C • Multiple pore sizes available	• Grav., Optical Microscopy (OM), Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), XRD

(continued)

Table 5-8 (continued)
Example of Types of Filter Media for Particulate Sampling

Filter type	Filter sizes (mm)	Characteristics: Chemical	Characteristics: Physical	Analysis Methods
Polycarbonate membrane	47	• Low blank levels • Low blank weight • No carbon analysis • Low hygroscopic tendency	• Light gray, nearly transparent surface • Minimal diffusion of transmitted light • Moderate flow resistance • Low particle collection efficiency for some pore sizes • Melts at 60°C • Multiple pore sizes available • Use for particle size classification • Retains static charge	• Grav., OA, OM, SEM, XRF, PIXE
Pure quartz filter	25 37 47 203 x 254	• Low blank level for ions • Contains large and variable quantities of Al and Si • Low hygroscopic tendency • Passive adsorption of organic vapors • Little adsorption of HNO_3, NO_2, and SO_2	• White opaque surface • Diffuses transmitted light • Moderate flow resistance • High particle collection efficiency • Melts at >900°C • Edges of filter flake in holders	• ICP, ICP/MS, IC, Thermal Carbon Analysis (TCA), Thermal Optical Transmission Carbon Analysis (TOT) Thermal Manganese Oxidation Carbon Analysis (TMO)
Mixed quart fiber (quartz filters with 5% borosilicate content)	203 x 254	• Contains large and variable quantities of Na, Al, and Si plus variable levels of other metals • High blank weight • Low hygroscopic tendency• Passive adsorption of organic vapors • Little adsorption of HNO_3, NO_2, and SO_2	• White opaque surface • Diffuses transmitted light • Low flow resistance • High particle collection efficiency • Can melt at 500°C • Becomes brittle on heating	• Grav., XRF, PIXE, AA, ICP, ICP/MS, IC, AC, T, TOR, TMO, TOT

(continued)

Table 5-8. (continued)
Example of Types of Filter Media for Particulate Sampling

Filter type	Filter sizes (mm)	Characteristics: Chemical	Characteristics: Physical	Analysis Methods
Teflon-coated glass fiber (borosilicate glass fiber mat with surface layer of Teflon)	37 47	• Low blank level for ions • High blank weight • Low hygroscopic tendency• Inert to adsorption of HNO_3, NO_2, and SO_2	• Low flow resistance • High particle collection efficiency • Melts at 60°C; glass at 500°C	• Grav., IC, AC
Glass fiber (borosilicate glass fiber)	203 x 254	• High blank levels • High blank weight • Low hygroscopic tendency • Adsorbs HNO_3, NO_2, SO_2, and organic vapors	• White opaque surface • Diffuses transmitted light•Low flow resistance • High particle collection efficiency • Melts at 500°C	• Grav., OA, XRF, PIXE, NAA, AA, ICP, IC, AC
Cellulose fiber ("paper" filter)	25 37 47	• Low blank levels; high purity • High blank weight • No carbon analysis • Highly hygroscopic • Most useful for adsorption of gases, e.g., HNO_3, SO_2, NH_3, and NO_2 after impregnated with reactive chemicals	• White opaque surface • Diffuses transmitted light • Variable flow resistance • Low particle collection efficiency possible • Burns at 150°C • High mechanical strength	• Grav., XRF, PIXE, NAA, AA, ICP, ICP/MS, IC, AC

Quartz fiber filters are the most commonly used filters for TSP/PM_{10} particulate sampling for determining mass loading as part of a collocated monitor in a FFMS. They are constructed from finely spun glass fiber and an organic binder compressed in a paper machine. They are quite fragile and must be handled with care. However, these filters have the ability to withstand high temperatures (up to 540°C). They are further typified by high-collection efficiency. In some cases, the organic binder may interfere with subsequent analysis, so the filter is flash-fired to remove the binder material. Quartz filters are nonhygroscopic, thus able to be used in areas where humidity is high. Because they are glass, they are the filter choice for most corrosive atmospheres. Because of their high silicate content, they are extremely difficult to ash by chemicals or heat. Therefore, extraction procedures are performed on these filters to remove the sample for subsequent chemical analysis. For this reason, flash-fired quartz filters are the preferred filter of choice as part of a collocated monitor in a FFMS.

(2) Equivalent methods. Equivalent or real-time methods for measuring TSP and PM_{10} rely on instruments equipped with either a radiometric detection device or an oscillating pendulum detection device. To date, the EPA has designated only two radiometric instruments and one oscillating pendulum instrument as equivalent methods. These are the Graseby and Thermo Environmental Beta Gauge instruments and the Rupprecht and Pataschnick (R&P) TEOM® Monitor, respectively.

As discussed in Chapter 4 and illustrated in Figure 5-27, the operation of the beta gauge involves particulate material being accumulated on a continuously moving filter tape that is passed between a source of low-energy

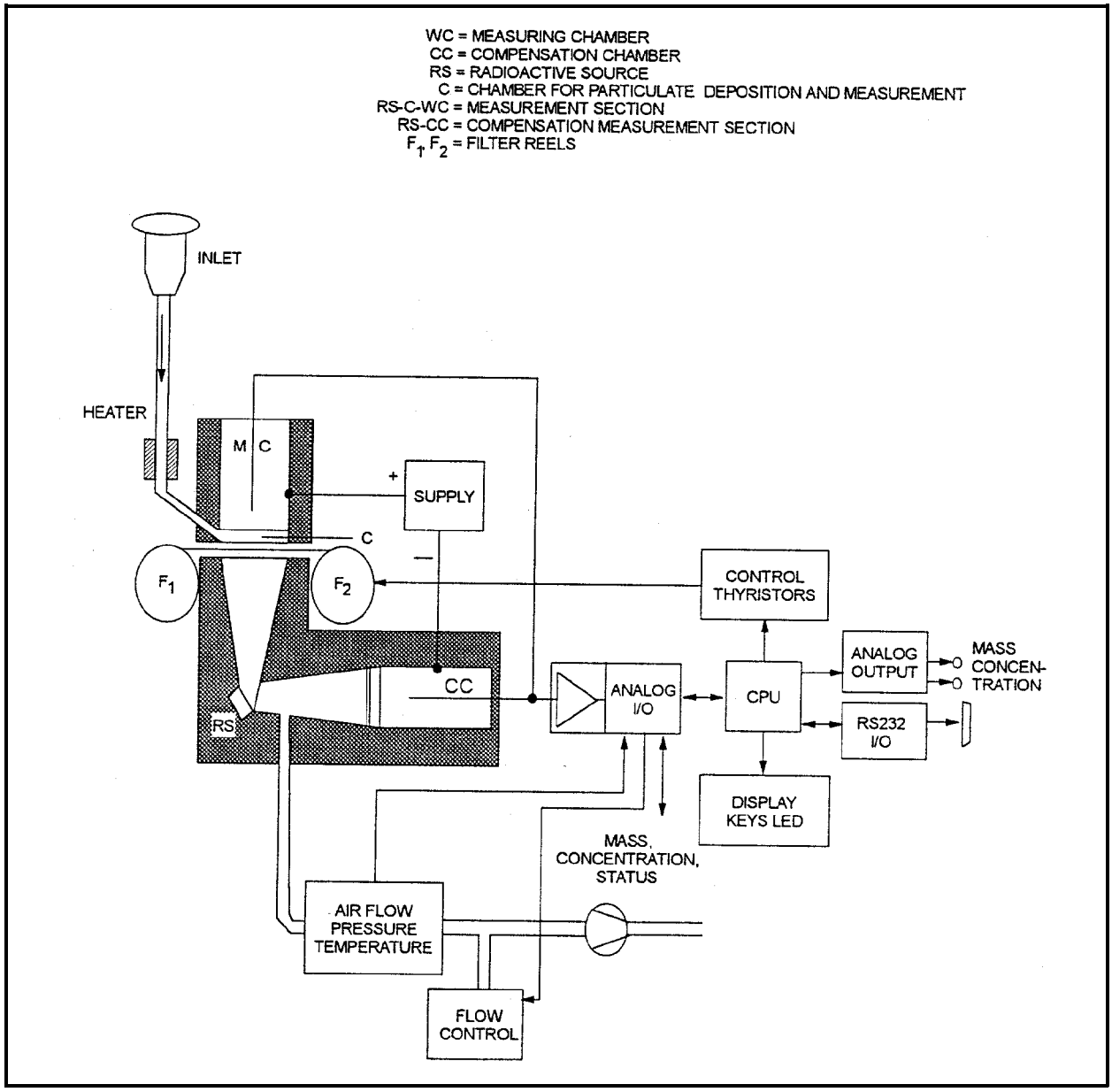


Figure 5-27. Example of operation of a typical commercial PM_{10} beta-gauge sampler

beta rays (i.e., 0.01 to 0.1 MeV electrons) and a detector at a designated feed rate. Beta radiation is attenuated by the filter tape according to the approximate exponential function of particulate mass loading (i.e., Beer's Law). Attenuation of blank filter tape prior to particulate loading, or some other "control" material, is also measured for comparison. The difference in attenuation between the blank and exposed filter is calculated as the blank corrected particulate mass concentration for the specific time period of exposure as determined by the tape feed rate. Beta gauge samplers are operated at a relatively low flow rate (nominally 16.7 liters/minute) with sampling

inlets designed for either TSP or PM_{10} size fractionation. While these monitors are capable of mass concentrations for averaging times as short as 30 minutes, 2-to 24-hour averaging periods are frequently required with typical ambient concentrations to obtain sufficient particulate deposition for an accurate determination.

The Rupprecht and Pataschnick tapering element oscillating microbalance (TEOM®) monitor shown in Figure 5-28 is based on an altogether different measurement principle. With this monitor, particulate is continuously accumulated on an exchangeable filter cartridge. The filter cartridge is fixed to a patented measurement device consisting of a TEOM®. Particle-laden air enters the monitor through a size fractionating sample inlet and then passes through the tapering element, which consists of a hollow glass tube that oscillates in an applied electric field. Particulate matter is deposited on the filter cartridge, which is mounted at the tip of the tapering element. Since the frequency of oscillation of the tube and filter is proportional to their combined inertial mass, particulate loading can be continuously measured. The monitor continuously measures particulate mass at concentrations between 5 micrograms per cubic meter ($\mu m/m^3$) and several grams per cubic meter (g/m^3). Mass loading rate, mass concentration, and total mass accumulation may be calculated. The exchangeable filter cartridges are designed to allow for future chemical and physical analysis. The monitor can be operated as either a TSP monitor or as a PM_{10} monitor, depending on the sampling head attached. Further size fractionation is possible with an optional sampling head designed to pre-separate particles at 2.5 and 10 µm diameter cut points. Both the beta and oscillating microbalance techniques are fully discussed in Chapter 2, Methods IO-1.1 through IO-1.3, as part of EPA's *Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air*.

Each of the reference and equivalent methods described above has its own unique operational requirements and characteristics. Obviously, each method has its own advantages and important interferences to be aware of. The most important of these factors are outlined in Table 5-9.

b. Sampling activities. As with other types of fenceline monitoring activities, particulate sampling is generally scheduled in coordination with remedial activities at the HTRW site. Often, several phases of a sampling program are planned to coincide with or precede the mobilization, construction, and operation phases of the remediation project. Phases typically include background monitoring, an intense (high frequency, multi-sampler, multi-analyte) start-up monitoring phase, and long-term monitoring.

Sampling activities generally include equipment mobilization or set-up, sampler calibration (initial and field), routine operation and maintenance of samplers, preparation and recovery of samples, and sample storage and transport. Appropriate procedures for each of the methods described above are outlined in detail within the Federal Register method references, the *Compendium Methods for the Determination of Inorganic Compounds in Ambient Air*, and instrument operating manuals available from individual vendors.

c. Siting requirements and location. The number and locations of TSP/PM_{10} samplers used in fixed-fenceline monitoring systems are determined on the basis of several factors. These generally include:

- The purpose(s) of the sampling program and data quality objectives.

- The size and shape of the waste site.

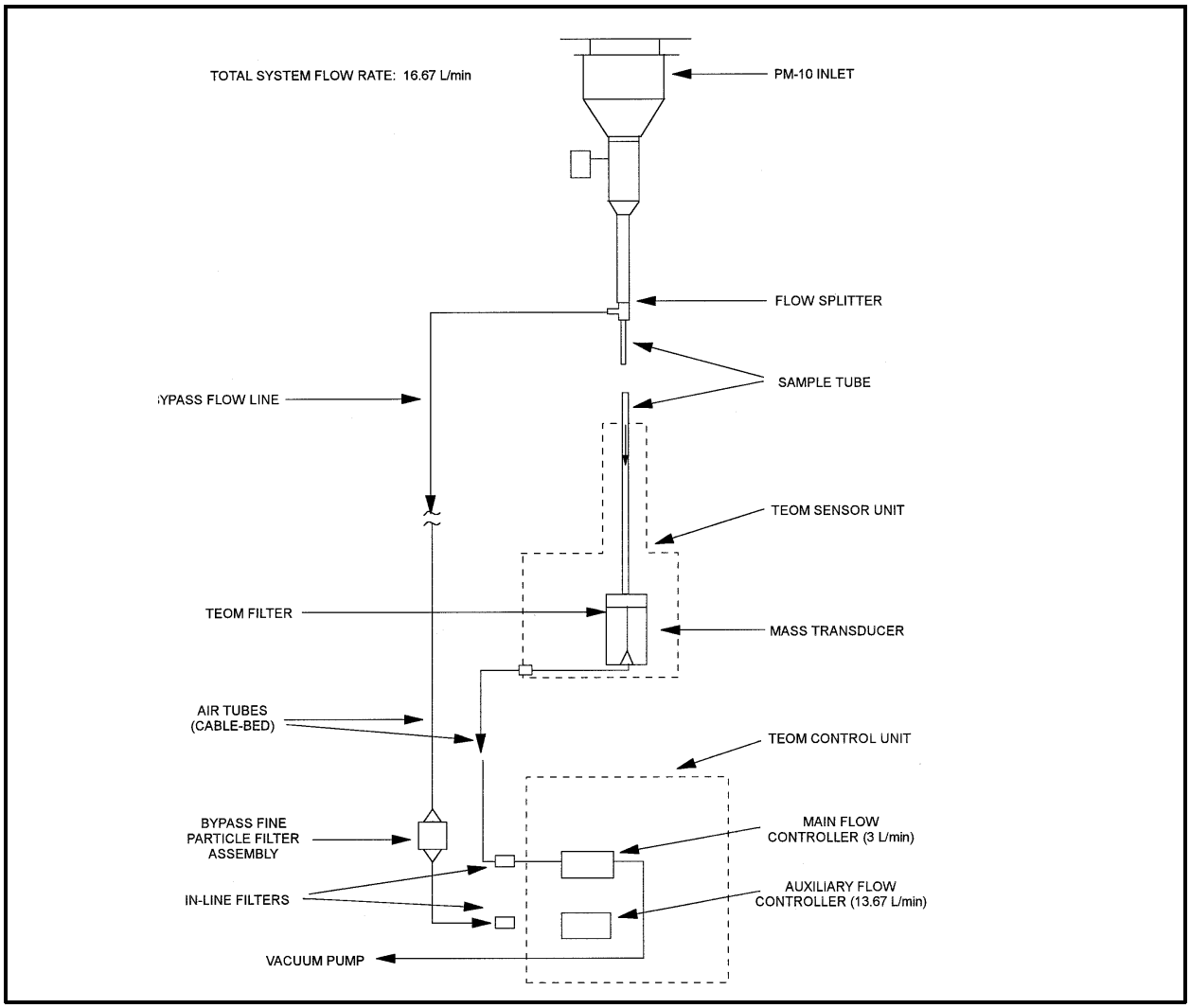


Figure 5-28. Example of a real-time PM_{10} sampler based upon the oscillating microbalance (TEOM®) technique

- The locations of potential on-site emission sources.
- The locations of topographic features that affect the dispersion and transport of site emissions
.
- The variability of local wind patterns.
- The locations of sensitive receptors such as schools, hospitals, and concerned citizens.
- The level of available funding.

Table 5-9
Example of Advantages/Disadvantages of Particulate Sampling Methods

Sampler Type	Advantages	Disadvantages
Hi--Vol Methodology	• High flow rate = more material captured = lower detection of ambient concentrations of inorganic materials (assuming identical filter medium and analysis technique). • Volumetric flow control ensures constant flow rate. • Highly durable and versatile.	• Filter may cause plugging and stress motor. • Weather can cause variable flows • Equipment and electrical not very durable in bad weather
Dichotomous Methodology	• Collects two fractions so information can be obtained about total PM_{10} and either/or both of the two fractions. • Analysis by XRF. • Operates at a low flow rate (about 0.6 ft^3/min) allowing use of filter media that would otherwise quickly clog at hi-vol flow rates.	• Filters may plug during sampling in inclement weather from rain. • Tripod needs to be secure to the sampling platform.
Beta-Gauge Methodology	• Measurement mechanism has no moving parts. • Heating of sample air stream generally not required. • Less sensitive to fluctuations of ambient temperature, pressure and humidity.	• May require a license from Nuclear Regulatory Commission for radioactive source. • Only authorized personnel can repair source. • Generally requires some protection from internal condensation.
Oscillating Microbalance Methodology	• Can provide highly precise measurements for averaging periods of 1-hour or less.	• Must be isolated from excessive mechanical noise and vibration. • Constant internal temperature must be maintained above ambient field temperature.

Typically, programs designed for determining long-term concentration levels or public health impacts require fewer monitoring locations than those intended to monitor compliance with short-term action levels because the long-term prevailing wind directions are usually more predictable than day-to-day wind patterns; therefore, samplers can be more accurately situated for measuring significant long-term effects. Dispersion modeling of source emissions, using climatological data as input, is often performed to determine the most appropriate sampling locations (i.e., areas of maximum or significant effects).

For determining concentration levels with respect to short-term effects, a fixed network of samplers ideally should be located around the perimeter of the HTRW site, with additional samplers located near working areas and near sensitive receptors. The number of samplers will depend, primarily, on the size and shape of the HTRW site. For large sites surrounded by nearby residences, a 12-station network would provide nearly complete spatial coverage of the fenceline (i.e., one sampling station every 30°). In some cases, only samples from stations located directly upwind or downwind of the site for a given sampling period might need to be analyzed. Alternatively, for smaller sites, fewer receptors, and/or smaller budgets, a smaller number of stations may be used; possibly as few as one sampling station in each compass quadrant. The minimum and maximum number of recommended monitoring locations for a typical HTRW site are shown in Figure 5-29.

As illustrated in Figure 5-29, the location of time-integrated with real-time perimeter volatile organic monitoring systems may be controlled by the Analytical Center coupled with the on-site meteorological station. In essence, during periods of on-site remediation, the Analytical Center would sense the wind direction from the meteorological station and turn-on the time integrated TSP/PM_{10} monitors to operate only when the wind comes from the upwind quadrant. Under this scenerio, sampling would occur only during periods of upwind designation, thus the user is able to determine upwind/downwind concentrations and the effect of the remediation activities on the surrounding community. This approach limits the number of samplers to be purchased and the number of samples to be analyzed. Sampling may, however, require several days to obtain enough sample for analysis, especially with the determination of metals from the filter material.

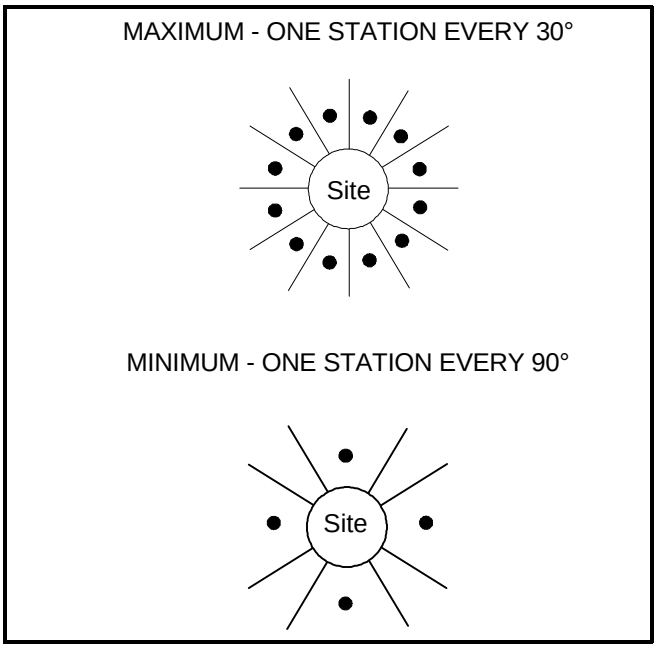


Figure 5-29. Depiction of maximum and minimum number of recommended monitoring locations for a typical HTRW site

Similiar to other monitoring systems, sampler placement is very important to ensure a representative sample is obtained. In many cases, wind flow obstructions caused by nearby buildings, trees, hills, or other obstacles may constrain sampler placement. Other constraints might be related to security, the accessibility of electrical power, or the proximity to roadways and other pollution sources that might affect the representativeness of the sample. Specific guidelines for selecting sites to achieve representative conditions are listed in Chapter 5,Paragraph 3c and repeated here:

- The most desirable height for sampler inlets is near the breathing zone (i.e., about 5 to 6 ft above ground). Practical factors, such as high impermeable fences surrounding the waste site, may sometimes require that sampling inlets be placed slightly higher (at least 1 meter above the top of the fence).

- Samplers should be located at least 20 meters from the dripline of nearby trees and <u>must</u> be at least 10 meters from the dripline of trees when the trees act as an obstruction to airflow.

- Samplers must be located away from obstacles and buildings such that the distance between the obstacles and the sampler inlet is at least twice the height that the obstacle extends above the sampler inlet. Airflow must be unrestricted in an arc of at least 270° around the sampler, and the predominant wind direction for the season of greatest pollutant concentration potential must be included in the 270° arc.

- The sampler and nearby roadways must be sufficiently separated to avoid the effects of dust re-entrainment and vehicular emissions on measured air concentrations.

- Stations located in unpaved areas should be placed on ground covers so that the effect of locally re-entrained or fugitive dusts will be kept to a minimum.

A properly collocated time-integrated TSP/PM_{10} and inlet probe for a real-time volatile organic monitoring system is pictured in Figure 5-24 and diagrammed in Figure 5-30. When utilizing collocated sites, each of the samplers must be separated by a minimum of 6 feet so representative parcels of air can be extracted by each unit. In addition, the sampler inlets must be at a minimum of 6 feet above the ground. The sampler platform should be anchored (2 feet) in cement. All electrical connections must be protected from the elements. Two receptacles should be installed for more complex collocated systems, as illustrated in Figure 5-30. It is recommended that the system be secured with a chain-link fence and outdoor lighting.

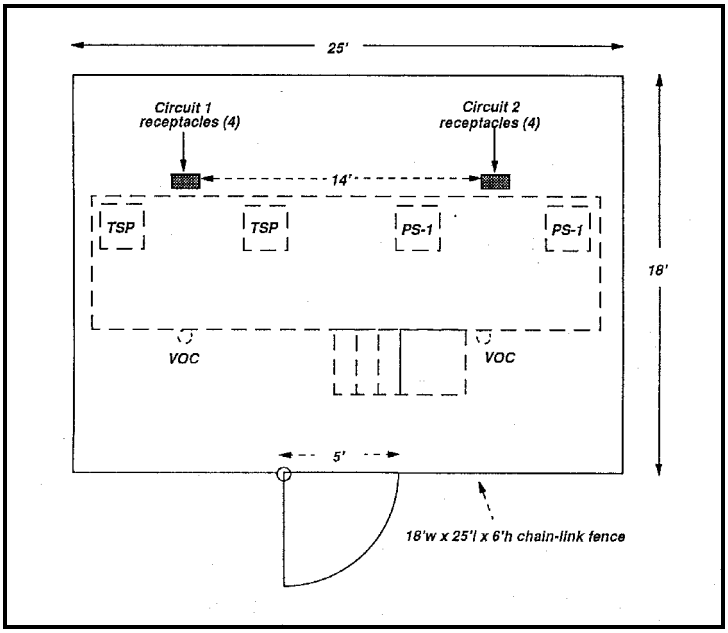


Figure 5-30. Example of a diagram of a collocated TSP and VOC inlet samplers

d. Sampling periods and frequencies. Sampling period refers to the length of time to which each measurement value is referenced (e.g., 30-minute, 1-hour, 24-hours, etc.). The sampling frequency is the number of sampling periods conducted within a given time interval (e.g., daily, one every third day, etc.). For typical HTRW monitoring programs, the sampling period may range from a few seconds to 72 hours, depending on the specific goals and data requirements of the program. Sampling periods of a few seconds are performed using real-time or grab sampling techniques, whereas longer sampling periods are usually performed using time-integrated methods. For real-time monitoring, the sampling frequency is usually continuous, although sampling may be limited to certain times of the day when remedial activity is occurring. Time-integrated sampling may be performed continuously (i.e., back-to-back sample collection, or at intermittent, discrete intervals. Specific program goals and available funding will normally dictate whether continuous or intermittent sampling intervals are performed. Grab sampling is only performed when an instantaneous spot check of the air constituents is required (e.g., as a pre-monitoring screen for constituent compounds), or is a specified corrective action.

Sampling periods must be chosen for comparability with relevant action levels or ARARs. For example, if the measurement data are to be compared with a 30-minute action level, a 30-minute sampling period is normally required (alternatively, continuous, real-time monitoring can be performed and the resulting data averaged over 30-minute intervals). Compliance with long-term action levels usually is determined using a series of 24-hour sampling periods. In some cases, sampling periods also may depend on the amount of sample volume needed

to achieve acceptable detection limits. A 1-hour sampling period, for instance, will yield a detection limit one-half that of the same technique operating with the same flow rate for 30 minutes.

The required frequency of sample collection depends primarily on:

- The variability of emission rates with respect to the time period associated with the action level.
- The variability of meteorological and other factors that might affect pollutant dispersion.
- The level of confidence needed for determining mean or maximum downwind concentrations.
- The level of available funding.

When action levels are based on short-term averages and the pollutant concentrations are expected to vary significantly over time, continuous sample collection may be needed to achieve an acceptable level of confidence that PALs are not exceeded. Note that the level of confidence required in the measurement results may depend on how close the measured ambient concentration levels are to the action level concentrations (i.e., the higher the measured concentrations, the greater the confidence required). For determining compliance with long-term action levels, a minimum sampling frequency of once every sixth day is normally required. However, if the measured concentration levels are near levels of concern, a greater frequency of collection, perhaps daily, will be required (e.g., operating schedule for PM_{10} sampling given in 40 CFR, Part 58. 13).

5-8. Verification of the Sample Collection System

Proper performance of the collection system should be verified regularly by measuring a number of critical parameters at selected locations along the sample path. The purpose of QC checks is to demonstrate that sample integrity is not lost during travel through the sample collection system. Sample integrity may be compromised through system leakage, system plugging, internal condensation of contaminants and/or water vapor, or absorbtion of contaminants on internal surfaces. Parameters typically included are various flow rates, pressures, temperatures, electrical resistances, and transfer efficiencies. The frequency of these checks will depend on the expected stability of the specific parameter. Table 5-10 provides a summary of the parameters that should be verified and recommended frequencies for these checks

The primary parameter requiring verification for the collection system is transfer efficiency as measured by percent recovery of gas sample of known concentration. An 80 to 120 percent tolerance recovery is typical. Measurements exceeding the tolerance threshold should trigger diagnostic procedures and/or corrective action. Secondary parameters needing verification are measurements of flow rates, pressures, sample line temperatures, and electrical resistances. Tolerances for each of these parameters should be established during system design based on the manufacturer's performance specifications for specific collection system components such as pumps and heated sample lines.

Figure 5-31 illustrates a typical equipment set-up for both a transfer efficiency check and a flow rate check of a FFMS collection system. As shown, flow rate is simply measured by attaching a rotameter to the sample inlet. For transfer efficiency, a supply of standard gas of known concentration is introduced at the sample inlet, drawn

Table 5-10
Example of Typical Collection System Audit Parameters

Audit Parameter	Measurement Location	Suggested Minimum Frequency	Application
Sample transfer efficiency	• introduction of standard gas at sample inlet	Weekly	Verification that sample integrity is maintained
Flow rate	• at sample inlet • at sample pump • at various ports to the analytical system	Weekly	Verification of unrestricted sample flow
Sample line temperature	• at heat trace sample line control panel • at junction box between each heat trace sample line segment	Each shift any weekly	Verification of performance of heat trace sample line according to specification
Sample line resistance	• at junction box between each sample line segment	Weekly	Verification of performance of heat trace sample line according to specification
Operating gas pressures	• at carrier gas canister • at calibration gas canisters • at auxiliary air compressor	Daily	Verification of performance operating gas supply according to specification

through the heated sample line by the primary sample pump, delivered to the sample conditioning system, and presented to the analytical system in the Analytical Center for quantitation. To accurately simulate actual sampling conditions, the pressurized standard gas must be introduced at the sample inlet at atmospheric pressure. Therefore, either a flow-through Tedlar® bag or a more elaborate equilibration apparatus with a sensitive pressure gauge is used. Experience has shown the Tedlar® bag arrangement to be the most reliable and simple to operate in the field, as illustrated in Figure 5-31.

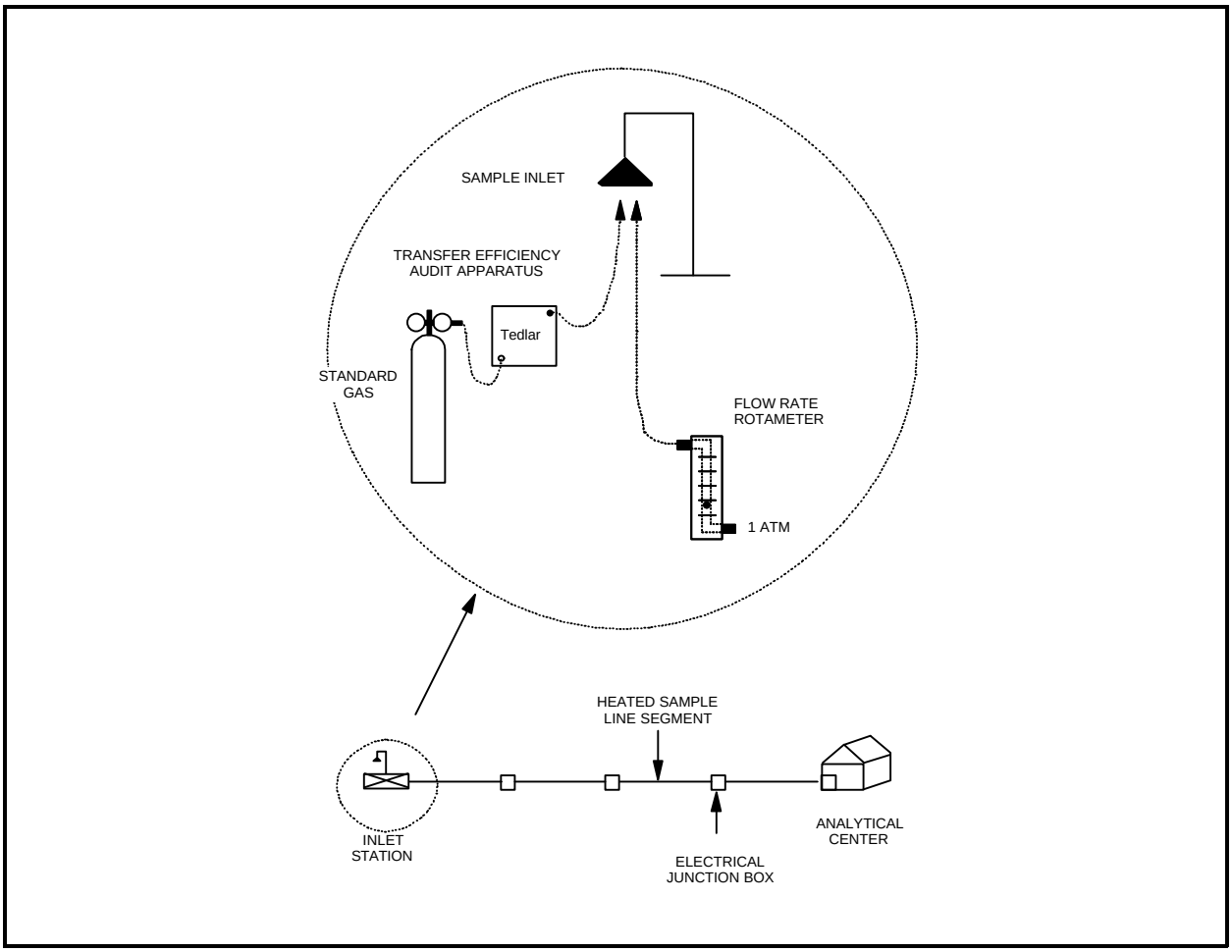
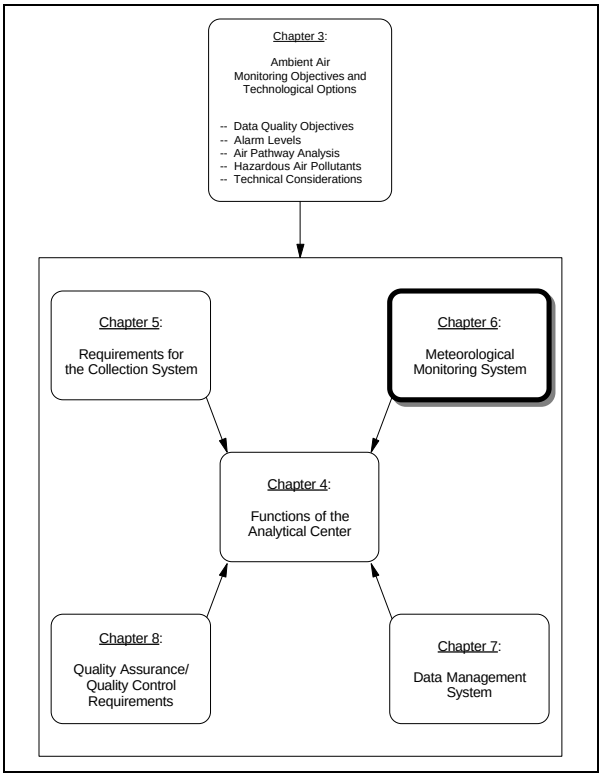


Figure 5-31. Example of QC procedures for evaluating transfer efficiency and flow rate of a FFMS

SUMMARY OF METEOROLOGICAL MONITORING SYSTEM

The meteorological system is an outreach of the analytical center and an integral component of any perimeter air monitoring program. This system collects meteorological data that is recorded and stored in the analytical center.



SECTION I: INTRODUCTION AND OBJECTIVE

- Meteorological System Overview
- Purpose of Meteorological System

SECTION II: METEOROLOGICAL MONITORING SYSTEM AND ORGANIZATION

- Introduction
- Meteorological Data Collection and Parameters
- Communication Process
- Data and Reporting Formats
- Data Quality Assurance/Quality Control (QA/QC)

SECTION III: INTEGRATION OF ANALYTICAL SYSTEM WITH METEOROLOGICAL MONITORING

- Introduction
- System Network and Design

SECTION IV: METEOROLOGICAL MONITORING AND PERIMETER ACTION LEVELS

- Introduction
- Alarm Level 1
- Alarm Level 2
- Alarm Level 3
- Alarm Level 4

The Meteorological System assists with determining the risk assessment to off-site receptors from contaminants leveling the site during remediation. Chapter 6 discusses the integration of the meteorological data with the perimeter air monitoring program. Users will be introduced to the meteorological parameters to be monitored, siting criteria and tower requirements, the communication process of the meteorological station with the analytical center, QA/QC, and data processing at the analytical center.

Panel 6-1. Overview of the Meteorological Monitoring System.

6-1. Introduction

Meteorological monitoring assists with determining the net site emissions and risk to off-site receptors from contaminants leaving the HTRW site during remediation. Meteorological monitoring coupled with pollutant monitoring allows an assessment of the air pathway during all times that air quality data is collected. In particular, most models used in determining emission rates of pollutants from a HTRW site require the input of wind speed, wind direction, temperature, precipitation, relative humidity, barometric pressure, and atmospheric stability.

The same QA/QC activities associated with FFMS pollutant monitoring must be implemented in the meteorological monitoring program. The monitoring of atmospheric conditions must be (1) representative of the atmospheric conditions that affect the pollutant being transported off the site, (2) comparable across the measurement network, and (3) of the same quality as the pollutant measurement program.

The objective of Chapter 6, Meteorological Monitoring System, is to discuss the integration of the meteorological data with the FFMS. This chapter will discuss the meteorological parameters to be monitored, siting criteria and tower requirements, communication of the meteorological station with the Analytical Center, QA/QC, and the processing of meteorological data for input to site-specific models.

Meteorological sensors must provide data of sufficient accuracy and resolution to enable a meaningful interpretation of the monitoring results.

6-2. Meteorological Monitoring System and Organization

a. Introduction. The purpose of this paragraph is to provide detailed information on meteorological monitoring stations that could be used to obtain continuous on-site meteorological data at an HTRW site. Included are an introduction that addresses the necessity for meteorological monitoring; a section on meteorological data collection parameters that discusses siting a station, tower requirements, and the parameters that need to be measured; descriptions of alternative communication processes, data and reporting formats, data QA/QC, and alternative data telemetry processes. The collection of meteorological data may often be required both prior to and during the remediation of contamination at an HTRW site. Meteorological data are often necessary to determine the potential risk to neighboring communities from contaminants released during the site remediation. Therefore, if representative meteorological data are not available from a neighboring National Weather Service (NWS) facility, these data will need to be collected on site.

Prior to the remediation of a contaminated HTRW site, an APA must usually be performed. The primary components of an APA are:

- Characterization of air emission sources (e.g., estimation of contaminant emission rates).
- Determination of the effects of atmospheric processes (e.g., transport and dilution).
- Evaluation of receptor exposure potential (i.e., what air contaminant concentrations are expected at receptors of interest for various exposure periods).

The overall goal of an APA is to evaluate the actual or potential effects of remediation on air quality. This evaluation is usually based upon the results of a computerized dispersion model of the effects of known releases of contamination from the HTRW site. Dispersion models usually require 1 year of representative wind data to define the path and concentration of the plume as a function of range from the site. If wind data are not available from the NWS, instrumentation probably will need to be established to collect it on-site.

The specific goal of any associated perimeter air monitoring network is to evaluate the potential exposure via the air pathway of residents and workers in neighboring communities to contaminants from the HTRW site. To determine this potential, the effects of measured releases on neighboring communities must be modeled. These models require meteorological data representative of the site during the episode. To complement the air monitoring network, instrumentation may be established on-site to collect meteorological data for site-specific windroses and receptor combinations.

b. Meteorological data collection and parameters. A meteorological station at a HTRW site must provide representative data for the area around the site and for each of the parameters required by dispersion models appropriate to that site. Careful consideration must be given to both the specification and siting of the appropriate equipment. The following sections contain discussions of meteorological station siting criteria, tower requirements, and the parameters to be measured.

(1) Siting criteria. The siting of a meteorological station is very important to the success of a remediation project. Siting of the meteorological station should follow guidance specified in three U.S. EPA documents:

- *Quality Assurance Handbook for Air Pollution Measurement Systems, Vol. IV, Meteorological Measurements*, EPA-600/R-94/038d, Office of Research and Development, Research Triangle Park, NC, March 1995.

- *On-site Meteorological Program Guidance for Regulatory Modeling Applications*, EPA-450/4-87-013, Office of Air Quality Planning and Standards, Research Triangle Park, NC, 1987.

- *Ambient Monitoring Guidelines for Prevention of Significant Deterioration (PSD)*, EPA-450/4-87-007, Office of Air Quality Planning and Standards, Research Triangle Park, NC, 1987.

As a general rule, the station should be sited away from the influence of obstructions such as trees and buildings and should be in such a position that it can make measurements that are representative of the HTRW site. Table 6-1 documents the key siting criteria, as provided from the above references, for properly locating long-term meteorological monitoring stations.

Table 6-1
Example of Key Siting Criteria for Meteorological Stations at HTRW sites

Factor	Criteria
1. Vertical Spacing Above	For long-term monitoring studies, sensors should be located 10 meters above the ground.
2. Horizontal Spacing	Optimum horizontal spacing for meteorological stations should be located away from nearby obstructions (trees, buildings, etc.) by a distance of 10 times the height of the obstruction.
3. Unrestricted Airflow	Unrestricted airflow must exist around the sensors.
4. Spacing from Roadways	Meteorological station must be placed at a distance greater than 25 meters from the edge of the nearest traffic lane.

The following are other practical guidelines for locating a meteorological station at a HTRW site:

- Locate the station in a portion of the site that allows for ease of access to security, power, and lighting.
- Meet siting criteria of 10 times the height of nearest obstructions (i.e., trees, buildings, etc.).
- Locate the meteorological station outside the exclusion zone to minimize intrusion into site during routine operation/ maintenance and quarterly audits of the system.

(2) Tower requirements. To representatively measure the wind speed and direction for the area around the HTRW site, meteorological wind sensors must be sited away from obstructions, as described above, and must be suspended 10 meters above the ground. A 10-meter, self-supporting meteorological tower should be erected on a 3-foot diameter by 3-foot deep concrete slab. This concrete slab will act as the anchor or primary support for the 10-meter meteorological tower. In addition, a lightening rod should be attached to the highest point on the tower and connected to the earth ground by a heavy copper wire, as illustrated in Figure 6-1.

(3) Meteorological parameters. Meteorological variables needed for most of the USACE and EPA computerized dispersion models include mean wind speed, wind direction, ambient air temperature and Pasquill stability category. The most accepted methods for determining stability category from HTRW sites are derived from (1) ambient air temperatures (i.e., measured at 2 and 10 meters) and solar radiation using the ΔT method, or (2) the standard deviation of the wind direction (σ_a). The measurement of precipitation, barometric pressure, and relative humidity in conjunction with ambient air monitoring at the HTRW site is highly recommended and is often a regulatory requirement. The time and date of each measurement must also be recorded. This section contains detailed information on the above meteorological variables.

Table 6-2 provides examples of system accuracy and measurement resolution for each of the measured meteorological variables. Locations of the specific instruments, frequency of measurements, units of measurements, required instrument accuracy, and measurement resolution for the meteorological instruments is included in this section.

Table 6-2
Example of System Accuracy and Measurement Resolution for Meteorological Systems at HTRW sites

Data Type	System Accuracy	Measurement Resolution
Wind Speed	+ or -0.5 m/s	0.1 m/s
Wind Direction	+ or -5°	1°
Ambient Temperature	+ or -0.5°C	0.1°C
Delta T (Vertical)	+ or -0.1°C	0.02°C
Radiation	50 W/m^2	10 W/m^2
Precipitation	+ or -0.5 mm	0.3 mm
Time	+ or -5 minutes	

Wind speed is one of the primary variables needed for a dispersion modeling analysis. It determines the amount of initial dilution encountered by the plume exiting the emission source, as well as the amount of plume rise. An instrument to measure wind speed should be located on the meteorological tower at a height of 10 meters above the ground surface (see Figure 6-1). Observations should be recorded continuously; at 1-hour intervals, the mean wind speed with standard deviation, and maximum and minimum values should be calculated. The wind speed should be recorded in units of meters per second (m/s) within a range of 0 to 20 m/s.

The wind direction, for meteorological purposes, defines the direction from which the wind is blowing and is measured in degrees clockwise from true North. Wind direction determines the direction a plume will travel. The instrument to measure wind direction should be located on the meteorological tower at a height of 10 meters above the ground surface, as illustrated in Figure 6-1. The wind direction should be recorded continuously; at 1-hour intervals; the mean wind direction and the standard deviation of wind direction should also be calculated. The wind direction should be recorded in units of degrees with an instrument resolution to the nearest 1°.

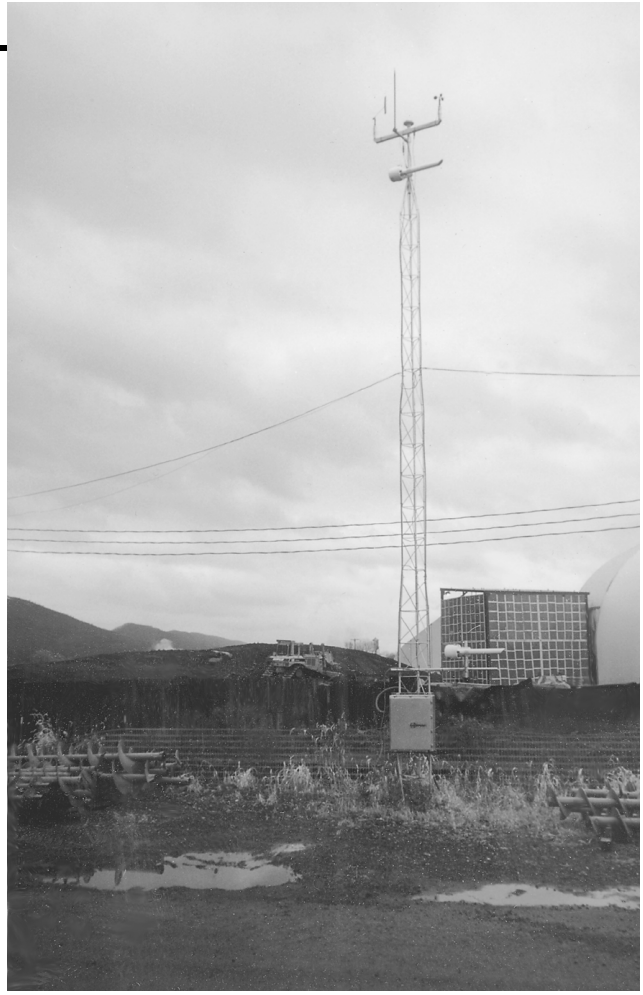


Figure 6-1. Example of a 10-meter meteorological station at a HTRW site

Because of problems associated with averaging wind direction as the vane crosses over the North (i.e., 0 to 360°), a 0° to 540° instrument should be used.

The ambient air temperature is used in determining the amount of rise experienced by a buoyant plume. If the ΔT method is used to calculate the Pasquill stability category, the ambient air temperature should be measured at both 2 meters and 10 meters above the ground, as illustrated in Figure 6-1. The temperature sensors should be housed in aspirated enclosures. The temperature at 10 meters and optionally the ΔT should be measured continuously; at 1-hour intervals, the mean temperature and ΔT, with maximum and minimum values, should be calculated. The temperature and ΔT should be recorded in units of degrees Celsius (°C) and converted to degrees Kelvin (K) for model input purposes. The ambient air temperature measurements are generally made over a nominal range of -50° to +50°C.

Solar radiation, which is related to the stability of the atmosphere, should also be measured at the meteorological station. As stated earlier, the solar radiation could be used with the ΔT measurement to estimate the stability category. The instrument measuring solar radiation should be mounted as the highest instrument at the 10-meter level above the ground, as illustrated in Figure 6-1. The solar radiation should be measured continuously; at 1-hour intervals, the mean, maximum, and minimum values should be calculated. The solar radiation should be recorded in units of watts per meter squared (W/m^2) with a measurement resolution of 10 W/m^2.

Barometric pressure (P_{bar}) and relative humidity (RH) are not typically required to perform dispersion modeling. However, this data is required to calculate air density and are often useful in the calibration of ambient air monitoring equipment as part of the FFMS. A meteorological station at an HTRW site should include these sensors. Both P_{bar} and RH should be measured continuously; at 1-hour intervals, the mean values should be recorded. The P_{bar} should be measured in units of mBars and the RH in units of percent moisture. The P_{bar} measurements should be made within a range of 800 to 1100 mBars, resolved to the nearest mBar, and accurate to within ±5 mBars. The RH measurements should be made within a range of 0 to 100 percent RH, resolved to the nearest percent, and accurate to within ±5 percent.

Precipitation should be recorded at the HTRW site even though it will not be used by the dispersion model. The precipitation measurements are useful information during remediation activity and for the data review and validation process. The precipitation gauge should be at least 6 inches in diameter and should be heated for winter operation. The precipitation gauge should be located away from the tower (10 meters), positioned on a level platform about 1 meter above ground. In some climates, a snow fence is suggested around the precipitation gauge. Precipitation should be totalized continuously; at 1-hour intervals, the total value should be recorded. Precipitation measurements should be made in units of inches. The selected instrument should measure precipitation within a range of 0 to 100 inches and accurate to within 0.1 inch.

A secondary parameter used in dispersion models requires the operator of the meteorological station and FFMS to calculate stability categories as indicators of atmospheric turbulence.

The amount of turbulence in the atmosphere has a major impact on the rise of on-site emission plumes and upon their subsequent dispersion by diffusion. Turbulence is a result of many factors, including windflow over rough terrain, trees, or buildings (mechanical turbulence); rising warm air (thermal turbulence); and migrating high and low pressure air masses. Any factor enhancing the vertical motion of air will increase the amount of turbulence. For a given wind speed, stable atmospheric conditions provide smaller levels of atmospheric turbulence than do unstable conditions and can lead to higher model-predicted concentrations.

For site perimeter impacts, dense gas releases will only be weakly affected by stability classification. As the release becomes neutrally buoyant, the plume will become more influenced by atmospheric conditions such as stability class.

Dispersion models currently use stability categories as indicators of atmospheric turbulence. Based on the work of Pasquill and Gifford, six stability categories have been defined, where Category A represents extremely unstable conditions and Category F represents moderately stable conditions. Methods for estimating atmospheric stability categories from on-site data are provided in the *Guideline on Air Quality Models (Revised) and On-Site Meteorological Program Guidance for Regulatory Modeling Applications*. The Pasquill-Gifford (P-G) stability classification method attempts to parameterize the results of turbulence in the atmosphere (stability) using observations of wind speed and subjective estimates of incoming solar radiation. The Pasquill categories are:

Pasquill Categories	Stability Classification
Extremely unstable	A
Moderately unstable	B
Slightly unstable	C
Neutral	D
Slightly stable	E
Moderately stable	F
Extremely stable	G

Modeling guidelines published by EPA identify four methods of using on-site data to determine the Pasquill stability class of a parcel of air at a HTRW site. In order of preference, these methods are:

- Turner's 1964 method using site-specific data, which include cloud cover, ceiling height, and surface (~10 meters) wind speeds.
- Vertical wind direction fluctuations (σ_e) from site-specific measurements. σ_e may be determined from elevation angle measurements or may be estimated from measurements of σ_w according to the transform: $\sigma_e = \sigma_w / \mu$.
- Horizontal wind direction fluctuation (σ_a) from site-specific measurements.
- Turner's 1964 method using wind speed with cloud cover and ceiling height from a nearby NWS site.
- Temperature changes with altitude. Two thermocouples positioned at the 10- and 2-meter location to give a ΔT output.

Turner's 1964 Method with Site-Specific Data. Turner provided an objective method for implementing the P-G method using routine airport observations. Stability using Turner's method is a function of wind speed and Turner's net radiation index. The latter is dependent on cloud cover and ceiling and the solar insolation class, which is a function of the solar elevation angle and is objectively determined based on location and time.

Turner's method in combination with the P-G stability categories provide practical procedures for routinely implementing the Gaussin dispersion models. By virtue of its historic precedence and widespread use, EPA considers Turner's method to be the benchmark procedure for determining P-G stability.

Vertical Wind Direction Fluctuations (σ_e). Next to the Turner 1964 system employing on-site observations, the EPA prefers that stability be determined from vertical wind direction fluctuations (σ_e). The most economical way of measuring vertical wind speed fluctuations is to install a lightweight propeller on a vertical axis. The propeller will rotate, first, one way and then the other as the air mass is alternatively buoyant and subsiding. Another way to measure vertical wind fluctuations is to use a bivane that pivots on a single point and has a circular band on the tail instead of the usual fins. The bivane will tilt in response to the combinations of vertical and horizontal winds. Further details, including the calculational procedure for vertical velocity fluctuations, can be found in EPA's *"On-Site Meteorological Program Guidance for Regulatory Modeling Applications."*

Horizontal Wind Direction Flucutation (σ_a). Next in order of EPA preference for determining stability is the method based on horizontal wind direction fluctuations. In contrast to vertical fluctuations, the

equipment to measure horizontal fluctuations is more reliable. A low mass wind vane is used in conjunction with a micro-computer to determine the standard deviation of the horizontal meander.

Turner's 1964 Method Using NWS Data. This method is similar to the Turner 1964 Method except NWS data is used in place of site-specific data. This is the least favored of the methods because there is generally a lack of proximity of a NWS to a HTRW site.

Temperature Change (ΔT) with Altitude. Temperature measurements made at two different elevations (i.e., 10- and 2-meter height) can be used to determine stability. This method normally employs a tower with motor-driven fans (aspirators) and a highly sensitive thermocouple or thermistor that measures the temperature differences. The use of this method is approved by the Nuclear Regulatory Commission but not by the EPA. The releases from nuclear facilities generally have no plume rise and occur at elevations of 30 to 45 meters. The emissions from warm stacks that are of greatest interest to EPA result in plume elevations of 50 to several hundred meters. The EPA believes that the ΔT scheme does not adequately assess the stability in the boundary layers in which most of its plumes disperse.

For fugitive sources and toxic gas releases that occur without plume rise, the ΔT method may provide a reasonable way of determining stability.

Finally, the solar radiation measurement can be combined with the ΔT to determine atmospheric stability at the site. The solar radiation/Δ-T (SRDT) method retains the basic structure and rationale of Turner's method, while eliminating the need for observations of cloud cover and ceiling. It is the recommended alternative procedure for use with on-site data.

The SRDT method (see Table 6-3) uses the 10 meter wind speed in combination with measurements of total solar radiation during the day and temperature difference (ΔT) at night. The method is based on Bowen (1983) with modifications as necessary to retain as much as possible of the structure of Turner's method as implemented in the EPA's recommended meteorological processors: *Meteorological Processor for Regulatory Models (MPRM) and RAMMET*. Results of an evaluation using three on-site data bases (19,540 combined valid hours) show that the SRDT method estimates the correct P-G stability category 62 percent of the time and is within one category of the P-G stability 89 percent of the time.

The stability classification method recommended for use at HTRW sites for a FFMS is either the horizontal wind direction fluctuation (σ_a) or the temperature change (ΔT) in conjunction with solar radiation measurement.

Communication process. Electronic signals provided by each of the meteorological instruments should be interpreted, summarized, and stored in a data logger intrinsic to the meteorological station. However, if real time ambient air monitoring is being performed as part of a FFMS, these data should be exported to the Air Monitoring Data Acquisition/Telemetry System (AMDAS) in the Analytical Center. This process allows access to air quality data from the FFMS which can be combined with meteorological data to provide real time upwind/downwind evaluation capability so site activities can be modified to reduce emissions during remediation.

If this method is selected, a data path must be established between the meteorological tower and the AMDAS. Three common methods of providing this path are:

- If the meteorological tower and the AMDAS are in close proximity to each other (~15 meters), signal conditioners can be used to convert the electrical signal from each instrument to an electrical current

loop (i.e., 4 to 20 mA). These conditions would be connected directly to the AMDAS in the Analytical Center

- If there is an unobstructed line of site between the meteorological tower and the AMDAS in the Analytical Center but it is not practical to use a data cable to connect them, a small data logger can be used to digitize the electrical signal from each instrument so it could be transmitted to the AMDAS using a pair of frequency modulated radio modems.

- If however, there is not an unobstructed line of site between the meteorological tower and the AMDAS and it is not practical to use a data cable to connect them, or if there is no AMDAS, a small data logger can be used to digitize the electrical signal from each instrument so that it can be transmitted to the AMDAS or a reporting computer using telephone modems and a commercial telephone line.

Table 6-3
Example of Use of Solar Radiation/Delta-T (SRDT) Method for Estimating Pasquill-Stability Categories

Wind Speed (m/s)	DAYTIME Solar Radiation (Wm^{-2})			
	≥925	675 → 925	175 → 675	<175
<2.0	A	A	B	D
2.0 → 3.0	A	B	C	D
3.0 → 5.0	B	B	C	D
5.0 → 6.0	C	C	D	D
>6.0	C	D	D	D

Wind Speed (m/s)	NIGHTTIME Temperature Difference (°C)	
	<0.0	≥0.0
<2.0	E	F
2.0 - 2.5	D	E
≥2.5	D	D

c. Data and reporting formats. Most modern DAS offer a host of reporting options for meteorological data. These reformatted reports meet the reporting requirements of most HTRW site meteorological monitoring applications. However, if specialized reporting is required, report writing languages are usually available to meet these needs.

A typical menu of reformatted reporting options could includes categories such as:

- Daily summary report.

- Status reports.
- Historical reports
- Graphs.
- EPA reports.

The measurements taken at the meteorological station should be recorded and stored on a DAS located in the Analytical Center. The DAS is one of the most important components of the meteorological program. The main function of the DAS is to collect air quality data (including meteorological data,) process and store the data, and report this data, which is then used as part of the HTRW site assessment. Data turnaround times are most stringent when the monitoring data are being compared with short-term action levels during remediation. In these cases, immediate or real-time monitoring of meteorological parameters are usually required. At a minimum, a daily summary report should be available for evaluation by the on-site personnel. The daily summary report should, at a minimum, include the following:

- Hourly averages for wind speed (m/sec), wind direction (degrees), stability class, 10-meter temperature (°C), barometric pressure (mBars), and precipitation (inches).
- Minimum, maximum, and average values for each of the parameters monitored.
- Indication of missing data points.

Figure 6-2 illustrates a typical daily HTRW site meteorological report.

Status reports generally refer to reports of the status of instrumentation, alarms, or data, as it is provided to the data logger. Historical reports get their data from the archived data files. Graphs, USACE, and EPA reports are specialized forms of historical reports.

Status reports should be generated if short-term action levels are exceeded by any of the individual data points. These data should then be used in conjunction with dispersion models. These data should be used to validate the model outputs for the HTRW site. This validation is done by comparing measured ambient air concentrations from the FFMS to the concentrations predicted by an atmospheric dispersion model that uses the actual meteorological conditions present during monitoring.

Dispersion models are inherently conservative, so the model output will usually over-predict ambient concentrations. The degree to which the model over (or under) predicts will depend on site-specific factors. The degree of over-prediction observed for a short-term dispersion modeling may be used, with limitations, as a correction factor when interpreting long-term dispersion modeling results.

Some useful examples of reformatted historical reports available with an integrated data acquisition system might include:

- Frequency Distribution Report — generates a frequency distribution report of a selected pollutant from the hourly data files. An averaging interval may be specified by the operator.
- Joint Frequency Distribution — generates a joint frequency distribution report and a wind or pollution rose on the screen, as illustrated in Figure 6-3.

- Data Recovery Report — prints out a report showing the number and percentage of valid scans from all instruments. The time period is defined by the operator.

- Calibration Report — generates a report that shows the zero and span data for all auto-calibration instruments.

Some examples of reformatted graphical reports available with an integrated DAS might include:

- Daily Two Parameter Graph — displays hourly averages for a selected day and parameter (see Figure 6-4).

- Five-Day Single Parameter Graph — displays hourly averages for a selected 5 days and parameter (see Figure 6-5).

- Monthly Single Parameter Graph —displays hourly averages for a selected month and parameter with zoom features to a selected 5-day span.

- Daily Multiple Site Graph— displays hourly averages for selected sites (up to 5) on one graph for a selected day.

- Five-Day Multiple Site Graph — displays hourly averages for selected sites (up to 5) on one graph for 5 days.

- Daily Multiple Parameter Graph — displays hourly averages for selected parameters (up to 3) on one graph for a selected day.

- Five-Day Multiple Parameter Graph — displays hourly averages for selected parameters (up to 3) on one

- Calibration Graph for One Month — displays calibration values for one parameter for 1 month. (Zero, Span 1, and Span 2 are all displayed on one graph.)

d. Data QA/QC. A comprehensive QA/QC program for the operation of a meteorological station at a HTRW site should include both (1) a timely and comprehensive review and validation of the data and (2) a rigorous inspection, maintenance, and calibration program.

(1) Data review. At regularly scheduled intervals, data must be downloaded from a meteorological station's data logger, reviewed for completeness and reasonableness, archived, and reported. These activities should be performed daily if possible and should not be performed less than once per month. If possible, data should be compared with climatological data from a nearby NWS station. If any missing or unreasonable data is identified, a corrective action report (see Figure 6-6) and a corrective action request (see Figure 6-7) should be completed and included in the DCQCR.

(2) Calibration procedures. The meteorological station should be factory calibrated prior to initial shipment to the site and at least once every 2 years thereafter. In addition, every time the meteorological station

is installed, and quarterly during its operation, the sensors should be checked for damage and all parameters should be verified as correct. Set-up and quarterly audits should be performed using their transfer standards listed in Table 6-4.

At the completion of a field verification, a site calibration report (see Figure 6-8) should be completed and included as part of the Site Inspection Form (see Figure 6-9). If any discrepancies are noted, a corrective action report and a corrective action request must also be completed and included in the DCQCR.

The remainder of this section describes a generic HTRW on-site maintenance program for the meteorological system that should be performed immediately following installation and quarterly thereafter.

Daily Meteorological Monitoring Report at a USACE HTRW site, Anytown, USA
Date: 30 Sep 96
Time: 00:00 to 23:00

Time	Wind Speed, (m/sec)	Wind Direction, °	Stability Class (A, B, C, D, E, F)	Temp., °C	Barometric Pressure, mB	Precipitation, inches.
00:00	1.4	292	F	12.1	995	9.60
01:00	1.0	261	E	10.5	995	9.59
02:00	0.9	239	E	9.1	995	9.59
03:00	0.7	265	F	8.6	995	9.59
04:00	0.8	266	F	8.0	995	9.59
05:00	1.0	306	F	8.0	996	9.59
06:00	0.8	316	F	7.6	996	9.59
07:00	1.7	329	A	8.5	996	9.59
08:00	2.0	342	B	9.4	996	9.59
09:00	1.2	340	A	10.8	996	9.59
10:00	1.0	336	A	13.2	996	9.60
11:00	1.1	97	A	15.8	995	9.60
12:00	1.6	77	A	18.8	994	9.60
13:00	2.0	83	A	21.6	993	9.60
14:00	2.1	88	B	23.3	991	9.60
15:00	1.7	105	A	24.6	990	9.60
16:00	1.7	116	D	24.6	989	9.60
17:00	1.4	102	F	23.3	989	9.60
18:00	2.0	138	F	33.2	989	9.60
19:00	1.8	142	F	22.7	989	9.60
20:00	1.7	150	F	22.6	989	9.60
21:00	1.6	176	F	22.2	989	9.60
22:00	2.5	215	E	21.7	989	9.60
23:00	2.4	233	D	31.3	988	9.60
MAX	3.4	342		24.6	996	9.60
MIN	0.7	77		7.6	988	9.59
SIGMA	0.6	95		6.6	3	0.00
AVG	1.5	211		16.3	993	9.60
GOOD	24.0	24		24.0	24	24.00

Figure 6-2. Example of daily meteorological report for a HTRW site

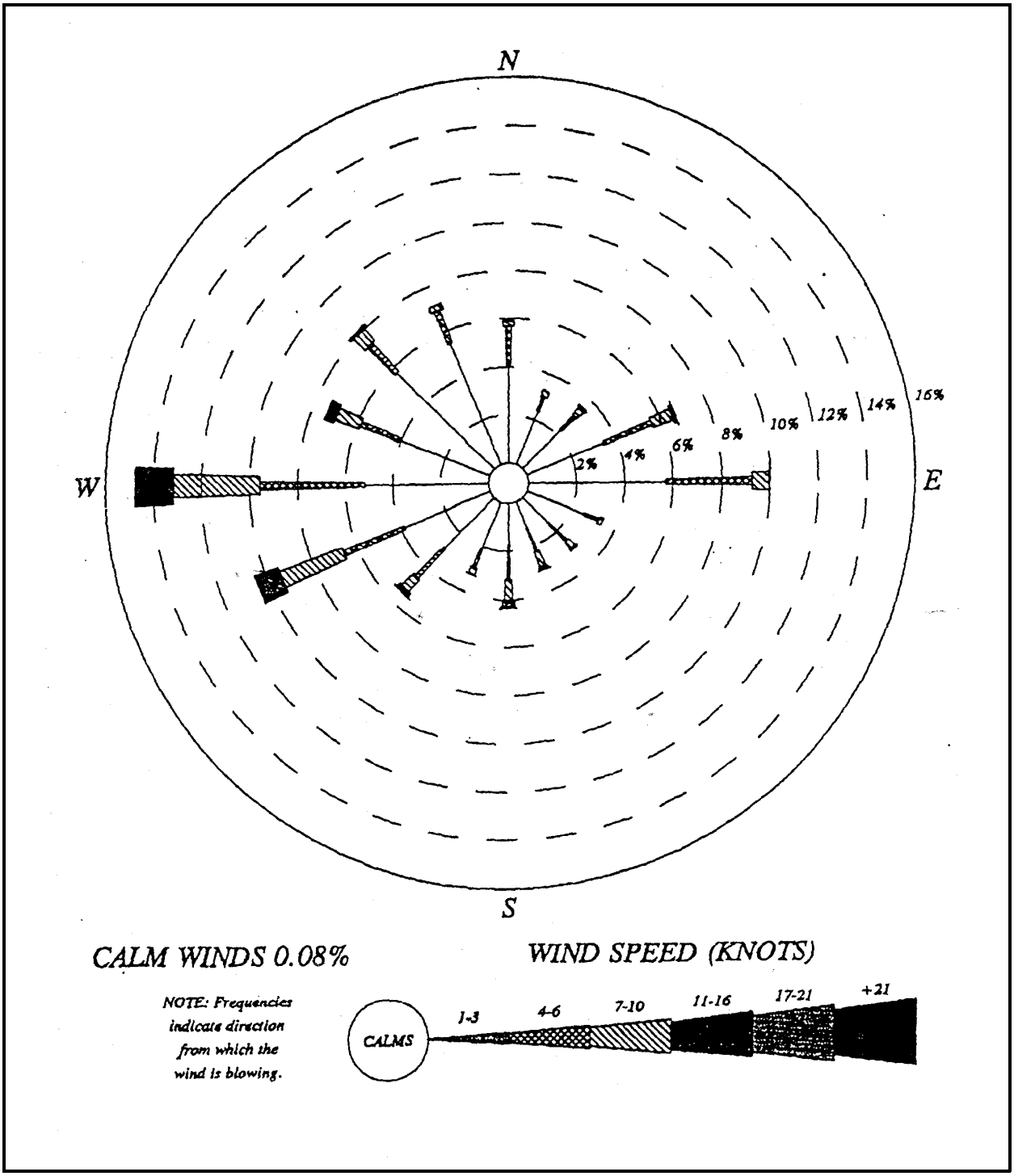


Figure 6-3. Example of typical meteorological display (wind rose) of wind speed and direction

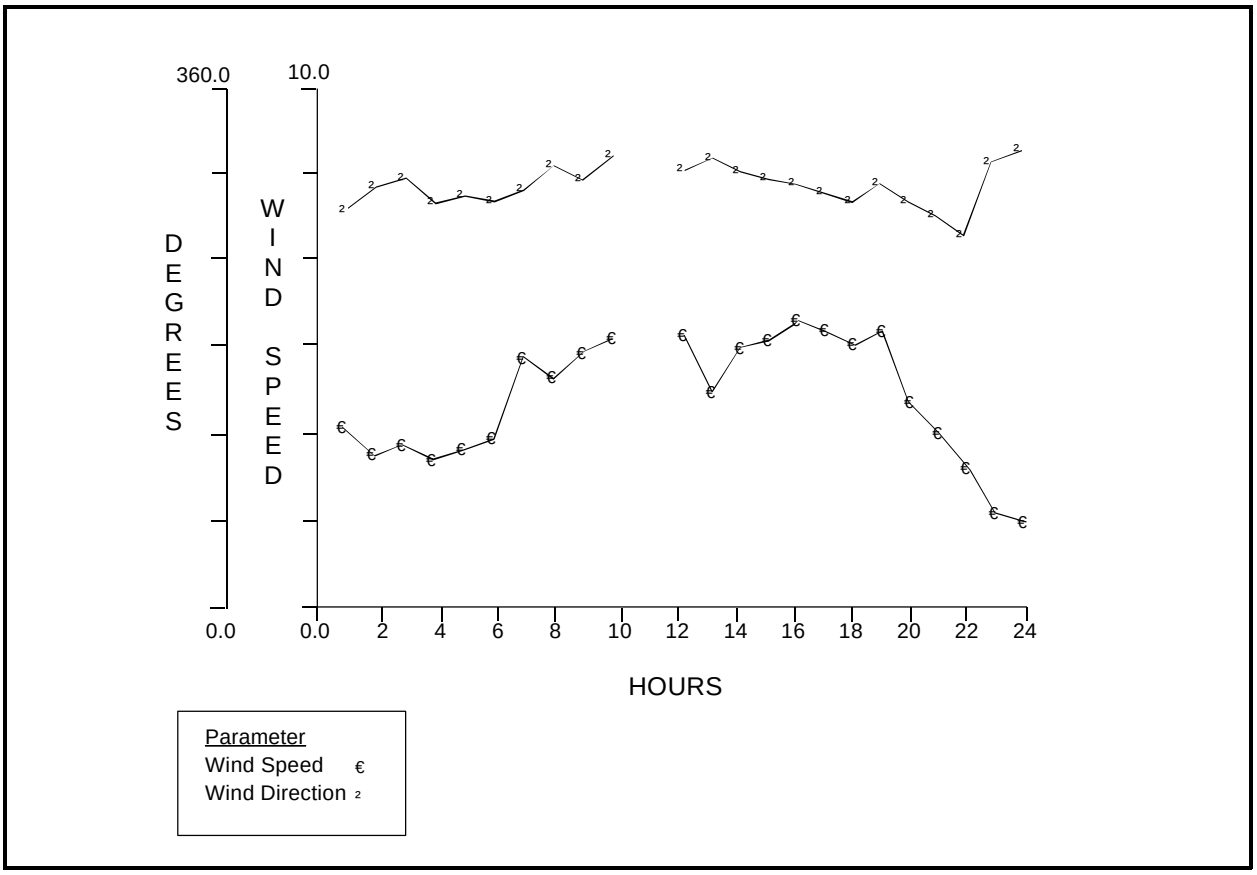


Figure 6-4. Example of meteorological report illustrating daily two parameter graph for a HTRW site, Any Town, USA

(a) Tower, enclosures, and cables. Before verifying the accuracy of the meteorological instrumentation, conduct a check of the support hardware necessary for its functionality. Using a carpenters lever, verify that the tower is level. If it is not, shims must be inserted below the tower and guide wires tightened to correct the problem. Verify that all electrical cables are firmly attached and not free to blow in the wind. If any electrical cables are loose, attach them to adjoining hardware. Verify that all weather-tight enclosures are closed and properly sealed. Check to see that fans on electronic cabinets or aspirated enclosures are operating properly.

(b) Wind speed anemometer. Check the physical integrity of the anemometer cups, shaft heater (i.e., if installed), and electrical cables. Replace any damaged equipment. Check to see if the cross-arm is level and if the anemometer spins easily and smoothly. Remove the

anemometer cups from the shaft and attach a thumb-wheel torque gauge (i.e., usually available from the instrument manufacturer) to ensure that the starting torque is less than the operating specification for the anemometer. Remove the thumb-wheel torque gauge and attach a frequency monitored servomotor (i.e., usually available from the instrument manufacturer) to verify that the indicated wind speed is within the accuracy specified by the instrument manufacturer. Repair or replace any damaged or worn parts. Attach the anemometer cups to the shaft. If any adjustments are necessary to the signal conditioning board, reset the zero and span according to the manufacturers recommended procedures.

Table 6-4
Standard Certification Instrumentation for Meteorological Station Audits

Parameter	Verification Method
1. Wind Direction	Compass
2. Wind speed	Frequency monitored servo motor
3. Temperature	Mercury in glass thermometer
4. Relative humidity	Sling psychrometer
5. Precipitation (rain gauge)	Graduated container

(c) Wind vane. Check the physical integrity of the wind vane, shaft heater (i.e., if installed), and electrical cables. Replace any damaged equipment. Check to see if the cross-arm is level, aligned with the North, and if the vane spins easily and smoothly. Remove the wind vane from the shaft and attach a thumb-wheel torque gauge (i.e., usually available from the instrument manufacturer) to ensure that the starting torque is less than the operating specification for the instrument. Remove the thumb-wheel torque gauge and replace the wind vane. Hold the wind vane in each of the cardinal directions while checking the accuracy of the indicated wind direction. Hold the wind vane in each of two known directions for consecutive halves of an integration period to verify the calculated standard deviation of wind direction. Repair or replace any damaged or worn parts. If any adjustments are necessary to the signal conditioning board, reset the zero and span using the manufacturers recommended procedures.

(d) Temperature sensor(s). Check the physical integrity of each temperature sensor, the enclosures, the fans (i.e., if installed), and the electrical cables. Verify the temperature indicated by each instrument against a National Institute of Standards and Technology (NIST) traceable thermometer with 1/10° F graduations, placed within the aspirated enclosure. If any adjustments are necessary to the signal conditioning board, reset the zero and span using the manufacturers recommended procedures.

(e) Barometer. Check the indicated station barometric pressure against a NIST traceable aneroid barometer or the station pressure reported by a nearby NWS reporting station at roughly the same altitude. If any adjustments are necessary to the signal conditioning board, reset the zero and span using the manufacturers recommended procedures.

(f) Relative humidity sensor. Check the indicated relative humidity against a sling psychrometer equipped with NIST traceable thermometers and a psychometric chart. If any adjustments are necessary to the signal conditioning board, reset the zero and span using the manufacturers recommended procedures.

(g) Precipitation gauge. Check the physical integrity of the rain gauge, heater, snow fence (if installed), and electrical cables. Verify that the rain gauge is level, that the mechanism moved freely, and that the rain path is free from obstructions. Slowly pour a known volume of water into the rain gauge. Divide the volume

of water introduced by the area of the top of the rain gauge for comparison with the indicated amount of rainfall from the DAS in the Analytical Center.

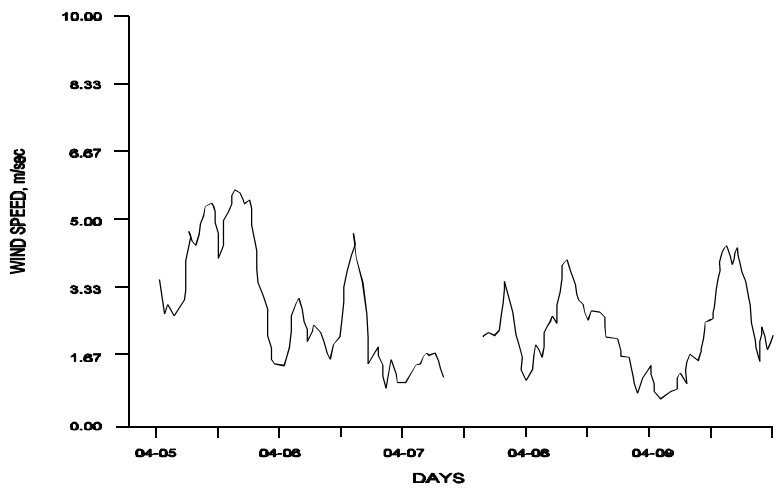


Figure 6-5. Example of meteorological report illustrating 5 day single parameter (wind speed) graph for a HTRW site, Any Town, USA

CORRECTIVE ACTION EXAMPLE
USACE HTRW SITE
ANY TOWN, USA

Originator's Name _____ Date _____
Reporting Facility _____ Refs. _____

_____

Component _____

_____

Failure found in:

☐ Installation ☐ Calibration ☐ Operational Use
☐ Unit Test ☐ System Test ☐ Service Call
☐ Other _____

_____

Originator's Statement of Failure

_____

Corrective Action Required in Field

Name Date

_____

Corrective Action Request
(see Figure 6-7)

_____

DISTRIBUTION

☐ Quality Assurance ☐ Project Manager
☐ Field Operations ☐ FILE
☐ Data Processing

Figure 6-6. Example of corrective action report for a HTRW site meteorological program

CORRECTIVE ACTION REQUEST EXAMPLE
USACE HTRW SITE
ANY TOWN, USA

Originator/Dept _____Site Name _____
_____Site No. _____
Part No. _____Part Name _____
Quantity _____ P.O. No. _____ Serial No. _____ R/R No. _____
Discrepancy: _____
_____
_____
_____
_____

Signature: _____Date _____

CORRECTIVE ACTION

Cause of Discrepancy: _____
_____
_____
_____
Action Taken to Prevent Recurrence: _____
_____
_____
_____

Correction Action is: ☐ APPROVED ☐ DISAPPROVED
Corrective Action Verified As Accomplished ☐

Signature: _____Date _____

DISTRIBUTION

☐ Quality Assurance

☐ Project Manager

☐ Field Operations

Figure 6-7. Example of corrective action request for a HTRW site meteorological program

SITE CALIBRATION EXAMPLE
USACE HTRW SITE
ANY TOWN, USA

Customer Name _____ Arrive Time/Date _____
Site Name/I.D. _____
Met Level _____ of _____ Levels.

I. Met System Information:
Manufactured By _____ Model No. _____
Wind Speed Sensor Type _____ Serial No. _____
Wind Direction Type _____ Serial No. _____
Translator Model No. _____ Serial No. _____

2. Condition of Met System:
W/S Sensor _____ Cups _____
W/D Sensor _____
Signal Cables _____
Translator _____
Orientation _____

3. Calibrator:
Manufactured By _____ Model No. _____ Serial No. _____

4. Before Calibration:

W/S/ Signal	SW Position	Expected	Actual Speed	=	Chart (Opt)
	1.				
	2.				
	3.				
	4.				

W/S/ Signal	SW Position	Expected Outlet	Actual Output	=	Chart (Opt)
	0	0 V			
	•	1.5 V			
	•	3.2 V			
	F	4.3 V			

5. After Calibration (If Required):
Reason: _____

W/S/ Signal	SW Position	Expected	Actual Speed	=	Chart (Opt)
	1.				
	2.				
	3.				
	4.				

6. Upon Completion of All Calibrations, This Site Mark Tape With “Calibration Data”

Calibration Performed By _____
Date/Completion Time _____
Calibration _____ of _____ this location _____
Regional Office _____

Figure 6-8. Example of site calibration for a HTRW site meteorological program

SITE INSPECTION EXAMPLE
USACE HTRW SITE
ANY TOWN, USA

Time Arrived _____

Customer Name _____

Site Name/I.D. _____ Location _____

No. of Levels _____

Type of Inspection:

Weekly Monthly Quarterly Bi-Annual Actual

1. Condition of met System:
   Met Model _____ S/N _____
   Manufactured By _____
   Sensors O.K.? _____
   Cups O.K.? _____ If No. Explain _____
   Vane O.K.? _____ If No. Explain _____
   Cables O.K.? _____ If No. Explain _____
2. Met Conditions:
   Wind Blowing? _____ Cloud Cover ( ) _____ Temp., °F _____
3. Met System:
   If Wind Blowing, Are Cups Moving? Level 1 _____ Level 2 _____
   Are Vanes Deflecting? Level 1 _____ Level 2 _____ Level 3 _____
4. Chart Recorder:
   Manufactured By _____ Model _____ S/N _____
   Chart Speed _____ Chart Time: Gain _____ Loss _____ (i.e., Minutes)
5. Data Logger:
   Manufactured By _____ Model _____ S/N _____
   Tape Started, Time/Data _____ Ended, Time/Date _____
   Tape Ran O.K.? _____ Error Signal _____
6. Power Supply:
   Batteries O.K.? _____ If No, Explain _____
   Voltage Level _____ If Failure, Approx. Time/Date _____
7. Station Check Information:
   Time Departed _____ Total Time _____
   State Checked By _____ Affiliation _____

Figure 6-9. Example of site inspection for a HTRW site meteorological program

(h) Telemetry process. Once a working meteorological station and data logging system are established, a data path must be established between the meteorological tower and the DAS in the Analytical Center used for data review, archiving, and reporting. Three common methods of providing this path are:

- If the meteorological station is unattended, the data logger and the data reduction computers can each be equipped with a dial-up telephone modems. The DAS can be used to call the station data logger and download data. The data can then be reviewed, reduced, and reported from the convenience of a remote location.

- If the meteorological station is attended and the data review, reduction, and reporting will be conducted on-site as part of the Analytical Center, the data can be downloaded by a standard serial or parallel computer interface to the on-site computer in the Analytical Center.

Table 6-5
Suggested Data Screening Criteria for a Meteorological System at a HTRW Site

Meteorological Variable	Screening Criteria (Flag data if the value:)
Wind speed	• Is less than zero or greater than 25 m/s • Does not vary by more than 0.1 m/s for 3 consecutive hours • Does not vary by more than 0.5 m/s for 12 consecutive hours
Wind direction	• Is less than 0 or greater than 360° • Does not vary by more than 1° for more than 3 consecutive hours • Does not vary by more than 10° for 18 consecutive hours
Temperature	• Is greater than the local record high • Is less than the local record low; (the above limits could be applied on a monthly basis) • Is greater than a 5° change from the previous hour • Does not vary by more than 0.5°C for 12 consecutive hours
Temperature difference	• Is greater than 0.1° C/m during the daytime • Is less than -0.1° C/m during the nighttime • Is greater than 5.0° C/m or less than -3.0°C/m

- If the meteorological station is attended but the data review, reduction, and reporting will be conducted off-site, the data can be downloaded as described in methods (1) or (2) above. If the data is downloaded on-site, as described in method (2), the data files could be copied to disks and mailed, downloaded to the remote location using a direct modem link, or downloaded through a corporate bulletin board service or the Internet.

(i) Processing of on-site meteorological data for modeling. The first review of the data involves a screening to identify suspect data points. The screening criteria are outlined in Table 6-5 for various meteorological parameters. Once the meteorological data has been screened and certified as accurate, it may be used in future dispersion models. The EPA has recently issued guidance on the use of meteorological data, collected via an on-site measurement program, for regulatory modeling applications. The meteorological processor currently available from EPA is the MPRM. The MPRM, Version 1.2, has been designed to construct meteorological data files of upper air, mixing height, surface observations, and on-site data for air pollution dispersion models

that are routinely used in regulatory decision making by EPA. Specifically, the processor is designed to accommodate those dispersion models recommended for use in the *Guidelines on Air Quality Models*.

As illustrated in Figure 6-10, the MPRM, Version 1.2, consist of a three-stage processing system:

(1) First stage processor (extraction and quality assessment). During the first stage, the processor extracts upper air, mixing height and surface data from the raw data files delivered from the National Climatic Data Center (NCDC) in Asheville, North Carolina, and on-site data from the raw data files developed from the on-site meteorological station. The extracted data are processed through a series of quality assessment checks. Missing and suspect values are identified and reported.

Consequently, the goal of this first stage of processing is to:

- Read the on-site and NWS meteorological data files.
- Find the data within the time period specified by the user.
- Store these data in American Standard Code for Information Interchange (ASCII) data files.
- Scan the stored values and report occurrences of missing or suspect values.

An additional capability of this first stage is assessing the quality of the data by checking for possible missing or suspect values. Any occurrences of missing or suspect data values are reported before the upper air soundings, mixing height data, surface observations, and on-site data are combined.

The output files from this first stage of processing should be edited using standard text

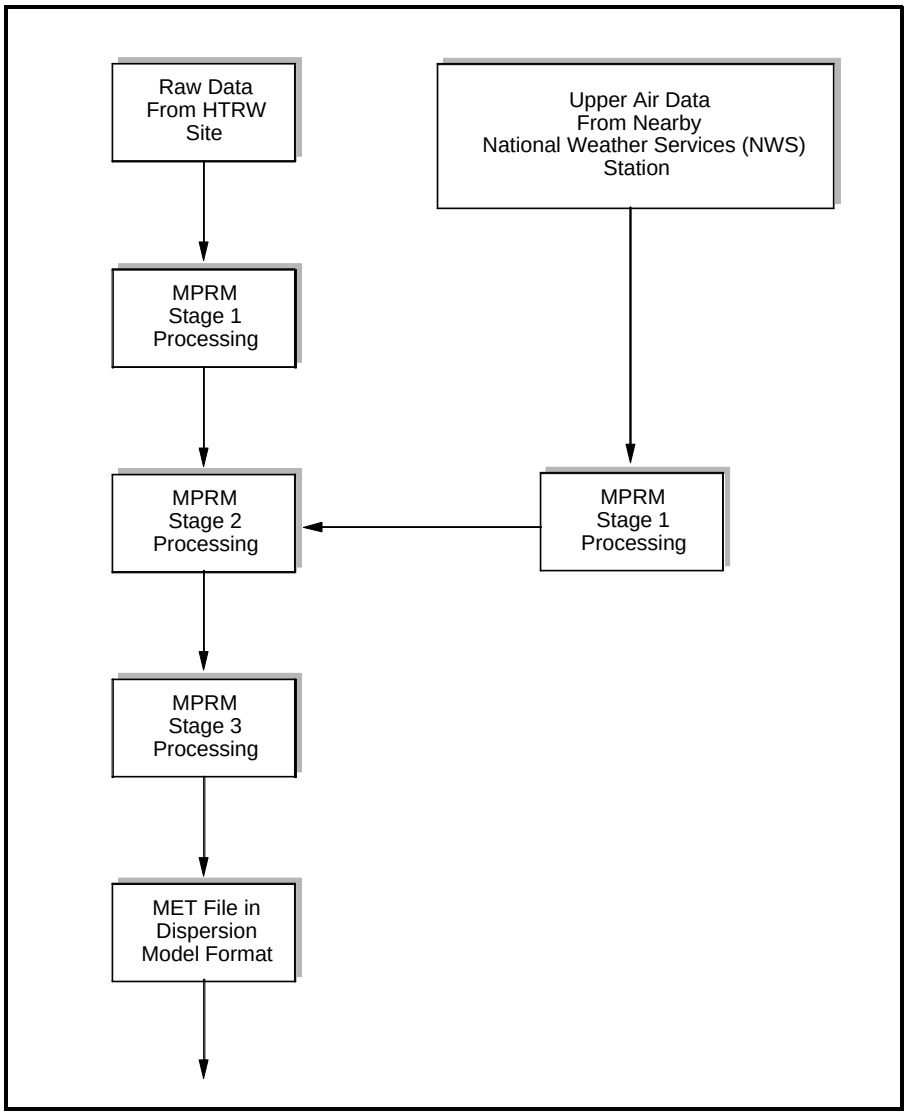


Figure 6-10. Example of EPA's three stage meteorological data processing, MPRM Version 1.2

editors routinely available on computer systems.

(2) Stage 2 processor (combining data). During the second stage, the processor combines the available data for each midnight-to-midnight, 24-hour period (twice-daily upper air soundings and mixing height data, hourly surface weather observations, and hourly on-site data) and stores these data in a combined (merged) format.

The goal of the second stage of processing is to:

- Combine into one file the available onsite and NWS meteorological data files created during Stage 1 processing.
- Store the data in a more compact format.

For specifying the dispersive state of the atmosphere, the physics of the atmosphere should be considered daily. Estimation of the depth of convective mixing (atmospheric stability) is the summation of effects starting with the heating of the surface shortly after sunrise. Thus, the merging of the available data for each 24-hour period is the next logical step in processing before developing the characterization of the input meteorological data files for the dispersion models.

The merged data are stored in unformatted form because this format is a more efficient use of storage than the formatted ASCII data file storage that is used during the first stage of processing. The ASCII files are convenient for test editors but are no longer needed once the quality assessment and editing are completed.

(3) Stage 3 processor (creating a model input file). During the third and final stages, the processor reads the merged data and develops a meteorological data file for the dispersion model selected by the user. The goal of this third stage is to create a meteorological data file for use with a regulatory dispersion model chosen by the user.

The MPRM can generate one of several output formats to meet the input requirements of the regulatory dispersion model chosen by the user. The RAMMET format can be selected as the default output with default methods for processing wind, temperature, stability category, and mixing heights. These methods employ the NWS hourly surface weather observations and the NCDC twice-daily mixing heights and duplicate the processing performed by the RAMMET meteorological processor.

6-3. Integration of Analytical System and Sample Collection System with Meteorological Monitoring

a. Introduction. Electronic signals provided by each of the on-site meteorological station could be interpreted, summarized, and stored in a data logger intrinsic to the meteorological station. If real-time information is needed, however, those data should be exported to a DAS located in the Analytical Center, as illustrated in Figure 6-11.

b. System network and design . Integrating and managing the meteorological data at a DAS within the Analytical Center ensures that the program objectives associated with meteorological parameters are met. At a minimum, the central DAS provides:

- Storage of all required meteorological data.

- Ability to enter and access pollutant-specific data with the meteorological data to generate histograms.
- Retrieval of data and preparation of standardized reports.

As identified in Figure 6-11, the analog inputs from the meteorological station for instruments measuring wind speed, wind direction, temperature, solar radiation, barometric pressure, and relative humidity are attached to the central DAS in the Analytical Center for storage and future reporting. The programs available allow the data to be retrieved and stored in 1-minute, 5-minute, 30-minute, or 1-hour averages. The user determines which averaging period is most appropriate for the program objectives. The DAS allows real-time calculations using meteorological data coupled to pollutant data.

6-4. Meteorological Monitoring and Perimeter Action Levels

a. Introduction. As previously documented, meteorological monitoring can be integrated to the real-time FFMS to provide information on the impact the remediation of the HTRW site is having on the surrounding community. The site-specific PALs are usually established by the regulatory authorities and become part of

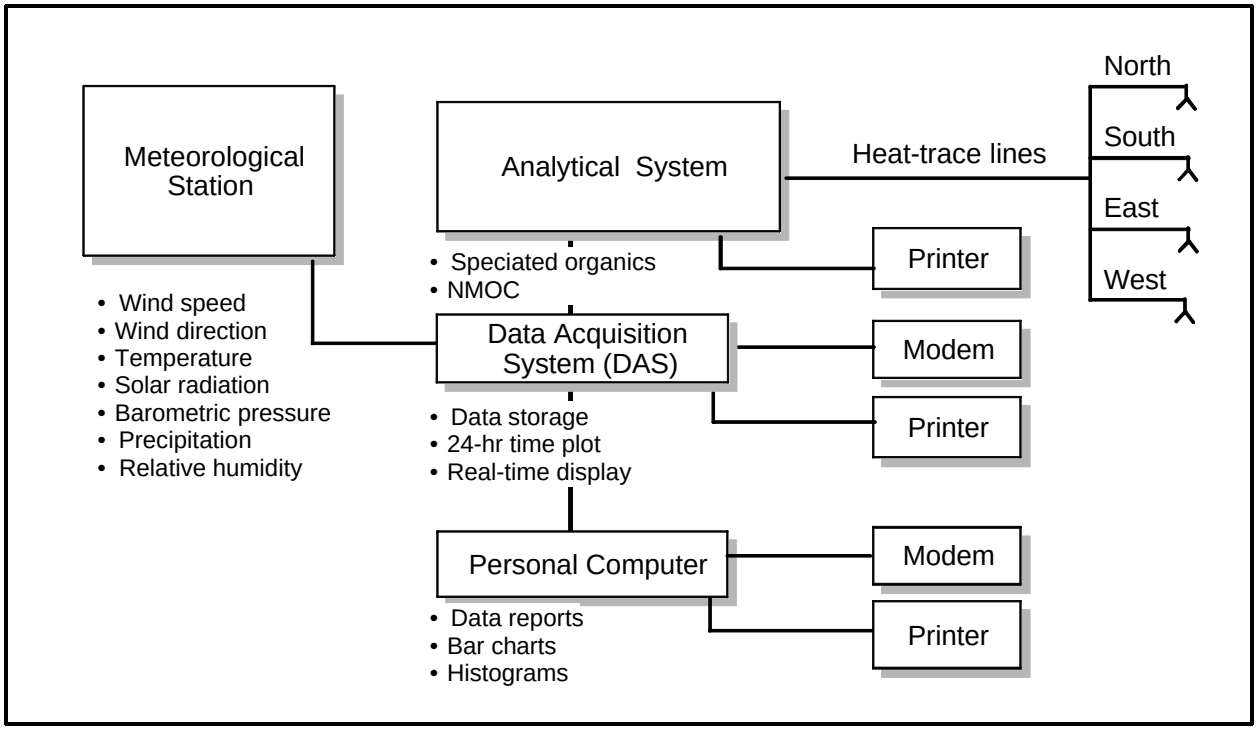


Figure 6-11. Example of connecting the HTRW site meteorological station with the sample collection system and the DAS in the Analytical Center.

the site Health and Safety Plan. The PALs require a progression of alarm levels that may trigger some or all of the following actions:

- Greater specificity in contaminant analysis.
- Correlation of analytical and meteorological data to evaluate source direction.
- Calculation of net downwind concentration.
- Investigation and documentation of probable causes of exceedance.
- Implementation of site management controls, if necessary.

b. Alert levels. Alert levels for all target analytes are preprogrammed within the data acquisition. During any sampling interval, exceedances of either a total NMOC threshold and/or site-specific target analyte thresholds may be determined depending on the specific mode of chromatograph operation. The DAS should cycle through the established sampling schedule, log the individual instrument measurements, and compare the measurements with the preset alert levels. When an exceedance is identified, the DAS should trigger audible alarm mechanisms within the Analytical Center and generate a report as well as initiate further analyses, data storage, and data correlation. A typical HTRW site alarm level operational scheme is described in the following sections.

(1) Alarm level 1 - NMOC exceedance. As described previously, the network of heated sample lines transport sample gas from locations around the HTRW site to the analytical system in the Analytical Center. The microprocessor controlled system allows sequential sampling of each sample line. During routine sampling, the analytical system (i.e., gas chromatograph) is typically operated in the RAM mode for total NMOC. As such, the analytical system extracts a sample gas from each sample line and directs the gas to a detector for gross quantification of NMOC concentration. Resultant data are automatically logged to the DAS. When the total NMOC concentration in a given sample is below the alarm level (i.e., <1 ppm), the manifold apparatus simply proceeds to the next sample line. When total NMOC concentrations exceed the present alert level (i.e., >1 ppm), the microprocessor generates a written report, and a speciated analysis for target analytes in the sample is typically initiated.

(2) Alarm level 2 - Compound Specific Exceedance. In the speciated mode, the sample gas is directed to the analytical system where separation of the total gas sample is performed. Individual contaminants elude from the analytical system (i.e., GC column) and are directed to a detector for quantification. Specific analytes are identified on the basis of chromatograph retention time as compared to regular multi-point calibration of the system. Again, all data are logged to the DAS. If the concentrations of any of the target compounds are below the pre-set alarm level, the microprocessor signals the manifold apparatus to proceed to the next sample line and analytical operation is shifted back to the total NMOC or RAM. If the concentration of any target compound exceeds the pre-set alarm level (2), the microprocessor typically generates a report and initiates a sequence of speciated analyses of sample gas from each of the remaining sample lines. All resultant data are logged in the data storage system. Once a complete circuit of speciated analyses has been completed, the microprocessor signals the manifold apparatus to proceed to the next sample line and shifts analytical operational back to the RAM mode.

(3) Alarm level 3 - Meteorological Data Evaluation and Upwind Compound Specific Exceedance. Subsequent to the speciated analysis for each sample line, the DAS queries the program to determine the location of the upwind sample. If the concentration of any target compound at the upwind location exceeds the pre-set alarm level, the DAS typically generates a report indicating further investigation with a portable organic vapor analyzer in the area of the exceedance is necessary.

To determine the upwind station, the HTRW site is divided into four quadrants, each 90°, as illustrated in Figure 6-12. The four quadrants are defined as:

- Quadrant 1 (Q1): <45°, >315° and <405°, north quadrant.
- Quadrant 2 (Q2): >45° and <135°, >405° and <495°; east quadrant.
- Quadrant 3 (Q3): >135° and <225, >495, south quadrant.
- Quadrant 4 (Q4): >225° and <315°, west quadrant.

To identify which station is the upwind station, time integrated channels in the data logger determine if the wind is in a certain quadrant. If the wind is in a certain quadrant (i.e., the north quadrant), the north time-integrated channel will change its value from 0 to 1. When the wind is no longer in this quadrant, the value will change back. The quadrants are defined by degree ranges that are easily adjustable. There are a total of seven time-integrated channels, one for each direction (North, South, East, West) and three to handle the extra 180° of the wind direction measuring device (range is 0° to 540°). The upwind channels will not activate if the wind speed is less than 1.5 m/s.

(4) Alarm level 4 - Meteorological Data Evaluation and Compound Specific Exceedance (net concentration). If the concentration of all target compounds at the upwind location are below the pre-set alarm level, the microprocessor subtracts the upwind concentrations from those reported for the downwind station to determine the HTRW site net concentration. If the net concentration of any target compound at the downwind location exceeds the pre-set alarm level, the microprocessor generates a report indicating further investigation with a portable organic vapor analyzer in the area of the exceedance, if necessary.

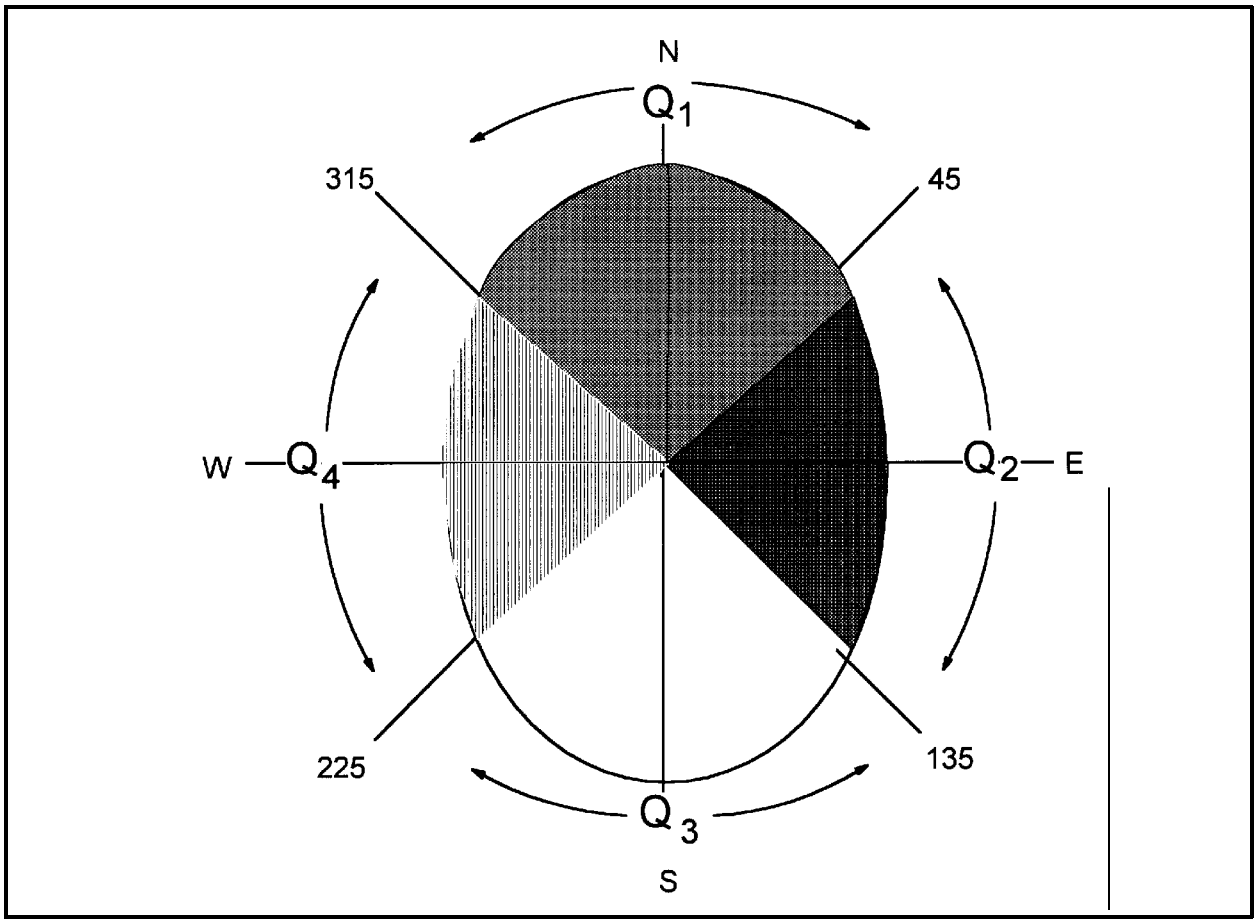
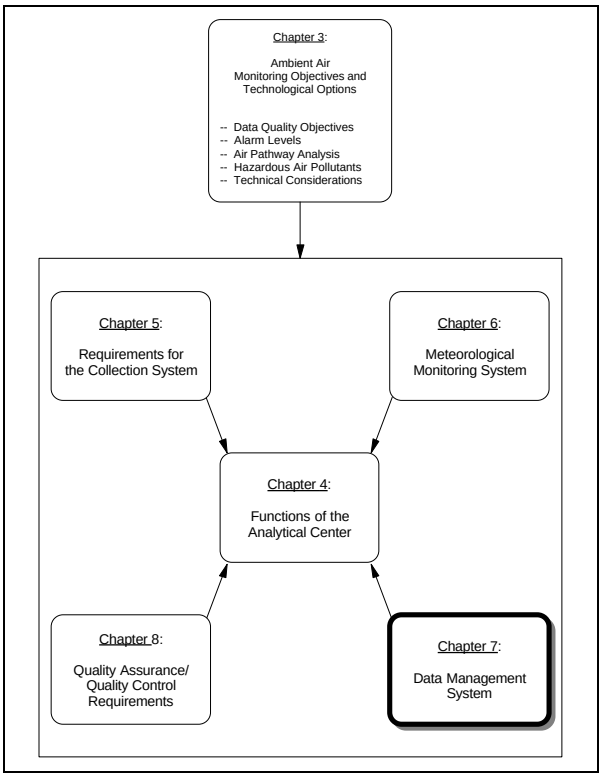


Figure 6-12. Example of HTRW site divided into 90° quadrants for calculating upwind/downwind net concentration of site specific target analytes

SUMMARY OF DATA MANAGEMENT SYSTEM

Developing an integrated data management system for the transfer, storage, and manipulation of data is an integral part of a FFMS at a HTRW site. The data management system encompasses the techniques used to gather and manage the data of a real-time, fixed fenceline monitoring system.



SECTION I: INTRODUCTION

SECTION II: DATA ACQUISITION SYSTEM DESIGN, OPERATION, AND USERS

- Introduction
- Data Acquisition System
- Network Configuration
- Data Receptors and Users
- Component Testing and Calibration

SECTION III: DATA COMPILATION, STORAGE, TRANSMISSION, AND REPORTING

- Data Files
- Data Reporting Forms and Electronic Files
- Daily and Monthly Reports
- Data Validation Procedures
- Meeting the Project DQOs

The main function of the Data Management System is to collect air quality data from remote sites, transmit it to a central point, process and store the data, then report the data to be used in site assessment reporting. Chapter 7 discusses data acquisition; data compilation, storage and reporting; and data validation.

Data management procedures for HTRW site perimeter ambient monitoring programs are characterized by the need to store and integrate large volumes of data derived from a variety of data sources. Because these data may be collected over a long period of time, developing an integrated DAS for the transfer, storage, and manipulation of data to create reports is an essential element of any monitoring program.

The integration and management of the perimeter air monitoring program data should be supported by a central, integrated data base system located in the Analytical Center. The design and structure of the selected software must be compatible with program objectives and, at a minimum, provide:

Panel 7-1. Overview of Data Management System.

- Storage of all acquired data.
- Ability to enter and access field and laboratory information.
- Retrieval of data and preparation of standardized reports.

Panel 7-1. Overview of Data Management System.

7-1. Introduction

The purpose of this chapter is to provide information on the techniques that will be used to gather and manage the data of a real-time FFMS. The types of data that will be processed are the chemical parameter and speciated compounds detailed in Chapters 4 and 5 of this manual and meteorological data as described in Chapter 6. Data acquisition, compilation, storage, reporting, and validation are discussed in this chapter.

7-2. Data Acquisition System Design, Operation, and Users

a. Introduction. The DAS is one of the most important components of the fixed-fenceline perimeter air monitoring program. In contrast to typical non-hazardous waste site applications where data turnaround times may be several weeks, data turnaround during remediation at HTRW sites typically must be within 1 or 2 days to compare long-term action levels and within hours to compare short-term action levels. Data turnaround times are most stringent when the monitoring data are being compared with short-term action levels during remediation at an HTRW site. In these cases, immediate or real-time feedback of perimeter ambient concentration levels is usually required. The main function of the DAS is to collect air quality data from FFMS sites, transmit it to a central point (usually in the Analytical Center), process and store the data, then report the data that is to be used in HTRW site assessment reporting involving the DCQCR.

Data management procedures for HTRW site perimeter ambient monitoring programs are characterized by the need to store and integrate large volumes of data derived from a variety of data sources. Because these data may be collected over a long period of time, developing an integrated DAS for the transfer, storage, and manipulation of data to create reports is an essential element of any monitoring program.

The integration and management of the perimeter air monitoring program data should be supported by a central, integrated data base system located in the Analytical Center. The design and structure of the selected software must be compatible with program objectives and, at a minimum, provide:

- Storage of all acquired data.
- Ability to enter and access field and laboratory information.
- Retrieval of data and preparation of standardized reports.

b. Data acquisition system. The DAS comprises a critical component of the perimeter FFMS. Data acquisition can be done with a device as simple as a strip-chart recorder that produces a physical printout of data collected from monitoring instruments. More typical data acquisition units receive analog or digital signals from monitoring instruments and average these numbers over 1 or more intervals as the data is stored electronically. Commercially available DASs used in HTRW perimeter monitoring systems can both store these numbers and also perform real-time calculations on the data. The ability to perform real-time

calculations on the data is essential for any HTRW perimeter monitoring program used for determining upwind/downwind and net concentrations.

The configuration of most data acquisition units (see Figure 7-1) has both analog and digital inputs. Analog inputs come from the meteorological station for instruments measuring wind speed, wind direction, temperature, delta T (ΔT), solar radiation, barometric pressure, relative humidity, and precipitation. Digital input from the real-time analytical system in the Analytical Center is received via an RS-232 port and passed into several data channels representing measured pollutants at each monitoring station. The DAS determines which station is upwind by monitoring the wind direction and then, using monitoring results, calculates a net concentration between the upwind and downwind stations. The upwind station is determined by which quadrant the wind direction falls, as described in Chapter 6. As discussed, the HTRW site is assigned quadrants as:

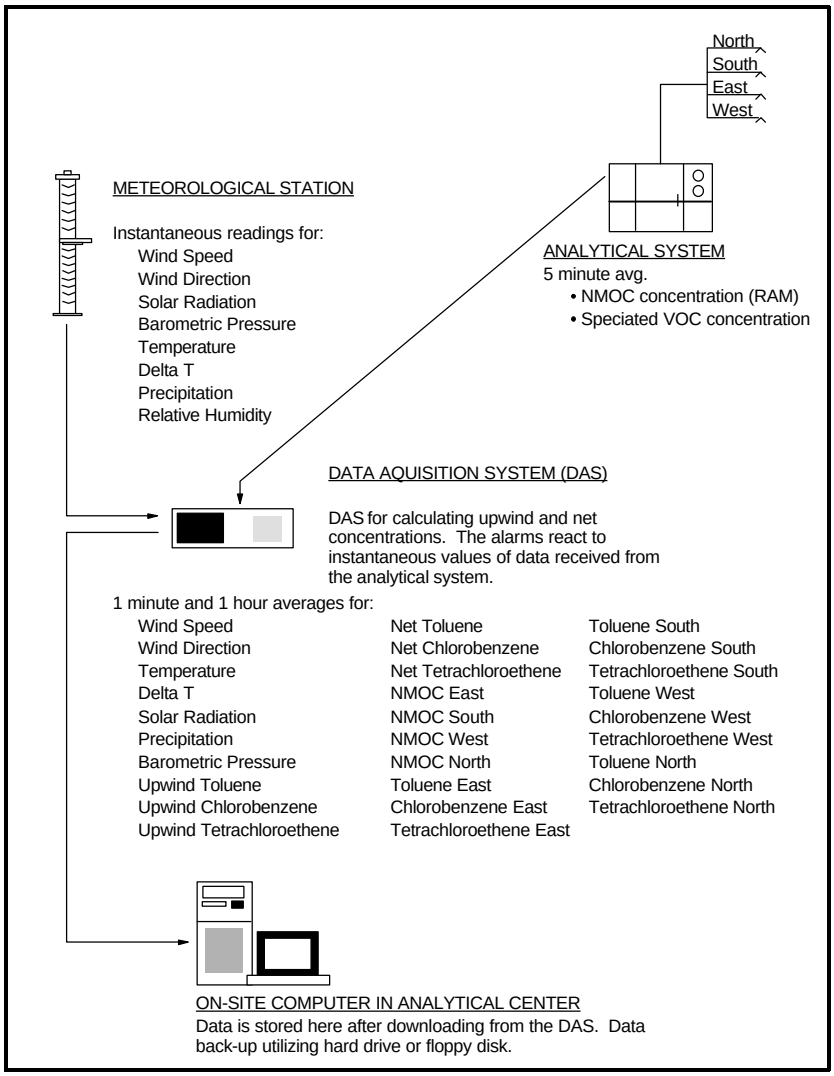


Figure 7-1. Example of data acquisition, storage, and reporting configuration, for a FFMS at a HTRW site.

- Q1: North<45°, >315° and <405°
- Q2: East>45° and < 135°,>405° and <495°
- Q3: South>135° and < 225°, >495°
- Q4: West>225° and <315°

The data logger holds instantaneous values, but only stores averaged values. For instance, the wind direction is updated whenever the meteorological instrument is capable of sending data. The data logger stores each of these values temporarily as it calculates auxiliary (operator determined average between 1 and 15 minutes) and 1-hour averages. These averages are transferred permanently from the DAS to the computer.

c. Network configuration. As shown in Figure 7-2, the DAS is part of a network of instruments. Typical DAS can store only up to a day's worth of data, so the data must be downloaded daily to a computer. This procedure can be done with a direct-cable connection or with a modem. The typical configuration is a direct-cable connection. Additionally, the data from the computer can be transferred via modem and the internet to other off-site offices where the data is stored and backed up with a tape device, as illustrated in Figure 7-2.

d. Data receptors and users. The data from the DAS is used by three categories of receptors. The first category is the Analytical Center. The on-site operators evaluate the real-time data and initiate any required responses for the four alarm-levels, as outlined in Chapter 4 (see Paragraph 4-3). These alarm-levels are based on data from the real-time analytical system and the meteorological station that exceed certain predetermined limits as explained earlier in Chapter 4. The second category is the analysts who perform data

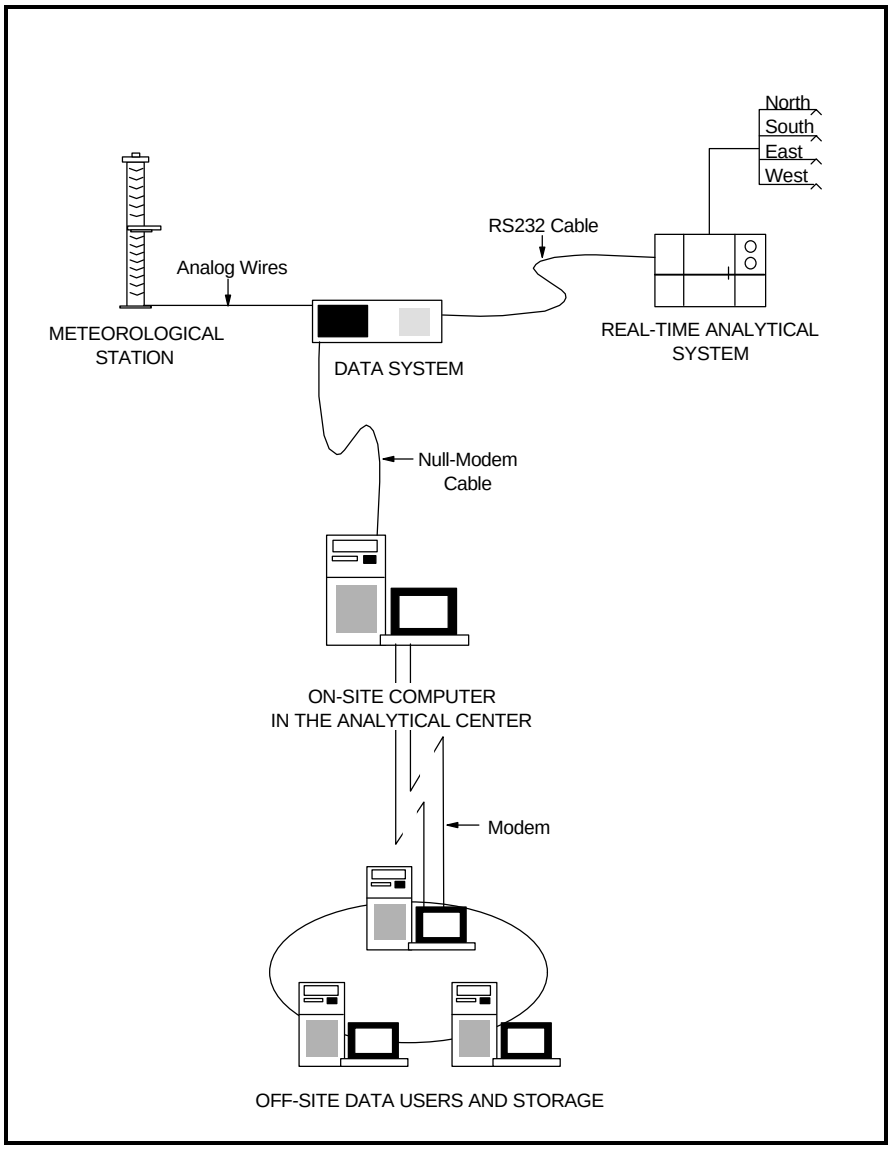


Figure 7-2. Example of HTRW DAS network configuration in the Analytical Center.

analysis and evaluation. The third category of users are the report receipients.

e. Component testing and calibration. The meteorological station components are tested by creating inputs and verifying the values on the data acquisition unit. For instance, the wind speed instrument would be held in place which should produce a specified voltage. In this example, the voltage should equate to zero velocity in the data acquisition unit, as discussed in Chapter 6. For the analytical system, known sample concentrations are measured with the analytical system for validation, and the DAS values are checked for accuracy and acceptable transfer of the data. Lastly, the data transferred to the computer is validated to ensure that the transfer took place.

7-3. Data Compilation, Storage, Transmission, and Reporting

a. Data files. The information from the DAS is downloaded (polled) daily (usually at 2400 hours) to the computer and stored in electronic files in the Analytical Center. All hourly and auxiliary averages and sigmas since the last polling, edit exceptions, changes in input line status, and any calibration data may be retrieved. These files can also be sent and stored in off-site office networks where tape backups are performed, as illustrated in Figure 7-3. The system keeps a "raw" database and a "validated" database for hourly values to ensure data integrity. Hourly data retrieved via polling is put into both databases. The Analytical Center may later edit only the validated database; the raw data can never be changed.

The data files can be stored in a binary format but can be converted to standard format with most commercially available software. As shown in Figure 7-4, this format allows the data to be analyzed in any appropriate software package.

b. Data reporting forms and electronic files. The DAS provides several reports for displaying both real-time and archived data. Real-time data, such as voltages, readings, and alarms, can be displayed on the data acquisition unit itself. Real-time bar graphs, historical graphs (plotting acquired points) and trending plots (plotting acquired points and adding real-time points) can also be displayed. For reviewing older data, software on the computer can generate several types of reports: status reports, historical reports, graphs, and monthly reports. With the exception of the "monthly report," which can report using either the raw or the validated data, the following reports can be produced from the validated database:

(1) Status reports. Status reports for calibration (if auto-calibration instruments are used) and data recovery are available. The data recovery report (see Figure 7-5) shows the number and percentages of valid scans from all instruments over an operator defined time period.

(2) Historical reports. These reports provide data for given parameters over specified time intervals. Hourly numbers, daily averages, and monthly averages can be reported. Figure 7-6 illustrates a single parameter 24-hour report.

(3) Graphs. There are several graphs available for displaying information listed below:

- Daily Single Parameter Graph--displays hourly averages for a selected day and parameter.

- Multi-Day Single Parameter Graph--displays hourly averages for a specified number of days.

- Monthly Single Parameter Graph--displays hourly averages for a selected month and parameter with zoom features to a focus on a specified number of days.

- Daily Multi-Site Graph--displays hourly averages for a selected day for a specified number of selected sites on one graph.

- Multi-Day Multi-Site Graph--displays one graph hourly averages for a specified number of days for a specified number of selected sites.

- Daily Multi-Parameter Graph--displays hourly averages for a selected day for a specified number of selected parameters on one graph.

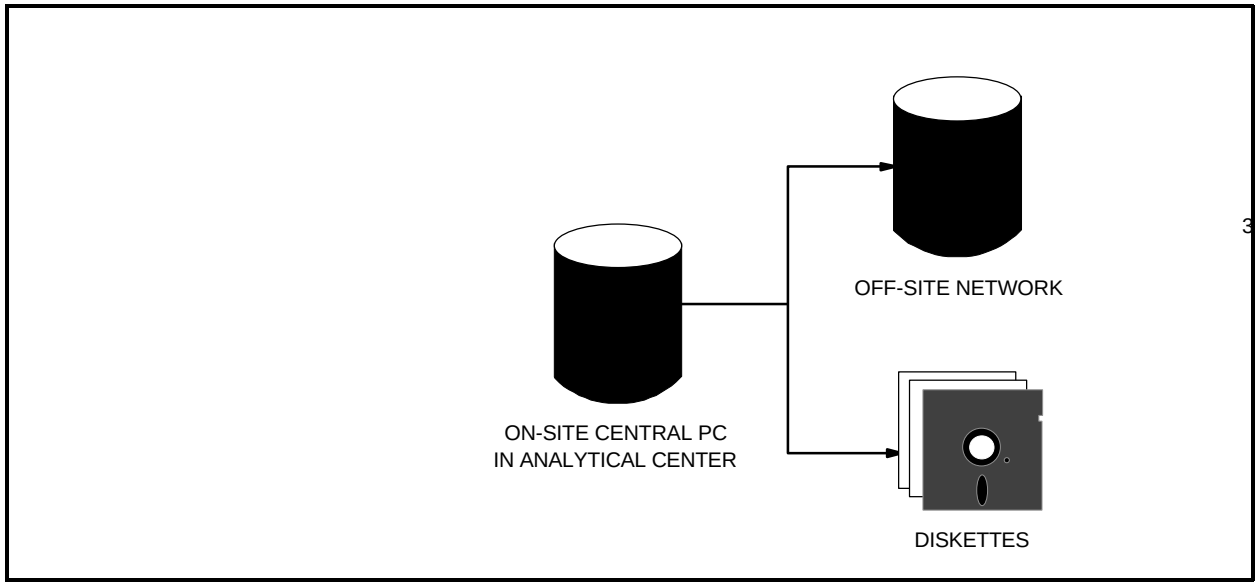


Figure 7-3. Example of data file transmission and storage as part of a HTRW DAS.

- Multi-Day Multi-Parameter Graph--displays hourly averages for a specified number of selected parameters for a specified number of days on one graph.

- Calibration Graph for 1 Month--displays calibration values for one parameter for 1 month.

(4) Frequency distribution. Frequency Distribution Reports are a report of a selected pollutant from the hourly data files. An averaging interval may be specified by the operator. A Joint Frequency Distribution Report shows two or more selected pollutants and a wind or pollution rose on the screen.

c. Daily and monthly reports. A meteorological report (see Chapter 6) summarizing meteorological information for the site is generated daily. This data may be required as part of the DCQCR.

The USACE may require a separate DCQCR for projects involving a large amount of onsite chemical parameter measurement activities. Minimum amounts of such measurement activity can be included in the contractor's daily CQC Report.

The FFMS information for the DCQCR shall be provided by the on-site personnel in the Analytical Center responsible for chemical parameter measurement and chemical sample acquisition, and signed by the contractor QC representative to assure that the chemical data resulting from these activities meets the contract documentation requirements.

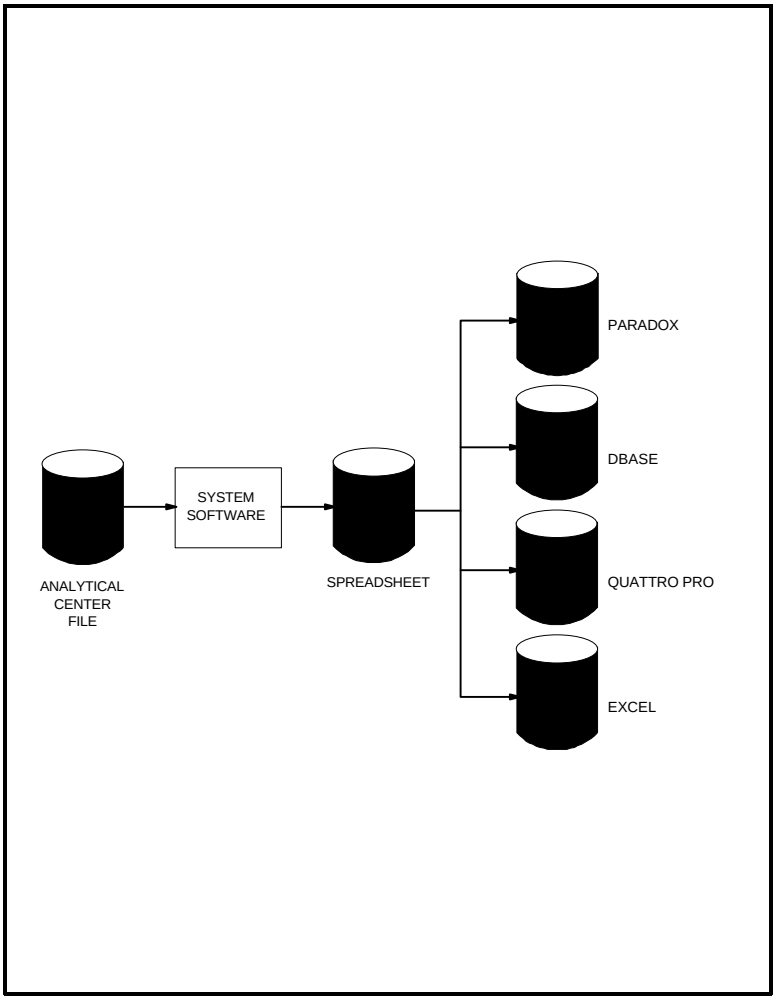


Figure 7-4. Example of data file formats.

The DCQCR should contain, as a minimum, the following:

- Job identification and site numbers.
- Weather including temperature, wind speed and direction, barometric reading, significant wind changes, etc.
- Chemical data acquisition work performed, including specific information identifying project and QA samples collected and calibrations.
- Sampling and sample shipments including shipment and delivery problems that affect project DQO requirements.
- Chemical parameter measurement problems that may affect project DQO requirements, including instrument malfunction, performance requirement failure, etc.

- Any sampling performed as contingency sampling.
- Corrective actions and/or deviations from the approved SAP, including approvals.
- Chemical quality control activities, as part of the three-phase control procedures that were implemented, and confirmation that deviations or actions jeopardizing project DQOs have been documented and

PERCENT RECOVERY REPORT

DAY: 06/25/95
SITE: USACE HTRW - ANYTOWN, USA
TOTAL NUMBER OF SCANS PER PARAMETER: 24

DCN ID	SITE NAME	PARAMETER NAME	NUMBER OF VALID AVG SCANS	NUMBER OF TOTAL OF CALIBRATION VALID SCANS	SCANS	PERCENT RECOVERY
01		WNDSP	24	0	24	100.0
		WNDDR	24	0	24	100.0
		TEMP	24	0	24	100.0
		DELTA	24	0	24	100.0
		SOLAR	24	0	24	100.0
		PRECI	24	0	24	100.0
		BARPR	24	0	24	100.0
		SIGMA	24	0	24	100.0
		UPTOU	24	0	24	100.0
		UPCLB	24	0	24	100.0
		UPTCL	24	0	24	100.0
		NETOU	24	0	24	100.0
		NECLB	24	0	24	100.0
		NETCL	24	0	24	100.0
		NMAST	24	0	24	100.0
		TOULN	24	0	24	100.0
		TOULS	24	0	24	100.0
		TOULE	24	0	24	100.0
		TOULW	24	0	24	100.0
		CLBZN	24	0	24	100.0
		CLBZS	24	0	24	100.0
		CLBZE	24	0	24	100.0
		CLBZW	24	0	24	100.0
		TCLEN	24	0	24	100.0
		TCLES	24	0	24	100.0
		TCLEE	24	0	24	100.0
		TCLEW	24	0	24	100.0
TOTAL FOR DCN 01			648	0	648	100.0

Figure 7-5. Example of data recovery report from DAS in Analytical Center.

forwarded to project management. A summary of the feedback procedure for any corrective actions taken.

- Signatures of responsible authority and initials of all persons conducting changes/corrective actions.

The DAS can be programmed to provide all minimum contact requirements for the DCQCR.

Monthly, a project summary report can be produced from the DAS with daily meteorological reports and daily wind-roses (joint frequency distribution graphs of wind speed and wind direction). These wind-roses, (See example in Fig. 6-3), are generated on-site and captured into a graphics file that can be sent electronically to any off-site office.

d. Data validation procedures. Data validation is the systematic review of measurement data for outlier and error detection. For FFMS data collected at a HTRW site, there can be three levels of validation: (1) preliminary consistency check and outlier identification, (2) review of data collection processes, and (3) statistical analysis of data to determine consistency between data sets and monitoring devices and to formally identify outliers. Data found to be questionable at any of these levels should be investigated, and an

explanation should be sought for the unusual readings. Data validation requirements are project specific and may involve different validation levels for various analytical procedures, as outlined in Figure 7-7.

- **Level 1**. Qualified chemists or air specialists, as part of the Analytical Center, should perform a preliminary visual check for noticeably improbable quantities, peaks or spikes in the data, obvious trends in the data that might result from monitoring equipment malfunction, and other data irregularities. The personnel should also compare data points that share deterministic relationships (e.g., high wind speed readings, wind direction, ambient temperature and wind speed, component quantitiy, and speciated organic concentrations) to identify irregularities. These reviews are performed shortly after the raw data is collected so that investigations can determine the validity of the readings.

- **Level 2**. Qualified personnel should review chain-of-custody, maintenance, calibration, and analysis records to detect any problems with laboratory or field processes or equipment parameters that might lead to nonstandard sampling intervals, insufficient sample volume, or other problems that may negate the sampling event or create questionable results.

- **Level 3**. Qualified statisticians should analyze data for subtle yet unacceptable abnormalities. They should assess the consistency of data collected over time and by different monitoring devices at the same site. They also should use statistical methods to identify outliers in the data that require investigation.

The data validation procedures just outlined are applicable for both real-time and time-integrated monitoring as part of a HTRW monitoring program, as indicated in Table 7-1. The levels of validation involve a QC review by each data collector or generator and an independent review of the entire data set by the Project Quality Assurance Officer. Activities for the integrated program (real-time and time-integrated) are identified in Figure 7-7 and include visual checks for improbable data, peaks or spikes, obvious trends, data relationships

02-09-1996
11:30:16
MET - AIR QUALITY DAILY DATA REPORT
Site: USACE HTRW Site
Any Town, USA
Date:6/25/95

Hour	WNDSP (m/sec)
0	1.20
1	0.80
2	1.20
3	1.10
4	1.20
5	0.80
6	1.30
7	2.00
8	2.20
9	1.60
10	1.00
11	1.50
12	1.60
13	2.50
14	2.20
15	2.70
16	2.30
17	1.80
18	1.70
19	1.60
20	1.30
21	1.10
22	1.10
23	1.10

Figure 7-6. Example of single-parameter 24-hour report from DAS in Analytical Center.

with other parameters (VOCs and wind direction), maintenance, calibration, and analysis records.

e. Meeting the project DQOs. The last step in data evaluation is data quality assessment which determines whether the data reported meets the project DQOs. As defined in Chapter 3, DQOs are defined as qualitative and quantitative statements which clarify project objectives, define appropriate types of data to collect, and specify the limits of uncertainty the decision maker is willing to accept in data that support project related decisions. The reviewer evaluates the data and compares their quality to the project DQOs. If it is determined that the data collected does not meet the project DQOs, then a plan for initiating and implementing corrective action should occur to bring the program back to compliance with the DQOs. The plan should specify (1) conditions that will require corrective actions, (2) personnel responsible for initiating, implementing, evaluating and approving the results of corrective actions, and (3) statement of resolution identifying that program DQOs have been met based upon corrective action or establishing new DQOs.

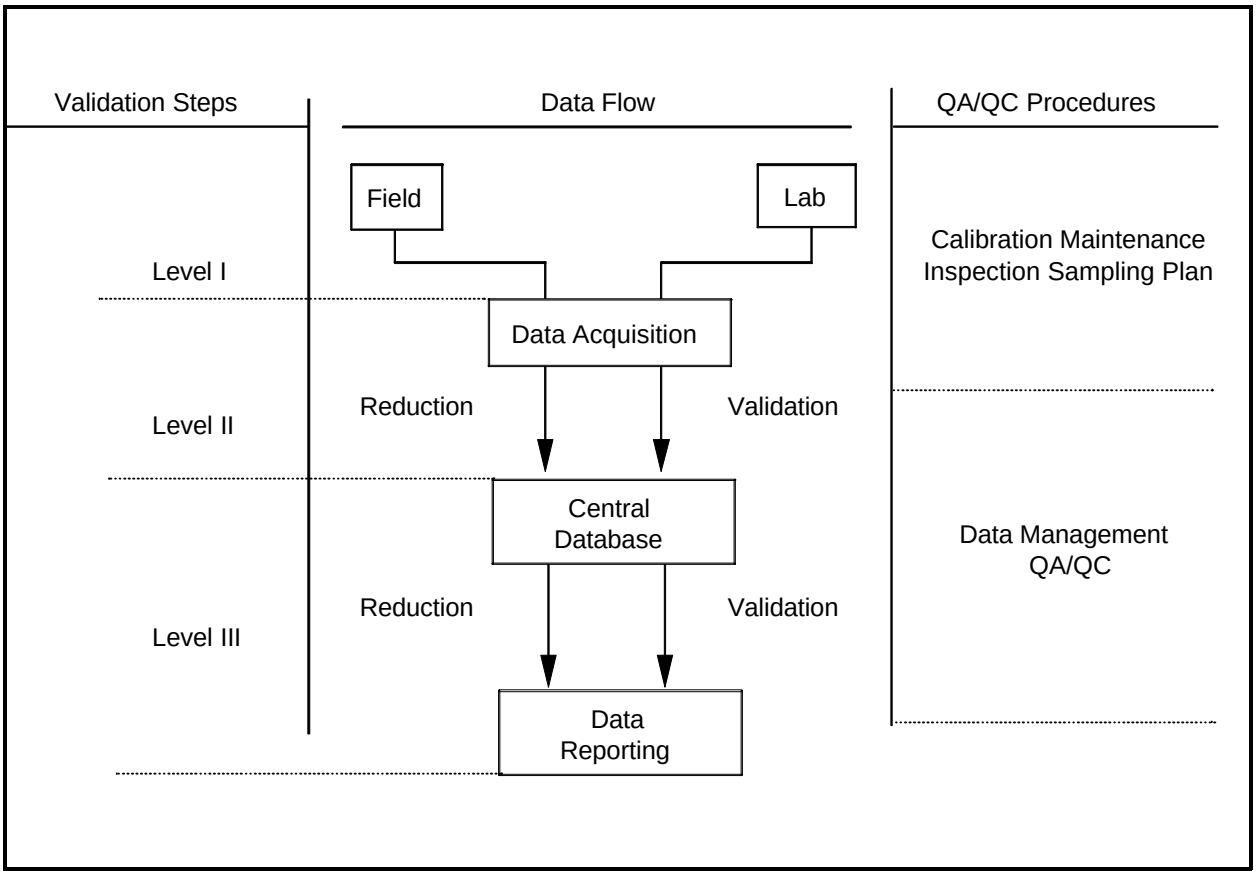


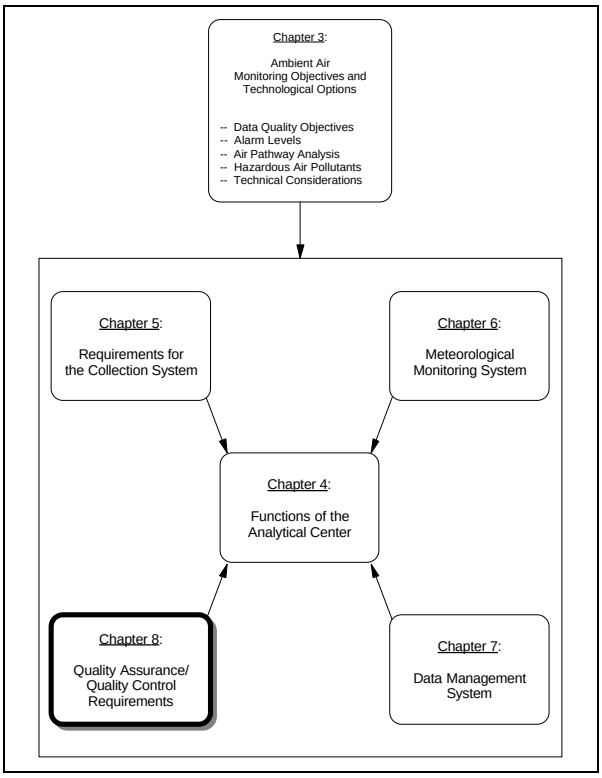
Figure 7-7. Example of levels of data validation recommended by EPA.

Table 7-1
Example of Applicable Levels of Data Validation for Real-Time and Collocated Time-Integrated Methods

Parameter	Example of sampling method	Example of analytical method	Example of level of data validation
Organics Volatile	Real-time sample collected through heat-trace sample lines and analyzed by analytical system	Gas chromatography equipped with photoionization detector for real time analysis	Level 1 and 2
	Time-integrated sample collected in stainless steel SUMMA® canisters utilizing pump system.	Analysis by cryogenic concentration followed by gas chromatography/ mass spectroscopy (GC/MS) analysis.	Level 1, 2, and 3
Semi-volatiles	Time-integrated sample collection on polyurethane foam (PUF/XAD-2) plugs using a high-volume sampling apparatus.	Soxhlet extraction, concentration of the extracts, and analysis using GC/MS detection for PAHs,	Level 1, 2 and 3
Inorganics Total Suspended Particulate (TSP) matter and materials	Time-integrated samples collected on 8 in. X 11 in. quartz fiber filters utilizing high volume sampling technique.	Filter weighted for total mass, then extracted in HCl/HNO_3 by microwave extraction, followed by inductively coupled argon plasma spectroscopy (ICP) analysis for metals.	Level 1, 2, and 3
Meteorological Wind speed, direction, solar radiation, temperature and precipitation	Time-integrated through various instrument specific for meteorological parameters.	No analysis required. Instantaneous value from on-site instruments	Level 1 and 2

SUMMARY OF QUALITY ASSURANCE/QUALITY CONTROL (QA/QC) REQUIREMENTS

A QA/QC system involves a systematic set of procedures, checks, audits, and corrective actions intended to ensure that all design, performance, environmental monitoring and sampling, and other technical and reporting activities related to achieving project related FFMS data quality objectives are met. Chapter 8 identifies and describes the steps in designing and executing QA/QC procedures for a FFMS sampling and analysis program.



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- Field Sampling Plan
- QA Project Plan

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Panel 8-1. Overview of Quality Assurance/Quality Control Requirements.

Panel 8-1. Overview of Quality Assurance/Quality Control Requirements.

8-1. Introduction

The QA/QC program for the FFMS involves a systematic set of procedures, checks, audits, and corrective actions to ensure that all design, performance, environmental monitoring and sampling, and other technical and reporting activities for achieving the project DQOs are met. Important components of the QA/QC planning process involve developing a clear understand of how the data will be used, defining the DQOs that are needed to ensure project success and establishing how data quality will be assessed. These and other QA/QC components are incorporated into the project's SAP, which is composed of two parts: the FSP and the QAPP.

Although QA and QC are both intended to provide for the production of quality data, the two concepts are fundamentally different in several regards. Quality control involves those controls and checks that are *routinely implemented by project staff* to maintain the integrity of the collected data. An example of a QC activity is the periodic calibration of an instrument as specified in the operating manual. In contrast, QA is a quality auditing function *performed occasionally by individuals external to the project team*. An example of a QA activity is the review of instrument calibration records to ensure that the calibrations have been performed correctly. For USACE projects, the QA and QC requirements may be project and/or contract specific or may otherwise default to ER 1110-1-263, EM 200-1-6 or other specified USACE guidelines.

8-2. Quality Planning

Quality planning is an integral part of the USACE's environmental programs, as addressed in EM-200-1-2 and should include FFMSs, when applicable, activities at HTRW sites. That EM provides project planning guidance to develop data collection programs and define DQOs for HTRW sites. The use of that manual as part of the quality planning of a project is intended to promote the identification of the type and quality of data required for HTRW site cleanup, progressing from site investigation and evaluation through remedial design and site close-out for USACE customers.

That EM-200-1-2 describes a four-phase data quality design process. The four phases are:

- Phase I - Identify project strategy.
- Phase II - Determine data needs.
- Phase III - Develop data collection options.
- Phase IV - Design data collection program.

Consistent with the philosophy described in EM 200-1-2, the design, installation and utilization of FFMSs at HTRW sites also requires technical project planning.

The most important step in designing and executing a fixed fenceline monitoring program at a HTRW site is the initial planning that takes place at the very beginning of the project. The extra effort put into this initial planning more than pays for itself in improved data quality and reduced rework. The essential elements of the initial planning process are discussed below and summarized in Figure 8-1.

a. Intended use of the data. The design of a FFMS for monitoring at HTRW projects can contain numerous deficiencies when there is poor understanding of the intended use of the data. When this deficiency occurs, the data collected do not address the needs of the program, and the resources that were devoted to the data collection effort may have been wasted. Thus, the first step in the initial planning process is to clearly define how the data will ultimately be used and to reach agreement concerning this use among all involved parties.

Agreement on the total intended uses of data is not always straightforward, especially where there may be multiple uses and differing priorities among the effected parties. If the data are to be used for risk assessment purposes, for example, a number of potentially hazardous air contaminants may need to be measured and instrument detection limits set at very low limits. Alternatively, if the data will be used to demonstrate compliance with air emission standards, an entirely different set of sampling and analysis requirements are involved.

For most USACE projects involving FFMS, the data collection efforts will typically support on-site remediation activities. *Pre-remediation* air quality monitoring may be conducted to establish background concentrations and site-specific meteorology to gain experience with the sampling and analytical methods to be used later in the project. Monitoring during the *remediation* phase generally has two objectives: (1) documenting any air quality impacts associated with the remediation activities and (2) triggering corrective actions in the event of an air contaminant release above a predetermined level, as discussed in Chapter 4. *Post-remediation* sampling may be conducted to confirm that air contaminant levels have returned to baseline levels and that any air quality impacts occurring during remediation have been eliminated. Given the diverse and complex data collection needs involved with a remediation project, the intended use of the data must be firmly established as a first step in the project planning process.

b. Data quality objectives. As discussed in Chapter 3, determining DQOs is also an essential step in the planning process. Once the DQOs have been established, it is possible to select those sampling and analysis procedures that will provide the required quality of data. Additionally, later in the project, the quality of measured data can be assessed by determining if the DQOs have been achieved.

c. Field Sampling Plan. Not until the intended use of the data and the project DQOs have been clearly established can the FSP be prepared. A depiction of the FSP and QAPP and their general contents is shown in Figure 8-1. The FSP specifies the sampling and analysis methods and procedures to be used and contains a number of elements that are crucial to achieving the desired levels of data quality. These elements include chain of custody procedures, sample packaging and shipping requirements, contractor quality control procedures, and a corrective action plan. Additionally, the FSP should reference or append SOPs (see Appendix C) for the selected sampling and analysis methods. For most on-site equipment operation and sampling procedures, these SOPs should be prepared specifically for the methods and site specific applicability. For USACE, projects, a required FSP should contain the required SOPs and should be reviewed and approved during the preparatory phase of the USACE three phase control system.

d. Quality Assurance Project Plan. The final step in the initial planning process is preparing the QAPP. The required elements of a QAPP are summarized in Figure 8-2. For FFMSs, the QAPP should include reference and audit sample analysis. Especially important are the sample custody and holding time requirements, calibration procedures and frequencies, internal QC checks, calculation of data quality indicators, and corrective actions. Additionally, the QAPP identifies the project's QA Officer, who officially approves and implements the QAPP. A QAPP review and approval checklist from EM 200-1-3 is presented in Figure 8-3.

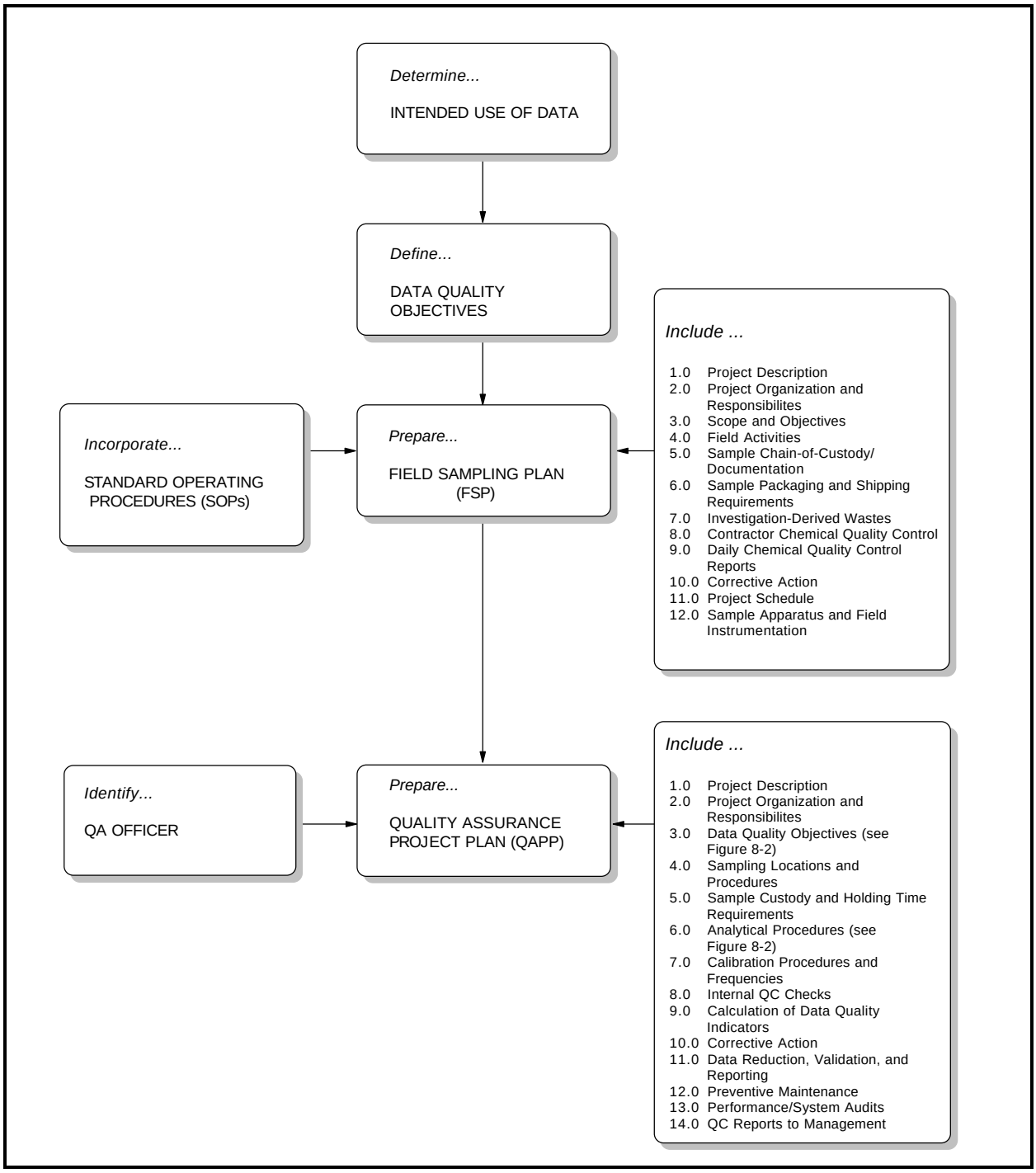

Figure 8-1. Example of essential elements of quality planning as part of a HTRW FFMS.

- ***Title Page***. Should include the name of the document and the date it was prepared. The QA officer should sign the title page, ensuring that field and laboratory personnel are aware of the requirements for precision, accuracy, completeness, representativeness, and comparability.
- ***Table of contents***. Includes a listing of the QAPP elements and any appendices, figures, and tables. A list of the recipients of official copies of the QAPP should also be provided.
- ***Project description***. Consists of a general paragraph describing the scope of work, general objectives, and required measurements. (If the project description is discussed in the field sampling plan, it does not need to be repeated in the QAPP.)
- ***Project organization and responsibility***. Identifies key field and laboratory personnel or organizations that are necessary for each analytical activity during the study. A table or chart showing the organization and lines of authority should be included. The organizational chart should also include all subcontractors and their key points of contact. The QA officer should be organizationally independent of project management so that the risk of conflict of interest is minimized.
- ***Data quality objectives (see Figure 8-1)*** . Describes the QA objectives for the data so that the data can achieve their intended use. Project-specific data quality objectives that have been identified for the project, short-term decisions that will be made during the project planning phase, and long-term decisions that will be made prior to project closeout should be highlighted.
- ***Sampling locations and procedures***. References the sections of the field sampling plan that discuss the general rationale for choosing sampling locations and the sampling procedures proposed for each matrix.
- ***Sample custody and holding times***. References the appropriate sections (e.g., sample custody/ documentation) of the field sampling plan for all custody and holding requirements pertaining to the field and laboratory activities.
- ***Sampling and analytical procedures***. (See Figure 8-1) Identifies the appropriate sampling and analytical test methods that should be used for each environmental sample. The field sampling plan can be referenced.
- ***Calibration procedures and frequencies***. Discusses the calibration procedures to be used, the number and concentration of calibration standards, and the calibration range and procedures to establish and verify the calibration of instruments.
- ***Internal QC checks***. Identifies the specific internal QC methods to be used, including analyses of method blanks; use of laboratory control samples, and use of environmental samples as duplicates, matrix spikes, and duplicates.
- ***Calculation of data quality indicators***. Discusses how precision, accuracy, completeness, representativeness, and comparability goals are to be calculated from the project data.
- ***Corrective actions***. Addresses corrective actions that must be implemented if QA specifications are not met. Corrective actions could include resampling, reanalyzing samples, or auditing laboratory procedures. Persons responsible for initiating these actions should be identified.
- ***Data reduction, review, validation, and reporting***. Discusses the data review process that is required to assure the validity of the data. Data reduction procedures should be summarized and the persons responsible for data reduction identified. The format for reporting the data and the data reporting schedule should be specified.
- ***Preventive maintenance***. Discusses the preventive maintenance plan that will be implemented to minimize downtime of field and laboratory instrumentation.
- ***Audits***. Describes the performance, systems, data quality, and management audits that will be performed onsite and at the laboratory.
- ***QC reports to management***. Discusses QC reports that will be prepared. These reports typically include an assessment of accuracy, precision, completeness, representativeness, and comparability; audit results; and significant QA problems encountered.

Figure 8-2. Example of required elements of a quality assurance project plan (QAPP) for a HTRW FFMS.

Quality Assurance Objectives

(This information should be referenced to the Project Work Plan or contract specifications)

a. Are field measurement objectives discussed? Y_____ N_____ N/A_____

b. Are analytical method detection limits defined? Y_____ N_____ N/A_____

c. Are quality control parameters defined? Y_____ N_____ N/A_____

1. Precision and accuracy Y_____ N_____ N/A_____
2. Completeness Y_____ N_____ N/A_____
3. Representativeness Y_____ N_____ N/A_____
4. Comparability Y_____ N_____ N/A_____

Sample Custody/Documentation

a Is a field logbook maintained with appropriate information concerning drilling/sampling? Y_____ N_____ N/A_____

b. Is method of identifying photographs discussed? Y_____ N_____ N/A_____

c. Is sample numbering system appropriate? Y_____ N_____ N/A_____

1. Project designator Y_____ N_____ N/A_____
2. Location designation Y_____ N_____ N/A_____
3. Matrix code Y_____ N_____ N/A_____
4. Sample sequence numbers Y_____ N_____ N/A_____
5. Depth interval (if required) Y_____ N_____ N/A_____

d. Sample Documentation

1. Does information on sample label include:
   - Site name Y_____ N_____ N/A_____
   - Identification of sample station number Y_____ N_____ N/A_____
   - Date and time of collection Y_____ N_____ N/A_____
   - Name of sampler Y_____ N_____ N/A_____
   - Analytical analyses requested Y_____ N_____ N/A_____
   - Media sampled Y_____ N_____ N/A_____
   - Preservation method Y_____ N_____ N/A_____
2. Are completed custody seals required over sample container (except VOA) lids? Y_____ N_____ N/A_____
3. Does chain-of-custody record contain appropriate information? Y_____ N_____ N/A_____
4. Are receipts for sample forms required? Y_____ N_____ N/A_____

Figure 8-3. Example of a QAPP review and approval checklist from EM 200-1-3.

TECHNICAL SYSTEMS AUDITS

A qualitative on-site evaluation of a measurement system used to assess and document all facilities, equipment, systems, recordkeeping, data validation, operation, maintenance, calibration, reporting, and quality control procedures. Since the above items should be defined in the approved QAPP, the QAPP provides the basis for the audit.During the audit, any undocumented or unauthorized deviations from the approved QAPP are cited and noted in the audit report.

Although quantitative information is not provided, the audit helps the auditor quickly determine whether the data quality is likely to be adequate for the intended use of the data, or whether problems present during testing may lead to erroneous results. Often, the collection of data is facilitated with the aid of checklists. A checklist not only provides a simple format for documentation, but also provides an indication of whether the auditor has examined all elements of the system under evaluation.

PERFORMANCE EVALUATION AUDITS

A quantitative evaluation of a measurement system. Although it is possible for each measurement of a test program to be subjected to a performance audit, it is more common for only the critical, or most important, measurements to be evaluated. The evaluation usually involves the measurement or analysis of a reference material having associated with it a known value or composition. It is important that the value or composition of the reference material be certified, or at least verified, prior to use, and that the certification or verification be adequately documented. Usually, the identity of the reference material is disguised so that the operator or analyst will treat it no differently from a test program sample.

A performance evaluation audit will answer the following questions:

- What were the accuracy and precision of the measurement system at the time of the audit?
- Do the qualitycontrol data collected during routine system operation correctly reflect data quality?
- Is the measurement system operating within the established control limits?
- If the results of previous audits are available, has data quality significantly changed?

DATA QUALITY AUDITS

An assessment of the methods used to collect, interpret, and report the information required to characterize data quality. This assessment involves a detailed review of the recording and transfer of raw data, data calculations, the documentation of procedures, and the selection and discussion of appropriate data quality indicators. A data quality audit answers the following questions:

- Is there sufficient documentation of all procedures used in the data collection effort to allow the repetition of the effort by a person or team with technical qualifications similar to those of the original data collector?
- Is there sufficient documentation to verify that the procedures specified for use in the data collection effort were properly followed?
- Is sufficient information presented to enable potential users to evaluate the limitations of the data and to determine whether the intended use of the data is appropriate?

The result of the audit help determine whether the data collection efforts need modification and if the quality control procedures are adequate.

MANAGEMENT SYSTEMS AUDITS

An on-site audit of an organization's quality assurance management system used to verify the existence and adequacy of the internal management systems necessary for the successful implementation of a quality assurance program. The primary purpose is to determine the extent to which quality assurance has been institutionalized within an organization and to recommend actions to correct any deficiencies found. Management systems audits are designed to answer the following questions:

- Does the management policy of the organization identify the specific role of quality assurance in its operations?
- Does the organization maintain official position descriptions for all QA personnel and provide for a quality assurance program that includes appropriate milestones and documentation of specific work assignments?
- Is it possible to identify specific resources that were allocated to the management of the organization's QA program?
- Does the QA Officer maintain an adequate system for determining the status of documents or activities required of individual projects?
- Is there adequate training in QA, and is there evidence of a routine concern for QA in organization activities?

Figure 8-4. Example of four types of quality assurance audits associated with a FFMS at a HTRW site

- ***Background (upwind) samples***. Samples similar to the sample under investigation, but outside the presumed area of contamination. These samples are taken to measure the concentration of analytes considered naturally occurring, due to another contaminant source, or due to the media used in sample acquisition.

- ***Trip Blanks***. Whenever the possibility exists for accidentally adding extraneous material into the sample during collection, shipment, or analysis, a trip blank sample should be used to assess the magnitude of this contamination. Blank samples associated with the field sampling effort include both field blanks and trip blanks.

- ***Field Control Samples***. General term assigned to field-generated replicates (duplicates/splits/spikes), blanks, background/upwind samples, etc., associated with reference method monitoring (RMM).

- ***Field Duplicate Sample***. Independent sample collected at approximately the same time and place, and using the same methods, as another sample (collocated). The duplicate and original sample are containerized, handled, and analyzed in an identical manner.

- ***Field QA***. A sample that is a collocated replicate of a field sample, except that the sample is sent to the USACE's QA laboratory for analysis; allows early detection of sampling, documentation, packaging, shipping, and analytical errors.

- ***Field QC Sample***. A field replicate (duplicate) sent blindly to the laboratory; results assess sampling precision and handling techniques.

- ***Field Replicate***. A general term for field duplicates/triplicates, field splits, or field spikes; used to evaluate the precision of handling, shipping, storage, preparation, and analysis procedures. Each replicate is containerized, handled, and analyzed in an identical manner.

- ***Laboratory Control Sample/QC Reference Sample***. A spiked blank sample prepared by the analyst (preferably obtained from an outside source) which combines a portion, or all, of the elements being analyzed; used for calculation of precision and accuracy and to verify that the analysis is under control.

- ***Laboratory Duplicate Samples***. Identical splits of individual samples that are taken and analyzed by the laboratory to assess method reproducibility.

- ***Matrix Duplicate/Laboratory Duplicate (DUP)***. Two representative aliquots of the same sample matrix subjected to identical analytical procedures to assess the procedural precision of the method through the calculation of relative percent difference (%RPD).

- ***Method Blank***. The use of extraction solution, zero air, and adsorption media prepared in the same manner as samples; used to determine if cross contamination or memory effects are present.

- ***Surrogate Compounds/System Monitoring Compounds***. Brominated, fluorinated, or isotopically labeled compounds (not expected to be detected within environmental samples) which are added to every field sample; used to evaluate sampling and analytical efficiency by measuring recovery.

- ***Trip Blank***. Trip blanks are transported with empty sample containers to the HTRW site and remain sealed until analyzed with collected environmental samples. Trip blanks permit evaluation of contamination generated from sample containers or occurring during the shipping and laboratory storage process.

Figure 8-5. Example of typical QC samples associated with a FFMS.

The QAPP also identifies the QA audits to be performed during the sampling and analytical phases of the

project. Audit results are very important because they can identify problems before it is too late to implement corrective actions. Additionally, audit results provide validation of the quality of data being collected. The four types of QA audits associated with a FFMS are summarized in Figure 8-4. For FFMSs, audits should address sample collection, system performance and analytical procedures and data analysis.

8-3. Characterizing Data Quality

A QC program makes use of a variety of *QC samples* and *data quality indicators* to assist in characterizing the quality of data collected. The types of QC samples used in the field will depend upon the nature of the data collection effort, but will likely include field replicates (duplicates, splits, and/or field spikes), field blanks (zero air, canister, and/or trip blanks), and background (upwind) samples. Laboratory QC procedures will usually include the analysis of replicates, standards, reference material, surrogates, and/or RAM spiked samples. These and other types of QC samples associated with a FFMS program are defined in Figure 8-5. For FFMSs, sampling and analysis may involve the Analytical Center and/or reference method monitoring (RMM). For the FFMS perimeter air monitoring program, prescribed data quality qualifiers are defined in terms of precision, accuracy, completeness, representativeness, and comparability. These data quality indicators can then be compared against the project DQOs to determine whether these aspects of the FFMS project's data quality needs have been met. Each of the five data quality indicators are described below.

a. Precision. Precision examines the distribution of measured values about their mean. The distribution of measured values refers to how different the individual measured values are from the average reported value. Precision may be affected by the natural variation of the matrix or contamination within that matrix as well as by indeterminate errors made in field and/or laboratory handling procedures. For chemical analysis of environmental samples, precision is commonly determined from duplicate sample analyses and expressed as relative percent difference (RPD), as follows:

$$\text{RPD (\%)} = \left[\frac{|C_1 - C_2|}{\overline{C}}\right] \times 100$$

where:

C_1 and C_2 = absolute value of the difference of the observed values.

$\overline{C}$ = the mean of the duplicate values $[(C_1 + C_2)/2]$.

For continuous monitors for which collocated sampling is not practical, precision is determined by the measurement of a certified gas. For these measurements, precision is calculated as follows:

$$\text{RPD (\%)} = \left[\frac{X_1 - X_2}{X_2}\right] \times 100$$

where:

X_1 = measured value as documented by real-time, on-line analytical system in the Analytical Center.
X_2 = certified value as documented by manufacturer certificate.

If sufficient replicate samples are taken (usually at least eight), precision can be estimated as the Relative Standard Deviation (RSD) or the Coefficient of Variation (CV), as follows:

$$CV = RSD = \left(\frac{S}{\overline{C}}\right) \times 100$$

where:

CV = coefficient of variation.
RSD = relative standard deviation.
S = standard deviation.
$\overline{C}$ = mean value of replicate observed values.

$$S = \left[\frac{1}{n-1} \sum_{i-1}^{n} (C_i - \overline{C})^2\right]^{\frac{1}{2}}$$

where:
C_i = observed value of the ith replicate.
$\overline{C}$ = mean of replicate observed values.
n = number of replicates.

and the mean, $\overline{C}$, is defined as:

$$\overline{C} = \frac{1}{n} \sum_{i=1}^{n} C_i$$

For a perimeter real-time, on-line volatile organic analytical system in the Analytical Center, precision is measured daily by challenging the system with a known reference gas or individual organic compounds and calculating the system RPD.

b. Accuracy. Accuracy measures the bias in a measurement system. Sources of bias may include the sampling process, field contamination, preservation methods, handling, sample preparation, and analysis techniques. Field equipment blanks and trip blanks can help assess the potential contaminant contribution from various outside sources. Analytical accuracy can be assessed through the use of known and unknown QC and spiked samples and is commonly represented as percent recovery (%A) or percent bias. Accuracy of a real-time, on-line volatile organic analytical system is determined by collocating a reference method or Compendium method sampling system (i.e., RMM) with the real-time system and calculating:

$$\%A = 100 \times \left[\frac{X_u}{X_s}\right]$$

where:

X_S = measured value as determined by the reference method monitoring (RMM)/Compendium method
monitoring.

X_U = measured value as determined by the real-time gas chromatographic system in the Analytical Center.

c. Completeness. Completeness is defined as the percentage of measurements made that are judged to be valid measurements compared to the total number of measurements planned. Specified levels of overall completeness, in addition to particular completeness goals for critical samples, should be established as part of the project DQOs. Percent completeness (%C) is calculated as follows:

$$\%C = \left[\frac{V}{N} \right] x\ 100$$

where:

V = number of measurements judged to be valid, as measured by the real-time monitoring system.

N = number of valid measurements needed to achieve a specified statistical level of confidence (i.e., 80%).

Overall completeness accounts for both sampling and analysis completeness, each of which may be specified separately. Valid samples include those analytes in which the concentration is determined to be below detection limits. There may also be different completeness goals for various parameters and time periods. Typically, completeness is expressed as overall completeness for a given parameter at a given site for a specified period, such as a year or the duration of monitoring. Typically, overall completeness goals of 80 to 90 percent for real-time monitoring data and greater than 90 percent for meteorological and RMM data should be readily available.

d. Representativeness. Representativeness expresses the degree to which sample data accurately and precisely represent (1) the characteristics of a population of samples, (2) parameter variations at a sampling point, or (3) environmental conditions. Representativeness is generally a qualitative parameter that is most concerned with proper siting and design of the sampling program. It can be accessed qualitatively or through the use of duplicate field and laboratory samples, which provides both precision and representativeness information.

Typically, for real-time FFMSs at HTRW sites, one or more locations may be chosen to represent background concentrations, short-term maximum exposures, long-term maximum exposures, worker exposure, or average concentrations at or downwind of the site. Meteorological data such as temperature, humidity, wind speed, direction, and precipitation should be reviewed to see if locations actually met the characteristics expected based on earlier modeling. A failure to achieve required representativeness with a FFMSs is generally the result of either system design or system operation failures.

e. Comparability. Comparability is a qualitative parameter expressing the confidence with which one data set can be compared with another. For example, sample data should be comparable with other measurement data for similar samples and sample conditions. Comparability is achieved by using compatible procedures to collect and analyze representative samples and to report analytical results in appropriate units.

8-4. QA/QC Applications to FFMS Programs

Although specific applications of QA/QC will vary among HTRW sites, a number of considerations are common to all FFMS projects. These considerations are discussed below, along with some recommendations and areas of concern.

a. Data Quality Objectives. The determination of DQOs will depend upon specific project needs. For the monitoring methods described in this EM, representative and achievable data quality indicators have been identified that will be appropriate for most applications. These are listed in Table 8-1. It is recommended that a table similar to Table 8-1, but with a column added that compares the DQOs with measured data quality indicators, be included in the SAP and each monthly HTRW project progress report.

b. Sampling site location. Sampling equipment needs to be located where representative samples can be collected. For most HTRW FFMS programs, representative sampling sites should be selected to assess (1) any increase in emissions from the HTRW site during remediation and (2) potential exposure to workers and nearby residents. Obviously, a critical factor in site selection should be wind direction. Although sometimes airport wind data can be relied upon, in most situations the airport is too far away to take into account local terrain and other factors (e.g., nearby buildings) that can affect localized wind speed and direction. Thus, it may be desirable to set up a meteorological station on site to establish prevailing wind direction. Depending on the duration and season of the sampling event, the meteorological station may need to be operated for an extended period of time (several months to a year) to determine representative conditions; or it may be necessary to operate the meteorological station for the duration of the project and select sampling locations based on this on-line information. Another site selection factor involves the location of potentially exposed workers and nearby residents (e.g., monitors may need to be set up between the emission source and these potentially exposed individuals).

c. Internal QC. Table 8-2 presents examples of the QC checks that are appropriate for the types of instrumentation described earlier in this EM as part of a HTRW FFMS program. Additionally, blanks involving one clean sampling device (e.g., a PUF/XAD-2 adsorbent cartridge, glass fiber filter, or SUMMA® canister) should accompany a certain percentage of the samples to the field and back to the laboratory to serve as trip and field blanks. The average amount of analyte found on the trip blank should be compared with the amount found in the actual samples; if the trip blank level is greater than 25 percent of the sample amounts, the data should be identified as suspect. During a specified number of sampling events at least one set of collocated samples using RMMs (two or more samples collected simultaneously) should be collected. If agreement between collocated samples is not within ±40 percent, the reason for non-agreement should be investigated.

d. Performance and systems audits. Example performance audits for the types of instruments described earlier in this EM as part of a HTRW FFMS program are presented in Table 8-3. This table is intended to be representative of audits that might be performed; however, additional and/or different performance audits may be needed, depending upon the specific equipment in use. The frequency of performance audits will depend on the intensity and duration of the sampling effort. Systems audits should be performed immediately before the sampling effort begins and again shortly after it begins (e.g., during the first week). Thereafter, systems audits should be performed as often as practicable. Table 8-4 documents the criteria and limits for the performance and system audits involving an HTRW FFMS program.

Table 8-1
Example Data Quality Indicators and Specifications for a FFMS Program at a HTRW Site

Measurement	Accuracy or Recovery (%)	Precision (RPD)	Completeness (%)
Real-time Monitoring Instrumentation			
Analytical system for RAM NMOC	±40	±30	>80
Analytical system for speciated organics	±40	±30	>80
Contingency analytical system for RAM and speciated organics	±40	±30	>80
Time-Integrated Monitoring Instrumentation			
High-volume (HV) TSP/metals	NA	±30	>90
PM_{10}/TSP sampling	±0.5 mg	NA	>90
TSP/PM_{10}/metal analysis	60-120	<30	>90
Semi-volatile sampling and analysis	60-120	<30	>90
Organic sampling and analysis	60-120	<30	>90
Meteorological Monitoring			
Wind speed	±0.2 m/s	NA	>90
Wind direction	±5°	NA	>90
Temperature	±0.5°C	NA	>90
Barometric Pressure	±0.5 in Hg	NA	>90
Relative humidity	±5%	±30	>90
Precipitation	±0.25 in H_2O	±30	>90

NA = not applicable.

As an additional tool for system audit, many USACE HTRW programs have specified the use of one or more mobile sampling station to be used as a data quality indicator. These stations are generally configured to be mobile units which can be collocated with any of the FFMS sample inlets or other perimeter or off-site monitoring stations for making simultaneous measurements. This approach allowed any problems with the stationary monitoring stations or FFMS sample and transport to be quickly detected. It also allows for additional precision calculations for the measurement system.

e. Preventive maintenance and corrective action. Many of the problems that occur during field sampling programs can be avoided with proper maintenance. Table 8-5 presents an example of a routine/preventive maintenance schedule for the equipment typically used during a HTRW FFMS program. Note that some maintenance procedures must be performed daily, whereas others are performed just twice a year. All preventive

Table 8-2
Example of QC Checks Associated with HTRW FFMS Program

QA/QC Sample Type	Suggested Minimum Frequency	Responsible Party	Application
FIELD			
Collocated samples for TSP/PM_{10} semi-volatiles and volatiles	10% of sampling events	Field crew	Used to determine variation due to sample collection and/or ambient conditions
Flow checks of samplers (single point)	All sampling events; must be within 10% of desired flow rate.	Field crew	Used to verify initial flow point calibration curve to laboratory standard curve
Sampler certification	Once per quarter	Field crew	Used to verify that sampler is not contaminated
Retention time (RT) check for real-time analytical system for 3-5 indicator organic compounds	Daily	GC operator	Used to verify that retention time differences for speciated organcis do not exceed 0.5 minutes from initial check
Single-point calibration check for real-time analytical system for 3-5 indicator organic compounds	Daily	GC operator	Used to verify calibration check for speciated organics do not exceed ±25% of initial calibration
Multi-point calibration check for real-time analytical system for 3-5 indicator organic compounds	Weekly	GC operator	Used to verify proper operation of GC system
RAM NMOC calibration at 1 ppm for real-time analytical - system	Daily	GC operator	Used to verify proper operation of GC RAM system, within ±10% of standard
Heated sample lines efficiency verification with 1 ppm NMOC and 100 ppb of 3-5 indicator organic compounds	Initially, quarterly	GC operator and field crew	Used to verify transfer efficiency of the heated sample lines extended out to 1,000 feet.
LABORATORY			
Field blank for canister, PUF/XAD-2 adsorbent and filters	Method dependent, typically not less than 5% of trip numbers	Field crew	Used to detect contamination during field operations and shipping
Trip blank for canister, PUF/XAD-2 adsorbent and filters	5% of trip numbers (0 if field blank used in lieu of trip blank)	Field crew	Used to detect contamination during shipping
Lot blank	1 per event per lot, 3-6 whenever new lot of adsorbent acquired	Laboratory	Used whenever manufacturers supply a lot of samplers or when a fresh lot of sampling media is cleaned
Reagent/method blank	1 per reagent blank per batch	Laboratory	Used for solvent desorbed sorbent media
Surrogate spike	Every sample when used (semi-volatile only)	Laboratory	Used to verify that bias results are not being reported high or low due to problems with a specific analysis.

Table 8-3
Example of HTRW FFMS Program Performance Audits

Instrument	Type of Performance Audit	Frequency	Criteria
Analytical system from NMOC/ speciated organics	• Flow audit of extractive system heat trace sample lines • Chemical audit of extractive system heat trace sample lines -- 1 ppm NMOC gas -- Indicator organic compounds • Leak check (positive/negative)	• Quarterly • Quarterly • Quarterly • Quarterly	±10% of set-point ±40% of accepted value ±40% of accepted value for individual analytes
Heat-trace lines	• Flow audit check • Leak check	• Quarterly • Quarterly	±10% of set-point
Time-integrated and collocated samples	• Flow audit check • Leak check	• Quarterly • Quarterly	±10% of set-point
Meteorological station	• Wind direction check • Wind speed check	• Quarterly • Quarterly	Wind direction: ±5° Wind speed: ±0.2 m/s
Data acquisition system	• Electronic Voltage Check	• Weekly	±10% of set-point

Table 8-4
Example of Criteria and Data Qualifier Limits for a FFMS Involving Real-Time, Perimeter Air Monitoring

Criteria	Limits
Quantitative Measurements	
• Replicate precision	±30%
• Audit accuracy	70-130% of accepted value
• Data completeness	80%
Qualitative Measurements	
• Representativeness	Documented
• Comparability	Documented

maintenance actions must be documented for later review by a QA auditor. A plan for initiating and implementing corrective action should be developed, specifying: (1) conditions that will require corrective actions; (2) personnel responsible for initiating, approving, implementing, and evaluating the resolution of corrective actions; and (3) specific corrective action procedures to be used when predetermined control limits are exceeded. Corrective actions are usually instrument-specific, and equipment manuals and EPA-approved standard operating procedures should be consulted for guidance. In general, it is appropriate to initiate corrective actions when the following conditions occur:

- When predetermined acceptance standards are not attained (e.g., objectives for precision, accuracy, and completeness).

- When sampling procedures or data compilation techniques are determined to be faulty.
- When faulty equipment or instrumentation are found.
- When samples and test results cannot be traced with certainty.
- When quality assurance requirements have been violated.
- When required approvals have not been obtained.
- When system and procedure audits indicate problems.
- When the results of management assessment indicates problems.
- When a laboratory/inter-laboratory comparison study result indicates problems.

All routine maintenance activities should be documented on a form such as the example provided as Figure 8-6. Such records must be traceable to the specific equipment item. These records will be subject to audit by USACE's designated project QA personnel. Preventative maintenance and corrective action activities should also
be documented in the instrument log book, site log books, and daily reports.

f. Special concerns. No matter how good a QA/QC program is, unexpected challenges will still occur. Several lessons learned from earlier fenceline monitoring projects include the following:

- Set-up and troubleshoot the complete system prior to field deployment
- Have all system plans and specifications available on-site and reviewed by an electrical engineer prior to the start of the monitoring program.
- Keep in mind that monitoring projects are not research projects; you do not have the luxury of trial and error.
- Make sure all systems can "talk" to each other.
- Know what has to be reported (including units) and develop appropriate reporting forms.
- Build contingency costs into cost estimates to address unexpected QA/QC problems.

USACE
HTRW FFMS
EQUIPMENT MAINTENANCE/REPAIR REPORT

Instrument/Equipment Item: _____ Date: _____

Description of Problem: _____

_____
_____
_____
_____
_____
_____
_____
_____

Action(s) Taken:

_____
_____
_____
_____
_____
_____
_____
_____

Date/Time Item Returned To Service: _____

Initials: _____

Figure 8-6. Example of maintenance/repair report form as part of a HTRW FFMS program.

Table 8-5
Example of Typical Routine/Preventative Maintenance Activities Associated with HTRW FFMS Program at a HTRW Site

Equipment/Instrument	Activity	Frequency
Inlet probes	Perform flow check	Monthly
	Replace filter cartridges	Monthly
Heat trace sample lines	Perform flow check	Weekly
	Determine line temperature	Weekly
	Inspect and clean electrical junction boxes	Annually
	Inspect and replace fuses	As needed
Sample intake manifold system	Disconnect individual lines and blow clean w/ compressed air	Monthly
	Lubricate valves	Monthly
Sample conditioning system	Inspect and clean sample dryer	Annually
	Remove, inspect, clean and test gas cylinder regulators	Annually
	Check performance of perma-pure dryer	Semi-annually
Analytical system for RAM NMOC	Remove, inspect, clean and replace lamp	Weekly
	Measure voltages at detector	Weekly
Analytical system for speciated organics	Remove, inspect, clean and replace lamp	Weekly
	Measure voltages at detector	Weekly
Data acquisition system	Remove housing, blow circuit boards clean w/ compressed air	Annually
	Inspect power cord	
	Inspect external port connections and linkages	Annually
	Replace fuses	Annually
		Annually
Printers	Remove and inspect ink cartridge	Weekly
External alarm & pager system	Replace fuses	Annually
Telephone/fax/modem system	Inspect com port connections	Annually
	Inspect cords	Annually

With regard to specific equipment, prior projects indicate that the following concerns are common to many HTRW real-time, on-line FFMS projects:

Heat-Trace Lines

- Provide a “reliable” source of power (power interruptions are common).
- Carefully evaluate the temperature control system prior to field deployment, to verify that it can maintain a constant temperature.
- Provide access to all line components so that the temperature of segments can be monitored.
- Provide security for lines and voltage points.
- Test the probe filter with target compounds prior to installation.

- Verify the cleanliness of the sample transfer lines prior to installation.

Meteorological Station

- Use a software package that is consistent with the reporting requirements.
- Determine the method for calculating stability classification prior to field deployment of the meteorological equipment.
- Know all of the required reporting units (i.e., Langleys, mbars, etc.).

Real-time Analytical System in Analytical Center

- Set up the screen display so that the elapsed chromatography time is shown; this way, the user knows where he is in the cycle for individual analyte determination.
- Ensure that all systems in the Analytical Center (i.e., DAS, meteorological, analytical) can "talk" to each other prior to field deployment.
- Keep in mind that compliance, not science, is required; do not turn the project into a research project.
- Become very familiar with the software package prior to running the system.

Data Acquisition System

- Keep in mind that repairs usually include changing the electronic chips; extra chips should be kept on-hand.
- Perform test calculations prior to field deployment.
- Incorporate proper "averaging" times consistent with contract specifications.
- Understand the "short falls" of the system and be prepared to work around them.

8-5. Generation of Standard Test Atmospheres

a. Introduction. As new and improved real-time, on-line analytical systems for monitoring VOCs at HTRW sites have developed, it was imperative that these systems could be field calibrated and audited so the data generated would achieve project required objectives. As a result, more emphasis has been placed on the development of technology for the field generation of test calibration gases for field calibration and audit purposes. This calibration and audit technology can be used to ensure that data generated is an accurate representation of the pollutant concentration being monitored.

Due to deterioration (electrical or mechanical), environmental effects and site activities, measurement monitors and apparatus designed to operate within a specific range of conditions are subject to unforeseen changes which may affect the data generated by the monitors. To continually evaluate the performance of a real-time system, known concentrations of the target analytes should be used to challenge the system. The response of the monitors to the known concentration is used for system evaluation and the calculation of the precision of the system, as discussed in Paragraph 8-3.

The technologies available for generating known concentrations of target analytes for precision calculations can be divided into two broad categories:

- Dynamic calibration systems.
  - gas cylinder dilution system (e.g., concentrated cylinder gas followed by a series of dilutions)
  - permeation systems
  - flash vaporization
  - water purge

- Static systems.
  - static dilution
  - high pressure gas cylinders

In considering these two categories for generating known concentrations of test atmospheres, the part per billion [ppb] to parts per million [ppm] concentration ranges for the target analytes are the highest priority. Attempts to prepare static standards in fixed volume containers and in flexible bags may be impossible. Such features as adsorption, absorption, stability, and other concerns must be considered. Dynamic calibrations overcome many of the inherent problems of static systems; but dynamic calibrations are not without their drawbacks. Traceability, stability, availability of standards, etc. are just some of the limitations associated with dynamic calibrations. The purpose of this section is to discuss the methods available for generating known standards of target analytes using both static and dynamic systems so that calibrations and precision calculations can be performed.

b. Generating standard test atmosphere using static dilution system.

(1) Cylinder gas concentration. The gas cylinder is probably the best example of a static calibration system. The cylinder can be made of different materials and produced in different sizes. The use of gas cylinders to generate a test atmosphere has been well established in FFMS programs. Highly accurate gas standards for such pollutants as SO_2, NO_x, CO_2, CO, NMOC, and speciated organics have been used routinely for calibration of FFMSs. Manufacturers supply gas mixtures with a certification of analysis and a statement of accuracy. Accuracy levels are generally quoted between 2 to 5 percent of the component values.

Gas cylinders come in different sizes, materials of construction, and weights. The contents of gas cylinders can be limited by the material of construction. Multiple gases are frequently incorporated into one cylinder. Inclusion of multiple analytes in one cylinder is greatly dependent upon their reactivity, compressibility, and stability.

Cylinders intended to contain specified pollutant gases mixtures are produced by adding a known volume of gas to the cylinder, then pressurizing the cylinder with a diluent gas to a total gas cylinder pressure. The concentration of the target analyte in the gas cylinder can be calculated by the following equation:

$$C_{ppm} = \frac{10^6 \text{ x } V_c}{V_a + V_c} = \frac{10^6 \ P_c}{P_t}$$

$$C_{\%} = \frac{10^2 \text{ x } V_c}{V_a + V_c} = \frac{10^2 \ P_c}{P_t}$$

where:

C_{ppm} = final concentration of analyte in gas cylinder, ppm.
$C_{\%}$ = final concentration of analyte in gas cylinder, %.
V_c = volume of analyte gas in the cylinder, L.
V_a = volume of diluent gas added to the cylinder, L.
P_c = pressure of analyte gas in the cylinder, mmHg.
P_t = final pressure of gas mixture in the cylinder, mmHg.

This technique of producing gas concentrations is fairly accurate for concentrations from 10 ppb to more than 6,000 ppm, depending on the stability of the gas mixtures.

Another technique of preparing cylinder standards is “by-weight.” During this process, the cylinders are evacuated, then filled to a weight and allowed to reach equilibrium with the target analyte. The cylinder is then filled to a final weight with diluent gas. All weighing is performed on a high precision balance. The final concentration is determined by the weight percent of target analyte in the gas mixture.

(2) Cylinder gas problems. Gas manufacturers have documented numerous problems associated with maintaining accuracy of prepared certified gas standards. The problems which have been documented and investigated and can be categorized as:

- Cylinder material related.

- Gas stability related.

c. Cylinder material. The material of construction plays an important part in the long-term stability of target analytes (i.e., VOCs, NMOC) in gas cylinders. When reactive gases such as oxides of nitrogen, carbon monoxide, or sulfur dioxide and volatile organics are blended in a steel cylinder with an inert balance gas, the concentration can vary with time, temperature, and pressure. The mixture’s instability is random and dependent on the condition of the individual cylinders. It has been documented that the instability is a function

of gas absorption or reaction with the cylinder walls. Gas cylinders were initially constructed of mild steel and consequently lacked long term stability. To alleviate this problem, many manufacturers have provided gases in materials of construction other than mild steel, including stainless steel, aluminum, and treated cylinders.

The following factors affect the stability of standards in pressurized cylinders:

- Contamination.
- Reaction.
- Absorption.
- Adsorption.

Another method of decreasing the reactivity between the target analyte and cylinder material is to "soak" the cylinder with a high concentration of the gas of interest.

The theory behind this "soaking process" is that, with time, all of the gas that is going to react with or be absorbed into the cylinder walls will do so during the conditioning period. When the cylinder is put into its final mixing stage, any further reaction or absorption is supposedly precluded.

This method of preconditioning has met with only limited success for volatile organics. When the pressure or temperature of the cylinder changes, the gas that was absorbed during the soaking process can desorb; therefore, the concentration that the cylinder delivers can actually increase.

d. Cylinder gas stability. Gas stability is one of the most serious problems associated with certified standards. Gas stability is defined as the ability of a gas mixture to maintain its original concentration with time, temperature and cylinder pressure. Many volatile organics, such as alcohols, esters, ethers, alkenes, etc., are unstable at very low concentrations (<50 ppb) in gas cylinders. The instability is due to:

- Reaction with moisture.
- Reaction with other trace gas impurities.
- Reactions with cylinder walls.

The stability of several criteria pollutants (SO_2, CO, NO, CO_2, NMOC, etc.) has been well documented.

The stability of VOCs in compressed gas cylinders is dependent on the particular hydrocarbon for which a standard is needed. In general, the more reactive hydrocarbons are less stable.

- Relatively less stable: Aromatics and oxygenated or halogenated hydrocarbons.
- Relatively more stable: Propane, butane, hexane, and methane.

Volatile organics that are stable in gas cylinders for 6 months at the 50 ppb level are listed in Table 8-6.

Table 8-6
Volatile Organics that are Stable for 6 Months in Gas Cylinders at the 50 ppb Level

• vinyl chloride	• 1,1,2,2-tetrachloroethane
• vinylidene chloride	• 1,3,5-trimethylbenzene
• chloroform	• 1,2,4-trimethylbenzene
• 1,2-dichloroethane	• m-dichlorobenzene
• benzene	• o-dichlorobenzene
• toluene	• p-dichlorobenzene
• Freon 12	• 1,2,4-trichlorobenzene
• methyl chloride	• methyl bromide
• 1,2-dichloro-1,1,2,2-tetrafluoroethane	• ethyl chloride
• hexachloro-1,3-butadiene	• Freon 11
• methyl chloroform	• dichloromethane
• carbon tetrachloride	• 1,1-dichloroethane
• cis-1,3-dichloropropene	• cis-1,2-dichloropropene
• trans-1,3-dichloropropene	• 1,2-dichloropropane
• ethyl benzene	• 1,1,2-trichloroethane
• o-xylene	• 1,2-dibromoethane
• m-xylene	• tetrachloroethylene
• p-xylene	• chlorobenzene
• styrene	• benzyl chloride

e. Cylinder gas certification techniques. Presently, several types of gas standards are available from the NIST and commercial manufacturers. They are:

- NIST--Standard Reference Materials (SRMs).
- Gas Manufacturers Primary Standard (GMPS).
- Gas Manufacturers Certified Reference Materials (CRMs).
- Unanalyzed gases.

The NIST-SRMs are sold by the NIST as primary standards. These standards are prepared gravimetrically on a high load, high sensitive balance, with a tolerance of ±1 percent of the component. GMPSs are traceable to NIST-SRMs and are used to calibrate instruments used in certifying Gas Manufacturer's Certified Standards (GMCSs). The GMCS are prepared by a variety of gravimetric and pressure-volume temperature techniques and analyzed by instrumentation that has been calibrated by NIST-SRMs or GMPSs. These standards normally have a certification tolerance of ±3 percent. The unanalyzed standards are normally prepared in

Table 8-7. Gas Standards Tolerances

Gas standard	Tolerance percent (%) of the component
NIST--SRMs	±1
GMPS	±1
CRM	±3
Unanalyzed	±15
GMCSs	±1 of SRM

the same manner as the GMCSs, but are not analyzed. Their certification tolerances are normally ±15 percent. For some HTRW projects, site-specific reference materials or custom ordered mixtures may be necessary. Table 8-7 summarizes the gas standards available and their associated tolerances.

(1) NIST SRMs. Standard Reference Materials have been characterized by the NIST for some chemical and physical properties and are issued with a Certificate that gives the results of the characterization. These results are obtained by one of the three methods of certification, including using (1) a previously validated reference method; (2) two or more independent, reliable measurement methods; or (3) a network of cooperating laboratories, technically competent and thoroughly knowledgeable with the material being tested.

The SRMs are defined as being well-characterized and certified materials. They are prepared and used for three main purposes: (1) to help develop accurate methods of analysis (reference methods); (2) to calibrate measurement systems used to facilitate the exchange of goods, institute quality control, determine performance characteristics, or measure some property at the limit of the state-of-the-art; and (3) to assure the long-term adequacy and integrity of quality control processes. In these ways, SRMs help ensure the compatibility and accuracy of environmental measurements.

NIST has offered SRM materials, such as "Ambient Toxic Organics in Nitrogen," SRM No. 1804. For a real-time, on-line volatile organic FFMS, the SRM would be used as an independent audit of the system on a semi-annual or annual basis. The limited use of the SRM is due to its high expense and limited availability.

(2) Certified Reference Materials. The SRMs and CRMs are gaseous standards developed by the NIST in cooperation with the EPA. The main objective of this program was to help supply gaseous standards to industry without depleting the SRM stock. The NIST could neither increase production nor allow "out-of-stock" situations to develop with their SRM inventory. Consequently, a method was developed that enabled the specialty gas industry to produce accurate gas standards while maintaining traceability to NIST-SRMs. The new CRMs duplicates SRMs in stock according to stability, homogeneity, and concentration.

Manufacturers generally certify CRMs by analyzing their concentrations with an analyzer that has been calibrated with SRMs. The idea is to calibrate the analyzer with two or three SRMs, then analyze a "batch" of CRMs with the calibrated analyzer. This process provides traceability to NIST-SRMs and increases the number of reference gases available for commercial usage.

f. Generating standard test atmospheres using gas cylinder dilution system

(1) Introduction. One of the simplest and most economical systems for providing a known concentration of target volatile organic analyte to a FFMS or analytical system is the single gas dilution system. A simple dilution system involves mixing a gas of known concentration of target analyte with a contaminant-free diluent gas to provide a known concentration of gas of lesser value than the original. By measuring the volumetric flowrates of each gas stream (see Figure 8-7) and knowing the concentration of the original gas to be diluted, one can calculate the final concentration with the following equation:

$$C_u Q_u = C_d (Q_u + Q_d)$$

where:

C_u = concentration of undiluted pollutant gas provided by manufacturer (usually a CRM), ppm.
Q_u = volumetric flow rate of undiluted pollutant gas, mL/min.
C_d = final concentration of diluted gas, ppm.
Q_d = final volumetric flow rate of the diluent gas, mL/min.

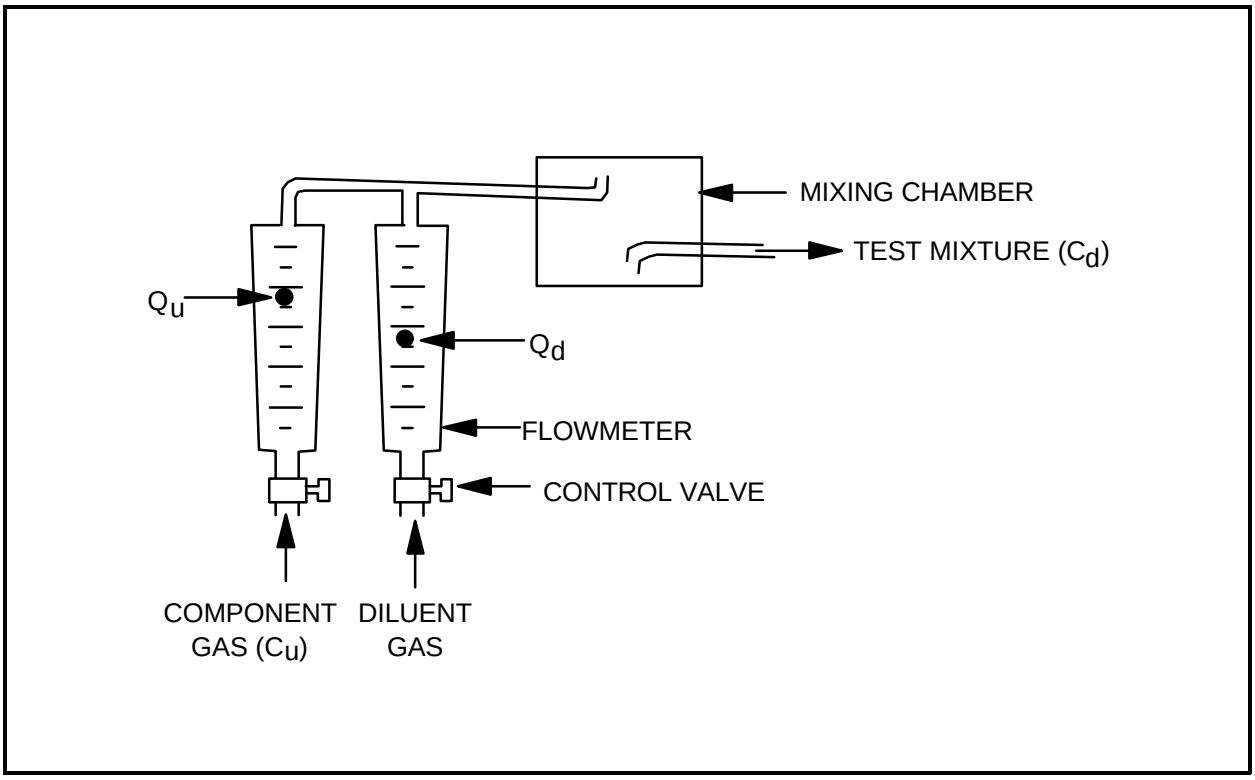

Figure 8-7. Example of gas dilution system using a single gas cylinder diluted with zero air as part of a HTRW FFMS program.

From the above equation, the following variables must be accurately measured to determine the final concentration: C_u, Q_u, and Q_d. Knowing these three values and rearranging the above equation, the final concentration of the diluted pollutant gas can be calculated with the following equation:

$$C_d = \frac{C_u Q_u}{Q_u + Q_d}$$

This procedure is the most common technique to produce low concentration standards of gaseous volatile organics from a higher gas concentration.

(2) Flow Measuring Devices

Three common methods for measuring flows in a gas dilution system are:

- Rotameters.
- Critical orifices.
- Mass flow controllers.

(a) *Rotameter*. One of the simplest means of measuring volumetric flows involves the use of rotameters. If calibrated, rotameters provide a direct correlation of volumetric flow.

The rotameter consists of a vertically graduated glass tube and a float located in the tapered vertical tube.

In operation, the fluid to be measured passes through the tapered tube, carrying the float to a position in the tub where its weight is balanced by the upward forces to the fluid flowing past it. At this point, a constant pressure differential across the float is reached, which is unique for each rotameter. The forces acting in the upward direction (buoyant and drag force) equal the force acting in the downward direction (gravity).

Most rotameters calibrate at room temperature with the downstream side open to the atmosphere. Correction for temperature and pressure variations from original calibration configuration are made by the following equation:

$$Q_u = Q_s \left[\frac{P_1 \times T_2}{P_2 \times T_1}\right]^{1/2}$$

where:

Q_u = volumetric flow rate of sampling configuration, corrected to present temperature and pressure, L/min.
Q_s = volumetric flow rate of calibration configuration, L/min.
P_1 = pressure at original calibration configuration, in Hg.

P_2 = pressure at sampling configuration, in Hg.
T_1 = temperature at calibration configuration, °R or °K.
T_2 = temperature at sampling configuration, °R or °K.

Because corrections of this nature are usually cumbersome and inaccurate, rotameters are usually calibrated under sampling configuration.

(b) *Critical orifices*. Critical orifices have progressively replaced rotameters in monitoring volumetric flow. If operated properly, the critical orifice ensures exact delivery of a gas stream with ±2 percent.

The orifice meter consists of some form of restriction located in a tube constructed of glass, metal, or other material. Two pressure taps, one upstream and one downstream of the orifice, serve as a means of measuring the pressure drop. As a fluid traverses the orifice, a pressure drop develops that can be correlated to flow rate.

As the pressure drop across the orifice increases, flow rates increase. The region of the calibration curve whose flow rate changes with pressure drop is termed noncritical flow and is associated with a variable orifice meter. Within this region of the calibration curve, the pressure drop across the orifice should be set to a desired number to generate a known flow.

If the pressure drop across the orifice is increased until the downstream pressure is equal to approximately 0.53 times the upstream pressure, the velocity of the gas stream becomes sonic. Even if the pressure is increased, no increase in flow will occur. The orifice meter has therefore become "critical." Under these conditions, a constant flow will occur as long as the 0.53 pressure relationship exists.

(c) *Mass flow controller*. This device operates on the principle that as a gas passes over a heated surface, heat is transferred from the surface to the gas. The amount of current required to keep the surface at a constant temperature is a measure of the velocity of the gas.

8-6. Reference Methods Requirements for Calculating System Accuracy

As part of a FFMS program, system accuracy of both real-time and time-integrated monitoring systems must be maintained within prescribed limits as defined in the program QAPP. As illustrated in Paragraph 8-2, system accuracy of a real-time, on-line, volatile organic analytical or a TSP/PM_{10} system is determined by comparing a RMM (i.e., Compendium method) with the on-site real-time VOC sampling system in the Analytical Center, as defined by the following equation:

$$\%A = 100 \times \left| \frac{X_u}{X_s} \right|$$

where:
%A = calculated accuracy, %.
X_u = measured value as a determined by the on-line, real-time analytical system, ppm.

X_s = measured value as determined by the RMM (i.e., Compendium method), ppm.

For TSP/PM_{10} time-integrated monitoring systems, system accuracy is determined by collocating a duplicate sampling system next to the on-site monitor and extracting a representative sample from the same general air parcel at the HTRW site. As specified in Chapter 4, the siting of the second sampler must meet the same monitoring siting requirements as the on-site sample, which are:

- 2-10 meters vertical spacing above ground.
- Unrestricted air flow around the reference method inlet.
- Greater than 2 meters away from the on-site sampler.
- Away from obstructions (i.e., trees, buildings, etc.) by a distance of 10 times the height of the obstacle.

Relative accuracy for real-time, on-line FFMS monitors at HTRW sites, can be determined either by collecting a second split sample at the analytical center, (using such methods as TO-1, TO-2, TO-3, TO-14, TO-15 or TO-17), at the FFMS sample inlet at a perimeter location or by taking a collocated sample adjacent to a sample inlet. The significant difference between the two approaches is that by taking a split sample the sample is assumed to be homogeneous for volatiles whereas collocated samples collected adjacent to a FFMS sample inlet provides a sample which may be a different atmosphere due to the required 2 meter separation from other samplers. The user must review the project DQOs and determine which method is best for the program. Since samples cannot be successfully "split" for particulate matter or a particulate related component such that homogeniety is maintained, collocated samplers are the acceptable compromise.

For real-time volatile organic perimeter air monitoring system, the two compendium methods used as "reference" methods in calculating percent accuracy for a FFMS are generally Compendium Methods TO-14 and TO-15, as previously discussed in Chapter 4 and are briefly reviewed here:

a. Compendium Method TO-14. Compendium Method TO-14 is applicable to specific VOCs at the sub-ppb level that have been tested and determined to be stable when stored in pressurized and subatmospheric pressure canisters. Numerous compounds, many which are chlorinated VOCs, have been successfully tested for storage stability in pressurized canisters. However, minimum documentation is currently available to demonstrate the stability of VOCs in subatmospheric pressure canisters.

Both subatmospheric pressure and pressurized sampling modes are initially used with an evacuated canister and a pump-ventilated sample line during sample collection. Pressurized sampling requires an additional pump to provide positive pressure to the sample canister. A sample of ambient air is drawn through a sampling train comprised of components that regulate the rate and duration of sampling into a pre-evacuated sampling canister.

After the air sample is collected, the canister valve is closed, an identification tag is attached to the canister, and the canister is transported to a predetermined laboratory for analysis. Upon receipt at the laboratory, the canister tag data is recorded and the canister is attached to the analytical system. During analysis, water vapor

is reduced in the gas stream by a Nafion® dryer (if applicable), and the VOCs are concentrated by collection in a cryogenically-cooled trap. The cryogen is then removed and the temperature of the trap is raised. The VOCs originally collected in the trap are revolatilized, separated on a GC column, then detected by one or more detectors for identification and quantification. The analytical strategy for Method TO-14 uses a high-resolution GC coupled to one or more appropriate GC detectors. The recorded values for the speciated organics are then compared to the on-site real-time FFMS to calculate an accuracy value.

b. Compendium Method TO-15. Compendium Method TO-15 is distinguished from Compendium Method TO-14 in that: (1) it addresses a large set of compounds (including polar organics); (2) it uses GC/MS technique as the only means of identifying and quantifying target compounds; and (3) it allows the use of alternative but equivalent methods through performance criteria standards.

In collocating reference methods with inlet probes for real-time monitoring systems, the same siting criteria must be met as locating a single system, as discussed in Paragraph 5-7, and listed earlier in this Paragraph for TSP/PM_{10}. They are:

Figure 8-8. Example of collocated time-integrated RMM (TSP and VOC) with perimeter real-time, on-line monitors at a HTRW site

- 2-10 meters vertical spacing above the ground.
- With unrestricted air flow around the reference method inlet.
- No closer than 2 meters to other sampling systems.
- Away from obstructions such as trees, building, etc., by a distance of 10 times the height of the obstruction.

Figures 8-8 and 8-9 document properly collocated sampling equipment at HTRW sites for calculating DQOs associated with accuracy indicators utilizing time-integrated RMM for TSP and volatile organics.

8-7. Corrective Action Requirements

Corrective action procedures should be developed as part of the Project SAP, FSP, QAPP, and SOPs. In the case of instrumentation and equipment, manufacturer's recommendations should be the starting point for all equipment diagnostics, maintenance, and repairs. Corrective action activities recommended as a result of system or performance audits will be recorded in the relevant audit report. In addition, all corrective action activities should also be documented as shown in the example provided in Figure 8-10. These recoeds must also be traceable to the specific equipment or procedural item. Corrective action activities should also be documented in the instrument log book, site log books, and daily reports.

In the event the real-time, on-line FFMS performance conditions are identified as adversely affecting data quality to any significant degree, the cause(s) should be determined and corrective actions taken to prevent reoccurrence. These actions may involve maintenance, repairs, or modifications to instrumentation or equipment and/or modification of operating procedures. Corrective actions may be initiated:

- When predetermined acceptance standards (objectives for precision, accuracy, and completeness) are not attained.
- When data compiled are determined to be faulty.
- When QA requirements have been violated.
- When routine, preventive maintenance activities are required.
- When system and performance audit reports are not acceptable.
- When a management assessment indicates the necessity.
- When required by the result of precision or accuracy comparison studies.
- When samples and test results cannot be traced with certainty.
- When designated approvals have been circumvented.
- When other operating procedures are determined to be faulty.

Figure 8-9. Utilization of RMM, Compendium Method TO-14, in calculating percent accuracy as a collocated unit at the perimeter of a HTRW site.

USACE HTRW FFMS
CORRECTIVE ACTION REPORT

Project I.D. _____ Date: _____

Measurement Parameter: ___ _____ Time: _____

Description of Problem: _____
_____
_____
_____
_____
_____

Recommended Corrective Action: _____
_____
_____
_____
_____
_____
_____

Action(s) Taken: _____
_____
_____
_____
_____
_____

Date/Time Action Implemented:
_____

Initials: _____

Figure 8-10. Example of corrective action report form as part of a FFMS at a HTRW site.