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## Chapter 2: Characterizing Facility Emissions

### What's Covered in Chapter 2:

- 2.1 Compiling Basic Facility Information
  - 2.2 Identifying Emission Sources & Estimating Emission Rates
  - 2.3 Identifying Compounds of Potential Concern (COPCs)
  - 2.4 Estimating COPC Concentrations for Non-Detects
  - 2.5 Evaluating Contamination In Blanks
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This chapter provides guidance on characterizing the nature and magnitude of facility emissions. Characterizing includes (1) compiling basic facility information, (2) identifying emission sources, (3) estimating emission rates, (4) identifying COPCs, (5) estimating COPC concentrations for non-detects, and (6) evaluating contamination in blanks. You can consider the information listed in the highlighted box at the end of each section the minimum that we recommend to ensure a risk assessment is scientifically sound. However, you may want to consult up front the more detailed discussions found in each section. A more complete understanding of the relevant issues will make sure that all appropriate information is collected simultaneously. This will help minimize the time and effort expended collecting site-specific information.

***PLEASE NOTE:*** for the purposes of this guidance, “we” refers to the U.S. EPA OSW.

The HHRAP is written for the benefit of a varied audience, including risk assessors, regulators, risk managers, and community relations personnel. However, the “you” to which we speak is the performer of a risk assessment: the person (or persons) who will actually put the recommended methods into practice.

### 2.1 COMPILING BASIC FACILITY INFORMATION

If you are a risk assessor, there is basic facility information you should consider while conducting the risk assessment, and include in the risk assessment report. Including this basic facility information in the report will enable reviewers to establish a contextual sense of how the facility relates to other facilities

and other hazardous waste combustors. It's also very important to thoroughly understand (and document) any regulatory limits evaluated in the risk assessment, because the risk assessment report informs the setting of risk-based permit limits. For example, specific emissions data might not be collected for a particular unit where waste feeds are controlled in lieu of demonstrating compliance with an emissions limit under the regulations (e.g., Tier I under the BIF rule for certain metals, MTEC under the HWC MACT rule). For transparency, we therefore recommend clearly identifying the basis for the assumptions and/or data to be used in the risk assessment, along with the rationale for how the information will be used.

### **RECOMMENDED INFORMATION FOR THE RISK ASSESSMENT REPORT**

- C Description of physical setting
- C Principal business and primary production processes
- C Normal and maximum production rates
- C Types of waste storage and treatment facilities
- C Type and quantity of wastes stored and treated
- C Process flow diagrams showing both mass and energy inputs and outputs
- < Relevant information from an existing or proposed permit and/or compliance documents (e.g., Waste Analysis Plan or Feedstream Analysis Plan; Startup, Shutdown, and Malfunction Plan; Certifications of Compliance; etc.)

## **2.2 IDENTIFYING EMISSION SOURCES & ESTIMATING EMISSION RATES**

Burning hazardous waste typically emits combustion by-products from a stack. In addition to emissions from a combustion stack, types of emissions associated with the combustion of hazardous waste may include (1) process upsets emissions, (2) accidental releases, (3) general RCRA fugitive emissions, and if the facility is a cement kiln (4) cement kiln dust (CKD) fugitive emissions. Each of these emission source types is defined below with regards to the context and scope of this guidance.

***Stack Emissions*** - Release of compounds or pollutants from a hazardous waste combustor into the ambient air while the unit is operated as intended and in compliance with a permit and/or regulation (for interim status).

***Process Upset Emissions*** - Release of compounds or pollutants from a hazardous waste combustor into the ambient air while the unit is not being operated as intended, or during periods of startup or shutdown. Upset emissions usually occur during events and times when the unit is not operating within the limits specified in a permit or regulation. Conditions within the combustion system during the process upset result in incomplete destruction of the wastes, or otherwise promote the formation and/or release of hazardous compounds from combustion stacks. Upset emissions are generally expected to be greater than stack emissions.

***Accidental Releases*** - an accidental release is defined in Section 112(r) of the Clean Air Act as an unanticipated emission of a regulated substance or other extremely hazardous substance into the ambient air from a stationary source. Accidental releases are typically associated with non-routine emissions from RCRA facilities, such as the failure of tanks or other material storage and handling equipment, complete failure of combustion and air pollution control systems (e.g. resulting from explosions, and fires), or transportation accidents.

***RCRA Fugitive Emissions*** - Release of compounds or pollutants into the ambient air from RCRA-regulated sources other than hazardous waste combustion stacks. RCRA fugitive emissions are typically associated with the release of pollutants from leaks in the combustion chamber (e.g., “puffs”); tanks, valves, flanges, and other material-handling equipment used in the storage and handling of RCRA hazardous wastes; residues from the combustion process such as ash or quench water; and other RCRA treatment, storage, or disposal units (e.g., landfills).

***CKD Fugitive Emissions*** - Release of pollutants into the ambient air caused by the handling, storage, and disposal of cement kiln dust.

We generally recommend that as applicable, all of these emission source types except accidental releases be addressed in the risk assessment. Accidental releases aren't within the scope of this guidance. We generally recommend evaluating accidental releases per Section 112(r) of the CAA and current Agency guidance (U.S. EPA 1996f) or the *RMP Offsite Consequence Analysis Guidance*, dated May 24, 1996. Despite this general guidance, it is for the permitting authority to decide on a site-specific basis whether the risk assessment will consider accidental releases.

The following subsections contain guidance for estimating emissions of the source types to be included in the risk assessment. Guidance on air dispersion modeling of stack and fugitive emissions is presented in Chapter 3.

### **2.2.1 Estimating Stack Emission Rates for Existing Facilities**

We generally consider it important to determine stack emission rates (in grams per second) of every COPC identified using the procedures outlined in Section 2.3. We anticipate that emission rates for existing facilities (i.e. already built and operational) will be based on direct stack measurements from regulatory performance tests, because permitting authorities generally require performance tests before

granting a permit to burn hazardous wastes, or in order to demonstrate compliance with emission standards.

As mentioned in the Special Note "How This Document Relates to Trial Burns" and elsewhere, we suggest incorporating data collection for a risk assessment into the regulatory performance testing program whenever possible. This will optimize the use of both facility and permitting agency resources,

and minimize expenditures associated with stack testing and subsequent data review, evaluation, and permitting. Incorporating risk assessment data collection into the performance test program can ensure that proper evaluation across test conditions is achieved for optimal data usability and versatility— both engineering considerations relating to unit operations flexibility, and streamlined data collection considerations for characterizing potential emissions.

#### **Test Design: Performance vs. Health Criteria**

Performance testing involves demonstrating compliance with emission standards or performance criteria under any operational circumstance. Facilities typically wish to maximize the flexibility of operating conditions allowed by their permit. This leads to performance tests designed to demonstrate compliance even while operating under extreme conditions (i.e., conditions that may only seldom occur or may only occur for brief durations over the course of a year).

Regulatory performance requirements are generally **national-scale**, technology-based **instantaneous** limits. Such performance requirements might not consider various **health impacts** to receptors located near **a particular facility**. Therefore, data needs to assess potential health risks are typically more comprehensive than those of a performance test. For example, a performance test will provide information to calculate destruction and removal efficiency (DRE) for a principal organic hazardous constituent (POHC) and perhaps measure total particulate matter, but will not typically quantify the various products of incomplete combustion (PICs) in the stack gases, nor establish particle size distribution for gases exiting the stack.

Situations have occurred in which some facilities assume that the only way to maximize permit flexibility and satisfy risk assessment data needs is to conduct separate tests. We encourage another interpretation. As mentioned elsewhere, we suggest modifying performance-based test protocols to include risk assessment data requirements as appropriate to evaluate both acute and chronic exposures posed by facility-specific operations that may occur under the terms of the permit.

Experience has shown us that in order to evaluate both acute and chronic reasonable maximum exposure estimates, the potential emissions evaluated in the risk assessment need to be based on actual operating scenarios that may occur under the terms of the permit. We acknowledge that proper design of a regulatory test program that includes risk assessment data collection is challenging for facilities that burn highly variable waste and/or have multiple operating conditions. At the same time, inadvertently omitting potential risk drivers from the risk assessment due to improper or oversimplified test design is to be avoided.

Therefore, if feed streams differ between the various test conditions in the regulatory test program, we generally recommend providing appropriate rationale for this difference in the test plan, and discussing in the risk assessment report any impacts the differences may have had upon the risk analysis.

In some cases, a facility may elect to focus data collection efforts for a risk assessment into one test condition in the regulatory testing program that demonstrates "normal operations" using feedstreams considered "worst-case" from an operational and potential emissions standpoint.

*Please Note:* We suggest such a test condition only for facilities that can identify and substantiate via historical operating records the typical (or day-to-day) operating mode for the hazardous waste combustion unit and ancillary equipment, regardless of the type of waste fed.

If combining multiple and variable feedstreams into a single "worst-case" feed, the mixture needs to represent those actual waste matrices and constituents that are the most difficult to burn (ensuring that the combustion unit is fairly challenged). A "worst-case" feed also needs to contain the most toxic substances managed in the unit, on a mass basis proportional to that fed at any time (ensuring that all potentially toxic emissions are quantified). Multiple and/or highly variable feedstreams that require different extremes of a wide operating envelope, or feedstreams that are combined on a disproportional mass basis to that fed at any time, may not be representative of actual operations. We're concerned that they might even result in emission estimates that are not sufficiently conservative for the risk assessment. Please see the Risk Burn Guidance for Hazardous Waste Combustion Facilities (U.S. EPA 2001c) for further information on designing a testing program that integrates risk assessment data collection into the regulatory testing of hazardous waste combustors.

**Test Conditions' Relation to Permit Conditions**

The feed and operating conditions demonstrated during the testing will define an operating envelope that not only establishes the working assumptions for the risk assessment, but also the final permit terms. If a facility collects emissions data for the risk assessment under "normal" operating conditions, additional permit limitations may be appropriate to ensure that conditions represented as normal during the test are, in fact, normal over the long-term operation of the facility.

We generally recommend including the risk assessor in the early planning efforts of the test program development, so that the test program can be more effectively streamlined while meeting multiple and complex data collection goals. At least three valid runs at steady state are needed to characterize a test condition. Since steady state conditions are typically outlined in the test plan for each test condition and verified by field observations during the test program, resulting emission rates for any particular COPC are likely to be fairly consistent between runs for each test condition. Test reports document any abnormalities in steady state operations for a particular run or test condition. If any one run experiences significant issues that may impact the data quality or comparability with the other runs, the facility and permitting authority might decide during the test to discontinue the problem run and initiate a new run to

ensure a valid test condition. Test reports also document this occurrence and identify those valid runs of the test condition.

For risk assessments, we generally recommend using the maximum of the three emission rates identified for each COPC during a particular test condition, adjusted for process upsets. This approach is consistent with implementing a steady state test designed for collecting risk data where the combustor burns representative, yet worst-case or challenging feeds, at operating conditions that are allowable and/or typical under the permit. This approach will also allow consistency in refinements to the final risk analysis that may involve several risk evaluations for different operating scenarios (i.e., across the various test conditions) in order to afford operational flexibility while maintaining permit provisions that ensure protection of human health.

*Please Note:* The recommendation to use the highest of the three emission rates is an update to Section 8.1.2 of U.S. EPA (2001c).

An alternative to a regulatory performance test is the use of data "in lieu of" testing. Permitting authorities generally consider this type of data on a case-by-case basis. Prior to accepting such data as a surrogate for use in the risk assessment, we recommend evaluating the data from both an engineering perspective and a data usability perspective. To evaluate the similarities between combustors, consider the design and construction of the combustor and associated air pollution control devices, along with the basic operating conditions of the process equipment as tested (e.g., capacity, flow rates, supplemental fuels used, etc.) to ensure comparable emissions. Stack test measurements from a similar combustor are useful if the combustor burns similar waste feed(s) in terms of constituents, type of waste matrix, and amount of waste fed on a mass basis. In addition, we recommend evaluating the methods used to quantify COPCs and associated detection limits achieved during the test, as well as verifying that the data quality documentation is acceptable for risk assessment purposes.

**SPECIAL NOTE: HOW THIS DOCUMENT RELATES TO TRIAL BURNS**

We believe that generating defensible emission rates for compounds of potential concern (COPCs) is one of the most important parts of the risk assessment process. This requires special consideration when planning a risk assessment. Therefore, we consider emissions testing, risk assessment planning, and implementation as interdependent aspects of the hazardous waste combustion site-specific risk assessment process.

As described elsewhere in this chapter, **traditional regulatory performance tests (e.g., RCRA trial burns designed solely to measure DRE) *do not* sufficiently characterize COPC emissions for performing site-specific risk assessments.** We therefore generally recommend that collecting emissions data for a site-specific risk assessment include a thorough understanding of the operating limits to be established in the regulatory permit and the possible emissions that may result under the permitted operations of the unit. Regardless of whether the emissions data for the risk assessment is collected in a separate test condition or in multiple test conditions that are part of a regulatory performance test program, we recommend that to the extent possible, the planning, regulatory agency review, and collecting of emissions data be conducted simultaneously, to ensure consistency in data evaluation across test conditions is achieved and actual operations allowable under the permit are appropriately evaluated. This approach also eliminates redundancy or the need to repeat activities and minimizes cost expenditures overall.

The guidance documents below relate to the RCRA hazardous waste combustion program. You may find the listed documents useful for developing and conducting trial burns:

U.S. EPA. 1989f. *Handbook: Guidance on Setting Permit Conditions and Reporting Trial Burn Results. Volume II of the Hazardous Waste Incineration Guidance Series.* Office of Research and Development (ORD). EPA/625/6-89/019. January.

U.S. EPA. 1989g. *Handbook: Hazardous Waste Incineration Measurement Guidance Manual. Volume III of the Hazardous Waste Incineration Guidance Series.* Office of Solid Waste and Emergency Response. EPA/625/6-89/021. June.

U.S. EPA 1990i. *Handbook: Quality Assurance/Quality Control (QA/QC) Procedures for Hazardous Waste Incineration.* Office of Research and Development. EPA/625/6-89/023. January.

U.S. EPA. 1992c. *Technical Implementation Document for EPA's Boiler and Industrial Furnace Regulations.* Office of Solid Waste and Emergency Response. EPA-530-R-92-011. March.

U.S. EPA. 2001c. *Risk Burn Guidance for Hazardous Waste Combustion Facilities.* U.S. EPA Region 4 and OSW. EPA 530/R/01/001. July.

Generic Trial Burn Plans and/or Quality Assurance Plans and Procedures (QAPP) developed by individual EPA regional offices or authorized states.

### **2.2.1.1 Additional Emissions Testing Considerations**

COPC emission rates demonstrated in a traditional regulatory performance test (such as a RCRA trial burn) are expected to be greater than normal emission rates because a facility “challenges” its combustor during a trial burn. These challenges introduce a wide range of conditions for automatic waste feed cutoff (AWFCO) systems. Regulatory performance tests are usually conducted under two conditions:

1. a high-temperature test, in which the emission rate of metals is maximized, and
2. a low-temperature test, in which the ability of the combustor to destroy principal organic hazardous constituents (POHCs) in the waste feed is challenged.

The combination of high POHC feed rates and extreme operating conditions tested during a low-temperature trial burn typically produce higher PIC emission rates. However, this is not true in all cases. For example, the formation of Polychlorinated dibenzo(p)dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) doesn’t depend on “POHC incinerability” low temperature conditions. PCDDs and PCDFs can be formed catalytically in the low-temperature regions of the combustion unit or APCS. We recommend basing the decision to test under low, high, or both temperature conditions on the characteristics of the facility as discussed in the preceding section, considering facility-specific unit operation information for the particular types of wastes burned in the combustion unit as well as the particular APCS.

**RECOMMENDED INFORMATION FOR THE RISK ASSESSMENT REPORT**

- C All stack sampling information (current and historical data relevant to the risk assessment) on emission rates from the combustor during normal or day-to-day operating conditions and/or regulatory performance test conditions.
- C A description of the waste feed streams burned during the stack sampling. This includes chemical composition and physical properties, which demonstrate that the waste feeds are representative of worst-case wastes relative to producing emissions that may pose a potential risk concern.
- C Description of the operating conditions under which each set of emission rate data being used was developed.

**\* \* \* NOTICE \* \* \***

The permitting authority might not request a risk assessment for every possible metal or PIC from a combustor. This doesn't imply, however, that it will only ask for targeted sampling for COPCs during regulatory performance tests. Based on permitting experience and discussions with analytical laboratories, we maintain that complete target analyte list analyses conducted when using U.S. EPA standard sampling methods (e.g., 0010 or 0030) don't subject facilities to significant additional costs or burdens during the trial burn process. We recommend that stack emission samplers strive to collect as much information as possible to characterize the stack gases generated from the combustion of hazardous waste. Facilities should, then, generally expect that data collected for the risk assessment may include the following tests: Method 0010, Method 0030 or 0031 (as appropriate), total organic compounds (using the Guidance for Total Organics, including Method 0040), Method 0023A, Method 26A or 26 (as appropriate), the multiple metals train, and method for particle size distribution (e.g., CARB 501 or Method 5 Modified with analysis by Scanning Electron Microscopy [SEM]). The permitting authority might also determine that using other test methods is appropriate for the performance test, to address detection limit or other site-specific issues. See Table B.1-4 of the *Risk Burn Guidance for Hazardous Waste Combustion Facilities* (U.S. EPA 2001c) for a complete list of methods.

**2.2.1.2 Estimating the Total Organic Emission (TOE) Rate**

We recognize that despite all efforts, it might not be possible to identify all the compounds in the emissions from a facility. This data gap has the potential to underestimate risks and represents a non-conservative uncertainty. Organic compounds that can't be identified by laboratory analysis can't be defensibly treated as COPC's in the risk calculations. However, these compounds might still contribute significantly to the overall risk, and so it's reasonable to consider them qualitatively in the risk assessment (DeCicco 1995; U.S. EPA 1994i).

U.S. EPA developed the total organic emissions (TOE) test as one approach to account for unidentified organic compounds because pre-existing methods, such as total hydrocarbon analyzers, don't fully determine the total mass of organics present in stack gas emissions (Johnson 1996). We anticipate that trial/risk burns will generally include the TOE test, in order to provide sufficient information to address concerns about the unknown fraction of organic emissions. The TOE test is used in conjunction with the identified organic compounds to calculate a TOE factor. We recommend using the TOE factor to qualitatively evaluate potential risks from the unidentified fraction of organic compounds in the stack gas.

The TOE test is the subject of other guidance, such as the *Guidance for Total Organics* (U.S. EPA 1996d) with additional clarification provided in Section B.7 of U.S. EPA (2001c). Proper use of TOE data depends on a good understanding of the test method and how the data is reported. The TOE method defines total organics as the sum of three fractions:

***Fraction 1: Total Volatile Organic Compounds (TO<sub>VOC</sub>) (referred to as Field GC Component in the TO Guidance)*** - The fraction of organic compounds with boiling points less than 100°C. This VOC fraction is collected using U.S. EPA Method 0040. U.S. EPA Method 0040 allows for quantification of the total mass of organic compounds with boiling points less than 100°C, determined by summing the gas chromatograph/flame ionization detector results as described in the TO Guidance.

***Fraction 2: Total Chromatographical Semivolatiles (TO<sub>SVOC</sub>) (referred to as Total Chromatographical Organics Component in the TO Guidance)*** - The fraction of organic compounds with boiling points from 100°C to and including 300°C. This VOC fraction is collected using modified U.S. EPA Method 0010 procedures as defined by U.S. EPA (1996d). The total mass of organic compounds with boiling points 100°C up to and including 300°C is determined by summing the total gas chromatograph/flame ionization detector results as described in the TO Guidance.

***Fraction 3: Total Gravimetric Compounds (TO<sub>GRAV</sub>) (referred to as Gravimetric component in the TO Guidance)*** - The fraction of organic compounds with boiling points greater than 300°C. This fraction is determined by using modified U.S. EPA Method 0010 procedures defined by U.S. EPA (1996d), which quantify the mass, above this fractions boiling point, by measuring the total mass by evaporation and gravimetry (weighing) for nonvolatile total organics.

Please note that the TO total (TO<sub>TOTAL</sub>) is the sum of the sums of each fraction. The sum of the TO fractions is described as follows:

$$TO_{TOTAL} = TO_{VOC} + TO_{SVOC} + TO_{GRAV} \quad \text{Equation 2-1}$$

where:

$TO_{TOTAL}$	=	stack concentration of TO, including identified and unidentified compounds (mg/m <sup>3</sup> )
$TO_{VOC}$	=	stack concentration of volatile TO, including identified and unidentified compounds (mg/m <sup>3</sup> )
$TO_{SVOC}$	=	stack concentration of SVOC TO, including identified and unidentified compounds (mg/m <sup>3</sup> )
$TO_{GRAV}$	=	stack concentration of GRAV TO, including identified and unidentified compounds (mg/m <sup>3</sup> )

Use the TOE data in conjunction with the identified data to compute a TOE factor. Previously-computed TOE factors range from 2 to 40. The HHRAP defines the TOE factor as the ratio of the  $TO_{TOTAL}$  mass to the mass of identified organic compounds, as calculated by the following equation:

$$F_{TOE} = \frac{TO_{TOTAL}}{\sum_i C_i} \quad \text{Equation 2-2}$$

where

$F_{TOE}$	=	TOE factor (unitless)
$TO_{TOTAL}$	=	total organic emission (mg/m <sup>3</sup> )
$C_i$	=	stack concentration of the <i>i</i> th identified COPC (mg/m <sup>3</sup> )

Identifying the organic compounds in the denominator of Equation 2-2 is one of the most critical components of the TOE factor. Although the permitting authority may not request that you analyze the organic compounds with all possible analytical methods, you may wish to consider the effects that gaps in compound-specific identification may have on the computation of the TOE factor. For example, hazardous waste-burning cement kilns have expressed concern about the amount of light hydrocarbons that may evolve from the raw materials processed in the cement kilns, because these light hydrocarbons have not typically been identified in trial burns. If such concerns are significant, you and the permitting authority might choose to use additional test methods in the trial burn in order to speciate the maximum number of organic compounds.

We also generally recommend including tentatively identified compounds (TICs) in the denominator when computing the TOE factor, so that appropriate credit is given to defensible efforts at identifying the

maximum number of organic compounds. Finally, we generally recommend that non-detect COPCs be treated consistently between the risk assessment and TOE evaluation. That is, if a non-detected constituent is deleted as a COPC (See Section 2.3), then it would not be included in the identified fraction of the TOE equation. COPCs identified per Section 2.3, but not detected, might be included in the TOE factor equation at the reliable detection limit (non-isotope dilution methods) or the estimated detection limit (isotope dilution methods).

It's important to carefully evaluate the results of the gravimetric fraction when using the TOE factor. Both regulated industry and U.S. EPA have expressed some concern that the gravimetric fraction may over-report the organic fraction. It's been suggested that the gravimetric fraction may consist of organic and/or inorganic mass not directly attributable to organic incinerator emissions (U.S. EPA 1997a). The U.S. EPA Office of Research and Development (ORD) National Risk Management Research Laboratory (NRMRL) recently conducted a series of experiments to investigate this issue. The results indicate that it is indeed possible for inorganic mass to become soluble and retained in the TOE train methylene chloride extract. More importantly, the ORD/NRMRL research identified and demonstrated techniques for successfully mitigating this problem. Details of the experiments, results, and procedures for mitigating the GRAV bias will be made available in a forthcoming ORD report. Ultimately, these procedures will be contained in the forthcoming TOE guidance currently being revised by ORD. Further information on this topic is also available in U.S. EPA (2001c).

We recommend using the TOE factor in the uncertainty section of the risk assessment report to evaluate the risks from the unknown fraction of organics. The permitting authority can then evaluate the TOE factor and assess to what extent actual risks may be greater than estimated risks. For example, if the risk from the known portion of the emissions show that risks may be borderline and/or the TOE method shows that the unknowns are a significant portion of the emission profile, the permitting authority has several options, including:

1. Describe in a narrative form what is known of the unknown portion of the emissions.
2. As a bounding estimate, attribute a risk to the unknown portion of the emissions.

An example is presented as a preferred option in U.S. EPA (1994f), which assumes that the unknown compounds are similar in toxicity and chemical properties to the known compounds taken as a whole. The referenced equation is as follows:

$$Q_{i,adj} = Q_i \cdot \frac{TO_{TOTAL}}{\sum_i C_i} \quad \text{Equation 2-2A}$$

where

$Q_{i,adj}$	=	adjusted emission rate of compound $i$ (g/s)
$Q_i$	=	emission rate of compound $i$ (g/s)
$TO_{TOTAL}$	=	total organic emission (mg/m <sup>3</sup> )
$C_i$	=	stack concentration of the $i$ th identified COPC (mg/m <sup>3</sup> )

3. Recommend additional testing to identify a greater fraction of the organic compounds.
4. Specify permit conditions that further control total organic emissions or that further control the risks associated with known emissions.

Variations of the TOE factor can be useful to address site-specific concerns. For example, compute three separate TOE factors based on the apportioning provided by the TOE test (i.e.,  $TO_{VOC}$ ,  $TO_{SVOC}$ , and  $TO_{GRAV}$ ). Then evaluate the unknowns associated with each fraction of unidentified organic compounds separately.

### 2.2.2 Estimating Emission Rates for Facilities with Multiple Stacks

We generally recommend that the risk assessment consider emissions from all combustors burning hazardous waste at a facility, not just the unit currently undergoing the permitting process. As discussed further in Chapter 3, air dispersion modeling for each combustor (source) is frequently conducted separately, to evaluate risk on a stack- or source-specific basis. An example case is a chemical manufacturing facility which operates both an on-site incinerator and several hazardous waste-burning boilers. Whether it is the incinerator or the boilers being permitted, the risk assessment considers the emissions from all the combustors in the estimate of facility risk. In addition to RCRA combustors, emissions from other RCRA treatment, storage, or disposal units (e.g., open burning/open detonation and thermal desorption) might also be included in the risk evaluation in some cases.

### 2.2.3 Estimating Stack Emission Rates for Facilities Not Yet Operational

The permitting process for new hazardous waste combustion facilities includes submitting information of sufficient detail for the regulatory authority to evaluate compliance with existing regulations, guidance, and standards of protectiveness. Stack (or other source) locations and dimensions, design flow and

emission rate estimates, waste feed characteristics, surrounding building dimension data, facility plot plans, and terrain data are frequently reviewed and used in a pre-operation risk assessment. This assists decision-making and designing permit requirements.

We generally recommend reviewing design emission rates, waste feed characteristics, and other design data, along with supplementary documentation, to make sure they are representative, accurate, and comprehensive. Good engineering practice dictates a check of, and comparison with, data from similar existing units. Stack test reports for facilities of similar technology, design, operation, capacity, auxiliary fuels, waste feed types, and APCSs can be useful in estimating COPC emission rates for new facilities that have not been constructed. In addition to design data, particle size distribution data from a similar type unit that is operational may be useful. Estimated emission rates used to complete pretrial burn risk assessments are frequently compared to the measured emission rates from actual performance tests completed after the new facility receives a permit, is constructed and operational.

If surrogate data from similar facilities aren't available, some state environmental agencies enforce emission rate limits based on state laws. Since these limits cannot be exceeded, you could use them to develop emission rate estimates for the risk assessment. A trial or risk burn could then demonstrate that facility emissions are less than those considered in the permit and risk assessment.

#### **2.2.4 Estimating Stack Emission Rates for Facilities Previously Operated**

We generally recommend that the risk assessment also consider emissions from the historical operation of other combustors burning hazardous waste at the facility, not just the unit currently undergoing the permitting process. The permitting authority will determine the appropriateness of this on a case-by-case basis. An example case might be when the emissions from historical operation of a source or sources have already resulted in potential risk concerns at or near the facility. You could model emissions from historical operations as a separate source or, if applicable, include them in the fate and transport equations by adding the previous years of operation to the anticipated time period of combustion for an existing or newly operating source. In some cases, you might also include historical emissions from other RCRA treatment, storage, or disposal units at the facility (e.g., open burning/open detonation and thermal desorption) in the risk assessment, in addition to RCRA combustors.

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**RECOMMENDED INFORMATION FOR THE RISK ASSESSMENT REPORT**

- C All stack test reports for combustors used to develop emission rate estimates
  - C If using surrogate data to assess a new facility, descriptions of how the combustion data used represent similar technology, design, operation, capacity, auxiliary fuels, waste feed types, APCs, and particle size distributions
  - C Demonstration that the data used to develop the emission rate estimates were collected using appropriate U.S. EPA sampling and analysis procedures
  - C The range of data obtained, and values used, in completing the risk assessment
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### 2.2.5 Emissions From Process Upsets

It is possible for unburned hazardous waste to be emitted through the stack as a result of various process upsets, such as start-ups, shutdowns, and malfunctions of the combustion unit or APCs. Emissions can also be caused by operating upsets in other areas of the facility (e.g., an upset in a reactor which vents gases to a boiler burning hazardous waste could trigger a process upset in the boiler, resulting in increased emissions). U.S. EPA (1994i) indicates that upsets aren't generally expected to significantly increase stack emissions over the lifetime of the facility.

To account for the increased emissions associated with process upsets, we generally recommend that the stack emission rates estimated from trial burn data be multiplied by an upset factor. The upset factor is not applied to non-PIC emission rate estimates where the total mass of a constituent in the waste feed is assumed to be emitted. When available, site-specific emissions or process data can be useful to estimate the upset factor. You may also want to consider and evaluate the following types of data to derive the upset factor:

- C Data from continuous emissions monitoring systems that measure stack carbon monoxide, oxygen, total hydrocarbon (if requested), or opacity (if appropriate)
- C Data on combustion chamber, APCs, or stack gas temperature
- C Data on hazardous waste residence time
- C Frequency and causes of automatic waste feed cutoffs (AWFCO)
- C Frequency of start-up and shut-down events
- C Ratio of AWFCO frequency and duration to operating time

- C APCS operating variables like baghouse pressure drop, liquid scrubber flow rate, or electrostatic precipitator voltage
- C Stack test data collected while the combustor was operated under upset conditions

You might use this information to estimate the magnitude of the increase in emissions and the percentage of time, on an annual basis, that the unit operates at upset conditions. Additional information regarding upset factors for liquid-burning BIFs is available in the Louisiana Chemical Association (LCA) Letter Report on Upset Factors, dated October 27, 1999, available on the U.S. EPA Region 6 web site ([www.epa.gov/region06/](http://www.epa.gov/region06/)).

If you don't have site-specific data, or they are inappropriate for deriving an upset factor, we generally recommend estimating upset emission rates using a procedure based on work by the California Air Resources Board (CARB) (1990).

***Estimating Emissions from Process Upsets:*** To represent stack emission rates during process upsets, multiply the emission rate developed from the trial burn data by 2.8 for organics and 1.45 for metals. These factors are derived by assuming that emissions during process upsets are 10 times greater than emissions measured during the trial burn. Since the unit doesn't operate under upset conditions continually, the factor is adjusted to account for only the period of time, on an annual basis, that the unit operates under upset conditions. For organic compounds, the facility is assumed to operate as measured during the trial burn 80 percent of the year and operate under upset conditions 20 percent of the year  $[(0.80)(1)+(0.20)(10)=2.8]$ . For metals, the combustor is assumed to operate as measured during the trial burn 95 percent of the year and operate under upset conditions the remaining 5 percent of the year  $[(0.95)(1)+(0.05)(10)=1.45]$ .

Catastrophic process upsets brought about by complete failure of combustion and air pollution control systems (e.g. resulting from non-routine events such as explosions, fires, and power failures) are typically considered accidental releases and consequently aren't addressed by this guidance.

#### **RECOMMENDED INFORMATION FOR THE RISK ASSESSMENT REPORT**

- C Historical operating data demonstrating the frequency and duration of process upsets
- C A discussion of the potential cause(s) of the process upsets
- C Estimates of upset magnitude or emissions
- C Calculations which describe the derivation of the upset factor.

### 2.2.6 RCRA Fugitive Emissions

RCRA fugitive emission sources frequently evaluated in site-specific risk assessments include waste storage tanks; process equipment ancillary to the combustor; and the handling and disposal of combustion system residues such as ash. Fugitive emissions from other RCRA treatment, storage, or disposal units (e.g., landfills) may also warrant evaluation in some cases.

This section contains guidance for quantitatively estimating fugitive emissions using procedures outlined in other U.S. EPA guidance. Guidance regarding air dispersion modeling of fugitive emissions is presented in Chapter 3.

#### 2.2.6.1 Quantitative Estimation of RCRA Fugitive Emissions from Process Equipment

We generally recommend the following series of steps to quantitatively estimate RCRA fugitive emissions: (1) identify equipment to evaluate as a fugitive emission source(s); (2) group equipment, as appropriate, into a combined source; and (3) estimate compound-specific emission rates for each resulting source. We illustrate an example in Figures 2-1 and 2-2 and Tables 2-1 and 2-2, to help explain the recommended steps. Figure 2-1 presents the plot plan of a hypothetical facility that includes one RCRA combustion unit (CU-1), two hazardous waste feed storage tanks (WST-1 and WST-2), and ancillary equipment identified in a RCRA Part B permit application.

**Step 1: Identify Fugitive Emission Sources** - Generally, identify RCRA fugitive emission sources such as waste storage tanks and process equipment that comes in contact with a RCRA hazardous waste. Such equipment is specified in Title 40, Code of Federal Regulations (40 CFR) Part 265, Subpart BB. Equipment covered under Subpart BB includes:

- C Pumps
- C Valves
- C Connectors (flanges, unions, tees, etc.)
- C Compressors
- C Pressure-relief devices
- C Open-ended lines
- C Product accumulator vessels
- C Sampling connecting systems
- C Closed vent systems

C Agitators

Note each fugitive emission source on a facility plot map with a descriptor and the location denoted with Universal Transverse Mercator (UTM) coordinates (specify if North American Datum [NAD] of 27 or NAD83).

**Step 2: Group Equipment Into a Combined Source** - To significantly reduce the effort required to complete air dispersion modeling and the subsequent risk assessment, group equipment in close proximity, and evaluate as a single combined source. The speciated emission rates for the group are the summation of the emissions from the grouped individuals. Clearly denote on a facility plot plan or map the area extent of the grouped or combined source, as defined by UTM coordinates (specify if NAD27 or NAD83). Define the area extent of the combined source using the actual locations of the equipment being grouped, without exaggeration to cover areas without fugitive sources. It may also be useful to consider how fugitive emission sources are to be defined when conducting the air dispersion modeling (see Chapter 3).

Equipment in two areas of the hypothetical facility shown in Figure 2-1 are grouped into combined sources; these consist of the Waste Feed Storage Area and the RCRA Combustor Area.

**Step 3: Estimate Fugitive Emissions from Tanks** - Obtain fugitive emission rates for waste storage tanks from the facility's emission inventory or Title V air permit application prepared in compliance with Clean Air Act Amendments of 1990 (see example provided as Figure 2-2). If that information is not available, fugitive emissions from storage tanks can be calculated using U.S. EPA's TANKS Program or by following the procedures outlined in U.S. EPA (1995a), "*Compilation of Air Pollution Emission Factors, January 1995.*"

The information needed to accurately estimate fugitive emission rates from storage tanks includes, but is not limited to:

- C Dimensions of the tanks
  - Shell height and diameter
  
- C Characteristics of the tank roof
  - Color and shade
  - Condition (e.g., poor, good)
  - Type (e.g., cone, dome)
  - Height
  - Radius or slope
  - Fixed or floating
  
- C Characteristics of the shell
  - Color and shade
  - Condition (e.g., poor, good)
  - Heated
  
- C Settings on breathe vents
  - Vacuum setting

- Pressure setting
- C Characteristics of the stored liquids
  - Maximum and annual average liquid height
  - Working volume
  - Turnovers per year
  - Net throughput
  - Average annual temperature
  - Vapor pressures of speciated constituents (at annual average temperature)

**Step 4: Estimate Fugitive Emissions from Process Equipment** - Estimate fugitive emissions for each type of equipment listed under 40 CFR Part 265, Subpart BB by using the following four approaches, listed in order of increasing refinement and data requirements:

- C Average Emission Factor Approach (AEFA)
- C Screening Ranges Approach (SRA)
- C U.S. EPA Correlation Approach (EPACA)
- C Unit-Specific Correlation Approach (USCA)

These four approaches would generally be applicable to estimate fugitive emission rates of volatile organic compounds (VOCs) from equipment on any facility. Except for the AEFA method, all of the approaches need screening data collected using a portable monitoring device (PMD). Because data on fugitive emissions at a facility is typically limited, the AEFA method is expected to be used in most cases, and therefore has been selected for use in the example illustrated in Figure 2-1, and Tables 2-1 and 2-2. However, we recommend using more refined approaches such as SRA, EPACA, or USCA, if sufficient data is available. U.S. EPA (1995k) provides a detailed discussion on these three approaches. Additional information on estimating fugitive emission rates is available in U.S. EPA (1995k), "*Protocol for Equipment Leak Emission Estimates, EPA-453/R-95-017.*"

FIGURE 2-1  
 EXAMPLE FACILITY PLOT MAP

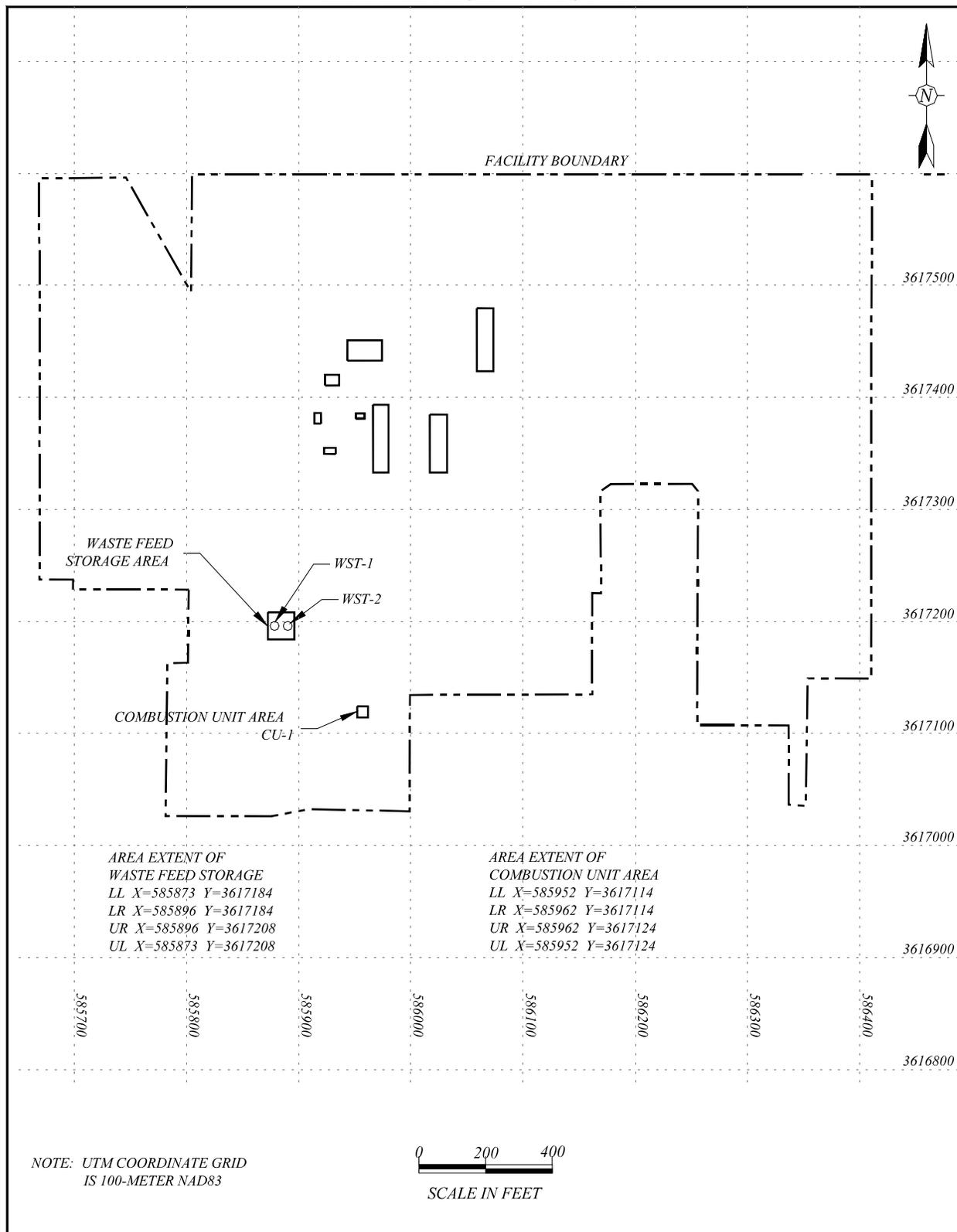


FIGURE 2-2  
EXAMPLE EMISSIONS INVENTORY

Department of Environmental Quality Air Quality Division P. O. Box 82135 Baton Rouge, LA 70884-2135 (504) 765-0219		<b>LOUISIANA</b> <b>SINGLE POINT SOURCE / AREA SOURCE</b> <b>Emission Inventory Questionnaire (EIQ)</b> <b>for Air Pollutants</b>					LA DEQ				
Company Name  Hypothetical Chemical Company			Plant location and name (if any)  Baton Rouge, LA Plant				Date of submittal  February 1996				
Source ID Number  WST - 1	Descriptive name of the equipment served by this stack or vent  Waste Feed Tank			Location of stack or vent (see instructions on how to determine location of area sources)  Horizontal Coordinate 589100 m E UTM zone no. 15 Vertical coordinate 3616200 m N							
STACK and DISCHARGE PHYSICAL CHARACTERISTICS  Change [ ] yes [x] no	Height of stack above grade [ft]  8	Diameter or stack discharge area  0.167 ft	Stack gas exit temperature (°F)  125	Stack gas flow at process conditions, <u>not at standard</u> (cfm)  24.27		Stack gas exit velocity (ft/sec)  18.32	For tanks, list volume (gals) 800  Date of construction				
Fuel a b c	Type of fuel used and heat input (see instructions)		Operating Characteristics	Percent of annual throughput of pollutants through this emission point				Normal operating time of this point	Normal operating rate		
	Type of Fuel			Heat input (MMBtu/hr)		Dec-Feb	Mar-May	Jun-Aug	Sep-Nov	hrs/ days/ weeks/ day week year	100%
						25	25	25	25	24.00 7 52.0	
<b>Air Pollutant Specific Information</b>											
Pollutant			Control equipment code	Control equipment efficiency	Emission Rate			Emission estimation method	Add, change, delete code	Concentration in gases exiting at stack	
					Average (lbs/hr)	Maximum (lbs/hr)	Annual (tons/yr)				
2-Nitropropane			000	0.0000	0.0023	0.3463	0.01	3	c	N/A ppm by vol	
Acetaldehyde			000	0.0000	0.0041	125.00	0.081	3	c	N/A ppm by vol	
Acetanitrile			000	0.0000	0.0023	21.1266	0.01	3	c	N/A ppm by vol	
Methanol			000	0.0000	0.0023	4.502	0.01	3	c	N/A ppm by vol	
Non-Toxic Voc			000	0.0000	0.0062	195.3347	0.028	3	c	N/A ppm by vol	

TABLE 2-1

EXAMPLE CALCULATION  
TOTAL FUGITIVE EMISSION RATES FOR EQUIPMENT IN WASTE FEED STORAGE AREA

1	2	3	4	5	6		7	8	9	10
Fugitive Emission Source	Waste Stream	Type of Waste Stream In Service	Equipment Type	Number of Each Equipment Type Per Waste Stream	Equipment Emission Factors		Total VOC Weight Fraction	Operational Time Period of Equipment (days)	Total VOC Emissions Rate by Equipment (g/sec)	Total Fugitive Emission Rate (g/sec)
					(kg/hr)	(g/sec)				
Waste Feed Storage Area	Process A Wastes	Light Liquid	Pumps	3	0.01990	0.00553	0.9	180	0.01493	0.14926
		Light Liquid	Valves	70	0.00403	0.00112	0.9	180	0.07056	
		Light Liquid	Connectors	30	0.00183	0.00051	0.9	180	0.01377	
		Light Liquid	Tank WST-1	1	--	--	0.9	180	0.02	
		Light Liquid	Tank WST-2	1	--	--	0.9	180	0.03	
	Process B Wastes	Heavy Liquid	Pumps	2	0.00862	0.00239	0.6	180	0.00287	0.06857
		Heavy Liquid	Valves	75	0.00023	0.00112	0.6	180	0.0504	
		Heavy Liquid	Connector	50	0.00183	0.00051	0.6	180	0.0153	
		Heavy Liquid	Tank WST-1	1	--	--	0.6	0	0	
		Heavy Liquid	Tank WST-2	1	--	--	0.6	0	0	

Notes:

- Column 1 Equipment in the Waste Feed Storage Area was identified and grouped as a combined RCRA fugitive emission source with an area extent defined by UTM coordinates (NAD83).
- Column 2 The waste streams serviced by equipment in the Waste Feed Storage Area can be determined through review of the facility's RCRA Part B Permit Application, Air Emission Standards.
- Column 3 The type of waste stream in service, defined as light or heavy for determination of equipment-specific emission factors, can be determined from review of waste stream vapor pressure.
- Column 4 Similar types of equipment can be grouped according to the most applicable equipment-specific emission factor and type of waste stream service (light or heavy) provided in U.S. EPA (1995k).

Column 5	The number of equipment type (per waste stream) identified in column 3.
Column 6	Emission factors specific to each type of equipment can be obtained from U.S. EPA (1995k), with the exception of storage tanks.
Column 7	Weight fraction of total volatile organic compounds was obtained from dividing the concentration of VOCs (mg/L) by the density of the waste stream (mg/L).
Column 8	Assumed the equipment is operational for 180 days a year.
Column 9	Equipment-specific fugitive emission rates were determined by multiplying Columns 5, 6, and 7. Emission rates for tanks were obtained from Title V air permit application. In the absence of such data, emission rates for tanks can be calculated using U.S. EPA's TANKS Program or by following the procedures outlined in U.S. EPA (1995a).
Column 10	The total fugitive emission rate for each waste stream is determined by summing emission rates for all the equipment. Table 2-2 presents calculations for estimating speciated fugitive emissions.

**TABLE 2-2**  
**EXAMPLE CALCULATION**  
**SPECIATED FUGITIVE EMISSIONS**  
**FOR EQUIPMENT IN WASTE FEED STORAGE AREA**

1	2	3	4	5	6
Fugitive Emission Source	Waste Stream	Waste Stream Composition	Weight Fraction of Each VOC In Waste Stream (%)	Total Fugitive Emission Rate (g/sec)	Speciated Fugitive Emissions (g/sec)
Waste Feed Storage Area	Process A Wastes	Acetaldehyde	0.20	0.14926	0.0030
		Acetonitrile	0.25		0.0037
		2-Nitropropane	0.25		0.0037
		Nitromethane	0.20		0.0030
	Process B Wastes	Acetaldehyde	0.20	0.06857	0.0137
		Acetonitrile	0.10		0.0069
		Methanol	0.20		0.0137
		Propionitrile	0.05		0.0034
Notes:					
Column 1	Equipment in the Waste Feed Storage Area was identified and grouped as a combined RCRA fugitive emission source with an aerial extent defined by UTM coordinates (NAD83).				
Column 2	The waste streams serviced by equipment in the Waste Feed Storage Area can be determined through review of the facility's RCRA Part B Permit Application, Air Emission Standards.				
Column 3	The waste stream composition can be determined from analytical data				
Column 4	Weight fraction of compounds in the waste stream can be determined from analytical data or review of the facility's Title V Air Permit Application, Emissions Inventory Questionnaire (EIQ) for Air Pollutants (see example in Figure 2-2).				
Column 5	The total fugitive emission rate for each waste stream was obtained from Column 10, Table 2-1.				
Column 6	Speciated fugitive emissions were obtained by multiplying Column 4 and 5.				

***An Example Calculation Using the AEFA Method***

Information needed to estimate fugitive emission rates using the AEFA method includes:

- C Type of waste stream associated with each equipment type (Columns 2 and 3, Table 2-1)
  - light liquids are those in which the sum of the concentration of individual constituents with a vapor pressure over 0.3 kilopascals (kPa) at 20°C is greater than or equal to 20 weight percent
  - heavy liquids are all others liquids not meeting the definition of light liquids as specified above

- C Number of each equipment type associated with each waste stream (Columns 4 and 5, Table 2-1)
- C Total VOC weight fraction of each waste stream (Column 7, Table 2-1)
- C Weight fraction of each VOC in each waste stream (Columns 3 and 4, Table 2-2)
- C Operational time period of equipment (Column 8, Table 2-1)

In the AEFA method, equipment is grouped by waste streams of similar characteristics and VOC composition (Columns 1 and 2, Table 2-1). However, the AEFA method doesn't account for different site-specific conditions such as temperature, vapor pressure, or screening values, among process units within a source category. Site-specific factors can significantly influence fugitive emission rates of leaks from equipment.

U.S. EPA (1995k) presents the average emission factors (Column 6, Table 2-1) for synthetic organic chemicals manufacturing industry process units, refineries, and natural gas plants. The following table is an excerpt from this guidance document. These emission factors are most valid for estimating rates of emissions from a grouping of equipment over a long time period.

**TABLE 2-3**

**SOCMI AVERAGE EMISSION FACTORS**

<b>Equipment type</b>	<b>Service</b>	<b>Emission factor (kg/hr/source)</b>
Valves	Gas	0.00597
	Light liquid	0.00403
	Heavy liquid	0.00023
Pump seals	Light liquid	0.0199
	Heavy liquid	0.00862
Compressor seals	Gas	0.228
Pressure relief valves	Gas	0.104
Connectors	All	0.00183
Open-ended lines	All	0.0017
Sampling connectors	All	0.0150
Source: U.S. EPA (1995k)		

To calculate the total VOC emissions rate for a specified equipment type, multiply the equipment emission factor by the total VOC weight fraction and the number of each equipment type per waste stream (Column 9, Table 2-1 = Column 6 x Column 7 x Column 5).

Generate the total fugitive emission rate for the waste stream (Column 10, Table 2-1) by summing the total VOC emission rates for each equipment type. Speciated fugitive emissions are then calculated by multiplying the weight fraction of each VOC in the waste stream and the total fugitive emission rate for the waste stream (Column 6, Table 2-2 = Column 4 x Column 5). This speciated emission rate is the emission rate used in the risk assessment.

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**RECOMMENDED INFORMATION FOR THE RISK ASSESSMENT REPORT**

- C Summary of the step-by-step process conducted to evaluate fugitive emissions
  - C Facility plot map clearly identifying each fugitive emission source with a descriptor and the location denoted with UTM coordinates (specify if NAD27 or NAD83).
  - C Speciated emission rate estimates for each waste stream serviced by each source, with supporting documentation
  - C Applicable discussion of monitoring and control measures used to mitigate fugitive emissions
- 

### **2.2.6.2 Fugitive Emissions from Combustor Leaks**

We recommend that when appropriate, the risk assessment evaluate fugitive emissions resulting from the construction, design, or operation of a hazardous waste combustor. Examples of fugitive emissions from combustor leaks include:

- C Combustors operating under negative pressure may experience temporary positive pressures (“puffing”) that cause fugitive emissions. This condition can occur when a slug of high BTU waste is combusted, causing a rapid expansion in the volume of combustion gases that exceeds the volume of the combustion chamber.
- C Fugitive emissions resulting from the day-to-day operation of the combustor and APCS. These emissions will typically include (1) leaks that occur due to a positive pressure in the APCS, and (2) routine maintenance activities such as replacement of baghouse collection bags.

Currently, we don't offer any specific guidance on how to quantitatively estimate fugitive emissions from hazardous waste combustors. However, if no site-specific quantitative methods are available, one option is to address risks associated with leaks in the uncertainty section of the risk assessment. Under such an approach, the permitting authority could review facility-specific data to determine whether or not the design addresses equipment leaks and whether the operational data indicate that equipment leaks may be a problem.

**RECOMMENDED INFORMATION FOR THE RISK ASSESSMENT REPORT**

- C Process design information and drawings (if necessary)
- C Past operating data indicating the frequency, duration, and magnitude of combustor leaks
- C Information regarding the probable cause of combustor leaks
- C Summary of procedures in place to monitor or minimize fugitive emissions resulting from combustor leaks

**2.2.7 RCRA Fugitive Ash Emissions**

Burning hazardous waste may produce flyash. Fugitive particle emissions may result from the associated collection, handling, and disposal of the flyash. Typically, fugitive emissions of flyash collected from an air pollution control device (APCD) will occur during transfer into covered trucks or other conveyance mechanisms prior to disposal. Emissions generated during the loading process can be controlled by APCDs or other types of equipment. However, some of the flyash may still escape into the atmosphere as fugitive emissions.

We generally recommend the following steps to quantitatively estimate RCRA fugitive ash emissions: (1) determine an empirical emission factor, (2) estimate the flyash generation rate, and (3) account for air pollution control equipment, if applicable. As demonstrated in the example calculation below, it is then possible to estimate the fugitive ash emission rate by multiplying the empirical emission factor by the flyash generation rate and, if applicable, the control deficiency of the air pollution control equipment.

**Step 1: Determine an Empirical Emission Factor** - One approach to estimate particle emissions associated with flyash loading and unloading is to use an empirical emission factor of 1.07 lb per ton flyash. This factor is based on a field testing program conducted at a coal fired power plant equipped with an electrostatic precipitator (ESP) (Muleski and Pendleton 1986). Because burning coal and hazardous wastes are similar activities, flyash generated from similar control devices is expected to behave similarly under the same conditions, with respect to fugitive emissions. In general, particle behavior is dependent more on the physical form of the flyash than on the feed (or waste) stream being burned. The emission factor determined during the empirical study (0.107 lb per ton flyash) can be adjusted by a factor (e.g., 10) to account for the fact that the flyash from burning coal (in the study) was wetted. Depending on the facility, the flyash from the hazardous waste combustion facility may or may not be wetted.

**Step 2: Estimate the Flyash Generation Rate** - Obtain the APCD flyash generation rate from the Part B Permit Application. Obtain the total ash content of the “generic” waste streams created from the waste profile. Both values should be approximately the same. Since a major portion of ash fed to the combustor is converted to bottom ash, it is likely that this value can be assumed to be a high estimate of the actual flyash generation rate.

**Step 3: Account for Air Pollution Control Equipment** - If an APCD is used for controlling emissions during flyash handling operations, you can generally apply an efficiency factor (e.g., 99.5 percent) to the emission rate. An efficiency factor of 99.5 percent is based on typical collection efficiencies of particulate matter control devices, for the particle sizes in the range of 2.5 to 10  $\mu\text{m}$  (U.S. EPA 1995a).

### Example Calculation

Multiply the empirical emission factor (Step 1) times the estimated flyash generation rate (Step 2):

$$[(1.07 \text{ lb per ton}) * (5,000 \text{ tons per year}) = 5,350 \text{ lbs per year}].$$

To account for the air pollution control equipment, multiply the product of Steps 1 and 2 times one minus the fabric filter efficiency (Step 3) to calculate the final RCRA fugitive ash emission rate for use in the risk assessment:

$$[(5,350 \text{ lbs per year}) * (1 - 0.995) = 26.75 \text{ lbs per year}].$$

### 2.2.8 Cement Kiln Dust (CKD) Fugitive Emissions

CKD is the particulate matter (PM) that is removed from combustion gas leaving a cement kiln. This PM is typically collected by an APCS—such as a cyclone, baghouse, ESP—or a combination of APCSs.

Many facilities recycle a part of the CKD back into the kiln. Current and applicable guidance on evaluating CKD includes (1) the *Technical Background Document for the Report to Congress* (U.S. EPA 1993g), and (2) the regulatory determination of CKD (60 FR 7366, February 7, 1995).

Most CKD constituents (for example, metals) aren't volatile but could be released to air through fugitive dust emissions as volatile or semivolatile organics. These emissions can be in gaseous form and present in relatively low concentrations, if at all (U.S. EPA 1993a). Dust particles may be suspended in the air by either wind erosion or mechanical disturbances. The extent to which dust is blown into the air by wind erosion depends on several site-specific characteristics, including (1) the texture (particle size distribution) and moisture content of the CKD on the surface of piles, (2) non-erodible elements, such as clumps of grass or stones on the pile, (3) presence of a surface crust, and (4) wind speeds. Mechanical disturbances that can suspend CKD constituents in the air include (1) vehicular traffic on and around CKD piles, (2) CKD dumping and loading operations, and (3) transportation of CKD around a plant site in uncovered trucks. Cement plants may use various control measures to limit the release of CKD to the air. For example, CKD may be pelletized in a pug mill, compacted, wetted, and covered to make the material less susceptible to wind erosion.

To keep the dust down, many facilities add water to CKD before disposal, to agglomerate individual particles. In addition, as CKD sits in a pile exposed to the elements, occasional wetting by rainfall may form a thin surface crust in inactive areas of the pile. This acts to mitigate air entrainment of particles. However, based on field observations by U.S. EPA (1993g), neither surface wetting nor natural surface crusting eliminates the potential for CKD to be blown into the air. Wetting the dust before disposal provides incomplete and temporary control because water is infrequently applied, and the dust ultimately dries and returns to a fine particulate that is available for suspension and transport. Similarly, a surface crust may develop, but (1) the crust breaks when vehicles or people move on the pile, and (2) fresh dust is regularly added to the pile, providing a continual, exposed reservoir of fine particles. Please note that a crust doesn't always form, for a variety of reasons such as weather and CKD chemistry.

CKD constituents that are released to the air are transported and dispersed by the winds, and are ultimately deposited onto land or water, either by settling in a dry form or by being entrained in precipitation.

### **2.2.8.1 Composition and Characteristics of CKD**

We evaluated the potential direct and indirect risks resulting from on-site and off-site management of CKD (U.S. EPA 1993g; 1993h). These studies highlight the limited amount of available information regarding variation in the chemical constituents of CKD generated by facilities burning hazardous waste

as fuel, and by facilities burning only fossil or nonhazardous waste fuels. There may also be differences in composition between the “as-generated” CKD -- a portion of which is recycled back into the system -- and the “as-managed” CKD that is disposed of on or offsite.

The air exposure pathway is generally of concern for CKD, because the dust is a fine PM that is readily suspendable, transportable, and respirable in air. In general, particles that are #100 micrometers can be suspended in the wind and transported. Within this range, particles that are #30 micrometers can be transported for considerable distances downwind. However, particles that are #10 micrometers are of primary concern for respiration by humans (U.S. EPA, 1993g). Virtually all of the dust generated at the 15 facilities evaluated by U.S. EPA (1993g) in the *Cement Kiln Dust Report to Congress* may be suspended and transported in the wind (that is, the vast majority of particles are #100 micrometers), and over two-thirds of all CKD particles generated may be transported over long distances. Additionally, a significant percentage of the total dust generated (from 22 to 95 percent, depending on kiln type) comprises respirable particles that are #10 micrometers.

**RECOMMENDED INFORMATION FOR THE RISK ASSESSMENT REPORT**

- C Physical data, including particle size distribution and density
- C Chemical data, including organic and inorganic analytical tests similar to those used for sampling combustion gases
- C Plant net CKD generation rate (how much CKD per year that is available for disposal)
- C Ambient air monitoring data
- C CKD management, transportation, storage, and disposal methods
- C Containment procedures, including fugitive dust prevention measures and the area of exposed CKD
- C Meteorological data, including wind speed and precipitation

**2.2.8.2 Estimating CKD Fugitive Emissions**

In general, the HHRAP doesn't address quantitative estimation of risk from fugitive CKD emissions. However, risk assessments of cement manufacturing facilities are still able to evaluate the fugitive CKD emissions qualitatively. The *Technical Background Document for the Report to Congress* (U.S. EPA

1993g), includes methods to estimate the magnitude of fugitive emissions from the handling, storage, and disposal of CKD. Sampling data of CKD collected during maximum waste metal feed rate conditions from the trial burn, risk burn and/or certification of compliance tests may also be useful in evaluating CKD fugitive emissions. You can then evaluate it qualitatively by comparing the risks estimated for the kiln stack emissions, to the high end national screening level estimated by U.S. EPA for CKD in U.S. EPA (1993g) and the regulatory determination of CKD (60 FR 7366, February 7, 1995). If the risks are equivalent, the combined risks appear significant, or the risks attributed to the CKD are greater than the risks estimated for the kiln stack emissions, it might be appropriate to evaluate the risk from CKD emissions in a more quantitative fashion. We generally recommend that the permitting authority make sure that any qualitative evaluation includes a comparison of the conditions at the facility to the conditions at the model facilities we evaluated in U.S. EPA (1993g; 1993h). In addition, an analysis of a specific facility's compliance with other risk-based environmental statutes and regulations is often an appropriate method to qualitatively evaluate risks associated with the handling, storage, and disposal of CKD.

### **2.3 IDENTIFYING COMPOUNDS OF POTENTIAL CONCERN**

Compounds of potential concern (COPCs) are those compounds evaluated throughout the risk assessment. There is no universal list of COPCs, because a compound that's a COPC for one combustor may not be a COPC for another combustor. COPCs in the emissions from hazardous waste combustors vary widely, depending on the type of

- < combustor,
- < fuel and hazardous waste feed being burned, and
- < APCS used.

COPCs include metals, products of incomplete combustion (PICs), and/or reformation products. PICs are any organic compounds emitted from a source that are present in the feed stream (even in trace amounts) and not completely destroyed in the combustion process. Reformation products are organic compounds that are formed immediately after combustion, due to interaction of specific constituents in the combustion gasses and specific unit operating conditions relative to a particular combustion process and associated air pollution control equipment.

PICs can be formed by trace toxic organic compounds in the waste feed stream. Therefore, we generally recommend evaluating these trace compounds as PIC precursors, in addition to those compounds more prevalent in the hazardous waste feed. *Don't confuse PICs with principal organic hazardous constituents (POHCs)*. POHCs are compounds in the waste feed stream used during a performance test burn to measure combustor DRE. Unburned POHCs and partially destroyed or reacted POHCs are PICs, but PICs are not necessarily POHCs. We've typically subdivided COPCs into seven different constituent categories (U.S. EPA 1994g; 1994i; 1994j; 1994n):

- C Polychlorinated dibenzo(p)dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs)
- C Polynuclear aromatic hydrocarbons (PAHs)
- C Polychlorinated biphenyls (PCBs)
- C Nitroaromatics
- C Phthalates
- C Other organics
- C Metals

Table A-1 (Appendix A) presents a comprehensive list of compounds typically found (1) in hazardous waste, and (2) in hazardous waste combustion stack gas emissions. Table A-1 identifies the Chemical Abstracts Service (CAS) number for each compound, and states whether the compound has been identified as a carcinogen. Table A-1 also indicates whether a compound has been identified as a potential COPC by

- U.S. EPA and state risk assessment reference documents,
- emission test results that have identified the compound in the emissions from hazardous waste combustion facilities, or
- other literature that suggests that the risks from the compound may be significant.

We provide Table A-1 to help you make sure that the performance test program considers the full range of compounds potentially emitted from a combustor, and the appropriate analytical method. A risk assessment won't necessarily evaluate every metal, potential PIC, and reformation product listed in Table A-1. Once the performance tests are completed, we recommend selecting the risk assessment COPCs from the stack test data and available facility-specific process information, rather than Table A-1.

Identify COPCs from the trial/risk burn data based on their potential to pose increased risk or hazard via one or more of the direct or indirect exposure pathways. We recommend focusing on compounds that

- are likely to be emitted because they (or their precursors) are present in the waste feed,

- are likely to be emitted because they are likely reformation products,
- are potentially toxic to humans, and/or
- have a tendency to bioaccumulate or bioconcentrate in food chains.

Appendix A discusses carcinogenic and noncarcinogenic toxicity of specific compounds. The toxicity information provided in the HHRAP Companion Database is for informational purposes, to help you explain the basis for selecting COPCs. Please keep in mind that toxicity benchmarks and slope factors might change as additional toxicity research is conducted. We recommend consulting the hierarchy of human health toxicity data (see Appendix A, Section A.2.6) before completing the risk assessment, to make sure that you use the most current toxicity data.

We generally recommend the following six-step approach (illustrated in Figure 2-3) for identifying the COPCs to evaluate in a site-specific risk assessment (U.S. EPA 1994i).

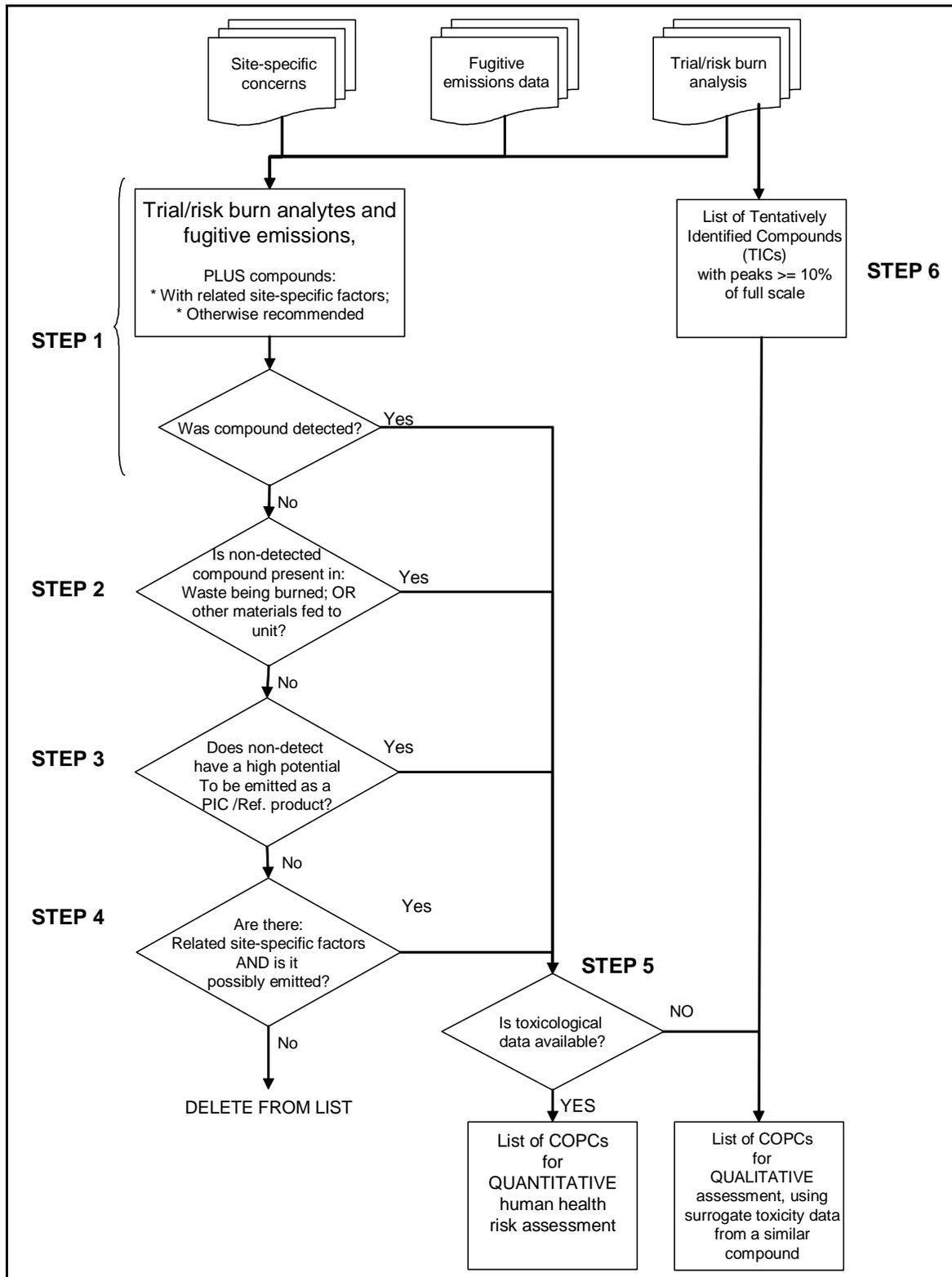
**Step 1:** Evaluate analytical data from the stack tests performed during the regulatory test burn program, and compounds associated with fugitive emissions (see Section 2.2.6). Prepare a list that includes all the compounds specified in the analytical methods performed in the stack tests, and all compounds found in the fugitive emissions evaluation. Also include compounds of concern due to site-specific factors (e.g., community and regulatory concern, high background concentrations), as well as PCDD/PCDFs, PAHs, and PCBs if not otherwise included. Notate whether each compound was detected or not detected.

In the recommended approach, a detection in any one of the sampling components (e.g., front half rinse, XAD resin, condensate, Tenax tube), in any run constitutes a detection for that specific compound. Evaluating blank contamination results [included in the quality assurance (QA) data section of the trial burn report] may be relevant when determining the non-detect status of the compounds (see Section 2.5).

Regardless of the analytical methods performed in the regulatory test burn program, we recommend that risk assessments consider PCDD/PCDFs, PAHs, and PCBs (the rationale for including these compounds is discussed in greater detail under Step 3 and in Sections 2.3.1 through 2.3.3).

Steps 2 through 4 are unnecessary for compounds detected in the stack test data analysis or identified in the fugitive emissions evaluation; they may jump to Step 5. All other compounds continue to Step 2.

FIGURE 2-3  
 COPC IDENTIFICATION



**Step 2:** Evaluate all wastes that the unit will be permitted to burn. Retain for evaluation any non-detected compound present in the waste (Section 2.4 discusses estimating concentrations for non-detects).

For example, if a facility is permitted to burn explosives which characteristically include nitroaromatic compounds, yet the stack test didn't detect any nitroaromatic compounds, it may be appropriate for nitroaromatic compounds to still be evaluated in the risk assessment. It is prudent to also consider other materials fed to the combustor (e.g. raw materials, or coal in a cement kiln).

Steps 3 and 4 are unnecessary for constituents retained as part of the Step 2 evaluation; they may jump to Step 5. All other compounds, i.e. non-detected compounds that did not satisfy Step 2, continue to Step 3.

**Step 3:** Retain for evaluation any non-detect with a high potential to be emitted as a Product of Incomplete Combustion (PIC).

As defined earlier, PICs are either present in the feed stream and not completely destroyed, or formed during the combustion process. It's therefore important to consider combustion chemistry in identifying COPCs. For example, PCDDs and PCDFs may not themselves be found in any feed stream yet still be emitted, because they can form when chlorine-containing chemicals react with organic matter in the low-temperature regions of the combustion unit or APCS. We therefore generally recommend that PCDDs and PCDFs be assessed. The potential for various PICs to be found in combustor emissions is dealt with in more detail in Sections 2.3.1 through 2.3.13, as well as EPA (2001c).

Identifying/including some compounds (nitroaromatics, phthalates, hexachlorobenzene, and pentachlorophenol) as PICs in the risk assessment may be warranted, considering waste feed composition and their potential to be emitted (e.g., nitrogenated wastes, plastics, or highly chlorinated organic waste streams) (see Sections 2.3.4 through 2.3.6).

Step 4 is unnecessary for PCDDs/PCDFs, PAH's, PCB's, and other compounds with high potential to be emitted as PICs; they may jump to Step 5. All other compounds, i.e. non-detected compounds that did not satisfy Steps 2 or 3, continue to Step 4.

**Step 4:** Retain for evaluation those compounds that (1) are a concern due to site-specific factors, and (2) may be emitted by the combustor.

As mentioned in Step 1, site-specific factors may contribute COPCs. For example, if there is community/regulatory concern about high background concentrations of a substance which would not have otherwise been assessed (i.e. it was neither a risk/trial burn analyte, nor found in the fugitive emissions evaluation), and there is reasonable potential for it to be emitted, it may be appropriate to include the compound. Also, if a compound found in the trial/risk burn analysis or fugitive emissions evaluation (and therefore included in the COPC list) doesn't satisfy Steps 2 or 3, yet is of concern for site-specific factors and has reasonable potential to be emitted, it may be appropriate for it to continue to Step 5.

If a compound doesn't have a reasonable potential of being present in the stack emissions, we generally recommend that the risk assessment report justify this assertion. This information will generally provide the risk manager with sufficient information to conclude that the facility has not overlooked a serious risk.

Compounds of concern due to site-specific factors with reasonable potential to be emitted continue to Step 5. Delete all other compounds (i.e. non-detected compounds that did not satisfy Steps 2 through 4) from consideration in the risk assessment.

**Step 5:** Research the recommended hierarchy of human health toxicity data (see Appendix A2.6) for available compound-specific health benchmarks. Add compounds with available toxicity data to the COPC list for **quantitative** assessment. Retain compounds that have no toxicity data on the COPC list for **qualitative** assessment, and use surrogate toxicity data from a toxicologically similar compound.

As detailed in Appendix A, we recommend a hierarchy of sources for toxicity data appropriate to use in the risk assessment. The tox hierarchy represents a library of sources for scientifically defensible, compound-specific human health benchmarks.

We generally recommend that the assessment of COPCs using surrogate toxicity data not be **quantitative** but rather **qualitative**, and be reported in the Uncertainty section of the risk assessment. The definition of a "toxicologically similar compound" will depend on the original compound, which in turn changes from

assessment to assessment. We recognize the uncertainties involved in even defining what constitutes “toxicologically similar.” We therefore recommend consulting with the permitting authority when identifying toxicologically similar compounds. It’s also within the permitting authority’s purview to determine that it’s technically appropriate (on a compound-specific basis) to use surrogate toxicity data quantitatively.

Previous guidance on how to qualitatively assess risk is inconsistent. Common practice is also highly variable. One option is to generate quantitative estimates for compounds using surrogate toxicity data. These results, however, aren’t typically reported with the rest of the COPCs, nor do they contribute to risk totals. Instead, the surrogate-based risk results are typically reported in the Uncertainty section of the risk assessment report, to inform risk management decision-makers.

**Please Note:** The above is only one option. We recommend consulting with the permitting authority regarding the appropriate level of effort in acquiring surrogate toxicity data, and other methods and processes to use in qualitative assessment.

**Step 6:** Evaluate the tentatively identified compound (TIC) peaks obtained during gas chromatography (GC) analysis, to determine whether any of the TICs have toxicities similar to the detected

### SPECIAL NOTE: REGARDING FATE & TRANSPORT DATA

Step 5 in Identifying COPCs focuses on availability of toxicity data because it tends to be the controlling factor: without toxicity parameter values, quantitative assessment is not possible. Depending on the compound, though, availability of fate & transport parameter values could also be a limiting factor.

If these parameter values are available, then it is scientifically reasonable, and in the interest of protecting human health and the environment, to evaluate exposure of receptors to the COPC via various direct and indirect pathways. However, if the necessary fate & transport properties for a particular exposure pathway aren’t available, then it seems reasonable to exclude that COPC from consideration for the affected pathway (or pathways). For example, if a biotransfer value for milk (see Chapter 5) is not available for a COPC then it can be assumed that, based on current information, the COPC won’t be assessed via the ingestion of milk exposure pathway. This principle holds true for other variables as well. Please note, though, that the lack of fate and transport data doesn’t automatically equate to an absence of potential exposure and risk. We generally recommend that as long as sufficient fate & transport properties are available, the calculations for each exposure pathway be completed, and any uncertainties introduced into the risk assessment described in the uncertainty discussion of the risk assessment report (see Chapter 8).

Fate & transport parameter data may be quite limited for some compounds, and acquiring that data can be a labor-intensive and time-consuming process. In an effort to streamline the risk assessment process, the fate & transport parameter values needed to follow this Protocol to assess the 200+ compounds most commonly found in hazardous waste combustor risk assessments are made available in a database companion to the HHRAP (available for download from the HHRAP web site). For those compounds not found in the database, the Superfund Chemical Data Matrix (SCDM, <http://www.epa.gov/superfund/resources/scdm/>) is a good first source to acquire the necessary values. When actual values aren’t directly available, HHRAP Appendix A also lists our recommended methods for estimating parameter values.

We generally recommend consulting with the permitting authority on the appropriate level of effort to expend acquiring/estimating fate & transport parameter values.

compounds. If they do, qualitatively assess using surrogate toxicity data, as recommended for identified compounds in Step 5.

All organic compounds that are identified and quantified are ultimately subtracted from the total organic emissions mass value. It is therefore beneficial for the laboratory to identify and quantify the maximum number of compounds, including TICs. Although it's in your interest to characterize as many TICs as possible, extensive characterization of TICs involves a significant commitment of time and expertise and can reach a point of diminishing returns. We therefore generally recommend characterizing TICs when the peak intensity is 10 percent or more of the full chromatographic scale, and obtaining a quantitative estimate of the value using the nearest eluting internal standard and a response factor of 1. Unless the identification of the TIC is confirmed by the analysis of an authentic standard, it may be appropriate to qualify the quantitative value as "estimated."

We recognize that for many compounds, only limited information on potential health effects is available. Also, for those chemicals with identified health effects, the relationship between dose and response may be poorly understood. We suggest that the risk assessment use the sum of the available toxicological information and evaluate the uncertainty associated with these issues. As stated previously, toxicity benchmarks and slope factors may change as additional toxicity research is conducted. You may wish to consult with the most current versions of the resources found in the tox hierarchy (see Appendix A, Section A2.6) before completing the risk assessment, to make sure that the toxicity data used in the risk assessment is the most current available.

Previous Agency guidance (1989e; 1994j; 1994n; 1998) recommended that the COPC list for indirect exposure analysis consist of only those constituents considered to present the most significant risks.

These constituents were selected based on the

1. quantity of the hazardous waste to be burned,
2. toxicity of the hazardous waste to be burned, and
3. potential for the hazardous waste to bioaccumulate.

For direct exposure analysis, however, previous guidance recommended including all constituents for which stack emission data and inhalation health benchmarks exist. We now recommend that a single COPC list apply to **both** indirect **and** direct exposure analysis. We believe that, through the use of computer-based calculations, you can efficiently assess all identified COPCs via both direct and indirect exposure pathways. Savings gained through computer-based calculations will provide for an efficient use

of facility and regulatory resources. Assessing the entire list of COPCs - rather than a subset as previously recommended - may help minimize public concern over the exclusion of some COPCs and reduce confusion for those interested in reviewing the results of the risk assessment.

**RECOMMENDED INFORMATION FOR THE RISK ASSESSMENT REPORT**

- C Complete evaluation of hazardous wastes to be burned in the combustor
- C Complete evaluation of any raw materials or primary fuels burned in the combustor
- C Waste analysis procedures used to monitor the composition of hazardous waste feed streams
- C Analytical data and calculations used to complete the COPC identification process

The following subsections provide specific information and guidance on identifying COPCs for each facility—with discussions for specific classes of compounds—that we typically recommend including in risk assessments. Emerging issues surrounding the class of compounds referred to as “endocrine disruptors” are also discussed.

The following subsections also focus on compounds that past experience has shown can drive risk assessments. These compounds include PCDDs/PCDFs, PAHs, PCBs, nitroaromatics, phthalates, hexachlorobenzene and pentachlorophenol, and metals. Volatile organic compounds are also discussed. We also discuss specific issues that affect the COPC identification process, and evaluating these compounds in the risk assessment.

**2.3.1 Criteria Pollutants**

Under the Clean Air Act, EPA establishes air quality standards to protect public health, including the health of "sensitive" populations such as people with asthma, children, and older adults. EPA has set national air quality standards (40 C.F.R. Part 40) for six principal air pollutants (also called the criteria pollutants): nitrogen dioxide (NO<sub>2</sub>), ozone (O<sub>3</sub>), sulfur dioxide (SO<sub>2</sub>), particulate matter (PM), carbon monoxide (CO), and lead (Pb). We discuss lead in Section 2.3.5.2, and PM in Section 2.3.7.

Nitrogen dioxide is a reddish brown, highly reactive gas that is formed in the ambient air through the oxidation of nitric oxide (NO). Nitrogen oxides (NO<sub>x</sub>), the generic term for a group of highly reactive

gases that contain nitrogen and oxygen in varying amounts, play a major role in the formation of ozone, PM, haze, and acid rain. The major sources of man-made NO<sub>x</sub> emissions are high-temperature combustion processes such as those that occur in automobiles and power plants. Short-term exposures (e.g., less than 3 hours) to low levels of NO<sub>2</sub> may lead to changes in airway responsiveness and lung function in individuals with preexisting respiratory illnesses. These exposures may also increase respiratory illnesses in children. Long-term exposures to NO<sub>2</sub> may lead to increased susceptibility to respiratory infection and may cause irreversible alterations in lung structure. NO<sub>x</sub> react in the air to form ground-level ozone and fine particle pollution, which are associated with adverse health effects (U.S. EPA 2005).

Ozone occurs naturally in the stratosphere approximately 10 to 30 miles above the earth's surface and forms a layer that protects life on earth from the sun's harmful rays. Ozone is also formed at ground level by a chemical reaction of various air pollutants combined with sunlight. The pollutants that contribute to ozone formation are oxides of nitrogen (NO<sub>x</sub>) and volatile organic compounds (VOCs). "Ground-level" ozone is an air pollutant that damages human health and the environment. Even at relatively low levels, ozone may cause inflammation and irritation of the respiratory tract, particularly during physical activity. The resulting symptoms can include breathing difficulty, coughing, and throat irritation. Breathing ozone can affect lung function and worsen asthma attacks. Ozone can increase the susceptibility of the lungs to infections, allergens, and other air pollutants. Medical studies have shown that ozone damages lung tissue and complete recovery may take several days after exposure has ended (U.S. EPA 2004a).

Sulfur dioxide (SO<sub>2</sub>) belongs to the family of SO<sub>x</sub> gases. These gases are formed when fuel containing sulfur (mainly coal and oil) is burned at power plants and during metal smelting and other industrial processes. High concentrations of SO<sub>2</sub> can result in temporary breathing impairment for asthmatic children and adults who are active outdoors. Short-term exposures of asthmatic individuals to elevated SO<sub>2</sub> levels during moderate activity may result in breathing difficulties that can be accompanied by symptoms such as wheezing, chest tightness, or shortness of breath. Other effects that have been associated with longer-term exposures to high concentrations of SO<sub>2</sub>, in conjunction with high levels of PM, include aggravation of existing cardiovascular disease, respiratory illness, and alterations in the lungs' defenses. The subgroups of the population that may be affected under these conditions include individuals with heart or lung disease, as well as the elderly and children (U.S. EPA 1986d; 2005).

Carbon monoxide is a colorless and odorless gas, formed when carbon in fuel is not burned completely. It is a component of motor vehicle exhaust, which contributes about 60 percent of all CO emissions

nationwide. Other sources of CO emissions include industrial processes, non-transportation fuel combustion, and natural sources such as wildfires. CO enters the bloodstream through the lungs and reduces oxygen delivery to the body's organs and tissues. The health threat from levels of CO sometimes found in the ambient air is most serious for those who suffer from cardiovascular disease such as angina pectoris. At much higher levels of exposure not commonly found in ambient air, CO can be poisonous, and even healthy individuals may be affected. Visual impairment, reduced work capacity, reduced manual dexterity, poor learning ability, and difficulty in performing complex tasks are all associated with exposure to elevated CO levels (U.S. EPA 2000d).

The permitting authority decides whether to include criteria pollutants in the quantitative risk assessment. For example, as noted in the November 14, 1997, decision of the Environmental Appeals Board in reference to the Ash Grove Cement Company Permit No. KSD031203318 and risks associated with exposure to cement kiln dust controlled through the state solid waste permit, compliance with other environmental statutes (e.g., CAA, CWA) may be an appropriate method to consider and control risks from non-RCRA related pollutants (Environmental Appeals Board 1997).

### **2.3.2 Endocrine Disruptors**

Endocrine disruptors are chemicals are thought to mimic natural hormones, inhibit the action of hormones, or alter the normal regulatory function of the immune, nervous, and endocrine systems. Possible human health endpoints affected by these agents include breast cancer and endometriosis in women, testicular and prostate cancers in men, abnormal sexual development, reduced male fertility, alteration in pituitary and thyroid gland functions, immune suppression, and neurobehavioral effects (U.S. EPA 1997g).

Problems were encountered while attempting to classify chemical compounds as endocrine disruptors. Only limited empirical data are available to support the designation of specific chemicals as endocrine disruptors, and some of the data are conflicting. There is a lack of clear structure-activity relationship, as well as a lack of unifying dose-response relationship, among the diverse groups of chemicals considered endocrine disruptors. Also, there are multiple modes of action for chemicals currently considered endocrine disruptors.

Because the information currently available on endocrine disruptors is inconsistent and limited, U.S. EPA has not yet developed a methodology for quantitative assessments of human health risk resulting from

exposure to potential endocrine disruptors (U.S. EPA 1996i). However, the methods for addressing endocrine disruptors are developing at a rapid pace. We therefore generally recommend contacting the Economics, Methods and Risk Analysis Division (EMRAD) of the Office of Solid Waste for the latest guidance on how to address endocrine disruptors in site-specific risk assessments. Additional information (e.g., U.S. EPA 1997g) is available for review at the web site <http://epa.gov/endocrine/pubs.html>.

### **2.3.3 Hexachlorobenzene and Pentachlorophenol**

In past guidance (U.S. EPA 1994g; 1994i; 1994j; 1994r) we recommended always including hexachlorobenzene and pentachlorophenol in risk assessments of hazardous waste combustors. However, we no longer recommend automatically including them. Rather, we generally recommend carefully considering the information and issues presented below before deciding whether to include hexachlorobenzene and pentachlorophenol as COPCs for quantitative assessment.

Hexachlorobenzene is an impurity in pentachlorophenol, while pentachlorophenol is formed from hexachlorobenzene in the body as well as in some factories (ATSDR 1994a; ATSDR 1994b). Hexachlorobenzene and pentachlorophenol, like all chlorinated aromatics, are synthesized by the reaction of elemental chlorine with a parent aromatic (Deichmann and Keplinger 1981; Grayson 1985). The addition of the first chlorine atom to the benzene or phenol molecule is rapid, but further chlorination becomes progressively more difficult, requiring ferric chloride or another Lewis acid catalyst to complete the reaction (March 1985). Therefore, these chlorinated compounds are difficult to make even under controlled conditions. Hexachlorobenzene, but not pentachlorophenol, has been reported in emissions from the combustion of municipal solid waste and from other processes (such as the chlorination of wood pulp) that also produce PCDDs and PCDFs (ATSDR 1994a; ATSDR 1994b). The combustion properties of these chlorinated compounds indicate that they aren't likely to be formed as PICs if they aren't present in the waste feed stream.

We consider it prudent to include hexachlorobenzene and pentachlorophenol as COPCs for combustors that burn waste feeds containing hexachlorobenzene and pentachlorophenol, wood preservatives, pesticides, or highly variable waste streams such as municipal solid waste. However, we don't recommend precluding these compounds from analytical testing during the trial burn based only on process knowledge and waste feed characteristics. Because PCDDs and PCDFs can be formed from fly ash-catalyzed reactions between halogens and undestroyed organic material from the furnace, other

Agency guidance (U.S. EPA 1994i; 1998c) recommends including potential precursor compounds in the risk assessment and trial burn (see Section 2.3). These precursor compounds might include chlorinated phenols (such as pentachlorophenol) and chlorinated aromatics (such as hexachlorobenzene). Also, the toxicity and uncertainties associated with combustion chemistry suggest that stack gas testing always confirm the absence of these compounds from stack emissions.

#### **2.3.4 Hydrogen Chloride/Chlorine Gas**

Hydrogen chloride (which becomes hydrochloric acid when dissolved in water) and chlorine are major products of the chemical industry, with uses too numerous to list. When chlorine gas dissolves in water (whether during drinking water treatment or when someone inhales chlorine), it hydrolyzes to form equal amounts of hydrochloric acid and hypochlorous acid; the adverse effects of which are similar but not identical (Stokinger 1981; ACGIH 1991).

Hydrochloric acid has many uses. It is used in the production of chlorides, fertilizers, and dyes, in electroplating, and in the photographic, textile, and rubber industries. Hydrochloric acid is corrosive to the eyes, skin, and mucous membranes. Acute (short-term) inhalation exposure may cause eye, nose, and respiratory tract irritation and inflammation and pulmonary edema in humans. Acute oral exposure may cause corrosion of the mucous membranes, esophagus, and stomach and dermal contact may produce severe burns, ulceration, and scarring in humans. Chronic (long-term) occupational exposure to hydrochloric acid has been reported to cause gastritis, chronic bronchitis, dermatitis, and photosensitization in workers. Prolonged exposure to low concentrations may also cause dental discoloration and erosion (U.S. DHHS 1993).

Chlorine is a potent irritant to the eyes, the upper respiratory tract, and lungs. Chronic (long-term) exposure to chlorine gas in workers has resulted in respiratory effects, including eye and throat irritation and airflow obstruction (Cal EPA 2000). Depending on the exposure concentration, acute (short-term) exposure to chlorine elicits reactions ranging from tickling of the nose and throat (Calabrese and Kenyon 1991) to chest pain, vomiting, dyspnea, and cough (U.S. DHHS 1993). Chlorine is also extremely irritating to the skin and can cause severe burns in humans (U.S. DHHS 1993).

### 2.3.5 Metals

Previous guidance (U.S. EPA 1994g; 1994i; 1998c; NC DEHNR 1997) recommends including the following inorganic substances in the risk assessment: antimony, arsenic, barium, beryllium, cadmium, hexavalent chromium, lead, mercury (elemental and divalent), nickel, selenium, silver, thallium, and zinc. All of these substances, except nickel, selenium, and zinc, are regulated by 40 CFR Part 266, Subpart H (the BIF regulations). We recommend evaluating nickel and selenium, to determine whether additional terms and conditions may need to be incorporated into the permit, pursuant to 42 USC § 6925(c)(3) and 40 CFR Part 270.32(b)(2)—i.e., U.S. EPA’s “omnibus” authority. In addition, U.S. EPA (2001c) recommends also characterizing the metals aluminum, copper, manganese, and vanadium. Another potential option is applying the BIF regulation Tier I or MACT MTEC assumptions, which assume that all metals in the waste feed pass through the combustion unit and APCS to the emission stream (U.S. EPA 1992c).

**Please Note:** It may be appropriate to include metals in the risk assessment even if they aren’t present in the combustor’s feed streams. Although metals cannot be formed as PICs, we are aware of combustors with metal emissions resulting from leaching from stainless steel feed piping.

#### RECOMMENDED INFORMATION FOR THE RISK ASSESSMENT REPORT

- C Waste feed, raw material, and secondary fuel stream analytical data
- C Metal emission rate sampling data or assumptions based on waste feed data
- C Explanations for excluding specific metals from evaluation during the risk assessment

The following subsections provide additional information on our recommended procedures for evaluating four metals—chromium, lead, mercury, and nickel. When evaluating stack emissions for the risk assessment, we highly recommend considering how each of these metals may be affected by the combustion process, including possible interactions with other constituents.

#### 2.3.5.1 Chromium

The oxidation state of chromium is a crucial issue in evaluating the toxicity of this metal, and the risks associated with exposure. Hexavalent chromium ( $\text{Cr}^{+6}$ ) is the most toxic valence state of chromium and

has been shown to be a human carcinogen through inhalation exposure (U.S. EPA 2005i). Trivalent chromium ( $\text{Cr}^{+3}$ ) is a commonly found, less-oxidized form of chromium. Trivalent chromium has not been shown to be carcinogenic in either humans or laboratory animals (U.S. EPA 2005i). U.S. EPA (1990a; 1990b) has indicated that chromium emitted from a combustor is not likely to be in the hexavalent form. However, there is not sufficient evidence to reliably estimate the partitioning of chromium emissions into these two valence states. In addition, we recognize that chromium may exist partially or in some cases entirely as trivalent chromium in various media. For example, Amdur et al. (1991) states that:

“Trivalent chromium is the most common form found in nature, and chromium in biological materials is probably always trivalent. There is no evidence that trivalent chromium is converted to hexavalent forms in biological systems. However, hexavalent chromium readily crosses cell membranes and is reduced intracellularly to trivalent chromium..”

We generally consider it best to use measured, speciated emissions data in the risk assessment. If site-specific speciated emissions data is unavailable, you may generate a default speciation. We generally recommend using the following method (developed by us through interpretation of data available in the MACT database, as documented in Appendix D) to generate a default speciation:

- When the measured amount of total chromium is  $<10$  : g/dscm, we recommend a default of 5 : g/dscm hexavalent chromium.
- When the measured amount of total chromium is in the range of 10 : g/dscm to 100 : g/dscm, we recommend assuming 45 percent is hexavalent chromium.
- When the measured amount of total chromium is  $>100$  : g/dscm, we recommend assuming 30 percent is hexavalent chromium.

### **2.3.5.2 Lead**

We generally recommend that risk assessments evaluating lead as a COPC use the IEUBK model when soil concentrations are calculated to be above the benchmark.

The Integrated Risk Information System (IRIS) doesn't currently list an RfD or RfC for lead, because a threshold level for exposure to lead has not been established. While the Agency has characterized lead as a probable human carcinogen, it has not developed a quantitative estimate of cancer risk due to a number of uncertainties, some of which may be unique to lead (U.S. EPA 2005b). The Agency has typically relied on the neurological effects observed in children as the sensitive endpoint for evaluating lead toxicity. Consequently, the Agency developed the integrated Exposure Uptake Biokinetic (IEUBK)

Model for Lead in Children. Developed through the efforts of U.S. EPA (1990c) and Kneip, et al. (1983), this model evaluates potential risks based on predicted blood lead levels associated with exposure to lead (U.S. EPA 1994e). The IEUBK model integrates several assumptions about the complex exposure patterns and physiological handling of lead by the body, and it has been validated at several sites at which lead exposure data and human blood lead levels are available (U.S. EPA 1990c). The U.S. EPA Science Advisory Board (U.S. EPA 1992b) and the U.S. EPA's Technical Review Workgroup for Lead have both reviewed and recommended the IEUBK model.

The Agency has developed a computerized version of the IEUBK model that predicts blood lead levels and distributions for children 0 to 7 years of age (U.S. EPA 1994e). The IEUBK model is available for download at <http://www.epa.gov/superfund/programs/lead/products.htm>. The IEUBK computer model cannot predict potential blood lead levels in adults. The Agency has developed an *Interim Approach to Assessing Risks Associated with Adult Exposures to Lead in Soil* (U.S. EPA 1996r). This interim model is intended for "assessing adult lead risks associated with nonresidential [industrial] exposure scenarios." However, in general, children are more susceptible to lead exposures than adults because of higher soil ingestion rates and greater absorption by the gut, in addition to nutritional variables and lower body weight. In fact, The Agency's interim approach for assessing adult exposures to lead is based not on limiting adult toxicity, but rather on limiting fetal toxicity by limiting indirect fetal exposure through direct maternal exposures to lead (U.S. EPA 1996r).

As stated before, we generally recommend that risk assessments evaluating lead as a COPC use the IEUBK model when soil concentrations are calculated to be above the benchmark. We don't generally recommend evaluating carcinogenic risks or noncarcinogenic hazards of lead. When run with standard recommended default values (these generally represent national averages, or "typical" values), the Agency's IEUBK model predicts that no more than 5 percent of children exposed to a lead concentration in soil of 400 mg/kg will have lead concentrations in blood exceeding 10 µg/dL (U.S. EPA 1994e and 1994o).

### **2.3.5.3 Mercury**

We generally recommend that the risk assessment evaluate exposure to three mercury species via varied pathways:

1. Assess elemental mercury only through direct inhalation of the vapor phase;

2. Assess divalent mercury through both direct inhalation and indirect exposure to vapor and particle-bound mercuric chloride; and.
3. Assess methyl mercury only through indirect exposure.

Air emissions of mercury contribute to local, regional, and global deposition. The U.S. Congress explicitly found this to be the case and required the Agency to prioritize maximum achievable control technology (MACT) controls for mercury (U.S. Congress 1989).

The *Mercury Study Report to Congress* (U.S. EPA 1997c) found that anthropogenic mercury releases are thought to be dominated on the national scale by industrial processes and combustion sources that release mercury into the atmosphere. A portion of these anthropogenic releases is in the form of elemental mercury, and a portion in the form of mercuric chloride. Coal combustion is responsible for more than half of all mercury emissions from U.S. anthropogenic sources. The fraction of coal combustion emissions in oxidized form (i.e. mercuric chloride) is thought to be less than the fraction in oxidized form from other combustion emission sources (including waste incineration).

Stack emissions include both vapor and particulate forms of mercury. Most of the total mercury emitted from the stack is in the vapor phase, although exit streams containing soot or particulates can bind up some fraction of the mercury. Vapor mercury emissions are thought to include both elemental ( $\text{Hg}^0$ ) and oxidized (e.g.,  $\text{Hg}^{+2}$ ) chemical species. Particulate mercury emissions are thought to be composed primarily of oxidized compounds, due to the relatively high vapor pressure of elemental mercury (U.S. EPA 1997c).

The methods for analyzing mercury speciation in emission plumes are being refined, and there is still controversy in this field. The speciation of mercury emissions is thought to depend on the fuel used, flue gas cleaning, and operating temperatures. True speciation of mercury emissions from the various source types is still uncertain and thought to vary not only among source types, but also between individual plants (U.S. EPA 1997c). Total mercury exiting the stack is assumed to consist entirely of elemental and divalent species, with no emissions of methyl mercury. The exit stream is thought to range from almost all elemental mercury to nearly all divalent mercury. Much of the divalent mercury is thought to be mercuric chloride ( $\text{HgCl}_2$ ) (U.S. EPA 1997c), particularly in the combustion of wastes containing chlorine. The divalent fraction is split between vapor and particle-bound phases (Lindqvist et al. 1991).

Please note that data on mercury speciation in stack emissions is very limited. Also, the behavior of mercury emissions close to the point of release has not been extensively studied. It is possible for chemical reactions to occur in the emission plume. This results in a significant degree of uncertainty implicit in modeling mercury emissions. Additional examples of uncertainties include the precision of measurement techniques, estimates of pollution control efficiency, limited data specific to source class and activity level. U.S. EPA (1997c) discusses uncertainty, and sensitivity analyses of several of the assumptions used in the modeling of mercury emissions. Additional discussions and examples of mercury modeling can be found in the proceedings of the IT3 conference (Kaleri 2000).

### **Site-Specific Mercury Sampling**

If site-specific mercury sampling information is available, one option is to estimate the oxidation state and phase distributions. We recommend basing the estimates on the concentration of mercury in various components of the Agency's multiple metals sampling train (i.e., U.S. EPA Method 29 or Method 0060) using the following guidelines:

- Mercury found in the acidic potassium permanganate impingers would be expected to be the elemental form of mercury ( $\text{Hg}^0$ ).
- Divalent mercury ( $\text{HgCl}_2$ ) is soluble in water and would be expected to be found in the dilute nitric acid/hydrogen peroxide impinges. This is also referred to as the ionic portion.
- Mercury found in the probe and filter can be assumed to be vapor-phase mercury adsorbed onto particulate matter or a solid-phase compound. This fraction is referred to as Hg(PM).

We understand that these methods can be biased by high  $\text{SO}_2$  and trace  $\text{Cl}_2$  in the feed. This bias results in the over-reporting of ionic vapor (or divalent form) and the under-reporting of elemental vapor mercury. For risk assessment purposes, we consider this protective.

### **Default Phase Allocation and Speciation of Mercury Exiting the Stack**

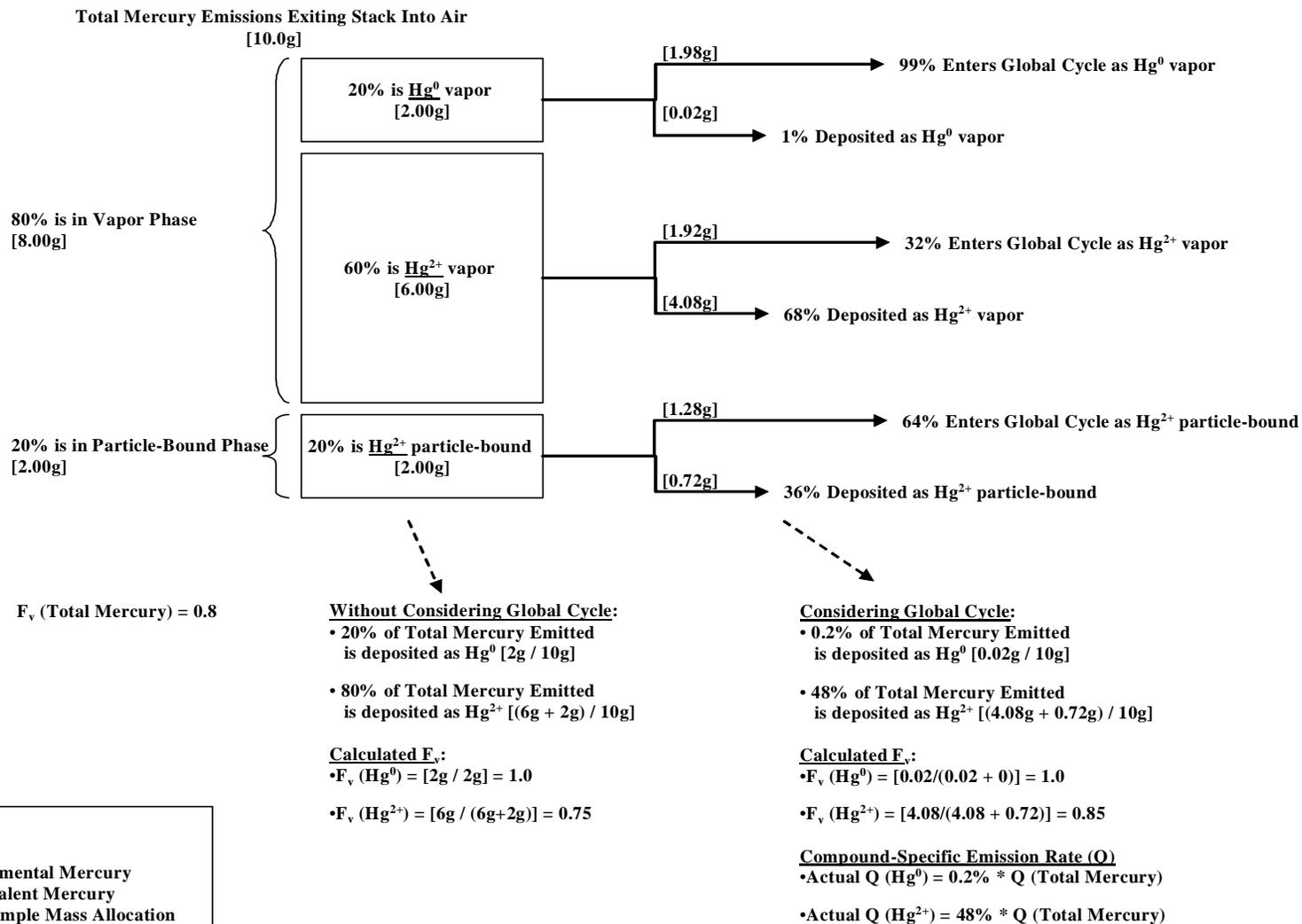
As discussed above, stack emissions are thought to be speciated into both divalent and elemental mercury, and include both vapor and particle-bound forms. Vapor-phase divalent mercury is thought to be more rapidly and effectively removed by both dry and wet deposition than particle-bound divalent mercury. This is a result of the reactivity and water solubility of vapor-phase divalent mercury (Lindberg et al. 1992; Peterson et al. 1995; Shannon and Voldner 1994). Also, divalent mercury emitted either in the

vapor phase or particle-bound, is thought to be subject to much faster atmospheric removal than elemental mercury (Lindberg et al. 1992; Peterson et al. 1995; Shannon and Voldner 1994). A small fraction (about one percent) of vapor-phase elemental mercury may be atmospherically transformed into divalent mercury by tropospheric ozone and adsorbed to particulate soot in the air and subsequently deposited in rainfall and snowfall (U.S. EPA 1997c).

Based on review of mercury emissions data presented for combustion sources in U.S. EPA (1997c) and published literature (Peterson et al. 1995), estimates for the percentage of vapor and particle-bound mercury emissions range widely from 20 to 80 percent. Therefore, unless site-specific mercury sampling information is available, we generally recommend a protective approach that assumes phase allocation of mercury emissions from hazardous waste combustion of 80 percent of total mercury in the vapor phase and 20 percent of total mercury in the particle-bound phase. As illustrated in Figure 2-4, of the 80 percent total mercury in the vapor phase, 20 percent of the total is in the elemental form and 60 percent of the total is in the divalent form (Peterson et al. 1995). Of the 20 percent of the total mercury that is particle-bound, 99 percent (assumed to be 100 percent in Figure 2-4) is in the divalent form. This allocation is:

- C Consistent with mercury emissions speciation data for hazardous waste combustion sources reported in literature (Peterson et al. 1995); and
- C Believed to be reasonably protective, since it results in the highest percentage of total mercury being deposited in proximity to the source, and therefore, indicative of the maximum indirect risk.

**FIGURE 2-4  
 PHASE ALLOCATION AND SPECIATION OF MERCURY IN AIR**



### **The Mercury Global Cycle**

According to information in U.S. EPA (1997c), a vast majority of mercury exiting the stack doesn't readily deposit, but is vertically diffused to the free atmosphere, transported outside the study area and into the global cycle. Regardless of the source of phase and speciation distribution values (i.e. either site-specific sampling data or default values), we generally recommend using the following fractions from U.S. EPA (1997c):

- A vast majority of the vapor-phase elemental mercury (over 99 percent) doesn't readily deposit, but becomes part of the global cycle;
- Of the mercury emitted as vapor-phase divalent mercury, about 68 percent deposits and about 32 percent diffuses vertically to the global cycle; and
- 36 percent of the particle-bound divalent mercury deposits, and the rest diffuses vertically to the global cycle.

### **Deposition and Modeling of Mercury**

Based on information in U.S. EPA (1997c) and as shown in Figure 2-4, we generally assume that deposition to the various environmental media is almost entirely divalent mercury in either the vapor or particle-bound form. Without considering the global cycle, 80 percent of total mercury would be deposited as divalent mercury and the remaining 20 percent would be deposited as elemental mercury.

We generally recommend using the percentages provided in U.S. EPA (1997c) to account for the global cycle. Using these figures, the percentage of total mercury deposited would be reduced to a total of 48.2 percent (40.8 percent as divalent vapor, 7.2 percent as divalent particle-bound, and 0.2 percent as elemental vapor). As discussed in Appendix A-2, these speciation splits result in fraction in vapor phase ( $F_v$ ) values of 0.85 (40.8/48.0) for divalent mercury, and 1.0 (0.2/0.2) for elemental mercury. Also, to account for the remaining 51.8 percent of the total mercury mass that is not deposited, the deposition and media concentration equations (presented in Appendix B), multiply the compound-specific emission rate ( $Q$ ) for elemental mercury by a default value of 0.002; and divalent mercury by a default value of 0.48.

### **Methylation of Mercury**

The net mercury methylation rate (the net result of methylation and demethylation) for most soils appears to be quite low; with much of the measured methyl mercury in soils potentially resulting from wet deposition (U.S. EPA 1997c). Based on the information in U.S. EPA (1997c), We assume that 98 percent

of the deposited mercury remains divalent mercury, and two percent speciates to organic mercury (methyl mercury) in soil. A significant and important exception to mercury methylation rate being low in soils appears to be wetland soils. Wetlands appear to convert a small but significant fraction of the deposited mercury into methyl mercury; which can migrate to nearby water bodies and potentially bioaccumulate in the aquatic food chain (U.S. EPA 1997c). Therefore, we assume the percentage of methyl mercury in wetland soils is higher than the 2 percent assumed for non-wetland soils. However, wetlands soils aren't specifically considered in any of the exposure pathways represented in the recommended human health exposure scenarios (see Chapter 4).

Both watershed erosion and direct atmospheric deposition can be important sources of mercury to a water body (U.S. EPA 1997c). There appears to be a great deal of variability in the processing of mercury among water bodies. As a result, you can generally expect different water body types to have different ranges of methylation, with wetlands generally expected to have higher percentages of methyl mercury than lakes, and lakes subsequently more than rivers or streams (Driscoll et al. 1994; Hurley et al. 1995; Krabbenhoft et al. 1999; Watras et al. 1995). Studies have also shown that rivers or lakes with wetland components (particularly riparian wetlands) have an increased methyl mercury content (Hurley et al. 1995; Krabbenhoft et al. 1999; St. Louis et al. 1996). The percentage of the water body that constitutes a riparian wetland also contributes (i.e., the higher percentage - the higher the methyl mercury concentration). The watershed is also an important factor in determining the methyl mercury concentration of the water body. Waterbodies that are surrounded by agricultural or forested land tend to have higher methylation fractions. Waterbodies that are surrounded by mining activities have high amounts of inorganic mercury in the water, and therefore have a lower methylation efficiency (Krabbenhoft et al. 1999). As briefly discussed later in this section, this variability in methylated mercury concentrations is primarily due to the characteristically wide range of chemical and physical properties of water bodies. Additionally, mercury entering the water body can be methylated predominantly through biotic processes (U.S. EPA 1997c).

In the absence of site-specific measurements to support evaluation of water body properties and biotic conditions relevant to mercury methylation, we generally recommend assuming that 85 percent of total mercury in surface water is divalent mercury, and the remaining mass is methyl mercury. This percentage (i.e., 15 percent as methyl mercury) is based on the average of reported values for the fraction of total mercury that is methyl mercury in surface water (Akagi et al. 1979; Bloom and Effler 1990; Bloom et al. 1991; Gill and Bruland 1990; Kudo et al. 1982; Lee and Hultberg 1990; Parks et al. 1989; Watras and Bloom 1992). These literature sources were originally presented in the SAB Review Draft of the

Mercury Study Report to Congress (U.S. EPA 1996s). The final Mercury Study Report to Congress (U.S. EPA 1997c, Volume III; Appendix D) also presents literature values for the fraction of methyl mercury in the water column. However, the data are specific to the epilimnion and hypolimnion. For the epilimnion, reported values range from 4.6 percent to 15 percent, with a point estimate of 7.8 percent. For the hypolimnion, reported values range from 27 percent to 44 percent, with a point estimate of 36 percent.

We are modifying our previous recommendation for applying the default mercury speciation (85 percent divalent mercury and 15 percent methyl mercury) to each calculated water body loading. Instead, we recommend that a dissolved water concentration first be calculated for total mercury using the fate and transport parameters specified for mercuric chloride. Then, the dissolved total mercury concentration should be apportioned based on an 85 percent divalent and 15 percent methyl mercury speciation split in the water body. Appendix B (Table B-4-24) presents the equations we recommend for applying the speciation assumptions.

For most environmental systems, the literature suggests that various physical and chemical conditions may influence the methylation of mercury. In some cases you might need to consider these conditions, and the magnitude of their potential impact, to assess the potential for over- or under-predicting mercury methylation in media and subsequent biotransfer up the food chain. There is extreme variation between modeled environmental systems, and at times disagreement in the literature regarding the quantitative influence of specific conditions on methylation. Table 2-4 summarizes the qualitative effects that some physical and chemical conditions, as reported in literature, may have on methylation. We therefore generally recommend conducting extensive research of literature specific to the conditions prevalent at the site, before deviating from the protective assumptions recommended above.

More recent advances in scientific understanding of the physical, chemical, and biological processes controlling mercury speciation and partitioning in water bodies are summarized in U.S. EPA (2005g).

TABLE 2-4

**QUALITATIVE EFFECTS OF  
 PHYSICAL & CHEMICAL CONDITIONS ON METHYLATION**

Physical or Chemical Condition	Qualitative Influence on Methylation	Referenced Literature
Low dissolved oxygen	Enhanced methylation	Rudd et al. 1983; Parks et al. 1989
Decreased pH	Enhanced methylation in water column	Xun 1987; Gilmour and Henry 1991; Miskimmin et al. 1992
Decreased pH	Decreased methylation in sediment	Ramlal et al. 1985; Steffan et al. 1988
Increased dissolved organic carbon (DOC)	Enhanced methylation in sediment	Chois and Bartha 1994
Increased dissolved organic carbon (DOC)	Decreased methylation in water column	Miskimmin et al. 1992
Increased salinity	Decreased methylation	Blum and Bartha 1980
Increased nutrient concentrations	Enhanced methylation	Wright and Hamilton 1982; Jackson 1986; Regnell 1994; Beckvar et al. 1996
Increased selenium concentrations	Decreased methylation	Beckvar et al. 1996
Increased temperature	Enhanced methylation	Wright and Hamilton 1982; Parks et al. 1989
Increased sulfate concentrations	Enhanced methylation	Gilmour and Henry 1991; Gilmour et al. 1992
Increased sulfide concentrations	Enhanced methylation	Beckvar et al. 1996

The deposition and media concentration equations that we generally recommend (presented in Chapter 5 and Appendix B) have been modified specifically to account for the methylation and subsequent biotransfer of mercury, assuming steady-state conditions. The HHRAP companion database provides the parameter values specific for methyl mercury, and Appendix A-2 includes additional discussion and reference on their origin.

As noted above, methylation can be highly variable between environmental systems. This results in a significant degree of uncertainty implicit in the modeling of mercury methylation. To expand on the qualitative information presented in Table 2-4, and to better understand conditions that may influence mercury methylation specific to a site, we recommend reviewing the related information presented in U.S. EPA (1997c; 2005).

We generally recommend using the equations and protective assumptions presented in this guidance to estimate risks associated with mercury. If estimated risks exceed target levels, it may be appropriate to use more extensive site-specific data (if available) and subsequently a more rigorous modeling effort, to further evaluate points of potential exposure. For example, if sufficient site-specific data is available, it could be used in a model that predicts transformation of chemical forms and biotransfer of mercury. One such model is the SERAFM (Spreadsheet Ecological Risk Assessment for the Fate of Mercury) model developed by EPA's Office of Research and Development, National Exposure Research Laboratory, Ecosystems Research Division. SERAFM updates the IEM-2M mercury fate and transport algorithms described in detail in U.S. EPA (1997c) by incorporating more recent advances in scientific understanding of the physical, chemical, and biological processes controlling mercury speciation and partitioning in water bodies. The SERAFM enhancements to IEM-2M are summarized in U.S. EPA (2005g).

SERAFM is written in an easy-to-implement Microsoft Excel format so that all manipulations, parameters and equations are readily available to the user. By specifying only a few additional water body parameters beyond those already utilized in this guidance (i.e., water body pH, dissolved organic carbon and color), the user is able to model specific water body mercury transformation processes instead of using the default speciation assumptions (i.e., 85 percent divalent/15 percent methyl). In the SERAFM model, mercury species are subject to several transformation reactions including photo-oxidation and dark oxidation of elemental mercury in the water column, photo-reduction and methylation of divalent mercury in the water column and sediment layers, and photo-degradation and demethylation of methyl mercury in the water column and sediment layers. For hazardous waste combustion sources, it is recommended that, watershed soil concentrations and water body loadings due to source deposition be calculated externally to SERAFM using the equations presented in Chapter 5 (Equations 5-1E and 5-28) and then linked to the appropriate SERAFM worksheets for calculation of speciated mercury concentrations in the water body.

The decision to use more complex mercury models in a risk assessment is not precluded just because they are different from the model we recommend in the HHRAP. It is for the permitting authority to decide whether the assessment will use more complex mercury models. If you use more complex mercury models, we recommend ensuring that sufficient and reliable site-specific data is readily available, and then carefully identifying and evaluating the models' associated limitations, and clearly documenting the evaluation in the Uncertainty section of the risk assessment report.

## **Conclusion**

We encourage all facilities to implement a combination of waste minimization and control technology options to reduce mercury emission rates on an ongoing basis. Realistic expectations for mercury emission reduction efforts may be established by considering various technology-based mercury emission limits that apply to waste combustors (for example, standards for European combustors, the MACT standards for hazardous waste combustors, or the MACT standards for municipal waste combustors). We acknowledge that site-specific risk assessments as currently conducted may not identify the entire potential risk from mercury emissions. Mercury that doesn't deposit locally will ultimately enter the global mercury cycle for potential deposition elsewhere.

### **2.3.5.4 Nickel**

We generally recommend evaluating nickel as an inhalation carcinogen using the inhalation unit risk factor for nickel refinery dust. We generally recommend evaluating nickel for other effects using the oral RfD for nickel soluble salts, the only available nickel-related RfD (see Appendix A-2 and the HHRAP companion database).

Nickel refinery dust is identified as a potential human inhalation carcinogen (U.S. EPA 2005i). Major components of nickel refinery dust include nickel subsulfide, nickel oxide and nickel sulfate. IRIS classifies nickel subsulfide - the primary component (roughly 50%) of nickel refinery dust - a Class A human carcinogen (U.S. EPA 2005e). However, all components responsible for the carcinogenicity of nickel refinery dust have not been conclusively established (U.S. EPA 2005c). Because the component (or components) of nickel refinery dust causing it to be carcinogenic have not been conclusively established, we consider it appropriate to evaluate nickel emissions as a potential carcinogen via the inhalation pathway. In addition, nickel oxides can be reduced to nickel sulfates (some of which are carcinogenic) in the presence of sulfuric acid (Weast 1986). Hazardous waste combustors which burn wet wastes containing significant amounts of nickel and sulfur may need to be especially concerned with nickel emissions.

We generally recommend evaluating nickel as an inhalation carcinogen because some forms of nickel—including nickel carbonyl, nickel subsulfide, and nickel refinery dust—are considered carcinogens (U.S. EPA 2005c,d,e). This is contrary to the Agency's previous analysis of the toxicity of

nickel emissions from hazardous waste combustors. These forms of nickel were not considered in developing the BIF regulations, because the BIF regulations assumed that nickel can only be emitted as nickel oxide, which by itself is not considered to be a carcinogen (U.S. EPA 1991a).

If the permitting authority has information at points of potential inhalation exposure that demonstrate the absence of nickel refinery dust components, or the presence only of noncarcinogenic nickel species, it may be appropriate to use this information as the basis for supplemental noncarcinogenic calculations. For exposure pathways other than inhalation, nickel has not been shown to be carcinogenic (U.S. EPA 2005i).

### **2.3.6 Nitroaromatics**

We generally recommend carefully considering the information in the following paragraphs before deciding the appropriateness of including nitroaromatic organic compounds in the risk assessment. It is reasonable to include nitroaromatics as COPCs if the combustor feed streams include nitroaromatic compounds or close relatives (TDA and TDI).

*Please Note:* In earlier guidance (U.S. EPA 1994g; 1994i; 1994j; 1994r) we recommended that risk assessments always include nitroaromatic organic compounds, including 1,3-dinitrobenzene; 2,4-dinitrotoluene; 2,6-dinitrotoluene; nitrobenzene; and pentachloronitrobenzene. We no longer recommend **automatically** including nitroaromatic organic compounds in risk assessments.

Nitroaromatic organic compounds such as 1,3-dinitrobenzene; 2,4-dinitrotoluene; 2,6-dinitrotoluene; nitrobenzene; and pentachloronitrobenzene (or close relatives such as toluenediamine [TDA] and toluene diisocyanate [TDI]—derivatives of dinitrotoluene) are typically associated with explosives and other highly nitrogenated hazardous wastes. Dinitrotoluene is used to make two products: trinitrotoluene and TDA. TDA is, in turn, used to make TDI. TDI readily reacts with water, and is therefore very unstable at ambient conditions. TDI is typically reacted with a polyol to form polyurethane (PU) plastics.

Combustion properties of these nitroaromatic compounds indicate that they won't be formed as PICs if they aren't present in the waste feed stream, mainly because of the thermodynamic and chemical difficulty of adding a nitro group to an aromatic. The process requires that (1) nitronium ions be generated, and (2) an aromatic ring react with the nitronium ion, with the nitronium ion attaching to the ring. This reaction process is not likely to occur in a hazardous waste combustor because (1) the reaction is typically carried out by using a "nitrating acid" solution consisting of three parts concentrated nitric

acid to one part sulfuric acid, and (2) nitronium ions aren't usually formed in a combustor environment (if they are, a thermodynamically more favorable reaction will occur, thereby eliminating the nitronium ion) (Hoggett, et al 1971; Schofield 1980; March 1985).

Combustion conditions most likely to result in nitrogenated PICs are associated with premature quenching of the primary flame—resulting from low temperature or excess air in the primary combustion chamber of the unit (U.S. EPA 1994j). Under such conditions, sampling for hydrogen cyanide is also recommended (U.S. EPA 1994j).

### **2.3.7 Particulate Matter**

We don't recommend evaluating PM as a separate COPC in the risk assessment. However, PM is generally quite useful as an indicator variable, because it can be measured in real time and is sensitive to changes in combustion conditions.

Particle pollution is a mixture of solid particles and liquid droplets found in the air. Some particles are emitted directly from a source, while others form in complicated chemical reactions in the atmosphere. In general, particle pollution consists of a mixture of larger materials, called "coarse particles," and smaller particles, called "fine particles." Coarse particles have diameters ranging from about 2.5 micrometers ( $\mu\text{m}$ ) to more than 40  $\mu\text{m}$ , while fine particles, also known as known as PM<sub>2.5</sub>, include particles with diameters equal to or smaller than 2.5  $\mu\text{m}$ . EPA also monitors and regulates PM<sub>10</sub>, which refers to particles less than or equal to 10  $\mu\text{m}$  in diameter. PM<sub>10</sub> includes coarse particles that are "inhalable" - particles ranging in size from 2.5 to 10  $\mu\text{m}$  that can penetrate the upper regions of the body's respiratory defense mechanisms (U.S. EPA 2004b).

Exposure to particles can lead to a variety of serious health effects. Scientific studies show links between these small particles and numerous adverse health effects. Long-term exposures to PM, such as those experienced by people living for many years in areas with high particle levels, are associated with problems such as decreased lung function, development of chronic bronchitis, and premature death. Short-term exposures to particle pollution (hours or days) are associated with a range of effects, including decreased lung function, increased respiratory symptoms, cardiac arrhythmias (heartbeat irregularities), heart attacks, hospital admissions or emergency room visits for heart or lung disease, and premature death. (U.S. EPA 1982c; 2004c).

Ambient PM is a complex mix of constituents derived from many sources, both natural and anthropogenic. Hence, the physicochemical composition of PM generally reflects the major contributing local and regional sources arising locally as well as regionally. It stands to reason that the contribution of any given component within the mix may not be equivalent in value or potency, but may well be highly dependent on other physicochemical attributes (e.g., co-constituents, specific bioavailability, or chelates), as well as the health status of the exposed individual. Evidence collected to date indicates that the discovery of a uniquely responsible physicochemical attribute of PM is not likely to occur (U.S. EPA 2004c).

### **2.3.8 Phthalates**

We generally recommend carefully considering the information in the following paragraphs before deciding the appropriateness of including phthalates in combustor risk assessments. At the same time, due to their toxicity and bioaccumulative potential, don't automatically discount the evaluation of phthalates in the risk assessment. If phthalates are included as COPCs in the risk assessment, we generally recommend using a metabolism factor (*MF*) of 0.01 for BEHP, and 1.0 for all other COPCs.

*Please Note:* In earlier guidance (U.S. EPA 1994g; 1994i; 1994j; 1994r) we recommended always including BEHP and DNOP in every risk assessment. We no longer recommend *automatically* including phthalates in risk assessments.

Phthalates such as bis(2-ethylhexyl)phthalate (BEHP) and di(n)octyl phthalate (DNOP) are synthesized by reacting alcohol with phthalic anhydride in the presence of an acidic catalyst in a nonaqueous solvent (ATSDR 1993; ATSDR 1995b). Among all phthalate plasticizers, BEHP—also referred to as di(2-ethylhexyl)phthalate or dioctyl phthalate—is produced in the largest volume; it is used in the manufacturing of polyvinyl chloride, the most widely produced plastic. DNOP is a plasticizer that is produced in large volumes, and is used in the manufacture of plastics and rubber materials. Because plastics have become so widely used in society, phthalate plasticizers such as BEHP and DNOP have become widely distributed in food, water, and the atmosphere (Howard 1990). The general public's exposure to phthalate-contaminated food averages 0.3 µg/day/individual, with an estimated maximum exposure of 2 mg/day/individual (ATSDR 1992). Phthalate plasticizers are commonly found in the environment and are practically impossible to avoid, especially at the trace concentrations that modern analyses can detect.

Phthalates and their predecessors are readily burned, as indicated by their flash points of 150 to 225 °C (NIOSH 1994). There is no apparent mechanism for phthalate PICs to be formed by burning other chemical compounds. Therefore, phthalates are very unlikely to be emitted from a combustor, although some degradation products, such as PAHs, are likely to be emitted when phthalates are included in the waste feed. However, facilities that burn plastics or materials with phthalate plasticizers should carefully consider the potential for phthalate plasticizers to exist in the stack gas emissions due to incomplete combustion. Also, the uncertainties associated with combustion chemistry suggest that stack gas testing confirm the absence of these compounds from stack emissions, rather than relying on process knowledge or waste feed characterization data.

Based on the findings of long-term animal carcinogenicity studies, the Agency has classified BEHP as a “probable human carcinogen” (class B2) (NTP 1982). Because of its octanol-water coefficient ( $K_{ow}$ ) value, BEHP has been presumed to have a high tendency to bioaccumulate (Mackay, Shiu, and Ma 1992; Karickhoff and Long 1995). Considering its ubiquity, B2 classification, and high tendency to bioaccumulate, BEHP is on most Agency lists of target chemicals (see Table A-1), including the Contract Laboratory Program (CLP) semivolatile organics analysis list; the Groundwater Monitoring List (40 CFR Part 264, Appendix IX); and the Hazardous Substances and Reportable Quantities List (40 CFR Part 302.4).

Evidence indicates BEHP is more readily metabolized and excreted by mammalian species than other contaminants (ATSDR 1987). As stated above, we generally recommend using an  $MF$  of 0.01 for BEHP, and 1.0 for all other COPCs. An  $MF$  represents the estimated amount of COPC that remains in fat and muscle. Based on a study by Ikeda et al. (1980), the Agency (EPA 1995h) used a COPC-specific  $MF$  to account for metabolism in animals and humans. Considering the recommended values for this variable,  $MF$  has a quantitative effect on animal and human concentrations only for BEHP. No information could be found on the metabolism or disposition of DNOP in the peer-reviewed literature. However, disposition data were found for an isomer of DNOP, diisooctyl phthalate (DIOP), a branched-chain phthalate (Ikeda et al., 1978). Based upon its similarity in structure, it may be assumed that DNOP would behave comparatively to DIOP and BEHP, and therefore, may be over estimated by approximately a factor of 100.

The  $MF$  applies only to mammalian species, including beef cattle, dairy cattle, and pigs. It does not relate to metabolism in produce, chicken, or fish. In addition, since exposures evaluated using this guidance are

intake driven, only apply a metabolism factor to evaluating indirect human exposure via ingestion of beef, milk, and pork. In summary, using an *MF* doesn't apply for direct exposures to air, soil, or water, or to ingestion of produce, chicken, or fish. Using an *MF* is further discussed in Section 5.4.4.7 and Appendix B, Tables B-3-10, B-3-11, and B-3-12.

### **2.3.9 Polychlorinated Biphenyls**

Because of evidence that PCBs can be emitted from combustion sources regardless of feed characteristics, and considering the significant toxicity of PCBs, we recommend conducting stack testing for PCBs to support the risk assessment. We also recommend automatically including PCBs as COPCs for combustors that burn PCB-contaminated wastes or waste oils, highly variable waste streams such as municipal and commercial wastes (for which PCB contamination is a reasonable assumption), and highly chlorinated waste streams. Due to the toxicity and uncertainties associated with combustion chemistries, we generally recommend that stack gas testing confirm the absence of these compounds from stack emissions.

The most commercially useful property of PCBs is that they are chemically stable in relatively adverse conditions, such as temperatures of several hundred degrees in an oxygen-containing atmosphere. The more chlorinated congeners are more resistant to reaction. PCBs were produced commercially by the reaction of the aromatic hydrocarbon biphenyl with chlorine gas in the presence of a suitable catalyst, generally ferric chloride or another Lewis acid (ATSDR 1995d). The degree of chlorination was controlled by manipulating the reaction conditions, including temperature, pressure, and the ratio of the reactants (Erickson 1992; Grayson 1985). The uses and distribution of polychlorinated biphenyls (PCBs) were severely restricted in the United States in the late 1970s—with additional bans and restrictions taking effect over the next decade (ATSDR 1995d).

Due to their stability in adverse conditions, destruction of PCBs by burning generally requires contact with high temperatures (at least 1,200°C) for an extended period of time (more than 2 seconds), under conditions with adequate oxygen (Erickson 1992). Waste combustors can contribute significantly to total emission inventories of PCBs (Alcock et al. 1999; U.S. EPA 1997e). An increasing body of information supports the likelihood that PCBs may be emitted as by-products of burning, regardless of PCB contamination in the combustor feed.

It is possible that PCBs can be formed by the same types of reactions that produce dioxins and furans, including gas-phase formation, heterogeneous formation from organic precursors, and *de novo* synthesis from flyash-bound carbon. Lemieux et al. (1999) hypothesized that if PCBs and dioxins and furans are formed by similar mechanisms, then emissions of PCBs should correlate with emissions of dioxins and furans. This hypothesis was tested by reviewing data where both PCBs and dioxins and furans were measured. An apparent trend was indeed found showing increased PCB emissions with increased emissions of dioxins and furans. In most cases, PCBs were found in the stack even when there were no PCBs in the combustor feed. Overall, PCB emissions exceeded dioxin and furan emissions by approximately a factor of 20, and this trend appeared to hold over five orders of magnitude in dioxin and furan emissions.

In addition, there is some limited data, from both laboratory and field studies, showing that PCBs may be formed from burning hazardous waste. Stack tests performed in U.S. EPA Region 10 on a boiler and an incinerator burning waste with 0.07 and 1.4 percent chlorine, respectively, confirmed the presence of PCBs in the stack gases (Kalama Chemical, Inc. 1996; Idaho National Engineering Laboratory 1997). The concentration of detected coplanar PCBs (as defined in Section 2.3.9.1) found in the boiler stack gas was 0.55 ng/dscm @ 7% O<sub>2</sub> at low temperature conditions (1,357° F) and 1.12 ng/dscm @ 7% O<sub>2</sub> at high temperature conditions (1,908° F). The concentration of total PCBs detected in the incinerator stack gas was 211 ng/dscm @ 7% O<sub>2</sub> at low temperature conditions (1,750 °F) and 205 ng/dscm @ 7% O<sub>2</sub> at high temperature conditions (2,075° F). PCBs with more than four chlorines comprised 51 percent of the total PCBs in the low temperature test and 59 percent of the total PCBs in the high temperature test.

Other laboratory studies suggest the possible formation of PCBs as PICs from burning hazardous waste with a high chlorine content. Bergman et al. (1984) heated samples of two chlorinated paraffins (CP) in conditions similar to incinerator conditions. A CP containing 70 percent chlorine did produce PCB (up to 0.3 percent of the amount of CP), as well as chlorinated benzenes (up to 0.5 percent), chlorinated toluenes (up to 0.6 percent), and chlorinated naphthalenes (up to 0.2 percent). Similar treatment of a CP containing 59 percent chlorine produced only chlorinated benzenes (up to 0.1 percent of the amount of CP, based on a detection limit of 0.0005 percent for each individual compound) and almost all of those (about 90 percent) were monochlorobenzene (Bergman 1984). This study indicates that burning highly chlorinated wastes (60 percent or greater chlorine) can produce PCBs. Also, in an experiment involving 4 percent charcoal, 7 percent chlorine, and 1 percent copper catalyst heated to 300° C, PCBs were formed

at levels approaching 300 ppb for the penta homologue, 200 ppb for the hexa homologue, 150 ppb for the hepta homologue, and less than 50 ppb for the tetra homologue (Stieglitz et al. 1989).

### **2.3.9.1 PCB Carcinogenic Risks**

In earlier guidance (1994g; 1994i; 1994j; 1994r) we recommended that risk assessments treat all 209 PCB congeners as a mixture having a single carcinogenic potency. This recommendation was based on the Agency drinking water criteria for PCBs (U.S. EPA 1988a), which used available toxicological information with the following limitations:

- C Aroclor 1260 was the only PCB for which a cancer *SF* had been developed; there was no agreed upon procedure for applying this *SF* for similar mixtures with less chlorine content.
- C Available physical, chemical, fate-and-transport, and toxicological information on individual congeners was limited (primarily because separation and synthesis of pure congeners can be technically difficult).
- C The number of tests conducted with various PCB mixtures and specific congeners to demonstrate similar toxicological effects was very limited.

Research on PCBs has continued since the compilation of U.S. EPA (1988a). The most important finding of this research is that some of the moderately chlorinated PCB congeners can have dioxin-like effects (U.S. EPA 1992e; 1994a; 1996q; ATSDR 1995d). This sub-category includes PCB congeners with four or more chlorine atoms and few substitutions in the ortho positions (positions designated 2, 2', 6, or 6'). They are sometimes referred to as "coplanar" PCBs, because the rings can rotate into the same plane if not blocked from rotation by ortho-substituted chlorine atoms. In this configuration, the shape of the PCB molecule is very similar to that of a PCDF molecule. Studies have shown that these dioxin-like congeners can react with the aryl hydrocarbon receptor; the same reaction believed to initiate the adverse effects of PCDDs and PCDFs. The World Health Organization (WHO) used various test results to derive interim toxicity equivalency factors (TEFs) ranging from 0.1 to 0.00001 for the dioxin-like coplanar PCB congeners (WHO 1998).

**TABLE 2-5**  
**TOXICITY EQUIVALENCY FACTORS**  
**FOR COPLANAR PCBs**

CAS Number	Chemical Structure	WHO 1998 TEFs (unitless)
32598-13-3	3,3',4,4'-tetrachlorobiphenyl	0.0001
70362-50-4	3,4,4',5-tetrachlorobiphenyl	0.0001
32598-14-4	2,3,3',4,4'-pentachlorobiphenyl	0.0001
74472-37-0	2,3,4,4',5-pentachlorobiphenyl	0.0005
31508-00-6	2,3',4,4',5-pentachlorobiphenyl	0.0001
65510-44-3	2',3,4,4',5-pentachlorobiphenyl	0.0001
157465-28-8	3,3',4,4',5-pentachlorobiphenyl	0.1
38380-08-4	2,3,3',4,4',5-hexachlorobiphenyl	0.0005
69782-90-7	2,3,3',4,4',5'-hexachlorobiphenyl	0.0005
52663-72-6	2,3',4,4',5,5'-hexachlorobiphenyl	0.00001
32774-16-6	3,3',4,4',5,5'-hexachlorobiphenyl	0.01
39635-31-9	2,3,3',4,4',5,5'-heptachlorobiphenyl	0.0001
Source: World Health Organization (1998)		

Additional congeners are suspected of producing similar reactions, but there is not yet enough data to derive TEF values for them. Since available analytical methods can now quantify most if not all individual PCB congeners, we generally consider it reasonable for the permitting authority to request that additional congeners be reported. For instance, 2,2',4,4',5,5'-Hexachlorobiphenyl (CAS No. 35065-27-1) is the most prevalent PCB congener found in human milk and fat (McFarland and Clark 1989). Work is currently underway to develop a separate slope factor for this particular compound (not a coplanar congener). However, until that work is complete, this compound can only be qualitatively assessed in the risk assessment.

We generally recommend estimating risks from coplanar PCBs by computing a toxicity equivalency quotient (TEQ) for PCBs, and then applying a slope factor for dioxin. High resolution gas chromatograph test methods, available at most commercial laboratories with dioxin/furan analytical capabilities, are able to identify the specific concentration of individual coplanar PCBs in stack gas.

In addition to the coplanar (dioxin-like) PCB congeners, We also generally recommend evaluating the remaining PCBs in the risk assessment. After considering the accumulated research on PCBs, especially a recent carcinogenesis study of Aroclors 1016, 1242, 1254, and 1260 and a number of studies of the transport and bioaccumulation of various congeners, USEPA (1996q) derived three new *SFs* to replace the former single *SF* for PCBs. These new *SFs* became effective in IRIS on October 1, 1996. These *SFs* are subject to revision as additional information from continuing research becomes available. The *SFs* and the criteria for their use are as follows (U.S. EPA 1996q):

**TABLE 2-6**

**ORAL SLOPE FACTORS FOR PCBs**

Slope Factor (milligrams per kilogram-day) <sup>-1</sup>	Criteria for Use
2	Food chain exposure Sediment or soil exposure Early-life (infant and child) exposure by all routes to all PCB mixtures Congeners with more than four chlorines comprise <i>more than</i> 0.5 percent of the total PCBs
0.4 (Not Typically Used)	Ingestion of water-soluble (less chlorinated) congeners Inhalation of evaporated (less chlorinated) congeners
0.07	Congeners with more than four chlorines comprise <i>less than</i> 0.5 percent of the total PCBs
Source: U.S. EPA 1996q	

An *SF* of 2 (milligrams per kilogram-day)<sup>-1</sup> is typically used in most circumstances when conducting a risk assessment. An *SF* of 0.07 (milligrams per kilogram-day)<sup>-1</sup> is generally scientifically defensible for adult exposures, when congener-specific analyses of emissions demonstrate that at least 99.5 percent of the mass of the released PCB mixture has fewer than five chlorine atoms per molecule (U.S. EPA 1996q). Acceptable congener-specific analyses include high-resolution gas chromatography/mass spectroscopy (or similar means) for total PCB concentrations for each mono- through deca-isomer group. We don't expect that the 0.4 *SF* will be widely used in combustion risk assessments, because the PCB mixture will usually contain 0.5 percent or more PCB congeners with more than 4 chlorines.

**2.3.9.2 Potential PCB Non-Cancer Effects**

In addition to cancer risk associated with all PCBs, we generally recommend determining noncancer hazard for those Aroclors having *RfDs*. IRIS specifies *RfDs* for Aroclor 1254 and Aroclor 1016 (U.S. EPA 2005i). The *RfD* for Aroclor 1254 (2x10<sup>-5</sup> milligrams per kilogram-day) will typically be used in

most circumstances when conducting a risk assessment. We consider this approach reasonable because approximately 77 percent of Aroclor 1254 is composed of PCB congeners with more than 4 chlorines (Hutzinger et al. 1974). The *RfD* for Aroclor 1016 ( $7 \times 10^{-5}$  milligrams per kilogram-day) is scientifically defensible for each homologue group demonstrating that at least 99.5 percent of the mass of the released PCB mixture has more than four chlorine atoms per molecule (U.S. EPA 1996q). We generally consider this approach reasonable because approximately 99 percent of Aroclor 1016 is comprised of PCB congeners with 4 or fewer chlorines (Hutzinger et al. 1974).

We also recommend evaluating the risks to infants from exposure to coplanar PCBs in human breast milk. Please see Section 2.3.10.2 for information on comparing estimated levels of coplanar PCBs (along with dioxins and furans) to background. More information on the breast milk pathway is in Chapter 4, and Tables C-3-1 and C-3-2.

### **2.3.9.3 Fate & Transport of PCBs**

When evaluating coplanar PCB congeners, or PCB congener mixtures of which greater than 0.5 percent contain more than 4 chlorines, we recommend using the fate and transport properties for Aroclor 1254. When assessing risks and hazards from PCB congener mixtures of which less than 0.5 percent contain more than 4 chlorines, we recommend using the fate and transport properties of Aroclor 1016.

### **2.3.10 Polychlorinated Dibenzo(p)dioxins and Dibenzofurans**

As was the case with previous Agency guidance (U.S. EPA 1994i, 1994j, 1994n, 1994r, and 1998c), we recommend including PCDDs and PCDFs in the risk assessment. Information in U.S. EPA (2000b) suggests that there is adequate evidence that exposure to PCDDs and PCDFs results in a broad spectrum of cancer and noncancer effects in animals, some of which may occur in humans.

PCDDs and PCDFs were first discovered as thermal decomposition products of polychlorinated compounds, including (1) the herbicide 2,4,5-T, (2) hexachlorophene, (3) PCBs, (4) pentachlorophenol, and (5) intermediate chemicals used to manufacture these compounds. One mode in which PCDDs and PCDFs form is in dry APCSSs, where fly ash catalyzes reactions between halogens and undestroyed organic material from the furnace. In recent years, as chemical analytical methods have become more sensitive, additional sources of PCDDs and PCDFs have been identified, including (1) effluent from

paper mills that use chlorine bleaches, and (2) combustion sources such as forest fires, municipal waste and medical incinerators, and hazardous waste combustors. Duarte-Davidson et al. (1997) noted that burning chlorine-containing materials in municipal solid waste is responsible for about two-thirds of the total annual emissions of newly formed TCDDs and TCDFs in the United Kingdom. In the United States, U.S. EPA (1998a) estimated that emissions of dioxin TEQs from municipal solid waste incinerators accounted for 37 percent of all emissions of dioxins into the environment in 1995. The current Agency draft dioxin sources inventory suggests that open barrel burning is the largest current single source of release of these compounds (U.S. EPA 2000).

PCDDs and PCDFs are formed at these combustion sources from the reaction of chlorine-containing chemicals and organic matter. Predicting the formation of PCDDs and PCDFs in a specific situation is difficult because dechlorination, which produces PAHs from PCDDs and PCDFs, occurs under similar conditions. Recent studies (Addink et al. 1996; Environment Canada 1987; Fröese and Hutzinger 1996a, 1996b; Gullett et al. 1994; Kilgroe et al. 1991; Luijk et al. 1994; and Shriver 1994) have explored some of these complexities, including (1) the formation of PCDDs and PCDFs from simple organics (such as ethane) and complex organics (such as dibenzofuran), and (2) the catalysis of these reactions by various common metals, such as copper. Wikström et al. (1996) found that the form of chlorine—whether organic, as with chlorinated solvents, or inorganic, as with bleach and salts—has little effect on the quantity of PCDDs and PCDFs formed. However, their study found that the total concentration of chlorine is important. In particular, if the waste being burned exceeds 1 percent chlorine, the PCDD and PCDF formation rate increases significantly. In contrast, Rigo et al. (1995) analyzed over 1,700 test results with varying chlorine feed concentrations and found no statistically significant relationship. The formation rate of PCDDs and PCDFs may also depend on the physical characteristics of the waste feed stream. Solid waste streams or high-ash-content liquid waste feed streams may increase particulate levels in the combustion system between the combustion unit and the APCS. The increased particulate levels provide additional surfaces for catalysis reactions to occur.

A review of currently available dioxin data for combustors reveals that total PCDD/PCDF emission rates vary by more than 28-fold between different facilities, even though they use similar combustion units and APCSs (U.S. EPA 1996b). Site-specific emission data are therefore needed to complete a more refined risk assessment of each combustor.

In evaluating fate-and-transport, it is important to consider the chemical and physical properties of dioxins. In soil, sediment, and the water column, PCDDs and PCDFs are primarily associated with particulate and organic matter because of their high lipophilicity and low water solubility. Ambient air monitoring studies, in which researchers studied the partitioning of dioxin-like compounds between the vapor and particle phases, suggest that the higher chlorinated congeners (the hexa through octa congeners) principally sorb to airborne particulates. The tetra and penta congeners significantly, if not predominantly, partition to the vapor phase (U.S. EPA 2000b). These findings are consistent with vapor/particle partitioning as theoretically modeled in Bidleman (1988). Dioxin-like compounds exhibit little potential for significant leaching or volatilization (U.S. EPA 2000b).

The following subsections clarify the procedures we recommend using (in conjunction with the procedures described in Chapter 7) to estimate risks associated with PCDDs and PCDFs. Also, we're aware of growing concern regarding the risks resulting from exposure to (1) fluorine- and bromine-substituted dioxins and furans, and (2) sulfur analogs of PCDDs and PCDFs. Research regarding these compounds is ongoing. Until such time as new information is released, though, you can consider the following subsections as our guidance on how to evaluate fluorine, bromine, and sulfur PCDD/PCDF Analogs as potential COPCs in hazardous waste combustor risk assessments.

### **2.3.10.1 PCDD/PCDF Cancer Risks**

We recommend using the TEF method to assess carcinogenic risk on the basis of toxicity relative to 2,3,7,8-TCDD, which is the most toxic dioxin.

There are 210 individual compounds or "congeners" of PCDDs and PCDFs. Seventeen of these 210 congeners are considered to have "dioxin-like" toxicity. In the TEF method, each of these 17 congeners is assigned a value, referred to as a toxicity equivalency factor (TEF), which compares its toxicity to that of 2,3,7,8-TCDD. 2,3,7,8-TCDD then has a TEF of 1.0, and other dioxin-like congeners have TEFs between 0.0 and 1.0. TEF values for these 17 congeners are listed in the Table 2-7.

TABLE 2-7

PCDD/PCDF TOXICITY EQUIVALENCY FACTOR VALUES

Dioxin Congener	TEF (unitless)	Furan Congener	TEF (unitless)
2,3,7,8-Tetrachlorodibenzo(p)dioxin	1.0	2,3,7,8-Tetrachlorodibenzofuran	0.1
1,2,3,7,8-Pentachlorodibenzo(p)dioxin	1.0	1,2,3,7,8-Pentachlorodibenzofuran	0.05
1,2,3,4,7,8-Hexachlorodibenzo(p)dioxin	0.1	2,3,4,7,8-Pentachlorodibenzofuran	0.5
1,2,3,6,7,8-Hexachlorodibenzo(p)dioxin	0.1	1,2,3,4,7,8-Hexachlorodibenzofuran	0.1
1,2,3,7,8,9-Hexachlorodibenzo(p)dioxin	0.1	1,2,3,6,7,8-Hexachlorodibenzofuran	0.1
1,2,3,4,6,7,8-Heptachlorodibenzo(p)dioxin	0.01	1,2,3,7,8,9-Hexachlorodibenzofuran	0.1
1,2,3,4,6,7,8,9-Octachlorodibenzo(p)dioxin	0.0001	2,3,4,6,7,8-Hexachlorodibenzofuran	0.1
		1,2,3,4,6,7,8-Heptachlorodibenzofuran	0.01
		1,2,3,4,7,8,9-Heptachlorodibenzofuran	0.01
		1,2,3,4,6,7,8,9-Octachlorodibenzofuran	0.0001

Source: World Health Organization (1998)  
 Van den Berg et al (1998).

To estimate the exposure media concentrations for PCDDs and PCDFs, we recommend using the congener-specific emission rates from the stack. Then, model the fate and transport of each of these 17 congeners to the exposure site to estimate congener-specific exposure media concentrations. The HHRAP companion database includes congener-specific fate and transport parameter values, and the media concentration equations are provided in Appendix B. After estimating congener-specific exposure media concentrations, we recommend using the TEFs to estimate a "toxic equivalent" (TEQ) exposure media concentration, and an overall TEQ exposure and cancer risk, as follows:

1. convert the exposure media concentrations of an individual congener to a TEQ concentration for that congener by multiplying the congener's media concentrations by the congener's TEF;
2. sum the TEQ concentrations of the individual congeners to get an overall exposure media concentration;
3. estimate the lifetime average daily dose (LADD) for the TEQ concentration; and
4. assess the cancer risk on a TEQ basis using the cancer slope factor for 2,3,7,8-TCDD, in combination with the TEQ-based LADD.

Please see Chapter 7 for a more complete discussion of the steps included in the TEF method.

### **2.3.10.2 PCDD/PCDF Noncancer Hazards**

We generally recommend comparing PCDD and PCDF oral exposure estimates to national average background exposure levels, using 1 pg TEQ/Kg/day for adults and 60 pg TEQ/kg/day for nursing infants. The pertinent exposure estimate would be the ADD, or Average Daily Dose, experienced over the course of the exposure duration, rather than the LADD, which is this ADD averaged over a lifetime.

The Agency typically evaluates noncancer effects of chemicals by comparing exposure levels to health-based reference doses or reference concentrations. However, for reasons discussed in the Agency's Draft Dioxin Reassessment (U.S. EPA 2000b), the Agency has not developed these non-cancer benchmarks for any of the PCDD or PCDF congeners, or for TEQ concentrations/doses.

One approach the Agency has taken to evaluate whether PCDDs and PCDFs emitted from hazardous waste combustion facilities are likely to cause significant noncancer health effects is to compare estimated TEQ exposures to national average background exposure levels (1 pg TEQ/kg/day for adults and 60 pg TEQ/kg/day for nursing infants). The average background level of PCDD/PCDFs and co-planar, dioxin-like PCBs in breast milk is 25 parts per trillion (ppt) of 2,3,7,8-TCDD TEQ (EPA 2000b). The 25- ppt 2,3,7,8-TCDD TEQ is the sum of the average breast milk concentration of 18-ppt TEQ from PCDD/PCDFs and 7-ppt TEQ from co-planar, dioxin-like PCBs (EPA 2000b). After normalization for infant body weight, this breast milk concentration of 25 ppt TEQ results in an average, background intake for the infant, ADIb-inf, of 93 picograms per kilogram per day (pg/kg-day) of 2,3,7,8-TCDD TEQ. If exposures due to the facility's emissions during the exposure duration of concern are low compared to background exposures, then the emissions aren't expected to cause an increase in noncancer effects.

In the future, the Agency may develop alternative approaches to evaluate noncancer effects from exposures to PCDDs and PCDFs. In that case, those approaches may be included in future risk assessments.

### **2.3.10.3 Fluorine, Bromine, and Sulfur PCDD/PCDF Analogs**

We generally recommend deciding on a site-specific basis whether to evaluate these compounds, in consultation with the permitting authority. Considering that neither the likelihood of the formation, nor

the toxicity of these compounds is well understood, the permitting authority is not likely to request a quantitative toxicity assessment of fluorine, bromine, and sulfur analogs.

The Agency is currently evaluating the potential for the formation of (1) fluorine- and bromine-substituted dioxins and furans, and (2) sulfur analogs of PCDDs and PCDFs (U.S. EPA 1996h; 1996m). Available information indicates that fluorinated dioxins and furans aren't likely to be formed as PICs; although the presence of free fluorine in the combustion gases may increase the formation of chlorinated dioxins (U.S. EPA 1996h). We aren't aware of any studies conducted to evaluate this relationship.

Available information indicates that there is potential for brominated or chlorobrominated dioxins to form (U.S. EPA 1996i). The Agency has not assigned TEF values for brominated dioxins or furans (U.S. EPA 1994k). However, the toxicity of bromo- and chlorobromo-substituted dioxin analogs is comparable to that of chlorinated dioxins in short-term toxicity assays (U.S. EPA 1996m).

Although chlorinated dibenzothiophenes (the sulfur analogs of dibenzofurans) have been reported to form, no information is available indicating the formation of chlorinated dioxin thioethers (the sulfur analogs of dibenzo[p]dioxins) (U.S. EPA 1996h). This may be because the carbon-oxygen bond is stronger than the carbon-sulfur bond, and the compound furan (which is part of the dibenzofuran structure) is more stable than thiophene (which is part of the dibenzothiophene structure) (U.S. EPA 1996c). Another possible reason that chlorinated dioxin thioethers have not been observed is the potential instability of these compounds. Chlorinated dioxin thioethers contain two carbon-sulfur bonds in the central ring of the structure (U.S. EPA 1996h).

***Please Note:*** There is currently no U.S. EPA-approved method for the sampling or analysis of these dioxin analogs.

We generally recommend using the TOE method (see Section 2.2.1.2) to account for the potential presence of these compounds. The Uncertainty section of the risk assessment report (See Chapter 8) could then discuss the potential for the formation of these analogs.

**RECOMMENDED INFORMATION FOR THE RISK ASSESSMENT REPORT**

- C Description of any combustor-specific operating conditions that may contribute to the formation of dioxins
- C Any facility-specific sampling information regarding PCDD and PCDF concentrations in air, soil, water, or biota
- C Information regarding the concentrations of sulfur, fluorine, and bromine in the combustor feed materials

**2.3.11 Polynuclear Aromatic Hydrocarbons (PAHs)**

As is the case in previous Agency guidance (U.S. EPA 1994i, 1994j, 1994r, 1998c), we recommend evaluating PAHs as COPCs. The following are commonly detected PAHs:

- benzo(a)pyrene (BaP);
- benzo(a)anthracene;
- benzo(b)fluoranthene;
- benzo(k)fluoranthene;
- chrysene;
- dibenz(a,h)anthracene; and
- indeno(1,2,3-cd)pyrene.

The Agency considers all of these compounds to be carcinogenic. However, an IRIS oral cancer slope factor is only available for benzo(a)pyrene.

PAHs are readily formed in combustors by either (1) dechlorination of other PAHs (such as dioxins) present in the waste feed or emissions stream, or (2) the reaction of simple aromatic compounds (benzene or toluene) present in the waste feed or emissions stream. PAHs are well-known as the principal organic components of emissions from all combustion sources, including coal fires (soot), wood fires, tobacco smoke ("tar"), diesel exhaust, and refuse burning (Sandmeyer 1981). They are generally the only chemicals of concern in particulate matter (Manahan 1991), although the presence of metals and other inorganics in the waste feed can add other contaminants of concern. Based on the toxicity and combustion chemistry of PAHs, we generally recommend that stack gas testing confirm the absence of these compounds from stack emissions.

At present, BaP is the most studied PAH and the only one for which a 2-year feeding rodent bioassay has been conducted (U.S. EPA 1991c). The studies available for the other carcinogenic PAHs were conducted by injection, dermal or gavage. Multiple animal studies in rodent and nonrodent species demonstrated BaP to be carcinogenic following administration by oral, intratracheal, inhalation, and dermal routes. BaP also produced positive results in several *in vitro* bacterial and mammalian genetic toxicity assays, in addition to numerous *in vivo* tests for deoxyribonucleic acid (DNA) damage. BaP metabolizes to reactive electrophiles that are capable of binding to DNA (U.S. EPA 1990h). Therefore, U.S. EPA (1993d) used various nonbioassay results to determine relative potency factors (RPFs) for the class B2 carcinogen PAHs. RPFs for these seven PAHs are listed in Table 2-8.

TABLE 2-8

RELATIVE POTENCY FACTORS  
FOR CLASS B2 CARCINOGEN PAHs

Compound	RPF
Benzo(a)pyrene	1.0
Benz(a)anthracene	0.1
Benzo(b)fluoranthene	0.1
Benzo(k)fluoranthene	0.01
Chrysene	0.001
Dibenz(a,h)anthracene	1.0
Indeno(1,2,3-cd)pyrene	0.1
Source: U.S. EPA (1993d)	

Obtaining test data for an individual chemical from a standard carcinogenesis bioassay that might be used to develop a cancer slope factor requires:

1. at least 1 kilogram of relatively pure chemical (greater than 98 percent purity is the most common specification),
2. \$500,000 to \$1,000,000, and
3. 5 to 6 years.

However, an alternative to the full carcinogenesis bioassay is to use *in vitro* studies to compare various PAHs. *In vitro* studies, such as those conducted by Knebel et al. (1994) and many other groups, require a few milligrams of each chemical, a few weeks, and about \$1,000 per chemical. Because of these

differences, we wouldn't anticipate that many full carcinogenesis bioassays of PAHs will be carried out in the near future.

As with previous guidance (U.S. EPA 1994g), we generally recommend evaluating PAHs using an approach similar to the BaP-RPF method. We generally recommend using the fate-and-transport properties of specific PAHs (versus those of benzo[a]pyrene) to estimate exposure concentrations. Then following the BaP-RPF method, you adjust the concentrations of the individual PAHs and sum them to obtain an equivalent total concentration of BaP. Multiply this summed concentration by the BaP cancer *SF* to estimate total risk from all carcinogenic PAHs.

We don't currently recommend a metabolism factor (MF) for PAHs. A published study (Hofelt et al. 2001), however, highlights the uncertainty in the HHRAP's approach and presents an alternative metabolism factor for use. If this alternative metabolism factor is used, you may wish to consider the following site-specific points:

1. If the PAHs under consideration are metabolized in the animal (beef, pork, etc) has it been determined that the degradation products/metabolites aren't persistent in the meat/and or milk? (This concern has been raised because it is the degradation products of PAHs that cause the toxicity.);
2. Is the extrapolation from the rat to larger animal appropriate?; and
3. If the metabolism factor is appropriate, should it be used equally for all the PAHs being evaluated?

Using an MF is discussed further in Section 5.4.4.7 and Appendix B, Table B-3-10.

In addition to carcinogenic effects, noncarcinogenic health effects are associated with exposure to PAHs. However, RPFs for noncarcinogenic effects of PAHs (similar to those developed for carcinogenic effects) have not been developed. The uncertainties associated with attempting to quantify the potential noncarcinogenic effects of PAHs without RfDs or RfCs is typically considered greater than the uncertainty associated with not evaluating these potential effects. However, if site-specific emissions data indicate that significant amounts of noncarcinogenic PAHs are emitted, we generally recommend that the potential to underestimate the noncarcinogenic health effects associated with exposure to PAHs be discussed in the Uncertainty section of the risk assessment report.

### 2.3.12 Radionuclides

Radionuclides exist in naturally occurring materials such as coal and other rocks, and as radioactive by-products of industrial processes. The HHRAP doesn't consider the naturally occurring concentrations of radioactive materials such as uranium and thorium (and their decay elements), based on Agency policy and technical limitations for measuring such low levels. However, radioactive wastes and materials, as defined by the U.S. Nuclear Regulatory Commission (NRC) and the U.S. Department of Energy (DOE), are subject to evaluation through interagency agreements on this subject. The U.S. NRC considers "radioactive waste" as waste that is, or contains, by-product material, source material, or special nuclear material (as defined in 10 CFR Part 20.1003). The U.S. NRC considers "mixed waste" as waste that contains both radioactive waste and hazardous waste (as defined by U.S. EPA). Both radioactive and mixed wastes must be handled in accordance with all relevant regulations, including U.S. EPA and U.S. NRC (10 CFR Part 20.2007) regulations. In particular, U.S. NRC licensees must comply with 10 CFR Part 20.2004—"Treatment or Disposal by Incineration"—and applicable U.S. EPA regulations.

We generally recommend evaluating the burning of mixed waste and radioactive material if those substances are components of the combustor feed. We also generally recommend including a radionuclide as a COPC if it is in the combustor's feed, and has an available toxicity value (e.g., slope factor). Slope factors for over 300 radionuclides are available in HEAST. The slope factor for a particular radionuclide is multiplied by the intake (pCi) or soil concentration and years of exposure (pCi/g times years of exposure) to estimate cancer risk.

Radionuclide exposure pathways typically evaluated in human health risk assessments include inhalation, ingestion of food products (e.g., meat, milk, vegetables), incidental soil ingestion, external exposure from ground surface deposits, and external exposure from air concentrations (air submersion). The submersion exposure pathway may be of particular concern for radionuclides that emit high-energy beta particles.

Environmental transport and subsequent human exposure are commonly evaluated through the use of radionuclide "dose" codes or computer code/spreadsheet combinations. A dose code combines air dispersion/deposition modeling with terrestrial transport models, human exposure parameters, and pre-calculated dose conversion factors [e.g., from *Federal Guidance Report No. 11* (U.S. EPA 1988c) and *Federal Guidance Report No. 12* (U.S. EPA 1993j)] to obtain dose and/or risk. The following are several available dose codes for evaluating radionuclides from mixed waste combustion facilities:

C	CAP-88	(Clean Air Act Assessment Package - 1988)
C	GENII	(The Hanford Environmental Radiation Dosimetry Software System)
C	MEPAS	(Multimedia Environmental Pollutant Assessment System)
C	ISCST3	(Industrial Source Complex Dispersion Model)
C	CALPUFF	(California Puff Model)

To calculate air concentrations and ground deposition rates of radionuclides, we generally recommend the ISCST3 air dispersion model using the exponential decay option. Intake can then be calculated with appropriate exposure scenario equations and parameters. ISCST3 is a good choice for facilities with multiple sources, complex terrain, building downwash, and wet/dry deposition requirements. A second option is to use the air concentration and ground deposition rate output from another dose code (e.g., CAP-88 if the facility has completed its NESHAPs analysis).

We generally recommend that equations for fate and transport of radionuclides in soil and water be consistent with those presented for non-radionuclides, while factoring in decay (and ingrowth if applicable). The recommended food chain biotransfer parameters used to determine food concentrations are available in the user's guides for most of the dose codes listed previously. However, a comprehensive reference for obtaining these values is the *Handbook of Parameter Values for the Prediction of Radionuclide Transfer in Temperate Environments; IAEA Technical Report Series No. 364* (International Atomic Energy Agency 1994).

Decay and ingrowth of radionuclides is a special consideration for integrating radioactive materials into risk calculations. Most radioactive materials undergo radioactive decay through a series of transformations rather than in a single step. Until the last step, these radionuclides emit energy or particles with each transformation and become other radionuclides. As radioactive decay progresses, the concentration of the original radionuclides decreases, while the concentration of their decay products increases and then decreases as the decay products themselves transform. The increasing concentration of decay products and activity is called ingrowth. We recommend that the assessment consider decay over both the air transport time and the surface exposure duration. Ingrowth may be important, and we generally recommend the assessment use radionuclide slope factors that include contributions from decay elements (“+D” slope factors). Ingrowth that involves change of physical state is another situation

needing special attention in the fate and transport modeling. For instance, solid radium-226 decays to gaseous radon-222, which then decays through solid polonium-218 to further decay elements.

Options for estimating cancer risks from exposure to radionuclides include using the slope factor methodology presented in the Agency's *Estimating Radiogenic Cancer Risks* (U.S. EPA 1994s), or using estimates of the relationship between radiation dose and cancer risk to convert dose to risk. Federal Guidance Report No. 13 (U.S. EPA 1999d) contains recent estimates of cancer risk for given radiation dose, based on low-dose, low-Linear Energy Transfer uniform irradiation of the body. For these conditions, radiation dose equivalent (rem) and absorbed dose (rad) are approximately equivalent. The Report provides risk estimates in terms of mortality and morbidity. It is important to use the estimate appropriate to the site and assessment in question.

The dose-conversion approach uses a single factor to convert dose to risk. It is limited, then, in that it doesn't take into account variations among radionuclides in the relationship between dose and risk. In general, though, this approach is protective. The slope factor approach generally provides a better estimate of risk. Limitations of the slope factor conversion methodology, however, include:

- C It assumes a single chemical form, which is not necessarily site-specific or most protective;
- C External radiation slope factors are only provided for soil contaminated to an infinite thickness, which will over-estimate exposure from radionuclide concentrations near the surface;
- C Slope factors aren't available for the submersion in water exposure pathway; and
- C Slope factors include decay chains for a limited number (18) of parent radionuclides (although these are the most significant decay chains)

Some radioactive materials, such as uranium, also present a non-carcinogenic hazard that it is possible to evaluate. We generally recommend also assessing these non-carcinogenic hazards. We also recommend that the risk summary table in the risk assessment report present the cancer risk from radiological contaminants alongside the risks from non-radiological contaminants.

To enhance transparency, we generally recommend that results include a discussion of additivity and the uncertainties of additivity when combining risks from radiological and non-radiological contaminants. There are fundamental differences between the slope factors for chemical and radionuclide carcinogens.

Most notably, the slope factors for chemical carcinogens generally represent an upper bound or 95<sup>th</sup> percent confidence limit value, while radionuclide slope factors are best estimate (50% confidence) values.

*Please Note:* A prescriptive method for calculating risk from combustion facilities burning mixed waste is beyond the scope of the HHRAP. The above information is provided to outline the method we recommend.

### **2.3.13 Volatile Organic Compounds**

U.S. EPA (1990e) reported that volatile organics listed as probable PICs (based on Freeman 1988 and 1989) produced by burning hazardous waste include:

- benzene;
- chloroform;
- tetrachloroethylene;
- 1,1,1-trichloroethane;
- toluene; and
- methylene chloride.

However, the validity of evaluating volatile organic COPCs through the various indirect exposure pathways (see Chapter 4) is subject to debate. One argument to exclude these COPCs from evaluation is that there is no empirical evidence that VOC emissions pose a hazard via indirect pathways. We're similarly not aware of any such evidence, but we're also unaware of any evidence to the contrary.

Another argument to exclude VOCs from evaluation is based on the conclusion that

1. volatile organic COPCs released into the air are expected to remain in the gas phase unless or until they are transformed into low-volatility compounds, and
2. this transformation (or atmospheric chemical reaction), and the subsequent removal of the reaction products, makes irrelevant the toxicity of the parent volatile organic COPC.

We disagree with both aspects of this argument. First, we're not aware of any information or research documenting the fate-and-transport of volatile organic COPCs from hazardous waste combustors. Second, although we agree that the toxicity of the parent COPC is irrelevant following transformation, this argument ignores the potential toxicity of the reaction products. We're not aware of any available quantitation methods that could be used to predict atmospheric chemical reactions of this nature. We therefore generally believe that evaluating the fate-and-transport (and toxicity) of the parent COPC

remains the best available method for protectively accounting for the potential reaction products to which receptors are ultimately exposed.

Finally, another argument to exclude VOCs from evaluation is the assertion that there is no firm technical basis for assessing the rate of deposition of VOCs to soils or uptake by plants (discussed in detail in Appendix A-2). Although we agree with the basic premise of this issue, we're unaware of any other method for evaluating the potential indirect exposure to volatile organic COPCs or their atmospheric reaction products (empirical data aren't available).

To summarize, we agree in principle that the science regarding the fate-and-transport of volatile organic COPCs in the environment is poorly understood. However, because the potential risks associated with indirect exposure to these COPCs is also poorly understood, we believe that evaluating volatile organic COPCs via the indirect exposure pathways—with the proper explanation of the uncertainties associated with this process—generally provides the most reasonable (based on current science) and protective estimate of these potential risks. We also believe that the risk equations generally address this issue because a calculation cannot be completed unless there are sufficient fate and transport properties values for each COPC.

Finally, current sampling and analytical methods aren't always able to positively identify all individual organic compound in stack emissions. We recommend accounting for the mass of unidentified organic compounds in stack emissions on the basis of TOE from the hazardous waste combustor. The methodology for using TOE in a risk assessment is discussed further in Section 2.2.1.2.

## 2.4 ESTIMATING COPC CONCENTRATIONS FOR NON-DETECTS

One particularly difficult issue in a risk assessment is how to treat data that are reported as below the “detection limit” (i.e. “Non-detects”). The following subsections:

1. define commonly reported detection limits;
2. describe the use of non-detect data in the risk assessment;
3. describe statistical distribution techniques applied to address this issue;
4. summarize our recommendations on quantifying non-detects for use in risk assessments; and
5. clarify use of data flagged as estimated maximum possible concentration (EMPC) in the risk assessment.

### 2.4.1 Definitions of Commonly Reported Detection Limits

Generically, a “detection limit” is the lowest level of an analyte that can be detected using a particular analytical method. The Agency’s commonly-used definition for the detection limit for non-isotope dilution methods is the method detection limit (MDL), as promulgated in 40 CFR Part 136, Appendix B (U.S. EPA 1995i). A level above the MDL is the level at which reliable quantitative measurements can be made; generically called the “quantitation limit” or “quantitation level.” In practice, numerous terms have been created to describe detection and quantitation levels. We have summarized below the significance and applicability of the levels most widely reported by analytical laboratories. These levels—listed generally from the lowest limit to the highest limit—include the following:

- C Instrument Detection Limit (IDL): The smallest signal above background that an instrument can reliably detect, but not quantify. Also commonly described as a function of the signal-to-noise (S/N) ratio.
- C Method Detection Limit (MDL): The minimum concentration of a substance that can be measured (via non-isotope dilution methods) and reported with 99 percent confidence that the analyte concentration is greater than zero. It is determined from analysis of a sample in a specific matrix type containing the analyte. The MDL is considered the lowest level at which a compound can be reliably detected. The MDL is based on statistical analyses of laboratory data. In practice, MDLs are determined on analytical reagents (e.g., water) and not on the matrix of concern. However, a laboratory may contract to do a matrix-specific “MDL Study” for a particular project or a particular facility’s waste matrix when needed. However, routine MDL determinations (water reagent) are conducted on at least an annual basis or whenever equipment changes occur. MDLs for a given method are laboratory- and compound-specific.

To determine the MDL as specified in 40 CFR Part 136, Appendix A, for example, at least seven replicate samples with a concentration of the compound of interest near the estimated MDL are analyzed. The standard deviation among these analyses is calculated and multiplied by 3.14. The result of the calculation becomes the MDL. The factor of 3.14 is based on a t-test with six degrees of freedom and provides a 99 percent confidence that the analyte can be detected at this concentration (U.S. EPA 1995i).

**Please Note:** 40 CFR Part 136 is specific to the Clean Water Act, and it identifies the use of water as the matrix for the MDL determination. The MDL was promulgated in 1984, and is incorporated in more than 130 Agency analytical methods for determining several hundred analytes.

- C **Reliable Detection Level (RDL):** A detection level recommended by the National Environmental Research Laboratory in Cincinnati. It is defined as 2.623 times the MDL (U.S. EPA 1995i).
- C **Estimated Detection Limit (EDL):** A quantitation level defined in SW-846 that has been applied to isotope dilution test methods (e.g., SW-846 Method 8290). A variation of the SW-846 defined EDL is also commonly reported by commercial laboratories, however, with the addition of a multiplication factor that generally elevates the EDL value by 3.5 to 5 times that of the SW-846 definition. Commercial laboratories sometimes report EDLs for non-isotope dilution methods, even though an EDL is not defined by the methods.

**As defined in SW-846:** The EDL is defined in SW-846 (presented in various methods, e.g., Method 8280A) as the estimate made by the laboratory of the concentration of a given analyte required to produce a signal with a peak height of at least 2.5 times the background signal level. The estimate is specific to a particular analysis of the sample and will be affected by sample size, dilution, etc. The presented equation defining EDL is as follows:

$$EDL = \frac{2.5 \cdot Q_{is} \cdot (H_n^1 + H_n^2) \cdot D}{V \cdot (H_{is}^1 + H_{is}^2) \cdot RF_n} \quad \text{Equation 2-3}$$

where

<i>EDL</i>	=	Estimated detection limit (ng/L)
2.5	=	Peak height multiplier (unitless)
<i>Q<sub>is</sub></i>	=	Nanograms of the appropriate internal standard added to the sample prior to extraction (ng)
<i>H<sub>n</sub><sup>1</sup> and H<sub>n</sub><sup>2</sup></i>	=	The peak heights of the noise for both of the quantitation ions of the isomer of interest
<i>H<sub>is</sub><sup>1</sup> and H<sub>is</sub><sup>2</sup></i>	=	The peak heights of both the quantitation ions of the appropriate internal standards
<i>D</i>	=	Dilution factor - the total volume of the sample aliquot in clean solvent divided by the volume of the sample aliquot that was diluted (unitless)
<i>V</i>	=	Volume of sample extracted (L)
<i>RF<sub>n</sub></i>	=	Calculated relative response factor from calibration verification (unitless)

**Common commercial laboratory practice:** The EDL generally reported by commercial laboratories is defined as the detection limit reported for a target analyte that is not detected or presents an analyte response that is less than 2.5 times the background level. The area of the compound is evaluated against the noise level measured in a region of the chromatogram clear of genuine GC signals times an empirically derived factor. This empirical factor approximates the area to height ratio for a GC signal. This factor is variable between laboratories and analyses performed, and commonly ranges from 3.5 to 5. The equation is as follows:

$$EDL = \frac{2.5 \cdot Q_{\beta} \cdot (F \cdot H) \cdot D}{W \cdot A_{\beta} \cdot RRF_{\sigma}} \quad \text{Equation 2-4}$$

where

$EDL$	=	Estimated detection limit
2.5	=	Minimum response required for a GC signal
$Q_{\beta}$	=	The amount of internal standard added to the sample before extraction
$F$	=	An empirical factor that approximates the area to height ratio for a GC signal
$H$	=	The height of the noise
$D$	=	Dilution factor
$W$	=	The sample weight or volume
$RRF_{\sigma}$	=	The mean analyte relative response factor from the initial calibration
$A_{\beta}$	=	The integrated current of the characteristic ions of the corresponding internal standard

- C Practical Quantitation Limit (PQL): A quantitation level that is defined in 50 FR 46908 and 52 FR 25699 as the lowest level that can be reliably achieved with specified limits of precision and accuracy during routine laboratory operating conditions (U.S. EPA 1992g; 1995i). The PQL is constructed by multiplying the MDL, as derived above, by a factor (subjective and variable between laboratories and analyses performed) usually in the range of 5 to 10. However, PQLs with multipliers as high as 50 have been reported (U.S. EPA 1995i).

The PQL has been criticized because of the ambiguous nature of the multiplier and because the resulting levels have been perceived as too high for regulatory compliance purposes (U.S. EPA 1995i).

- C Target Detection Limit (TDL): A quantitation level constructed similar to the PQL.
- C Reporting Limit (RL): A quantitation level constructed similar to the PQL.
- C Estimated Quantitation Limit (EQL): A quantitation level constructed similar to the PQL.
- C Sample Quantitation Limit (SQL): A quantitation level that is sample-specific and highly matrix-dependent because it accounts for sample volume or weight, aliquot size, moisture content, and dilution. SQLs for the same compound generally vary between samples as moisture

content, analyte concentration, and concentrations of interfering compounds vary. The SQL is generally 5 to 10 times the MDL, however, it is often reported at much higher levels due to matrix interferences.

- C Contract Required Quantitation Limit (CRQL)/Contract Required Detection Limit (CRDL): A quantitation pre-set by contract, which may incorporate SW-846 methods, Office of Water methods, or other methods deemed necessary to meet study objectives. These limits are typically administrative limits and may actually be one or two orders of magnitude above the MDL.

#### **2.4.2 Using Non-Detect Data In the Risk Assessment**

In collecting waste feed or emissions data for use in risk assessments, or in setting regulatory compliance levels, a permitting authority is often faced with data quality objectives that require analyses near or below analytical detection or quantitation levels. In such situations, permittees often argue that the detection levels should be set with a large factor of certainty in order to be confident that measurements are reliable. Environmental groups frequently argue that a level of zero, or a level at which a single researcher can demonstrate that the compound can be detected, should be used as the set level. Measurements made below analytical detection and quantitation levels are associated with increased measurement uncertainty, so it is important to understand the impact they may have when they are applied.

Because of the quantitative differences between the various types of detection levels, “non-detected” compounds pose two questions:

1. Is the compound really present?, and
2. If so, at what concentration?

The first question is generally hard to answer, and is dependent mainly on the analytical resources available. The answer to the second question is “somewhere between true zero and the quantitation level applied.” In earlier guidance (U.S. EPA 1994i) we recommended applying emission rates of one-half the “detection limit” for non-detects. However, which detection limit to use was not explicitly defined or presented in quantitative terms.

For *waste feed* data (e.g., used as a surrogate when emissions data is not available), we generally recommend using the SQL, since waste feeds are typically highly concentrated organic or inorganic matrices that require special analytical clean-up procedures and dilutions of the sample. This approach is consistent with that used in other program offices for highly contaminated media requiring quantification

specifically for risk assessment purposes. However, in dealing with stack emissions data, concentrations of constituents are typically found only at trace levels (assuming good combustion). Therefore, to increase consistency and reproducibility in dealing with non-detects for *emissions data*, we generally recommend using the MDL-derived RDL to quantify non-detects for COPCs analyzed with non-isotope dilution methods, and using the method-defined EDL to quantify non-detects for COPCs analyzed with isotope dilution methods. The procedures are as follows:

***For COPCs Analyzed With Non-isotope Dilution Methods:*** Quantify non-detects by using an MDL-derived RDL.

1. Require the laboratory to report the actual MDL as specified in the chosen SW-846 analytical method. The laboratory should report MDLs for every non-detect compound analyzed, in addition to the commonly used reporting limit, such as an EDL, EQL, or PQL.

Commonly used SW-846 non-isotope dilution methods such as Method 8260 (volatiles), and Method 8270 (semivolatiles) don't themselves define the MDL. They reference 40 CFR Part 136 instead. Though specified in the Method, some laboratories do not always report MDLs as defined in 40 CFR Part 136.

This would apply to the analysis of each individual component of multiple-component samples (e.g., front half rinse, XAD resin, condensate, Tenax tube).

**Note:** Laboratories typically produce MDLs specific to each non-isotope dilution method performed by the laboratory on an annual basis.

2. Calculate an MDL-derived RDL for each COPC non-detect by multiplying the MDL by 2.623 (interim factor) (U.S. EPA 1995i).

Another option is to request that the laboratory derive the RDLs for you (per the definition above), as part of the analysis. Good quality assurance/quality control (QA/QC) suggests you check to make sure the RDLs have been generated properly.

3. Adjust the RDL, as appropriate, to account for sample-specific volumetric treatments (e.g., splits and dilutions) that differ from those used in the Part 136 MDL determinations.

Again, an option is to have the laboratory perform the adjustments for you. We recommend you check to make sure the adjustments have been done properly.

***For COPCs Analyzed With Isotope Dilution Methods:*** Quantify non-detects using the EDL as defined by the analytical method, without the use of empirical factors or other mathematical manipulations specific to the laboratory. Commonly used isotope dilution methods include SW-846 Methods 8290, 1624, and 1625, as well as CARB 429.

***Methods for Metals Analysis:*** Quantify non-detects for metal analysis in the risk assessment by using the IDL as defined by the analytical method, without the use of empirical factors or other mathematical manipulations specific to the laboratory.

*Please note* this recommendation is an update to the information provided in U.S. EPA [2001c] *Risk Burn Guidance for Hazardous Waste Combustion Facilities.*)

The MDL definition used in 40 CFR Part 136 addresses errors of the first type (i.e. false negatives). The 99 percent confidence limit states that the MDL has only a 1 percent chance the detects will be misidentified as negative, when the compound of concern is actually present. Errors of the second type (false positives) aren't addressed. By not addressing false positives, the statistically-defined default value becomes 50 percent. In other words, where 40 CFR did not address false positives, the system required that 50 percent of the detects at the MDL would be false positives. This is a very protective approach, and biased toward not missing any compounds of potential concern that may be present. The MDL-derived RDL, and to a lesser extent the EDL, somewhat indirectly addresses the false positive issue. As described in defining the RDL (see Section 2.4.1), by the time the standard deviation has been multiplied by 8, the possibility of false positives is usually less than 1 percent.

### **2.4.3 Statistical Distribution Techniques**

Many statistical distribution techniques are available for calculating a range of standard deviations to quantify non-detect concentrations of COPCs. These include random replacement scenarios, such as (Cohen and Ryan 1989; Rao, Ku, and Rao 1991):

- the uniform fill-in (UFI) method, in which each LOD value is replaced with a randomly generated data point by using a uniform distribution;
- the log fill-in (LFI) method which is the same as UFI, except using a logarithmic distribution;
- the normal fill-in (NFI) method which is the same as UFI, except using a log-normal distribution; and
- the maximum likelihood estimation (MLE) technique.

Also, if the permitting authority determines it to be applicable, a Monte Carlo simulation might be used to determine a “statistical” value for each non-detect concentration.

### **2.4.4 Our Recommendations on Quantifying Non-Detects**

Using non-detects in a risk assessment depends on the analytical method(s) used to produce the data. In most cases, the Agency estimates emission rates for undetected COPCs (see Section 2.3) by assuming that COPCs are present at a concentration equivalent to the MDL-derived RDL for non-isotope dilution

methods, or to the method-defined EDL for isotope dilution methods. We consider these methods reasonable, and believe they represent a scientifically sound approach that supports maximum protection of human health and the environment while recognizing the uncertainty associated with analytical measurements at very low concentrations in a real world sample matrix. We also recognize that there are subjective components and limitations to each of the non-detect methodologies presented in this and previous guidance, including the recommended methods.

Some risk assessors have expressed the desire to obtain and use non-routine data (e.g., uncensored data) of defensible quality in risk assessments, as a way to deal with non-detect issues. The HHRAP doesn't address what forms or how such data might be used. The decision to use non-routine data in a risk assessment is not precluded just because it is different. Neither does the HHRAP necessarily endorse using non-routine data. We generally recommend consulting with the permitting authority on the appropriateness of using non-routine data. If non-routine data is used, we generally recommend carefully identifying and evaluating the limitations associated with the data, and clearly document this discussion in the Uncertainty section of the risk assessment report.

As stated previously, a pretrial burn risk assessment can help to make sure that the trial burn test will achieve the desired quantitation limit (and, therefore, DREs and COPC stack gas emission rates).

#### **2.4.5 Estimated Maximum Possible Concentration (EMPC)**

The EMPC as defined in SW-846 is in most cases only used with the isotope dilution methods. An EMPC is calculated *for dioxin isomers* that:

- have a response with a signal to noise ratio of at least 2.5 for both the quantitation ions; and
- meet all the relevant identification criteria specified in the analytical method, except the ion abundance ratio.

Ion abundance ratios are affected by co-eluting interferences that contribute to the quantitative ion signals. As a result, one or both of the quantitative ions signals may possess positive biases.

An EMPC is a worst-case estimate of the concentration. An EMPC is not a detection limit and should not be treated as a detection limit in the risk assessment. We generally recommend using EMPC values as detections without any further manipulation (e.g., dividing by 2). However, because EMPCs are worst-

case estimates, you may wish to consult with the permitting authority on techniques to minimize EMPCs when reporting trial and risk burn results. This is especially true when the EMPC values result in risk estimates above regulatory levels of concern. Some techniques to minimize EMPCs include performing additional cleanup procedures (as defined by the analytical method) on the sample or archived extract, and/or reanalyzing the sample under different chromatographic conditions.

**Please Note:** using alternative quantitation ions might be acceptable, if the signal-to-noise ratio of the ion signal is at least 2.5 and if the tune data indicate that the mass spectrometer is operating within specifications.

Such actions to reduce the EMPC are expected to be more cost effective than the additional sample cleanup and/or reanalysis.

#### **RECOMMENDED INFORMATION FOR THE RISK ASSESSMENT REPORT**

- C Actual MDLs for all non-detect stack emissions data, non-isotope dilution methods
- C EDLs for all non-detect stack emissions data, isotope dilution methods
- C SQLs for all non-detect waste feed or feedstream data used
- C Description of the method applied to quantify the concentration of non-detects

### **2.5 EVALUATING CONTAMINATION IN BLANKS**

Blank samples are intended to provide a measure of any contamination that may have been introduced into a sample:

1. in the field while the samples were being collected,
2. in transport to the laboratory, or
3. in the laboratory during sample preparation or analysis.

Blank samples are analyzed the same way as the site samples from the trial burn. To prevent including non-site related compounds in the risk assessment, we generally recommend comparing the concentrations of compounds detected in blanks to concentrations detected in site samples collected during the trial burn. Four types of blanks are defined in the *Risk Assessment Guidance for Superfund*

(U.S. EPA 1989e): trip blanks, field blanks, laboratory calibration blanks, and laboratory reagent or method blanks. Detailed definitions of each are provided below.

***Trip Blank*** - A trip blank is used to indicate potential contamination due to migration of volatile organic compounds from the air on the site or in sample shipping containers, through the septum or around the lid of sampling vials, and into the sample. The blank accompanies the empty sample bottles to the field as well as with the site samples returning to the laboratory for analysis. The blank sample is not opened until it is analyzed in the lab with the site samples, thus making the laboratory “blind” to the identity of the blanks.

***Field Blank*** - A field blank is used to determine if field sampling or cleaning procedures (e.g., insufficient cleaning of sample equipment) result in cross-contamination of site samples. Like the trip blank, the field blank is transported to the field with empty sample bottles and is analyzed in the laboratory along with the site samples. Unlike the trip blank, however, the field blank sample is opened in the field and recovered in the same manner as the collected samples. As with trip blanks, the field blanks’ containers and labels may be the same as for site samples and blind to the laboratory.

***Instrument Blank*** - An instrument blank is distilled, deionized water injected directly into an instrument without having been treated with reagents appropriate to the analytical method used to analyze actual site samples. This type of blank is used to indicate contamination in the instrument itself.

***Laboratory Reagent or Method Blank*** - A laboratory reagent or method blank results from the treatment of distilled, deionized water with all of the reagents and manipulations (e.g., digestions or extractions) to which site samples will be subjected. Positive results in the reagent blank may indicate either contamination of the chemical reagents or the glassware and implements used to store or prepare the sample and resulting solutions. Although a laboratory following good laboratory practices will have its analytical processed under control, in some instances method blank contaminants cannot be entirely eliminated.

***Water Used for Blanks*** - For all the blanks described above, results are reliable only if the water comprising the blank was clean. For example, if the laboratory water comprising the trip blank was contaminated with VOCs prior to being taken to the field, then the source of VOC contamination in the trip blank cannot be isolated.

Blank data is generally compared to the results with which the blanks are associated. However, if the association between blanks and data can’t be made, blank data is compared to the results from the entire sample data set.

U.S. EPA (1989e) makes a distinction between blanks containing common laboratory contaminants and blanks containing contaminants not commonly used in laboratories. Compounds considered to be common laboratory contaminants are

- acetone,
- 2-butanone (methyl ethyl ketone),
- methylene chloride,
- toluene, and
- the phthalate esters.

If compounds considered to be common laboratory contaminants are detected in the blanks, then sample results are usually not considered to be detected unless the concentrations in the sample are equal to or exceed ten times the maximum amount detected in the applicable blanks. If the concentration of a common laboratory contaminant in a sample is less than ten times the blank concentration, then the compound is usually treated as a non-detect in that particular sample.

In some limited cases, it may be appropriate to consider blanks which contain compounds that aren't considered by the Agency to be common laboratory contaminants. In these limited cases, sample results aren't considered to be detected unless the concentrations in the sample exceed five times the maximum amount detected in the applicable blanks. If the concentration in a sample is less than five times the blank concentration, then the compound would be treated as a non-detect in that particular sample.

Carefully consider the evaluation of blank data in the overall context of the risk assessment and permitting process. We generally expect issues related to non-laboratory contaminant blanks to be minimal, because data collection and analysis efforts in support of trial/risk burns are expected to be of high quality and in strict conformance to QA/QC plans and SOPs. Carefully evaluating the trial/risk burn data will avoid the potential for contaminated blanks to compromise the integrity of the data. It will also help prevent the need for retesting to properly address data quality issues.

We highly recommend practicing caution in applying blank results to correct or qualify sample results for any purpose, as blanks are provided in minimal quantities (e.g., one per test condition or one per test) and therefore are at best qualitative indicators of the validity of a data set. Blank correction can reduce accuracy and often represent a non-conservative uncertainty. Consequently a permit authority might decide not to allow blank correction as a conservative assumption (consistent with a screening level risk assessment).

When considering blank contamination in the COPC selection process, we recommend that permitting authorities ensure that:

- (1) The facility or data gatherer has made every reasonable attempt to ensure good data quality and has rigorously implemented the QA/QC Plan and good industry sampling and testing practices.
- (2) Trial/risk burn data has not been submitted to the permitting authority as “blank corrected.” Rather, the permitting authority has the full opportunity to review the data absent additional manipulation by the data gatherer.
- (3) The effect of the blank correction on the overall risk estimates, if such an effect is considered, is clearly described in the uncertainty section of the risk assessment report.
- (4) The risk assessment report lists emissions rates both as measured, and as blank corrected, in situations where there is a significant difference between the two values.