

US EPA ARCHIVE DOCUMENT

Chapter 2

Facility Characterization

What's Covered in Chapter 2:

- ◆ Compiling Basic Facility Information
 - ◆ Identifying Emission Sources
 - ◆ Estimating Emission Rates
 - ◆ Identifying Compounds of Potential Concern (COPCs)
 - ◆ Estimating COPC Concentrations for Non-Detects
 - ◆ Evaluating Contamination In Blanks
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This chapter provides guidance on characterizing the nature and magnitude of emissions released from facility sources. The characterization 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.

2.1 COMPILING BASIC FACILITY INFORMATION

Basic facility information should be considered in conducting the risk evaluation, and provided to enable reviewers to establish a contextual sense of the facility regarding how it relates to other facilities and other hazardous waste combustion units. At a minimum, the basic facility information listed in the highlighted box at the end of this and other sections should be considered in the risk evaluation. The following sections and chapters describe the collection of this information in more detail; however, users may want to consult these discussions so that all site-specific information needed to complete the risk assessment can be collected simultaneously, when appropriate, for up front consideration. The risk assessor is also referred to *Briefing the BTAG: Initial Description of Setting, History, and Ecology of a Site* (U.S. EPA 1992a) (see web site www.epa.gov/superfund/program/risk/tooleco.htm) for more guidance on compiling basic facility information.

RECOMMENDED INFORMATION FOR RISK ASSESSMENT REPORT

- Principal business and primary production processes
- Normal and maximum production rates
- Types of waste storage and treatment facilities
- Type and quantity of wastes stored and treated
- Process flow diagrams showing both mass and energy inputs and outputs
- Type of air pollution control system (APCS) associated with each unit

2.2 IDENTIFYING EMISSION SOURCES

Combustion of a hazardous waste generally results in combustion by-products being emitted from a stack. In addition to emissions from the combustion stack, additional types of emissions of concern that may be associated with the combustion of hazardous waste include (1) process upsets, (2) general RCRA fugitive emissions, (3) cement kiln dust (CKD) fugitive emissions, and (4) accidental releases. Each of these emission source types are defined below with regards to the context and scope of this guidance.

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

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

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 compounds or 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 compounds or pollutants into the ambient air caused by the handling, storage, and disposal of cement kiln dust.

Accidental Release - 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, or transportation accidents.

Consistent with previous U.S. EPA guidance (U.S. EPA 1994d), U.S. EPA OSW recommends that, with the exception of accidental releases, all of these emission source types be addressed in the risk assessment, as applicable. Accidental releases are not considered within the scope of this guidance, and should be evaluated as recommended in Section 112(r) of the CAA and current U.S. EPA guidance (U.S. EPA 1996k) or the *RMP Offsite Consequence Analysis Guidance*, dated May 24, 1996. A decision to consider accidental releases in risk assessments for hazardous waste combustion facilities should be made on a site specific basis by the relevant permitting authority.

The following subsections contain guidance for estimating emissions for the source types specified for inclusion 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

Stack emission rates (in grams per second) need to be determined for every compound of potential concern (COPC) identified using the procedures outlined in Section 2.3. U.S. EPA OSW expects that emission rates used to complete the risk assessment will be (1) long-term average emission rates adjusted for upsets, or (2) reasonable maximum emission rates measured during trial burn conditions in order to assure that risk assessments are conservative. Maximum emission rates measured during trial burn conditions (see Section 2.2.1.1) represent reasonable maximum emission rates. These emission rates can be controlled by hourly rolling average permit limits traditionally found in combustion unit operating permits, and are more conservative than emission estimates that are based on long-term average emission rates. Long-term

average emission rates (see Section 2.2.1.2) are based on tests of the combustion unit burning worst-case wastes at operating conditions that are representative of normal operating conditions over a long-term period. If long-term average emission rate estimates are used in the risk assessment, the final permit will likely specify limitations in addition to any hourly rolling average limit typically used to regulate hazardous waste combustion facilities.

A permitting agency's decision to allow a facility to use emission rate data developed from either normal or maximum operating conditions will be made on a case-by-case basis. Some facilities may be required to use emission rate data developed from maximum operating conditions because the variability in waste feed and operating conditions is too great to make permit decisions based on emission data collected during normal operating conditions, or because the emissions from combustion of the waste feed material are anticipated to be highly toxic and only a conservative risk assessment can adequately ensure protection.

2.2.1.1 Estimates from Trial Burns

For existing facilities (such as those built and operational), emission rate information will generally be determined by direct stack measurements during pretrial burn or trial burn tests, because trial burn tests are generally part of the permitting process to burn hazardous wastes. This policy is consistent with U.S. EPA 1998 *Guidance on Collection of Emissions Data to Support Site-Specific Risk Assessments at Hazardous Waste Combustion Facilities*, prepared by U.S. EPA Region 4 and OSW (U.S. EPA 1998b). For new facilities (see Section 2.2.3), estimated emission rates used to complete pretrial burn risk assessments should be compared to the emission rates estimated from actual trial burns completed after the new facility receives a permit and is constructed. Trial burn tests are designed to produce emission rates higher than those anticipated under normal operating conditions. U.S. EPA OSW recommends that sampling be conducted, in accordance with U.S. EPA guidance on conducting trial burns, by using compound-specific stack sampling, analytical, and quality assurance/quality control (QA/QC) protocols and procedures approved by the permitting authority. An alternative to a trial burn test is the submittal of data "in lieu of" a trial burn. U.S. EPA OSW will consider this type of data for on-site units on a case-by-case basis. U.S. EPA OSW expects that this data to be based on recent stack test measurements from a similar type of combustion unit with similar waste feed, capacity, operating conditions, and air pollution control systems (APCSs) to ensure comparable emission rates and destruction and removal efficiencies (DREs).

U.S. EPA OSW expects that using data from a trial burn as a basis for estimating COPC emission rates will tend to overestimate risk. COPC emission rates measured during trial burns are expected to be greater than emission rates during normal unit operations, because a facility “challenges” its combustion unit during a trial burn to develop a wide range of conditions for automatic waste feed cutoff (AWFCO) systems. Trial burn 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 combustion unit to destroy principal organic hazardous constituents (POHCs) in the waste feed is challenged. The lesser of the 95th percentile of the mean or maximum stack gas concentration from the three trial burn runs should be used to develop the emission rate estimate used in the risk assessment.

High POHC feed rates and extreme operating conditions tested during the low-temperature trial burn test are usually expected to result in greater product of incomplete combustion (PIC) emission rates. However, this is not true in all cases. For example, the formation of PCDDs and PCDFs does not necessarily depend on “POHC incinerability” low temperature conditions. Polychlorinated dibenzo(p)dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) can be formed as a result of (1) catalytic formation in the low-temperature regions of the combustion unit or APCS during the low temperature test, or (2) catalytic formation that is dependent on high APCS temperatures typically experienced during the high temperature test.

Because the amount of testing required to develop estimates of COPC emission rates is so extensive and time consuming, U.S. EPA OSW places the responsibility for selecting the test conditions first on the facility and then on the permit writer. If a facility desires to receive a permit with no limits other than those traditionally based on hourly rolling average data gathered during a trial burn, then risk testing should be conducted during trial burn or “worst case” conditions. Whether the permit writer requires testing to be conducted at low, high, or both temperature conditions is a decision that must be made by the permit writer based on the characteristics of the facility and policy set forth by the senior management of the appropriate regulatory agency.

RECOMMENDED INFORMATION FOR RISK ASSESSMENT REPORT

- All (current and historical) stack sampling information regarding rates of emissions from the combustion unit during normal or trial burn conditions
- Description of the waste feed streams burned during the stack sampling, including chemical composition and physical properties, which demonstrate that the waste feeds are representative of worst case site-specific "real" wastes

*** NOTICE ***

Although U.S. EPA OSW will not require a risk assessment for every possible metal or PIC from a combustion unit, this does not imply that U.S. EPA OSW will allow only targeted sampling for COPCs during trial burn tests. Based on regional permitting experience and discussions with regional analytical laboratories, U.S. EPA OSW maintains that complete target analyte list analyses conducted when using U.S. EPA standard sampling methods (e.g., 0010 or 0030), do not subject facilities to significant additional costs or burdens during the trial burn process. Facilities conducting stack emission sampling should strive to collect as much information as possible which characterizes the stack gases generated from the combustion of hazardous waste. Therefore, every trial burn or "risk burn" should include, at a minimum, the following tests: Method 0010, Method 0030 or 0031 (as appropriate), total organic compounds (using the Guidance for Total Organics, including Method 0040), Method 23A, and the multiple metals train. Other test methods may be approved by the permitting authority for use in the trial burn to address detection limit or other site-specific issues.

2.2.1.2 Normal Operation Emission Rate Data

Facilities with limited waste feed characteristics and operational variability may be allowed to conduct risk testing at normal operational conditions (U.S. EPA 1994c). The collection of COPC data during normal operating conditions is referred to as a "risk burn" throughout the remainder of this guidance. It is important to note, however, that a risk burn does not replace a traditional trial burn conducted to measure DRE. Instead, U.S. EPA OSW considers a risk burn as an additional operating condition of the trial burn during which data is collected for the purpose of completing a risk assessment.

Because operational data collected during the risk burn would not normally be extrapolated to hourly rolling average AWFCO limits specified in an operating permit; the regulatory agency permit writer should

craft the permit with conditions designed to ensure that the facility does not operate at conditions in “excess” of the normal conditions over the long-term operation of the facility (for example, waste feed rate or stack gas flowrate). These additional permit limits are anticipated to take the form of quarterly or annual mass feed limitations on the waste feed, quarterly or annual average temperatures or stack gas flow rates, and other appropriate limitations.

It may also be necessary for the permit to contain appropriate reporting requirements to ensure that the regulatory agency can verify that the facility does not normally operate at conditions in excess of those tested during the risk burn. Monthly, quarterly, or annual reports which document long-term operations will likely be required of the facility. If a facility violates a long-term permit condition, the permit writer may also include language that requires the facility to cease waste burning immediately until a new test, risk assessment, and/or revised permit are completed. More detailed guidance on the development of permit limits can be found in U.S. EPA Region 6's *Hazardous Waste Combustion Permitting Manual*; which can be obtained from the U.S. EPA Region 6 web page (www.epa.gov/region06/).

One of the most important criteria which should be evaluated when considering the collection of data during a risk burn rather than a trial burn is the ability of the facility to document that the test is conducted with “worst case” waste. Worst case waste should be the waste feed material or combination of materials that are most likely to result in significant emissions of COPCs. The potential for both PIC and metal emissions should be considered in the selection of the worst case waste. For example, if a facility burns two types of waste—one waste with a high chlorine content and a significant concentration of aromatic organic compounds and a second with a low chlorine content and a significant concentration of alkanes—the former waste should be considered to be the “worst case” for PIC formation and should be used during the risk burn. A similar evaluation should be considered when selecting the worst case waste for metal emissions.

If a facility chooses to develop—and the appropriate regulatory agency allows the use of—emission rate estimates from a risk burn rather than a trial burn, the data set for each COPC should be the 95th percentile of the mean COPC emission rate over all the acceptable test runs *or* the maximum COPC emission rate value from all acceptable test runs, whichever value is lower. U.S. EPA OSW does not believe that it is reasonable to perform a risk assessment with the 95th percentile of the mean emission rate

if the maximum rate is less than this value. U.S. EPA OSW also recommends that, where possible, the COPC emission rate value from the trial burn test and the risk burn test be compared in the risk assessment report along with a comparison of the operational conditions at these two test conditions. For example, if the POHC used for the DRE test in the trial burn is a semivolatile organic compound (SVOC), the facility should analyze for all SVOCs (Method 0010) during the trial burn, and compare these values to those reported for the risk burn. The difference between the emission rates from the trial burn and risk burn should be evaluated in the uncertainty section of the risk assessment.

RECOMMENDED INFORMATION FOR RISK ASSESSMENT REPORT

- Sampling and analytical data for trial burn and risk burn (if the risk assessment is completed by using risk burn data) operating conditions
- Description of the operating conditions, under which each set of emission rate data being used was developed
- Complete evaluation of the differences between trial burn and risk burn operating conditions, with an explanation of the expected resultant risk differences

2.2.1.3 Estimates of the Total Organic Emission (TOE) Rate

Organic compounds that cannot be identified by laboratory analysis will not be treated as COPC's in the risk calculations. However, these compounds still may contribute significantly to the overall risk, and therefore, should be considered in the risk assessment (DeCicco 1995; U.S. EPA 1994d). U.S. EPA developed the total organic emissions (TOE) test to account for unidentified organic compounds because existing methods, such as total hydrocarbon analyzers, do not fully determine the total mass of organics present in stack gas emissions (Johnson 1996). U.S. EPA OSW anticipates that trial and risk burns will include sampling for TOE in order to provide permitting authorities with the information needed to address concerns about the unknown fraction organic emissions. The TOE can be used in conjunction with the identified organic compounds to calculate a TOE factor which can then be used to facilitate a evaluation of potential risks from the unidentified fraction of organic compounds in the stack gas.

The TOE test is the subject of other guidance; see the *Guidance for Total Organics* (U.S. EPA 1996b). Use of the TOE data is dependent 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_{VOC}) (referred to as Field GC Component in the TO Guidance) - TO_{VOC} is defined as the fraction of organic compounds having a boiling point 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_{SVOC}) (referred to as Total Chromatographical Organics Component in the TO Guidance) - TO_{SVOC} is defined as the fraction of organic compounds having boiling points between 100°C and 300°C. This VOC fraction is collected using modified U.S. EPA Method 0010 procedures as defined by U.S. EPA (1996b). The total mass of organic compounds with boiling points 100°C to 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_{GRAV}) (referred to as Gravimetric component in the TO Guidance) - TO_{GRAV} is defined as the fraction of organic compounds having boiling points greater than 300°C. This fraction includes two types of compounds: (1) Identified SVOCs collected using U.S. EPA Method 0010 having boiling points greater than 300°C and (2) unidentified nonvolatile organics having boiling points greater than 300°C. This fraction is determined by using modified U.S. EPA Method 0010 procedures defined by U.S. EPA (1996b), which quantifies the mass, above this fractions boiling point, by measuring the total mass by evaporation and gravimetry (weighing) for nonvolatile total organics.

It should be noted that the TO total (TO_{TOTAL}) is the sum of the sums of each fraction. The sum of the TO fractions are 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/m³)
 TO_{VOC} = stack concentration of volatile TO, including identified and unidentified compounds (mg/m³)

TO_{SVOC}	=	stack concentration of SVOC TO, including identified and unidentified compounds (mg/m^3)
TO_{GRAV}	=	stack concentration of GRAV TO, including identified and unidentified compounds (mg/m^3)

The TOE data is used in conjunction with the identified data to compute a TOE factor. TOE factors have been computed which range from 2 to 40. The TOE factor is defined by this guidance as the ratio of the TO_{TOTAL} mass to the mass of identified organic compounds and 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^3)
C_i	=	stack concentration of the <i>i</i> th identified COPC (mg/m^3)

One of the most critical components of the TOE factor is the identification of the organic compounds in the denominator of Equation 2-2. Although the permitting authority may not require a facility to analyze the organic compounds with all possible analytical methods, facilities should 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 be evolved 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, permitting authorities and facilities may choose to use additional test methods in the trial burn in order to speciate the maximum number of organic compounds.

U.S. EPA OSW also recommends that permitting authorities include tentatively identified compounds (TICs) in the denominator when computing the TOE factor to ensure that appropriate credit is given to defensible efforts at identifying the maximum number of organic compounds. Finally, U.S. EPA OSW recommends that non-detect compounds of potential concern be treated consistently between the risk assessment and TOE evaluation. That is, if a non-detected constituent is deleted as a compound of

potential concern (See Section 2.3), then it would not be included in the identified fraction of the TOE equation. Compounds of potential concern identified as per Section 2.3, but not detected, should be included in the TOE factor equation at the reliable detection limit (non-isotope dilution methods) or the estimated detection limit (isotope dilution methods).

The results of the gravimetric fraction should also be carefully evaluated when using the TOE factor. Both regulated industry and U.S. EPA scientists have expressed some concern that the gravimetric fraction of TOE test may contain materials that are not organic. U.S. EPA Office of Research and Development National Risk Management Research Laboratory (NRMRL) recently completed a study conducted to identify products of incomplete combustion (U.S. EPA 1997a). U.S. EPA NRMRL suggested in the study report that the gravimetric fraction of the TOE test may consist of organic and/or inorganic mass not directly attributable to organic incinerator emissions. U.S. EPA NRMRL theorized that these artifacts could consist of inorganic salts, super-fine particulate, or fractured XAD-2 resin. U.S. EPA NRMRL also concluded in this study report that the vast majority of the non-target semivolatile organic compounds detected, but not fully identified, were alkanes with more than 10 carbon atoms, esters of high molecular weight carboxylic acids, and phthlates. Most problems associated with accurately determining the gravimetric fraction attributable to incinerator emissions can be minimized; see the U.S. EPA 1998 *Guidance on Collection of Emissions Data to Support Site-Specific Risk Assessments at Hazardous Waste Combustion Facilities* (U.S. EPA 1998b) for minimizing sample errors.

The TOE factor is used in the uncertainty section of the risk assessment report to evaluate the risks from the unknown fraction of organics. Permitting authorities can 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 may decide to do any or all of the following:

1. Describe in a narrative form what is known of the unknown portion of the emissions.
2. Attribute a risk to the unknown portion of the emissions. An example was presented as a preferred option in U.S. EPA (1994d) which assumed 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 ³)
C_i	=	stack concentration of the i th identified COPC (mg/m ³)

3. Require 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.

Permitting authorities may use variations of the TOE factor to address site-specific concerns. For example, some permitting authorities may compute three separate TOE factors based on the apportioning provided by the TOE test (i.e., TO_{VOC} , TO_{SVOC} , and TO_{GRAV}). The unknowns associated with each separate fraction of unidentified organic compounds can then be evaluated separately.

2.2.2 Estimating Emission Rates for Facilities with Multiple Stacks

Emissions from all combustion units burning hazardous waste at a facility, not just the unit currently undergoing the permitting process, should be considered in the risk assessment. As discussed further in Chapter 3, air dispersion modeling for each combustion unit (source) should be conducted separate from the other combustion units, to allow evaluation of risk on a stack or source-specific basis. A case example is where a chemical manufacturing facility may operate both an on-site incinerator and several hazardous waste burning boilers. Whether it is the incinerator or the boilers undergoing the permitting process, the risk assessment should consider the emissions from all the combustion units in the estimate of facility risk. In addition to RCRA combustion units, emissions from other RCRA treatment, storage, or disposal units (e.g., open burning/open detonation and thermal desorption) may also be included in the risk evaluation in some cases.

2.2.3 Estimating Stack Emission Rates for Facilities Not Yet Operational

New hazardous waste combustion facilities should submit a Part B permit application, go through an extensive permitting process, and, if successful, receive a final permit to commencement of operation. The permitting process requires submittal of sufficiently detailed information for the regulatory authorities to evaluate compliance with existing regulations, guidance, and protectiveness. Stack (source) locations and dimensions, design flow and emission rate estimates, waste feed characteristics, surrounding building dimension data, facility plot plans, and terrain data should be reviewed and used in a pre-operation risk assessment. This will assist in decision-making and designing permit requirements.

The design emission rates, waste feed characteristics, and other design data should be reviewed along with supplementing documentation to assure 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 APCs should be used to estimate COPC emission rates for new facilities that have not been constructed.

If the preferred option of using surrogate data from similar facilities is not available, some state environmental agencies enforce emission rate limits based on state laws. Since these limits cannot be exceeded, they can be used to develop emission rate estimates for the risk assessment. The facility will demonstrate that its emissions are less than the those considered in the permit and risk assessment during the trial or risk burn.

Other data which may cause problems when performing risk assessments for new facilities is particle size distribution. A default particle size distribution is presented in Chapter 3 for use if particle size distribution data from a similar type of facility are not available.

2.2.4 Estimating Stack Emission Rates for Facilities Previously Operated

Emissions from the historical operation of combustion units burning hazardous waste at a facility, not just the unit currently undergoing the permitting process, may also be considered in the risk assessment on a

case-by-case basis as determined by the permitting authority. Such a case may be when the emissions from historical operation of a source or sources may have already resulted in potential risk concerns at or surrounding the facility. Emissions from historical operations could be taken into consideration by modeling as a separate source or, if applicable, in the fate and transport equations by adding the previous years of operation to the anticipated time period of combustion for a new or existing operating source. In addition to RCRA combustion units, historical emissions from other RCRA treatment, storage, or disposal units (e.g., open burning/open detonation and thermal desorption) at the facility under evaluation may also be included in the risk assessment in some cases.

RECOMMENDED INFORMATION FOR RISK ASSESSMENT REPORT

- All stack test reports for combustion units used to develop emission rate estimates
- If using surrogate data for a new facility, descriptions of how the combustion data used represent similar technology, design, operation, capacity, auxiliary fuels, waste feed types, and APCSs
- Demonstration that the data used to develop the emission rate estimates were collected by using appropriate U.S. EPA sampling and analysis procedures
- The range of data obtained, and values used, in completing the risk assessment

*** NOTICE ***

Facilities may use estimated emission rate data from other combustion units only to determine whether the construction of a new combustion unit should be completed. After a combustion unit has been constructed, U.S. EPA OSW will require an additional risk assessment using emission rates collected during actual trial burn conditions.

2.2.5 Emissions From Process Upsets

Uncombusted hazardous waste can 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 (1994d) indicates that upsets are not generally expected to significantly increase stack emissions over the lifetime of the facility.

Process upsets occur when the hazardous waste combustion unit is not being operated as intended, or during periods of startup or shutdown. Upset emissions are generally expected to be greater than stack emissions (over short periods of time) because the process upset results in incomplete destruction of the wastes or other physical or chemical conditions within the combustion system that promote the formation and/or release of hazardous compounds from combustion stacks. Upset emissions usually occur during events and times when the hazardous waste combustion unit is not operating within the limits specified in a permit or regulation.

To account for the increased emissions associated with process upsets, the stack emission rate estimated from trial burn data (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) is multiplied by an upset factor. When available, facilities should use site specific emissions or process data to estimate the upset factor. The following types of data may be considered and evaluated to derive the upset factor:

- Data for continuous emissions monitoring systems that measure stack carbon monoxide, oxygen, total hydrocarbon (if required), or opacity (if appropriate)
- Data on combustion chamber, APCS, or stack gas temperature
- Frequency and causes of automatic waste feed cutoffs (AWFCO)
- Ratio of AWFCO frequency and duration to operating time
- APCS operating variables, such as baghouse pressure drop, liquid scrubber flow rate, or electrostatic precipitator voltage
- Stack test collected while the combustion unit was operated under upset conditions

This information may be analyzed with the objective of estimating the magnitude of the increase in emissions and the percentage of time on an annual basis that the unit operates at upset conditions.

When site specific data are not available or are inappropriate for deriving an upset factor, consistent with previous guidance (U.S. EPA 1993h), U.S. EPA OSW recommends that upset emissions be estimated by 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 does not operate under upset conditions continually, the factor must be adjusted to account for only the period of time, on an annual basis, that the units 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 combustion unit 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 resulting from non-routine events such as explosions, fires, and power failures are considered accidental releases and are not addressed by this guidance.

RECOMMENDED INFORMATION FOR RISK ASSESSMENT REPORT

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

2.2.6 RCRA Fugitive Emissions

RCRA fugitive emission sources that should be evaluated in the risk assessment include waste storage tanks; process equipment ancillary to the combustion unit; 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 require evaluation in some cases.

This section contains guidance for quantitatively estimating fugitive emissions on the basis of procedures outlined by 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

Quantitative estimation of RCRA fugitive emissions includes (1) identifying equipment to be evaluated as fugitive emission source(s), (2) grouping equipment, as appropriate, into a combined source, and (3) estimating compound specific emission rates for each source. Figure 2-1 is an example of a facility plot plan 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 for a hypothetical example facility. This figure, as well as Tables 2-1 and 2-2, have been provided as an example to facilitate understanding of each of the steps presented for estimating fugitive emissions.

Step 1: Identifying Fugitive Emission Sources - Generally, RCRA fugitive emission sources to be evaluated in the risk assessment should include waste storage tanks and process equipment that comes in contact with a RCRA hazardous waste such as equipment specified in Title 40, Code of Federal Regulations (40 CFR) Part 265, Subpart BB. Equipment covered under Subpart BB includes the following:

**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 (1995f).
- Column 5 The number of equipment per type at the source was multiplied by the equipment specific emission factor (Column 6) to obtain equipment specific emission rate for that respective type of equipment (Column 7).
- Column 6 Emission factors specific to each type of equipment can be obtained from U.S. EPA (1995f), 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.

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

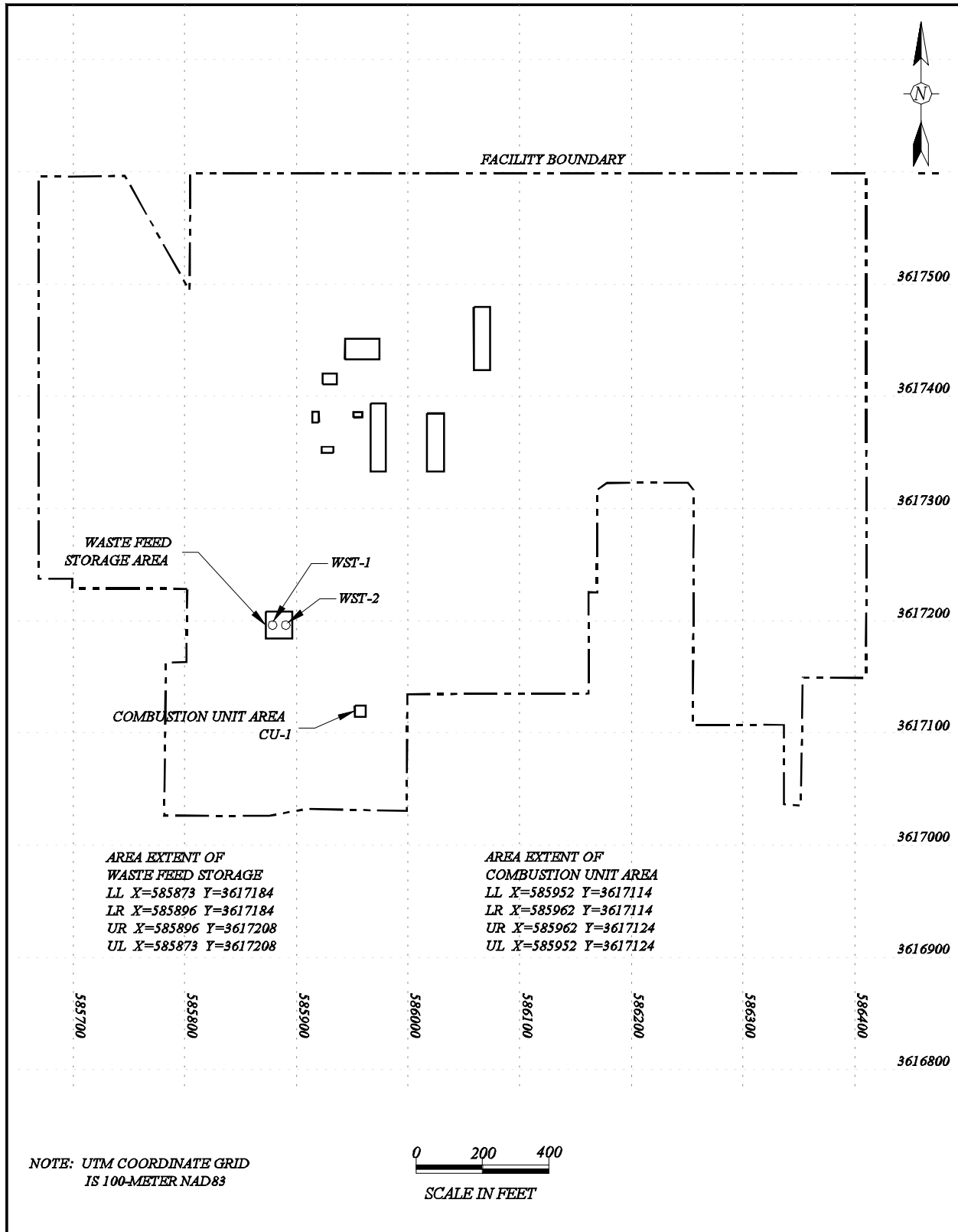
Each fugitive emission source should be identified on a facility plot map with a descriptor and the location denoted with Universal Transverse Mercator (UTM) coordinates (specify if North American Datum [NAD] of 27 or NAD83).

Step 2: Grouping Equipment Into a Combined Source - To significantly reduce the effort required to complete air dispersion modeling and subsequent risk assessment, equipment in close proximity may be grouped and evaluated as a single combined source with the speciated emission rates for each piece of equipment summed. The area extent of the grouped or combined source, as defined by UTM coordinates (specify if NAD27 or NAD83), should be clearly denoted on a facility plot map. The area extent of the combined source should be defined by the actual locations of the equipment being grouped, without exaggeration to cover areas without fugitive sources. Consideration should also be made for how fugitive emission sources are to be defined when conducting the air dispersion modeling (see Chapter 3).

As shown in Figure 2-1, equipment in two areas at the hypothetical facility have been grouped into combined sources; these consist of the Waste Feed Storage Area and the RCRA Combustion Unit Area.

Step 3: Estimating Fugitive Emissions from Tanks - Fugitive emission rates for waste storage tanks can be obtained 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 the facility does not have such information 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 guidance document (1995a), "*Compilation of Air Pollution Emission Factors, January 1995.*"

FIGURE 2-1
EXAMPLE FACILITY PLOT MAP



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**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		LOUISIANA SINGLE POINT SOURCE / AREA SOURCE Emission Inventory Questionnaire (EIQ) for Air Pollutants					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, not at standard (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) Type of Fuel Heat input (MMBtu/hr)		Operating Characteristics	Percent of annual throughput of pollutants through this emission point				Normal operating time of this point		Normal operating rate 100%
	Dec-Feb 25	Mar-May 25		Jun-Aug 25	Sep-Nov 25	hrs/ day 24.00	days/ week 7	weeks/ year 52.0		
	Air Pollutant Specific Information			Pollutant	Control equipment code	Control equipment efficiency	Emission Rate			
				Average (lbs/hr)	Maximum (lbs/hr)	Annual (tons/yr)				
				0.0023	0.3463	0.01	3	c	N/A ppm by vol	
				0.0041	125.00	0.081	3	c	N/A ppm by vol	
				0.0023	21.1266	0.01	3	c	N/A ppm by vol	
				0.0023	4.502	0.01	3	c	N/A ppm by vol	
				0.0062	195.3347	0.028	3	c	N/A ppm by vol	

The information required for estimating fugitive emission rates from storage tanks includes, but is not limited to, the following:

- Dimensions of the tanks
 - Shell height and diameter
- 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
- Characteristics of the shell
 - Color and shade
 - Condition (e.g., poor, good)
 - Heated
- Settings on breathe vents
 - Vacuum setting
 - Pressure setting
- 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: Estimating Fugitive Emissions from Process Equipment - Based on guidelines provided in U.S. EPA (1995f), "*Protocol for Equipment Leak Emission Estimates, EPA-453/R-93-017*," fugitive emissions for each equipment listed under 40 CFR Part 265, Subpart BB can be estimated by the following four approaches, in order of increasing refinement and data requirements:

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

These four approaches can be used at any facility to estimate fugitive emission rates of volatile organic compounds (VOCs) from equipment. Except for the AEFA method, all of the approaches require screening data collected by using a portable monitoring device (PMD). Because data on fugitive emissions at a facility is generally limited, the AEFA method will apply in most cases, and therefore, has been selected for use in the example demonstrated in Figure 2-1, and Tables 2-1 and 2-2. However, U.S. EPA OSW recommends that facilities use more refined approaches such as SRA, EPACA, or USCA, if sufficient data is available. U.S. EPA (1995f) provides a detailed discussion on these three approaches.

An Example Calculation Using the AEFA Method

Information for estimating fugitive emission rates using the AEFA method is as follows:

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

When this approach is used, equipment can be grouped by waste streams of similar characteristics and VOC composition (Columns 1 and 2, Table 2-1). However, the AEFA approach does not 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.

The average emission factors for synthetic organic chemicals manufacturing industry process units, refineries, and natural gas plants are presented in U.S. EPA (1995f) (Column 6, Table 2-1). 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.

SOCMI AVERAGE EMISSION FACTORS		
Equipment type	Service	Emission factor (kg/hr/source)
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 (1993e)

The total VOC emissions rate for a specified equipment type can be calculated by multiplying 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).

The total VOC emission rates for each equipment type are summed to generate the total fugitive emission rate for the waste stream by (Column 10, Table 2-1). Speciated fugitive emissions can then be 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 RISK ASSESSMENT REPORT

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

2.2.6.2 Fugitive Emissions from Combustion Unit Leaks

Fugitive emissions that result from the construction, design, or operation of a combustion unit burning hazardous waste should be evaluated, as appropriate. Examples of fugitive emissions from combustion unit leaks include the following:

- Combustion units that operate 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.
- Fugitive emissions resulting from the day-to-day operation of the combustion unit 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, U.S. EPA OSW does not offer any specific quantitative guidance on how to estimate fugitive emissions from hazardous waste combustion units. However, risks associated with emissions from hazardous waste combustion unit leaks can be addressed in the uncertainty section of the risk assessment if no site specific quantitative methods are available. Specifically, the permitting authority can review facility specific data to determine whether or not the design addresses equipment leaks and whether the operational data indicates that equipment leaks may be a problem.

RECOMMENDED INFORMATION FOR RISK ASSESSMENT REPORT

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

2.2.7 RCRA Fugitive Ash Emissions

The combustion of hazardous waste materials may result in the production of flyash. Fugitive particle emissions may result from the subsequent 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 equipment, however, a fraction of the flyash may still escape into the atmosphere as fugitive emissions.

2.2.7.1 Quantitative Estimation of RCRA Fugitive Ash Emissions

Steps for the quantitative estimation of RCRA fugitive ash emissions include (1) determining an empirical emission factor, (2) estimating the flyash generation rate, and (3) accounting for air pollution control equipment, if applicable. As demonstrated in the example calculation below, the fugitive ash emission rate can then be estimated by multiplying the empirical emission factor by the flyash generation rate and the control deficiency of the air pollution control equipment, if applicable.

Step 1: Determining an Empirical Emission Factor - Particle emissions associated with flyash loading and unloading can be estimated using 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 the combustion of 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 combusted. 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 the combustion of coal (as in the study) was wetted. Flyash from the hazardous waste combustion facility may not be wetted depending on the facility.

Step 2: Estimating the Flyash Generation Rate - The flyash generation rate from the APCD can be obtained from the Part B Permit Application and 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 is a conservatively high estimate of the actual flyash generation rate.

Step 3: Accounting for Air Pollution Control Equipment - If an APCD is used for controlling emissions during flyash handling operations, an efficiency factor (e.g., 99.5 percent) can be applied to the emission rate. An efficiency factor of 99.5 percent is based on U.S. EPA (1995a) for typical collection efficiencies of particulate matter control devices, for the particle sizes in the range of 2.5 to 10 μm .

Example Calculation

The fugitive ash emission rate is calculated by multiplying the empirical emission factor (Step 1) times the estimated flyash generation rate (Step 2) [(1.07 lb per ton) * (5,000 tons per year) = 5,350 lbs per year].

Accounting for the air pollution control equipment, the product of Steps 1 and 2 is multiplied times one minus the fabric filter efficiency (Step 3) to obtain the final RCRA fugitive ash emission rate for use in the risk assessment [(5,350 lbs per year) * (1 - 0.995) = 26.75 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 more recent regulatory determination of CKD (60 FR 7366, February 7, 1995).

Most CKD constituents (for example, metals) are not volatile but could be released to air through fugitive dust emissions as a volatile or semivolatile organic that can be released 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) nonerodible elements, such as clumps of grass or stones on the pile, (3) 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 (1) infrequent application of water, and (2) 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. It should be noted that a crust does not always form for a variety of reasons such as weather and chemistry of the CKD.

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

U.S. EPA (1993g) highlighted the limited amount of available information regarding the variation in 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 that is recycled back into the system and the “as-managed” CKD that is disposed on or offsite.

Transport in air is 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 may be suspended in

the wind and transported. Within this range, particles that are ≤ 30 micrometers can be transported for considerable distances downwind. 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 particles that are ≤ 10 micrometers.

RECOMMENDED INFORMATION FOR RISK ASSESSMENT REPORT

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

2.2.8.2 Estimation of CKD Fugitive Emissions

In general, this guidance does not address CKD risks in a quantitative fashion. However, risk assessments conducted for cement manufacturing facilities should, at a minimum, evaluate the fugitive emissions due to CKD on a qualitative basis. Readers are referred to the *Technical Background Document for the Report to Congress* (U.S. EPA 1993g), for methods to estimate the magnitude of fugitive emissions from the handling, storage, and disposal of CKD. In addition, an analysis of a specific facility's compliance with other environmental statutes and regulations may be an appropriate method to qualitatively evaluate risks associated 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. The purposes of identifying COPCs are to focus the risk assessment on those compounds that are likely to pose the most risk to ecological receptors exposed to hazardous waste combustion emissions. The COPC identification process is conservative by design to avoid not including compounds that might pose an ecological risk.

There is no one definition of a COPC, because a compound that is a COPC at one hazardous waste combustion unit may not be a COPC at another combustion unit. COPCs in the emissions from hazardous waste combustion units vary widely, depending on (1) the type of combustion unit, (2) the type of hazardous waste feed being burned, and (3) the type of APCS used. Also considered as COPCs are products of incomplete combustion (PICs); which are any organic compounds emitted from a stack, such as (1) compounds initially present in the hazardous waste feed stream and not completely destroyed in the combustion process, and (2) compounds that are formed during the combustion process. Because PICs may be formed by trace toxic organic compounds in the waste feed stream, these compounds should be evaluated as PIC precursors, in addition to those compounds that constitute most of the hazardous waste feed.

PICs should not be confused with principal organic hazardous constituents (POHC), which are compounds in the waste feed stream used to measure DRE of the combustion unit during a trial burn test. Unburned POHCs and partially destroyed or reacted POHCs are PICs, but PICs are not necessarily related to POHCs.

Table A-1 (Appendix A) presents a comprehensive list of compounds typically identified (1) in hazardous waste, and (2) in hazardous waste combustion stack gas emissions. For each compound, Table A-1 identifies the Chemical Abstracts Service (CAS) number and also indicates whether a compound has been identified as a potential COPC by (1) U.S. EPA and state risk assessment reference documents, (2) emission test results that have identified the compound in the emissions from hazardous waste combustion facilities, or (3) other literature that suggests that the compound may be significant from a risk perspective. Table A-1 has been provided in this guidance in order to help risk assessors ensure that the trial burn considers the full range of compounds potentially emitted from a combustion unit and the

appropriate analytical method. Once the trial burn stack tests are completed, the COPC selection process is initiated based on the universe of stack test data, not Table A-1. The purpose of a risk assessment is not to arbitrarily evaluate every potential compound listed in Table A-1.

Based on U.S. EPA OSW review, COPCs previously identified in ecological risk assessments at combustion facilities are as follows:

- Polychlorinated dibenzo(p)dioxins (PCDD) and polychlorinated dibenzofurans (PCDF)
- Polynuclear aromatic hydrocarbons (PAH)
- Polychlorinated biphenyls (PCB)
- Pesticides
- Nitroaromatics
- Phthalates
- Other organics
- Metals

This list was compiled based on professional experience and is not meant to be either limiting or inclusive. The list enabled U.S. EPA OSW to focus on (1) developing receptor-specific and compound-specific bioconcentration factors as provided in Appendices C and D, (2) developing compound- and receptor-specific TRVs as provided in Appendix E, and (3) developing receptor exposure parameters and exposure equations discussed in Chapter 5 and provided in Appendix F. These focused compound-specific parameters and information are included to facilitate the performance of ecological risk assessments, and are not meant to be either limiting or inclusive for hazardous waste combustion facilities. Experience has shown that developing compound-specific and receptor-specific parameters for risk assessments can be one of the most labor- and time-intensive parts of completing the risk assessment, and U.S. EPA OSW intends that the information included in the Appendices of this guidance facilitates the risk process.

COPCs are identified from the trial burn data based on their potential to pose an increased risk. This identification process should focus on compounds that (1) are likely to be emitted, based on the potential presence of the compound or its precursors in the waste feed, (2) are potentially toxic to ecological

receptors, and/or (3) have a definite propensity for bioconcentrating in ecological receptors and bioaccumulating in food chains. Appendix E presents toxicity reference values of specific compounds to specific receptors. The toxicity information provided in this guidance is for informational purposes to help permitting authorities explain the basis for identifying compounds as COPCs and facilitate completing the risk assessment. Since toxicity information may change as additional research is conducted, permitting authorities should review the most current available information before completing a risk assessment to ensure that the toxicity data used in the risk assessment is based upon the most current Agency consensus.

As illustrated in Figure 2-3, the following steps should be used to identify the COPCs that will be evaluated for each facility (U.S. EPA 1993h; 1994d).

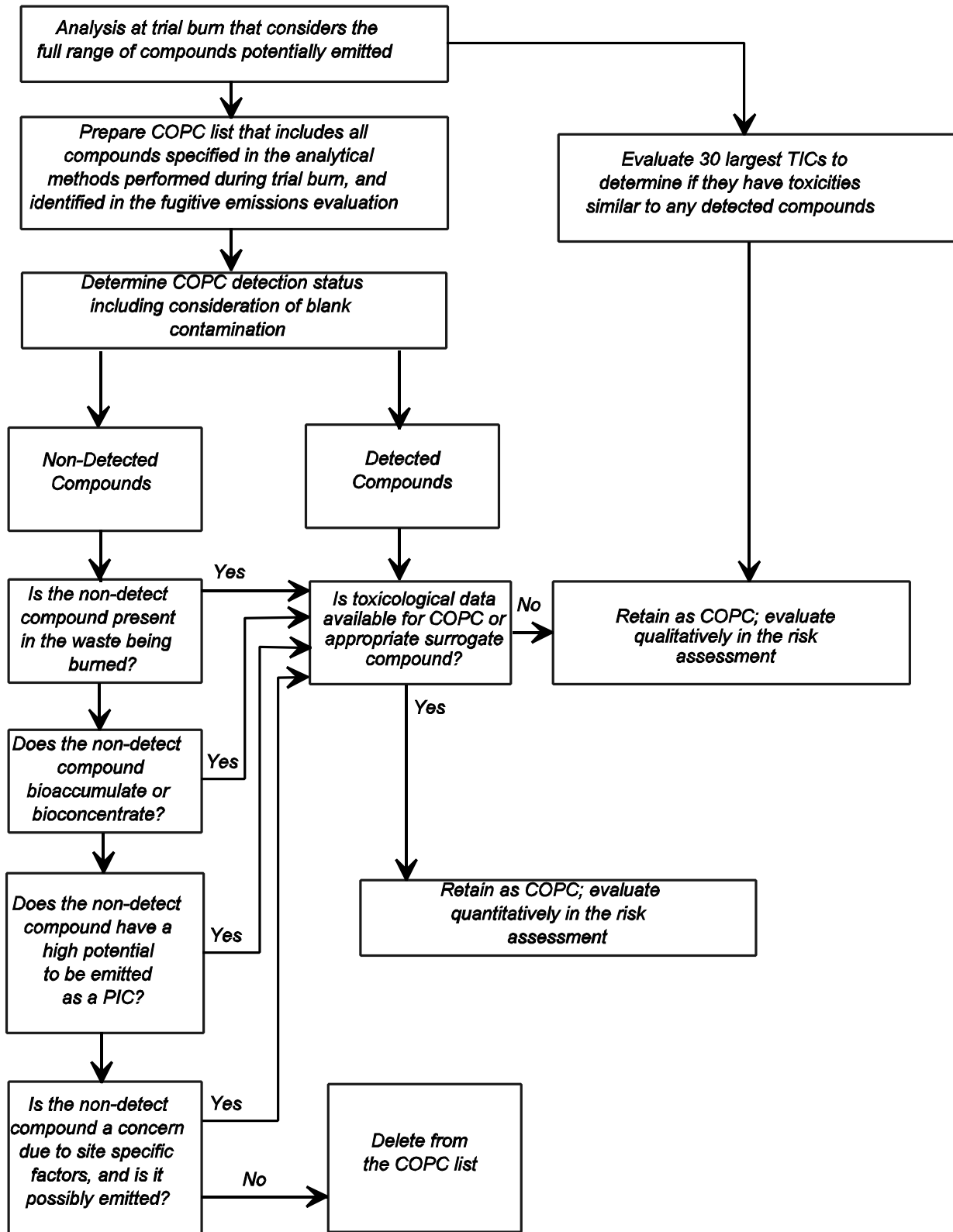
Step 1: Evaluate analytical data from the stack tests performed during the trial burn and compounds associated with fugitive emissions (see Section 2.2.5). Prepare a list which includes all the compounds specified in the analytical methods performed in the trial burn, and fugitive emission evaluation. Describe whether the compound was detected or not detected.

A detection in any one of the sample components (e.g., front half rinse, XAD resin, condensate, Tenax tube) in any run constitutes a detection for that specific compound. Evaluation of blank contamination results, included in the quality assurance (QA) data section of the trial burn report, should be considered when determining the non-detect status of the compounds (see Section 2.5).

Step 2: Evaluate the type of hazardous waste burned in the combustion unit—including all wastes that the unit will be permitted to burn—to determine whether any of the non-detect compounds should be retained for evaluation as COPCs because they are potentially present in the waste.

For example, if a facility is permitted to burn explosives which characteristically include nitroaromatic compounds, yet the stack test showed non-detect status for all nitroaromatic compounds, nitroaromatic compounds should still be evaluated in the risk assessment. This evaluation should also consider other materials fed to the combustion unit (e.g., raw materials or coal in a cement kiln). Regardless of the type of hazardous waste being burned in the combustion unit, every risk assessment should include PCDD/PCDFs and PAHs (the rationale for including these compounds is discussed in greater detail in Sections 2.3.1 and 2.3.2).

COPC IDENTIFICATION



US EPA ARCHIVE DOCUMENT

Step 3: Include as COPCs those compounds that are non-detect, but have a high potential to be emitted as PICs.

Although some compounds (nitroaromatics, phthalates, hexachlorobenzene, and petachlorophenol) have traditionally been automatically identified as PICs in previous U.S. EPA guidance, inclusion of these compounds should be based on consideration of potential to be emitted and waste feed composition (e.g., nitrogenated wastes, plastics, or highly chlorinated organic waste streams) (see Sections 2.3.4 through 2.3.6).

Step 4: Include as COPCs those compounds that are non-detect, but have a tendency to bioaccumulate or bioconcentrate. This includes organic chemicals with $\log K_{ow}$ values equal to or greater than 4.0 (Connolly and Pederson 1987), and inorganic compounds with a whole-body BCF equal to or greater than 100.

U.S. EPA OSW understands that this step would not retain some nondetected compounds (such as VOCs with $\log K_{ow}$ values less than 4.0) for further evaluation in the risk assessment and appears to provide the opportunity for detection limits for these compounds to be increased intentionally by the facility to escape the risk assessment process. However, U.S. EPA OSW anticipates that stack test data used in conducting the risk assessment will also be subject to evaluation in the human health risk assessment process, which would subsequently determine increased risk due to nondetected compounds with high detection limits. Therefore, the lowest achievable detection limits possible with standard U.S. EPA methods for all compounds are recommended, ensuring that the risk assessment process will result in the risk manager obtaining the information necessary to conclude that the facility has not potentially overlooked a serious risk.

Step 5: Evaluate the 30 largest tentatively identified compound (TIC) peaks obtained during gas chromatography (GC) analysis, to determine whether any of the TICs have toxicities similar to the detected compounds. If they do, consider surrogate toxicity data, as recommended for detected COPCs without toxicity information.

Step 6: Evaluate any compound that may be of concern due to other site-specific factors (e.g., community and regulatory concern, high background concentrations). Include as COPCs those compounds that (1) are a concern due to site-specific factors, and (2) may be emitted by the combustion unit.

If the compound in question does not have a reasonable potential of being present in the stack emissions, the risk assessment report should justify this assertion. This information will provide the risk manager with

the information necessary to evaluate potential for risk. By following Steps 1 through 6, the risk assessor will be able to identify COPCs from the typically exhaustive list of compounds tested in during the trial burn. To complete Step 4, log K_{ow} and BCF values for compounds typically identified in risk assessments as COPCs and listed at the beginning of this section are located in Appendices A and C, respectively.

The following subsections also focus on compounds that can drive risk assessments as indicated by past experience. These compounds include polychlorinated dibenzo(p)dioxins and dibenzofurans, polynuclear aromatic hydrocarbons, polychlorinated biphenyls, nitroaromatics, phthalates, hexachlorobenzene and pentachlorophenol, and metals. Volatile organic compounds are also discussed. Specific issues that affect the COPC identification process and evaluation of these compounds in the risk assessment are discussed. Because U.S. EPA's boiler and industrial furnace (BIF) regulations also regulate emission rates of PM and hydrochloric acid and chlorine gas, the risks associated with these compounds are also discussed. There is also a discussion of the emerging issues surrounding the class of compounds called "endocrine disruptors."

U.S. EPA OSW recognizes that, for many compounds, only limited information is available regarding potential effects. In addition, for some compounds for which effects have been identified, the relationship between dose and response may be poorly understood. U.S. EPA OSW advocates 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 information may change as additional research is conducted, permitting authorities should consult with the most current information before completing a risk assessment. Toxicity profiles for many of the compounds typically evaluated in ecological risk assessments are presented in Appendix H. U.S. EPA OSW prepared these profiles to promote consistency in risk assessments and to assist the uncertainty analysis.

RECOMMENDED INFORMATION FOR RISK ASSESSMENT REPORT

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

2.3.1 Polychlorinated Dibenzo(p)dioxins and Dibenzofurans

Based on their combustion properties and toxicity, U.S. EPA OSW recommends that PCDDs and PCDFs should be included in every risk assessment. The general combustion properties and guidance for addressing toxicity of PCDDs and PCDFs are discussed in the following paragraphs and subsections, respectively.

One mode in which PCDDs and PCDFs form in dry APCSS is fly ash catalyzed reactions between halogens and undestroyed organic material from the furnace. 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. 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, including forest fires, municipal waste and medical incinerators, and hazardous waste combustion units. Duarte-Davidson et al. (1997) noted that the combustion of 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.

PCDDs and PCDFs are formed at these combustion sources from the reaction of chlorine-containing chemicals and organic matter. Predicting the production 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; Robert 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 organic compound 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. 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 combustion units reveals that total PCDD/PCDF emission rates vary by more than 28-fold between different facilities, even though they use similar combustion units and APCs (U.S. EPA 1996h). Site-specific emission data are needed to enable completion of a more refined risk assessment at each combustion unit.

In evaluating fate-and-transport pathways, 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 of the PCDDs and PCDFs. Evaluation of ambient air monitoring studies, in which researchers evaluated the partitioning of dioxin-like compounds between the vapor and particle phases, suggests that the higher chlorinated congeners (the hexa through hepta congeners) were principally sorbed to airborne particulates, whereas the tetra and penta congeners were significantly, if not predominantly, partitioned to the vapor phase (U.S. EPA 1994e). This finding is consistent with vapor/particle partitioning as theoretically modeled in Bidleman (1988). Dioxin-like compounds exhibit little potential for significant leaching or volatilization after they have been sorbed to particulate matter (U.S. EPA 1994e).

The guidance in Chapter 5 for modeling exposure to a COPC also applies generally to exposure assessment for PCDDs and PCDFs. However, procedures specific for these compounds should be followed because

congener-specific toxicity and bioaccumulation information is limited. As discussed below, exposure of receptors to PCDDs and PCDFs should be assessed using 2,3,7,8-TCDD toxicity equivalency factors (*TEF*) and 2,3,7,8-TCDD bioaccumulation equivalency factors (*BEF*) to convert the exposure media concentration of individual congeners to a 2,3,7,8-TCDD Toxicity Equivalent (TEQ).

U.S. EPA OSW is also aware of growing concern regarding the risks resulting from (1) fluorine- and bromine-substituted dioxins and furans, and (2) sulfur analogs of PCDDs and PCDFs. U.S. EPA guidance on considering these compounds as potential COPCs is discussed in Section 2.3.1.5.

2.3.1.1 Toxicity Equivalency Factors for PCDDs and PCDFs

There are 210 individual compounds or “congeners” of PCDDs and PCDFs. Evidence indicates that low levels of PCDD and PCDF congeners adversely affect ecological receptors, especially the 2,3,7,8-substituted congeners (U.S. EPA 1993p; Hodson et al. 1992; Walker and Peterson 1992). The 17 congeners containing chlorine substituents in at least the 2-, 3-, 7-, and 8-ring positions have been found to display dioxin-like toxicity (U.S. EPA 1993g; 1994h). Therefore, U.S. EPA OSW and other U.S. EPA guidance (1998; 1993h) recommend that all risk assessments include all PCDDs and PCDFs with chlorine molecules substituted in the 2, 3, 7, and 8 positions. In Appendix A, the 17 PCDD and PCDF congeners that should be evaluated in every risk assessment for potential risk are listed. Any other PCDD and PCDF congener identified as a COPC should be treated as an uncertainty (see Chapter 6).

As noted above, the toxicity of PCDDs and PCDFs is related to their structure and chlorine substitution pattern. The 17 listed congeners are known to share a common mechanism of toxicity involving binding to the Ah-receptor. Planar PCDDs and PCDFs are characteristic for high Ah-receptor affinity. Toxicity is also related to the chlorine substitution pattern, especially for chlorine atoms in the 2,3,7,8-positions. By extension, it is assumed that an additivity model may be used to characterize the toxicity of mixtures of these PCDDs and PCDFs. While these congeners share a similar toxicity mechanism, available information indicates that the toxicity of these PCDDs and PCDFs is congener-specific, resulting in a wide range of toxicities (U.S. EPA 1993p, World Health Organization [WHO] 1997). This has resulted in the development of TEFs for these 17 congeners to convert the exposure media concentration of individual congeners to a 2,3,7,8-TCDD TEQ; which are widely used to assess the risk of dioxin and dioxin-like compounds (U.S. EPA 1993p; WHO 1997).

The procedure used to assess risk on the basis of the relative toxicity of 2,3,7,8-TCDD, which is assumed the most toxic dioxin (U.S. EPA 1994f), assigns a TEF value to each congener relative to its toxicity in relation to 2,3,7,8-TCDD. For example, 2,3,7,8-TCDD has a TEF of 1.0, and the other PCDDs and PCDFs have TEF values between 0.0 and 1.0. To estimate the exposure media concentration, U.S. EPA OSW recommends that a risk assessment for PCDDs and PCDFs be completed using the congener-specific emission rates from the stack and fate and transport properties in the media concentration equations (see Chapter 3 and Appendix B) and food web equations (see Chapter 5 and Appendix F). For quantifying risk, the exposure media (e.g., may be sediment for evaluating risk to sediment community measurement receptors, or it may be the dose of one or more prey species for evaluating risk to class-specific guild measurement receptors) concentrations of the individual congeners should be converted to a 2,3,7,8-TCDD TEQ by multiplying by the congener-specific TEFs corresponding to the respective measurement receptor being evaluated. Use of the TEFs allows for the combined risk resulting from exposure to a mixture of the 17 dioxin-like congeners to be computed assuming that the risks are additive.

WHO (1997) recently convened a conference to discuss the derivation of TEFs for humans and wildlife. WHO (1997) discussed the compilation and review of relevant scientific information on the PCDD and PCDF toxicity to wildlife, and utilized this information to assist in identifying TEFs. The following table (see Table 2-3) lists congener-specific TEFs reported for fish, mammals, and birds (WHO 1997). U.S. EPA OSW believes that these conference proceedings reflect the best available information for screening the ecological risk of PCDDs and PCDFs. However, it should be noted that TEFs based on long term in-vivo studies should be used when available.

TABLE 2-3

POLYCHLORINATED DIBENZO-P-DIOXIN AND POLYCHLORINATED DIBENZOFURAN CONGENER
 TOXICITY EQUIVALENCY FACTORS (TEFs) FOR FISH, MAMMALS, AND BIRDS

Congener	Receptor		
	Fish TEF	Mammal TEF	Bird TEF
2,3,7,8-TCDD	1.0	1.0	1.0
1,2,3,7,8-PeCDD	1.0	1.0	1.0
1,2,3,4,7,8-HxCDD	0.5	0.1	0.05
1,2,3,6,7,8-HxCDD	0.01	0.1	0.01
1,2,3,7,8,9-HxCDD	0.01	0.1	0.1
1,2,3,4,6,7,8-HpCDD	0.001	0.01	<0.001 ^a
OCDD	Not available	0.0001	Not available
2,3,7,8-TCDF	0.05	0.1	1.0
1,2,3,7,8-PeCDF	0.05	0.05	0.1
2,3,4,7,8-PeCDF	0.5	0.5	1.0
1,2,3,4,7,8-HxCDF	0.1	0.1	0.1
1,2,3,6,7,8-HxCDF	0.1	0.1	0.1
2,3,4,6,7,8-HxCDF	0.1	0.1	0.1
1,2,3,7,8,9-HxCDF	0.1	0.1	0.1
1,2,3,4,6,7,8-HpCDF	0.01	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.01	0.01	0.01
OCDF	0.0001	0.0001	0.0001

Notes:

^a For exposure assessment, a value of 0.001, which estimates upper range of true value, should be used.

Toxicity Equivalency Factors for Fish

WHO (1997) reported the review of three scientific studies on the relative overt toxicity of PCDDs and PCDFs to fish from which TEFs could be determined. These included evaluation of rainbow trout sac fry mortality after egg injection (Walker and Peterson 1991; Zabel et al. 1995) and evaluation of rainbow trout sac fry mortality following waterborne exposure (Bol et al. 1989). WHO (1997) concluded that TEFs from the egg injection studies were more appropriate than the waterborne exposure study. WHO (1997)

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also noted that since these TEFs were determined from the toxicity of each congener in relation to concentration in eggs, site-specific differences in exposure and bioavailability, and species-specific differences in toxicokinetic factors (deposition and metabolism) are accommodated. TEFs for PCDD and PCDF congeners in fish are presented in Table 2-3.

Toxicity Equivalency Factors for Mammals

Current TEFs for mammals (for evaluating human health risk to PCDDs and PCDFs) are largely based on studies in rodents. To supplement existing rodent-based TEFs, WHO (1997) discussed a mink reproductive study (Tillitt et al. 1996) and a study which analyzed available data from mink reproductive toxicity tests (Leonard et al. 1994). WHO (1997) reported that the relative potencies of PCDD and PCDF congeners toward mink reproductive toxicity were similar to the rodent models. WHO (1997) also discussed recent information on *in vivo* tumor promotion and *in vivo* ethoxyresorufin-o-deethylase (EROD) induction potency. However, specific studies reporting this information were not cited. Based on their review, WHO (1997) reported updated TEFs for mammals, including new values for 1,2,3,7,8-PeCDD, OCDD, and OCDF. TEFs for PCDD and PCDF congeners in mammals are presented in Table 2-3.

Toxicity Equivalency Factors for Birds

The experimental design of studies on the overt toxicity of PCDDs and PCDFs to birds precluded determination of the relative potency of these congeners. Other types of studies evaluated included embryo mortality following egg injection, *in vivo* biochemical effects following egg injection, biochemical effects in *in vitro* systems (Kennedy et al. 1996), and quantitative-structure activity relationship (QSAR) studies (Tysklind et al. 1995). The reviewed information indicated no significant differences between the *TEF* ranges for EROD induction and embryo mortality. Based on these results, WHO (1997) reported *TEFs* determined from EROD induction and QSAR studies. *TEFs* for PCDD and PCDF congeners in birds are presented in Table 2-3.

2.3.1.2 Exposure Assessment for Community Measurement Receptors

To evaluate exposure of water, sediment, and soil communities to PCDDs and PCDFs, congener-specific concentrations in the respective media to which the community is exposed should be converted to a

2,3,7,8-TCDD *TEQ*; which allows for direct comparison to 2,3,7,8-TCDD toxicity benchmarks. A media-specific 2,3,7,8-TCDD *TEQ* is calculated and used in the exposure assessment because limited congener-specific toxicity information is available for community receptors (WHO 1997). The congener-specific concentrations in the media to which the community being evaluated is exposed, should be calculated consistent with the guidance presented in Chapters 4 and 5, and Appendix F, for assessing exposure of community measurement receptors to other COPCs. The concentration of each PCDD and PCDF congener in the media of exposure should then be multiplied by the congener-specific *TEF* for fish (see Table 2-3), and summed, to obtain the 2,3,7,8-TCDD *TEQ* (see Equation 2-3).

$$TEQ = \sum (C_{Mi} \cdot TEF_i) \quad \text{Equation 2-3}$$

where

<i>TEQ</i>	=	2,3,7,8-TCDD toxicity equivalence concentration ($\mu\text{g/l}$ [water] or $\mu\text{g/kg}$ [soil or sediment])
C_{Mi}	=	Concentration of <i>i</i> th congener in abiotic media ($\mu\text{g/L}$ [water] or $\mu\text{g/kg}$ [soil or sediment])
TEF_i	=	Toxicity equivalency factor (fish) for <i>i</i> th congener (unitless)

U.S. EPA OSW assumes that *TEFs* for fish accurately reflect the relative toxicity of PCDD and PCDF congeners to community receptors. This assumption is based on the requirement for congener-specific *TEFs* for this analysis, as an alternative to the overly conservative assumption that all congener concentrations in the media be evaluated directly as 2,3,7,8-TCDD. Evaluation of all congeners directly as 2,3,7,8-TCDD is assumed overly conservative based on the limited evidence of the Ah receptor or TCDD-like toxicity in invertebrates, and that invertebrates appear to be less sensitive to the toxic effects of dioxin-like compounds (WHO 1997). For the same reasons, *TEF* values specific to invertebrate have not been developed; requiring use of the surrogate *TEF* values for fish. The reported findings in WHO (1997) support the use of *TEFs*, in combination with chemical residue data, for the calculation of *TEQ* concentrations in various media, including animal tissues, soil, sediment, and water. However, in relation to the use of *TEFs* for abiotic media, it should be noted that the biological meaning of these values is obscure due to the fact that the assumed biological or toxicological effect is influenced by many physico-chemical factors before uptake occurs (WHO 1997). Nevertheless, *TEF* values can be used as relative measurements of concentrations within media.

Use of the *TEFs* allows for the combined risk resulting from exposure to a mixture of the 17 dioxin-like congeners to be computed assuming that the risks are additive. As discussed in Chapters 5 and 6, risk to the water, sediment, or soil community being evaluated is then subsequently estimated by comparing the media-specific 2,3,7,8-TCDD *TEQ* to the corresponding media-specific toxicity benchmark for 2,3,7,8-TCDD.

2.3.1.3 Exposure Assessment for Class-Specific Guild Measurement Receptors

To evaluate the exposure of class-specific guilds to PCDDs and PCDFs, congener-specific daily doses of all food items (i.e., media, plants, and animals) ingested by a measurement receptor should be converted to a 2,3,7,8-TCDD *TEQ* daily dose (DD_{TEQ}); which allows for direct comparison to 2,3,7,8-TCDD toxicity benchmarks. The congener-specific daily doses of food items ingested by a measurement receptor should be calculated consistent with the guidance presented in Chapters 4 and 5, and Appendix F, for assessing exposure of class-specific guild measurement receptors to other COPCs. This includes the use of congener-specific media concentrations, congener-specific bioconcentration factors (*BCF*), and congener-specific food chain multipliers (*FCM*). The daily dose of each PCDD and PCDF congener ingested by a measurement receptor should then be multiplied by the congener-specific *TEFs* (see Table 2-3) that correspond to the respective measurement receptor, and summed, to obtain the DD_{TEQ} . Use of the *TEFs* allows for the combined risk resulting from exposure to a mixture of the 17 dioxin-like congeners to be computed assuming that the risks are additive. Following the general guidance provided in Chapters 5 and 6, risk to the class-specific guild being evaluated is then subsequently estimated by comparing the dose ingested term (represented by DD_{TEQ}) of the measurement receptor to the receptor specific toxicity benchmark for 2,3,7,8-TCDD.

The DD_{TEQ} for each measurement receptor should be determined as indicated in the following equation:

$$DD_{TEQ} = \sum DD_i \cdot TEF_{(MeasurementReceptor)} \quad \text{Equation 2-4}$$

where

$$DD_{TEQ} = \text{Daily dose of 2,3,7,8-TCDD } TEQ \text{ } (\mu\text{g/kg BW/d})$$

DD_i	=	Daily dose of <i>i</i> th congener ($\mu\text{g}/\text{kg BW}/\text{d}$)
TEF	=	Toxicity equivalency factor (specific to measurement receptor) (unitless)

As noted above, the congener-specific daily doses ingested by the measurement receptor should be determined following guidance in Chapter 5 and using equations in Appendix F. These equations include the use of congener-specific *BCF* and *FCM* values. As discussed in Section 2.3.1.4, the limited availability of congener-specific *BCFs* requires that media to receptor *BCF* values for 2,3,7,8-TCDD be utilized in conjunction with congener-specific *BEF* values to obtain estimated congener-specific *BCF* values. The estimation of congener-specific *BCFs* and their resulting numeric values are further discussed in Appendices C and D. Calculation of a congener-specific daily dose also requires the use of congener-specific *FCMs*. Guidance on the appropriate use of *FCMs* in modeling exposure and congener-specific values are provided in Chapter 5 and Appendix A-2, respectively.

2.3.1.4 Bioaccumulation Equivalency Factors

As discussed in Section 2.3.1.3, modeling the exposure of PCDD and PCDF congeners through the food web requires the quantification of bioaccumulation potential. However, similar to the limited availability of congener-specific toxicity information, measured bioaccumulation data specific to each congener is also limited. Therefore, for use with *TEFs* in the development of wildlife water quality criteria for the Great Lakes, U.S. EPA (1995j) developed bioaccumulation equivalency factors (*BEFs*) as a measure of a congeners bioaccumulation potential relative to 2,3,7,8-TCDD. As indicated in Equation 2-5, *BEFs* are estimated as a ratio between each PCDD and PCDF congener-specific *BASF* to that of 2,3,7,8-TCDD (Lodge et al. 1994; U.S. EPA 1995j).

$$BEF_i = \frac{BSAF_i}{BSAF_{TCDD}} \quad \text{Equation 2-5}$$

where

BEF_i	=	Bioaccumulation equivalency factor for <i>i</i> th congener (unitless)
$BSAF_i$	=	Biota-sediment accumulation factor for <i>i</i> th congener (unitless)
$BSAF_{TCDD}$	=	Biota-sediment accumulation factor for 2,3,7,8-TCDD

BEF values reported by U.S. EPA (1995k) for the 17 PCDD and PCDF congeners are provided in Table 2-4. Although developed based on concentration data of PCDDs and PCDFs in sediment and surface water for application of *TEFs* in fish, U.S. EPA OSW assumes that these *BEFs* are applicable to other pathways and receptors. The estimation of PCDD and PCDF congener-specific *BCF* values using *BEFs* is indicated in Equation 2-5. Further discussion and resulting numeric values for congener-specific *BCFs* are provided in Appendices C and D.

$$BCF_i = BCF_{TCDD} \cdot BEF_i \quad \text{Equation 2-6}$$

where

BCF_i	=	Media-to-animal or media-to-plant bioconcentration factor for <i>i</i> th congener (L/kg [water], unitless [soil and sediment])
BCF_{TCDD}	=	Media-to-receptor BCF for 2,3,7,8-TCDD (L/kg [aquatic receptor], unitless [soil and sediment receptor])
BEF_i	=	Bioaccumulation equivalency factor for <i>i</i> th congener (unitless)

TABLE 2-4

PCDD AND PCDF BIOACCUMULATION EQUIVALENCY FACTORS (BEFs)

PCDD Congener	Bioaccumulation Equivalency Factor (unitless)	PCDF Congener	Bioaccumulation Equivalency Factor (unitless)
2,3,7,8-TCDD	1.0	2,3,7,8-TCDF	0.80
1,2,3,7,8-PeCDD	0.92	1,2,3,7,8-PeCDF	0.22
1,2,3,4,7,8-HxCDD	0.31	2,3,4,7,8-PeCDF	1.6
1,2,3,6,7,8-HxCDD	0.12	1,2,3,4,7,8-HxCDF	0.076
1,2,3,7,8,9-HxCDD	0.14	1,2,3,6,7,8-HxCDF	0.19
1,2,3,4,6,7,8-HpCDD	0.051	2,3,4,6,7,8-HxCDF	0.67
OCDD	0.012	1,2,3,7,8,9-HxCDF	0.63
		1,2,3,4,6,7,8-HpCDF	0.011
		1,2,3,4,7,8,9-HpCDF	0.39
		OCDF	0.016

Source: U.S. EPA 1995k

2.3.1.5 Fluorine, Bromine, and Sulfur PCDD/PCDF Analogs

U.S. EPA (U.S. EPA 1996l; 1996m) 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. Available information indicates that fluorinated dioxins and furans are not likely to be formed as PICs; however, the presence of free fluorine in the combustion gases may increase the formation of chlorinated dioxins (U.S. EPA 1996l). U.S. EPA OSW is not aware of any studies conducted to evaluate this relationship. Available information indicates the potential for the formation of brominated or chlorobrominated dioxins (U.S. EPA 1996d).

Although chlorinated dibenzothiophenes (the sulfur analogs of dibenzofurans) have been reported to form, no information is available to indicate the formation of chlorinated dioxin thioethers (the sulfur analogs of dibenzo[p]dioxins) (U.S. EPA 1996l). 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 1996n). Another possible

reason that chlorinated dioxin thioethers have not been observed is the potential instability of these compounds, which contain two carbon-sulfur bonds in the central ring of the structure (U.S. EPA 1996l). The likelihood of the formation or associated toxicity of these compounds is not currently well understood. Therefore, a quantitative toxicity assessment of fluorine, bromine, and sulfur analogs is not required for inclusion in the risk assessment report. Instead, the uncertainty section of the risk assessment report should discuss the potential for the formation of these analogs. It should be noted that there is currently no U.S. EPA approved method for the sampling or analysis of these dioxin analogs. The use of the method for total organics (see Section 2.2.1.3) is currently recommended to account for the potential presence of these compounds.

TEF values for brominated dioxins or furans have not been developed (U.S. EPA 1994e; WHO 1997). 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).

RECOMMENDED INFORMATION FOR RISK ASSESSMENT REPORT

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

2.3.2 Polynuclear Aromatic Hydrocarbons

Based on their combustion properties and toxicity, U.S. EPA OSW recommends that PAHs be included in every risk assessment. 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 general combustion properties and guidance for addressing toxicity of PAHs are discussed in the following paragraph and subsection, respectively.

PAHs are readily formed in combustion units by either (1) dechlorination of other PAHs present in the waste feed or emissions stream (such as dioxins), 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. Therefore, based on the toxicity and combustion chemistry of PAHs, the absence of these compounds from stack emissions should always be confirmed via stack gas testing.

2.3.2.1 Exposure Assessment for PAHs

U.S. EPA OSW recommends that individual PAH compounds be modeled from the emission source to media (i.e., soil, surface water, soil) and plants, using compound-specific emission rates and fate and transport properties, as required in the media concentration equations (see Chapter 3 and Appendix B). Evaluation of exposure of community and class-specific guild measurement receptors to individual PAHs, should be conducted consistent with guidance provided in Chapters 4 and 5, and utilizing equations in Appendix F.

2.3.3 Polychlorinated Biphenyls

The use 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). 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 manipulation of the reaction conditions, including temperature, pressure, and the ratio of the reactants (Erickson 1992; Grayson 1985).

The most commercially useful property of PCBs is that they are chemically stable in relatively adverse conditions, such as a temperature of several hundred degrees in an oxygen-containing atmosphere; the more chlorinated congeners are more resistant to reaction. Therefore, destruction of PCBs by combustion

generally requires conditions of high temperatures (at least 1,200 °C) and an extended contact time (more than 2 seconds) in that temperature with adequate oxygen (Erickson 1992).

Limited data and studies, including laboratory and field, show that PCBs may be formed from the combustion of 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 (see definition in Section 2.3.3.1) found in the boiler stack gas was 0.55 ng/dscm @ 7% O₂ at low temperature conditions (1,357° F) and 1.12 ng/dscm @ 7% O₂ at high temperature conditions (1,908° F). The concentration of total PCBs detected in the incinerator stack gas was 211 ng/dscm @ 7% O₂ at low temperature conditions (1,750 °F) and 205 ng/dscm @ 7% O₂ 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 the combustion of 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 et al. 1984). This study indicates that the combustion of highly chlorinated (60 percent or greater chlorine) wastes can produce PCBs.

PCBs should automatically be included as COPCs for combustion units that burn PCB-contaminated wastes or waste oils, highly variable waste streams such as municipal and commercial wastes for which PCB contamination is reasonable, and highly chlorinated waste streams.

Due to the toxicity and uncertainties associated with combustion chemistries the permitting authority may choose to confirm that the absence of these compounds from stack emissions via stack gas testing for units burning hazardous wastes.

2.3.3.1 Exposure Assessment for PCBs

Previous U.S. EPA combustion risk assessment guidance (1994b; 1994d; 1994c; 1994l) has recommended that all PCB congeners (209 different chemicals) be treated in a risk assessment as a mixture having a single toxicity. This recommendation was based on the U.S. EPA drinking water criteria for PCBs (U.S. EPA 1988).

However, since the compilation of U.S. EPA (1988), additional research on PCBs has been reported. The most important result of this research is the demonstration that some of the moderately chlorinated PCB congeners can have dioxin-like effects (U.S. EPA 1992f; U.S. EPA 1994i; ATSDR 1995d; WHO 1997).

WHO (1997) recently convened a conference to discuss the derivation of *TEFs* for humans and wildlife. Conference participants discussed the compilation and review of relevant scientific information on the PCB toxicity to wildlife, and utilized this information to assist in identifying *TEFs* for congeners that can have dioxin-like effects. U.S. EPA OSW believes that these conference proceedings reflect the best available information for screening the ecological risk of PCBs. The following table (see Table 2-5) lists PCB *TEFs* reported for fish, mammals, and birds (WHO 1997).

TABLE 2-5

PCB CONGENER TOXICITY EQUIVALENCY FACTORS (TEFs) FOR FISH, MAMMALS, AND BIRDS

PCB Congener	Receptor		
	Fish TEF	Mammals TEF	Birds TEF
3,4,4',5-TCB	0.0005	0.0001	0.1
3,3',4,4'-TCB	0.0001	0.0001	0.05
3,3',4,4',5-PeCB	0.005	0.1	0.1
3,3',4,4',5,5'-HxCB	0.00005	0.01	0.001
2,3,3',4,4'-PeCB	<0.000005	0.0001	0.0001
2,3,4,4',5-PeCB	<0.000005	0.0005	0.0001
2,3',4,4',5-PeCB	<0.000005	0.0001	0.00001
2',3,4,4',5-PeCB	<0.000005	0.0001	0.00001
2,3,3',4,4',5-HxCB	<0.000005	0.0005	0.0001
2,3,3',4,4',5-HxCB	<0.000005	0.0005	0.0001
2,3',4,4',5,5'-HxCB	<0.000005	0.00001	0.00001
2,3,3',4,4',5,5'-HpCB	<0.000005	0.0001	0.00001
2,2',3,3',4,4',5'-HpCB	Not Available	Not Available	Not Available
2,2',3,4,4',5,5'-HpCB	Not Available	Not Available	Not Available

Source: WHO (1997)

The listed congeners have four or more chlorine atoms with 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 then react with the aryl hydrocarbon receptor; this same reaction is believed to initiate the adverse effects of PCDDs and PCDFs. Additional congeners are suspected of producing similar reactions, but there is not yet enough data to derive *TEF* values for them.

High resolution gas chromatograph test methods (e.g., draft Method 1668), available at most commercial laboratories with dioxin/furan analytical capabilities, should be used to identify the specific concentration of individual coplanar PCBs in stack gas. U.S. EPA OSW recommends that permitting authorities estimate risks to community and class-specific guild measurement receptors from coplanar PCBs by computing a *TEQ* for PCBs, and then comparing to the appropriate toxicity benchmark for 2,3,7,8-TCDD.

The specific guidance, provided in Sections 2.3.1.2 and 2.3.1.2 for evaluating exposure to PCDDs and PCDFs, should be followed in evaluating exposure to dioxin-like PCBs. However, TEF values listed in Table 2-5 should be utilized in the *TEQ* calculations. Also, since congener-specific fate and transport and bioaccumulation data are not available for each of the PCBs listed in Table 2-5, U.S. EPA OSW recommends that the fate and transport properties for Aroclor 1254 be used in the modeling. This approach is reasonable because approximately 77 percent of Aroclor 1254 is composed of PCB congeners with more than 4 chlorines (Hutzinger et al. 1974).

In addition to the coplanar (dioxin-like) PCB congeners, the remaining PCBs should also be evaluated in the risk assessment consistent with the guidance provided in Chapters 4 and 5. When evaluating PCB mixtures containing isomers with more than 4 chlorines in quantities greater than 0.5 percent of the total PCBs, U.S. EPA OSW recommends that the fate and transport properties for Aroclor 1254 be used in the modeling. As discussed above for evaluating coplanar PCBs, this approach is reasonable because approximately 77 percent of Aroclor 1254 is composed of PCB congeners with more than 4 chlorines (Hutzinger et al. 1974). When assessing risks from PCB mixtures which contain less than 0.5 percent of PCB congeners with more than 4 chlorines, U.S. EPA OSW recommends that the fate and transport properties of Aroclor 1016 be used in the modeling. This approach is reasonable because approximately 99 percent of Aroclor 1016 is comprised of PCB congeners with 4 or less chlorines (Hutzinger et al. 1974).

2.3.4 Nitroaromatics

Careful consideration should be made before the automatic inclusion of nitroaromatic organic compounds, including 1,3-dinitrobenzene; 2,4-dinitrotoluene; 2,6-dinitrotoluene; nitrobenzene; and pentachloronitrobenzene, in risk assessments for combustion units. These compounds 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, which 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 will not be formed as PICs if they are not 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 be reacted with the nitronium ion, resulting in the attachment of the nitronium ion to the ring. This reaction process is not likely to occur in a hazardous waste combustion unit 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 are not usually formed in a combustion unit environment (if they are, a further thermodynamically favorable reaction will occur, thereby eliminating the nitronium ion) (Hoggett et al. 1971; Schofield 1980; March 1985).

Nitroaromatics should be included as COPCs if the hazardous waste feed streams include nitroaromatic compounds or close relatives (TDA and TDI). Also, combustion of feed streams containing unusually high amounts of fuel-bound nitrogen (greater than 5 percent) may lead to increased levels of nitrogenated PICs (U.S. EPA 1994c). Examples of waste feeds identified include heavy distillation fractions and bottoms streams from the production of coal tars and petroleum distillation. 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 1994c). Sampling for hydrogen cyanide is also recommended (U.S. EPA 1994c).

2.3.5 Phthalates

Careful consideration should be made before the automatic inclusion of phthalates, including bis(2-ethylhexyl)phthalate (BEHP) and di(n)octyl phthalate (DNOP), in risk assessments for combustion units. 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, which is 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). 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 are synthesized by reacting alcohol with phthalic anhydride in the presence of an acidic catalyst in a nonaqueous solvent (ATSDR 1993; ATSDR 1995b). Phthalates and their predecessors are readily combusted compounds, 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 the combustion of other chemical compounds. Therefore, phthalates are very unlikely to be emissions from a combustion unit, 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.

The evaluation of phthalate plasticizers in risk assessments should not be automatically discounted due to the toxicity and bioaccumulative potential of these compounds. Moreover, the uncertainties associated with combustion chemistry suggest that the absence of these compounds from stack emissions should always be confirmed via stack gas testing rather than process knowledge or waste feed characterization data. U.S. EPA OSW recommends that careful consideration should be given to including phthalates as COPCs based on the information presented above.

2.3.6 Hexachlorobenzene and Pentachlorophenol

Careful consideration should be made before the automatic inclusion of hexachlorobenzene and pentachlorophenol in risk assessments for combustion units. Hexachlorobenzene and pentachlorophenol, like all chlorinated aromatics, are synthesized by the reaction of elemental chlorine with the 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 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). Hexachlorobenzene is an impurity in pentachlorophenol while pentachlorophenol is formed from hexachlorobenzene in some factories (ATSDR 1994a; ATSDR 1994b). The combustion

properties of these chlorinated compounds indicate that they are not likely to be formed as PICs if they are not present in the waste feed stream.

Hexachlorobenzene and pentachlorophenol should be included as COPCs for units that burn waste feeds containing hexachlorobenzene and pentachlorophenol, wood preservatives, pesticides, and highly variable waste streams such as municipal solid waste. However, precluding these compounds from analytical testing during the trial burn based on process knowledge and waste feed characterization is not recommended. Because PCDDs and PCDFs can be formed from fly ash-catalyzed reactions between halogens and undestroyed organic material from the furnace, U.S. EPA guidance (U.S. EPA 1993h; 1994d) has recommended that potential precursor compounds be included in the risk assessment and trial burn (see Section 2.3). These precursor compounds may include chlorinated phenols (such as pentachlorophenol) and chlorinated aromatics (such as hexachlorobenzene). Furthermore, the toxicity and uncertainties associated with combustion chemistry suggest that the absence of these compounds from stack emissions should always be confirmed via stack gas testing. U.S. EPA OSW recommends that careful consideration should be given to including hexachlorobenzene and pentachlorophenol as COPCs based on the information presented above.

2.3.7 Metals

U.S. EPA OSW recommends that the following inorganic substances be considered for evaluation in the risk assessment: aluminum, antimony, arsenic, barium, beryllium, cadmium, hexavalent chromium, copper, lead, mercury (elemental and divalent), nickel, selenium, silver, thallium, and zinc. All of these substances, except aluminum, copper, nickel, selenium, and zinc, are regulated by 40 CFR Part 266, Subpart H (the BIF regulations). In the case of metals not regulated by the BIF regulations, U.S. EPA has recommended that these metals be evaluated, to determine whether additional terms and conditions should be incorporated into the permit, by using U.S. EPA's omnibus authority provided under 40 CFR Part 270.32(b)(2) (U.S. EPA 1992c). Facilities may also apply the BIF regulation Tier I assumptions, that assume all metals in the waste feed pass through the combustion unit and APCS and are passed through to the emission stream (U.S. EPA 1992e).

It should be noted, that the presence of metals in the combustion unit's feed stream is not required for inclusion in the risk assessment. Although metals cannot be formed as PICs, U.S. EPA OSW is aware of combustion units with metal emissions resulting from waste feed leaching of stainless steel feed piping.

RECOMMENDED INFORMATION FOR RISK ASSESSMENT REPORT

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

The following subsections provide additional information regarding U.S. EPA-recommended procedures for evaluating metals—chromium, mercury, and nickel—that may be specifically altered during the combustion process or require specific considerations in the risk assessment.

2.3.7.1 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 (Cr^{+6}) is the most toxic valence state of chromium. Trivalent chromium (Cr^{+3}), a commonly found less oxidized and toxic form of chromium, is more commonly found in the environment. U.S. EPA (1990c; 1990d) has indicated that chromium emitted from a combustion unit 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. Also, media-specific chromium speciation information is often difficult to obtain within the scope of a screening risk assessment. However, U.S. EPA OSW recognizes that chromium may exist partially or in some cases entirely as trivalent chromium in various media. Therefore, unless site-sampling or process-specific information is provided to support a less conservative approach, the worst-case assumption—that 100 percent of the facility chromium emissions are in the hexavalent form—should be used as the initial assumption that all exposure is to hexavalent chromium.

The assumption that receptors are exposed to hexavalent chromium should be maintained in the absence of site specific data. However, permitting authorities may prepare supplemental calculations (that is, in addition to the site-specific data described above) considering chromium speciation at the points of potential exposure.

2.3.7.2 Mercury

Consistent with previous U.S. EPA combustion risk assessment guidance (U.S. EPA 1993h, 1994d, 1994c, 1994l), U.S. EPA OSW recommends that mercury be evaluated as COPCs in the risk assessment. Air emissions of mercury contribute to local, regional, and global deposition. The U.S. Congress explicitly found this to be the case and required U.S. EPA to prioritize maximum achievable control technology (MACT) controls for mercury (U.S. Congress 1989).

Anthropogenic mercury releases are thought to be dominated on the national scale by industrial processes and combustion sources that release mercury into the atmosphere (U.S. EPA 1997b). Stack emissions containing mercury include both vapor and particulate forms. Vapor mercury emissions are thought to include both elemental (Hg^0) and oxidized (e.g., Hg^{+2}) chemical species, while 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 1997b). While coal combustion is responsible for more than half of all emissions of mercury in the U.S. anthropogenic sources, the fraction of coal combustion emissions in oxidized form is thought to be less than that from waste incineration and combustion (U.S. EPA 1997b).

The analytical methods for mercury speciation of exit vapors and emission plumes are being refined, and there is still controversy in this field. Chemical reactions occurring in the emission plume are also possible. The speciation of mercury emissions is thought to depend on the fuel used, flue gas cleaning, and operating temperatures. The exit stream is thought to range from almost all divalent mercury to nearly all elemental mercury; with true speciation of mercury emissions from the various source types still uncertain and thought to vary, not only among source types, but also for individual plants as feed stock and operating conditions change (U.S. EPA 1997b). Most of the total mercury emitted at the stack outlet is found in the vapor phase; although exit streams containing soot or particulate can bind up some fraction of the mercury (U.S. EPA 1997b). Total mercury exiting the stack is assumed to consist of elemental and divalent species,

with no emissions of methylmercury assumed. The divalent fraction is split between vapor and particle-bound phases (Lindqvist et al. 1991). Much of the divalent mercury is thought to be mercuric chloride (HgCl_2) (U.S. EPA 1997b); this is particularly the case for the combustion of wastes containing chlorine.

It should be noted that data on mercury speciation in emissions exiting the stack is very limited, as well as, the behavior of mercury emissions close to the point of release has not been extensively studied. This results in a significant degree of uncertainty implicit in modeling of 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. Discussions of uncertainty and sensitivity analyses of several of the assumptions used in the modeling of mercury emissions are presented in the *Mercury Study Report to Congress* (U.S. EPA 1997b).

Phase Allocation and Speciation of Mercury Exiting the Stack

As discussed above, stack emissions are thought to include both vapor and particle-bound forms; and speciated as both divalent and elemental mercury. Based on review of mercury emissions data presented for combustion sources in U.S. EPA (1997b) 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, at this time U.S. EPA OSW recommends a conservative approach that assumes phase allocation of mercury emissions from hazardous waste combustion of 80 percent of the total mercury in the vapor phase and 20 percent of total mercury in the particle-bound phase. This allocation is:

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

As indicated in the global cycle mass percentages in Figure 2-4, mercury exits the stack in both the elemental and divalent vapor forms. Based on U.S. EPA (1997b), a vast majority of mercury exiting the stack does not readily deposit and is transported outside of the U.S. or vertically diffused to the free atmosphere to become part of the global cycle (see Figure 2-4). The divalent form emitted, either in the

vapor phase or particle-bound, are thought to be subject to much faster atmospheric removal than elemental mercury (Lindberg et al. 1992; Peterson et al. 1995; and Shannon and Voldner 1994). In addition, vapor phase divalent mercury is thought to be more rapidly and effectively removed by both dry and wet deposition than particle-bound divalent mercury, as a result of the reactivity and water solubility of vapor divalent mercury (Lindberg et al. 1992; Peterson et al. 1995; and Shannon and Voldner 1994).

Vapor Phase Mercury

As illustrated in Figure 2-4, of the 80 percent total mercury in the vapor phase, 20 percent of the total mercury is in the elemental vapor form and 60 percent of the total mercury is in the divalent vapor form (Peterson et al. 1995). A vast majority (assumed to be 99 percent) of the 20 percent vapor phase elemental mercury does not readily deposit and is transported outside of the U.S. or is vertically diffused to the free atmosphere to become part of the global cycle (U.S. EPA 1997b). Only a small fraction (assumed to be one percent) of vapor-phase elemental mercury either is adsorbed to particulates in the air and is deposited or converted to the divalent form to be deposited (assumed to be deposited as elemental mercury, see Figure 2-4). Of the 60 percent vapor phase divalent mercury, about 68 percent is deposited and about 32 percent is transported outside of the U.S. or is vertically diffused to the free atmosphere to become part of the global cycle (U.S. EPA 1997b).

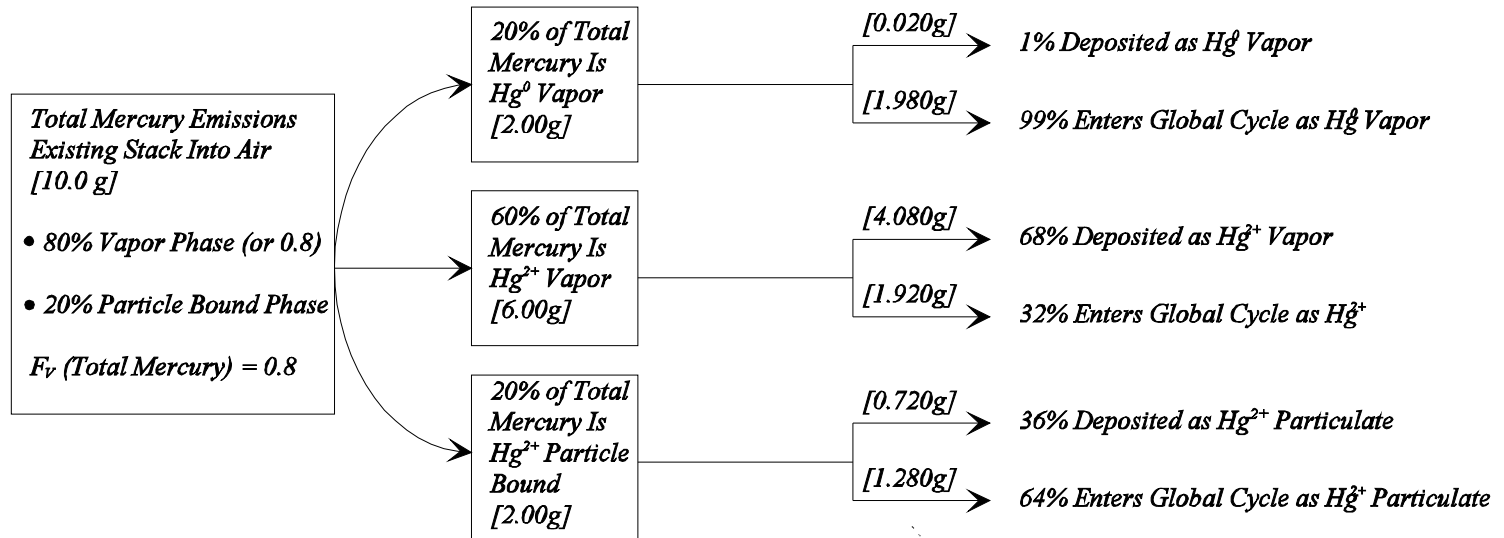
Particle-bound Mercury

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. U.S. EPA (1997b) indicates that only 36 percent of the particle-bound divalent mercury is deposited, and the rest is either transported outside of the U.S. or is vertically diffused to the free atmosphere to become part of the global cycle.

Deposition and Modeling of Mercury

Consistent with U.S. EPA (1997b) and as shown in Figure 2-4, it is assumed that deposition to the various environmental media is entirely divalent mercury in either the vapor or particle-bound form. Without consideration of the global cycle, mercury speciations will result in 80 percent of the total mercury emitted being deposited as divalent mercury and the remaining 20 percent being deposited as elemental mercury.

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



LEGEND

Hg^0 - Elemental Mercury
 Hg^{2+} - Divalent Mercury
 [] - Example Mass Allocation

Without Consideration of Global Cycle

• 80% of Total Mercury Emitted is Deposited as Hg^{2+} [(6g + 2g) / 10g]

• 20% of Total Mercury Emitted is Deposited as Hg^0 [2g / 10g]

Calculated F_V

• $F_V (Hg^{2+}) = [6g / (6g + 2g)] = 0.75$

• $F_V (Hg^0) = [2g / 2g] = 1.0$

With Consideration of Global Cycle

• 48% of Total Mercury Emitted is Deposited as Hg^{2+} [(4.08g + 0.72g) / 10g]

• 0.2% of Total Mercury Emitted is Deposited as Hg^0 [0.02g / 10g]

Calculated F_V

• $F_V (Hg^{2+}) = [4.08g / (4.08g + 0.72g)] = 0.85$

• $F_V (Hg^0) = [0.02g / (0.02g + 0g)] = 1.0$

Compound Specific Emission Rate Q

• Actual $Q (Hg^{2+}) = 48\% * Q$ (Total Mercury)

• Actual $Q (Hg^0) = 0.2\% * Q$ (Total Mercury)

U.S. EPA OSW recommends utilizing the percentages provided in U.S. EPA (1997b) to account for the global cycle, the percentage of total mercury deposited is 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 (40.8/48.2) 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.

Consistent with U.S. EPA (1997b) and as shown in Figure 2-4, it is assumed that deposition to the various environmental media is entirely divalent mercury in either the vapor or particle-bound form. Deposited divalent mercury is also considered as a source of methyl mercury, which is assumed as a media-specific percentage of the total mercury deposited.

Also, only a small fraction (assumed to be one percent) of elemental mercury is in the vapor phase and is assumed to be deposited in its original form. Therefore, any resulting exposure to elemental mercury is considered to be much less significant, and will not be considered in the pathways of the ecological risk assessment.

Appendix A-2 provides the parameter values specific to the various forms of mercury, and Appendix B provides media concentration equations for modeling mercury through the exposure pathways assuming steady-state conditions.

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 1997b). Consistent with U.S. EPA (1997b), a fraction of the divalent mercury that is deposited is assumed to speciate to organic mercury (methyl mercury) in soil. In soil, 98 percent of total mercury is assumed to be divalent mercury and the remaining mass as methyl mercury (U.S. EPA 1997b). 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 be

exported to nearby water bodies and potentially bioaccumulated in the aquatic food chain (U.S. EPA 1997b). Therefore, the assumed percentage of methyl mercury in wetland soils may be higher than the 2 percent assumed for non-wetland soils, and may closer approximate the 15 percent assumed for sediments.

Both watershed erosion and direct atmospheric deposition can be important sources of mercury to a water body (U.S. EPA 1997b). There appears to be a great deal of variability in the processing of mercury among water bodies. This variability is primarily a result of the characteristically wide range of chemical and physical properties of water bodies that influence the levels of methylated mercury. Some of the mercury entering the water body is methylated predominately through biotic processes (U.S. EPA 1997b). In the absence of modeling site-specific water body properties and biotic conditions, consistent with U.S. EPA (1997b), U.S. EPA OSW recommends 85 percent of total mercury in surface water is assumed to be divalent mercury and the remaining mass as methyl mercury.

For most environmental systems, the literature suggests that various physical and chemical conditions may influence the methylation of mercury. Consideration of these conditions, and the magnitude of their potential impact, may be required in some cases to assess the potential for over or under predicting mercury methylation in media and subsequent biotransfer up the food chain. Due to the extreme variance between environmental systems modeled, and at times disagreement, identified in literature reviewed regarding the quantitative influence of specific conditions on methylation, U.S. EPA OSW recommends that extensive research of literature, specific to the conditions prevalent at the site, be conducted before application and deviation from the conservative assumptions recommended above. The following table summarizes the qualitative effect some of the physical and chemical conditions, as reported in literature, may have on methylating:

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

To account for methylation of mercury in the media and its subsequent biotransfer assuming steady-state conditions, the deposition and media concentration equations (presented in Appendix B) have been modified specifically for modeling methyl mercury. Appendix A-2 provides the parameter values specific for methylmercury, and 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 modeling of mercury methylation. To expand on the qualitative information presented in the above table, and better understand conditions that may influence mercury methylation specific to a site, U.S. EPA OSW recommends review of information on this subject presented in the *Mercury Study Report to Congress* (U.S. EPA 1997b).

Exposure Assessment for Mercury

For assessing exposure of community and class-specific guild measurement receptors to mercury, guidance provided in Chapters 4 and 5 should generally be followed. However, special consideration is required in evaluating the various forms of mercury modeled to the point of exposure.

To evaluate exposure of water, sediment, and soil communities to mercury, species-specific concentrations of divalent mercury and methyl mercury, in the respective media to which the community is exposed, should be directly compared to toxicity benchmarks specific to those compounds. The species-specific media concentrations should be calculated using equations and guidance presented in Chapter 3 and Appendix B. Media-specific toxicity benchmarks for divalent and methyl mercury are provided in Appendix E.

To evaluate the exposure of class-specific guilds to mercury, the media-specific concentrations of both divalent and methyl mercury should be modeled as independent COPCs through the food web, assuming no methylation of divalent mercury to the methyl mercury form within organisms. Therefore, the daily doses of all food items (i.e., media, plants, and animals) ingested by a measurement receptor should be considered for both divalent and methyl mercury, and compared to the respective toxicity benchmarks that are representative of the measurement receptor (see Appendix E). The daily doses of food items ingested by a measurement receptor should be calculated consistent with the guidance presented in Chapters 4 and 5, and Appendix F, for assessing exposure of class-specific guild measurement receptors to other COPCs. This includes the use of species-specific media concentrations, and methyl mercury bioconcentration factors (*BCF*) and food chain multipliers (*FCM*).

Conclusion

In the event risks associated with mercury exceed target levels based on modeling with equations and initial conservative assumptions presented in this guidance, the permitting authority may approve use of more complex models that utilize more extensive site-specific data to predict transformation of chemical forms and biotransfer of mercury for evaluation at points of potential exposure. For example, the draft version of the ISCST3 dry gas algorithm for estimating dry gas deposition may be utilized. This draft model can be found

on the SCRAM bulletin (see Chapter 3); and specific default parameter values for mercury are presented in U.S. EPA (1997b). While this guidance does not address what models should be used or how data to support such models should be collected, the decision to use site-specific mercury models in a risk assessment is not precluded just because it is different; nor does this guidance automatically approve the use of such models. A permitting authority that chooses to use complex mercury models should carefully identify and evaluate their associated limitations, and clearly document these limitations in the uncertainty section of the risk assessment report.

U.S. EPA OSW encourages 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 proposed MACT standards for hazardous waste combustors, or the MACT standards for municipal waste combustors). U.S. EPA OSW acknowledges that site-specific risk assessments as currently conducted may not identify the entire potential risk from mercury emissions. Mercury that does not deposit locally will ultimately enter the global mercury cycle for potential deposition elsewhere.

2.3.8 Particulate Matter

PM is all condensed material suspended in air that has a mean aerodynamic diameter of 10 micrometers or less (PM₁₀). PM can be classified as aerosols, dusts, fogs, fumes, mists, smogs, or smokes, depending on its physical state and origin. Anecdotal evidence suggests that uncontrolled particulate emissions from coal-burning industries has adversely affected local populations of wildlife (U.S. Fish and Wildlife Service [U.S. FWS] 1980). For wildlife, PM can adsorb to external surfaces or membranes, for example causing corneal damage. Wildlife exposure can also occur through ingestion of contaminated food, water, and hair (through grooming) (U.S. FWS 1980). However, PM dose-response information to evaluate risk of particulate matter to ecological receptors is limited. For this reason, U.S. EPA OSW does not recommend that PM be evaluated as a separate COPC in a risk assessment. However, PM is useful as an indicator parameter for other contaminants because it can be measured in real time and is sensitive to changes in combustion conditions.

2.3.9 Hydrogen Chloride/Chlorine Gas

Hydrogen chloride (which becomes hydrochloric acid when dissolved in water) and chlorine are two of the 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.

Hydrogen chloride, as all other strong acids and bases, is an irritant on contact; adverse effects are seen only in the upper respiratory tract (including the nose, mouth, and throat). High concentrations can become corrosive and destroy tissues, producing chemical burns. Unless it is highly concentrated, ingested hydrochloric acid has only minimal adverse effects.

Because of the high concentrations of these compounds needed to produce observable effects, they are not expected to pose an ecological risk. Therefore, U.S. EPA OSW does not recommend that hydrogen chloride and chlorine gas be included as separate COPCs in the risk assessment.

2.3.10 Endocrine Disruptors

Endocrine disruptors are chemical compounds that interfere with the endocrine system's normal function and homeostasis in cells, tissues, and organisms. It has been hypothesized by U.S. EPA OSW that endocrine disruptors adversely affect the reproductive system by interfering with production, release, transport, receptor binding action, or elimination of natural blood-borne hormones and ligands.

Several studies have been conducted and serve as the basis for further experimentation to determine whether the hypothesis is correct. These studies include (1) wildlife reproduction (feminization of birds, alligators, and certain terrestrial mammals), (2) wildlife population ecology (population decline), (3) human reproductive physiology (decreased sperm count in males in industrialized nations), (4) molecular biology (data on receptor-mediated mode of action), and (5) endocrinology (increased understanding of mechanisms of hormone regulation and impacts of perturbations).

Some have attempted to classify chemical compounds as endocrine disruptors; however, several problems have been encountered. Only limited empirical data are available to support the designation of specific

chemicals as endocrine disruptors, and some of the data are conflicting. An absence of a clear structure-activity relationship is evident among the diverse groups of chemicals considered as endocrine disruptors. There is a lack of unifying dose-response relationship among the diverse group of chemicals. Also, multiple modes of action for chemicals are currently considered as 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 risk resulting from potential endocrine disruptors (U.S. EPA 1996d). Currently, no quantitative U.S. EPA methods exist to specifically address the effects of endocrine disruptors in a risk assessment. Because the methods for addressing endocrine disruptors are developing at a rapid pace, permits writers and risk assessors should contact the Economics, Methods and Risk Analysis Division (EMRAD) of the Office of Solid Waste for the latest policy on how to deal with endocrine disruptors in site specific risk assessments. Additional information can also be obtained from review of available publications (e.g., EPA Special Report on Endocrine Disruption) at the web site “www.epa.gov/ORD/WebPubs/endocrine/”.

2.3.11 Radionuclides

Radionuclides exist in (1) naturally occurring radioactive materials such as coal and other rocks, as (2) radioactive by-products of industrial processes. This risk assessment guidance does not consider the naturally occurring radioactive materials such as uranium and thorium (and their decay elements) based on U.S. EPA doctrine 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 is radioactive waste and hazardous waste defined by U.S. EPA. Radioactive and mixed waste 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.

U.S. EPA OSW recommends that the combustion of mixed waste and radioactive material should be evaluated in the risk assessment. Direct radiation (e.g., radiation from sealed sources such as instruments

that are not released to the environment) does not need to be evaluated in the risk assessment. Risk from both radiological and non-radiological contaminants should be presented along side each other in a risk summary table. Results should include a discussion of additivity and the uncertainties of additivity when combining risks from radiological and non-radiological contaminants. A radionuclide should be included as a COPC if it is in the combustion unit's waste feed.

U.S. EPA OSW recommends using the ISCST3 air dispersion model, utilizing the exponential decay option to calculate air concentrations and ground deposition rates. Intake should 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 special consideration in integrating radioactive materials into risk calculations is related to decay and ingrowth of radionuclides, especially the few decay processes that involve a change of state. Decay should always be considered, both over the air transport time and the surface exposure duration. Ingrowth may be important, and special care must be taken in the use of radionuclide slope factors that include contributions from daughters ('+D' slope factors). Ingrowth involving change of physical states is another situation that will require special handling 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.

Equations for fate and transport of radionuclides in soil and water should be consistent with those presented for non-radionuclides factoring in decay (and ingrowth if applicable). Food chain biotransfer parameters necessary to determine food concentrations are available in the *Handbook of Parameter Values for the Prediction of Radionuclide Transfer in Temperate Environments; IAEA Technical Report Series No. 364* (International Atomic Energy 1994).

Because the information currently available on ecological fate and effects for radionuclides is very limited, U.S. EPA OSW has not yet developed a methodology for quantitative assessments of ecological risk resulting from exposure. Ecological screening levels currently being used in some regions include 1 rad/day for aquatic receptors, based on population effects, (National Council on Radiation Protection and Measurements 1991), and 0.1 rad/day for terrestrial receptors (with the exception of pine trees and mammalian embryos) (International Atomic Energy Agency 1992). Additional references on evaluating ecological exposures to radiation include Barnthouse (1995) and Blaylock et al. (1993).

USER NOTE

Prescriptive methodology for calculating risk from combustion facilities burning mixed waste is beyond the scope of the current document. The above information is provided to outline the methodology recommended by U.S. EPA OSW.

2.4 ESTIMATES OF COPC CONCENTRATIONS FOR NON-DETECTS

The lowest level of an analyte that can be detected using an analytical method is generally termed the “detection limit.” One particularly difficult issue is the treatment of data in the risk assessment that are reported as below the “detection limit.” The following subsections (1) define commonly reported “detection limits,” (2) describe use in the risk assessment of data reported as non-detect, (3) describe statistical distribution techniques applied to address this issue, (4) summarize U.S. EPA OSW recommendations regarding quantification of non-detect issues in preparation of a risk assessment, and (5) clarify data flagged as estimated maximum possible concentration (EMPC) in the risk assessment.

2.4.1 Definitions of Commonly Reported Detection Limits

U.S. EPA’s commonly-used definition for the detection limit for non-isotope dilution methods has been 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 termed the “quantitation limit” or “quantitation level.” In practice, numerous terms have been created to describe detection and quantitation levels. The significance and applicability of the more widely reported of these detection and quantitation levels by analytical laboratories are summarized below. These levels—listed generally from the lowest limit to the highest limit—include the following:

- Instrument Detection Limit (IDL) is 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.
- Method Detection Limit (MDL) is 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, and 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, the MDLs are determined on analytical reagents (e.g., water)

and not on the matrix of concern. 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).

It should be noted that 40 CFR Part 136 is specific to the Clean Water Act, and therefore, 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 U.S. EPA analytical methods for the determination of several hundred analytes.

- Reliable Detection Level (RDL) is 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). The RDL is a total of 8 standard deviations above the MDL developmental test data (3.14 times 2.623).
- Estimated Detection Limit (EDL) is 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 such as SW-846 Method 8270, even though an EDL is not defined by the method.

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:

$$EDL = \frac{2.5 \cdot Q_{is} \cdot (H_n^1 + H_n^2) \cdot D}{V \cdot (H_{is}^1 + H_{is}^2) \cdot RF_n} \quad \text{Equation 2-7}$$

where

<i>EDL</i>	=	Estimated detection limit (ng/L)
2.5	=	Peak height multiplier (unitless)
<i>Q_{is}</i>	=	Nanograms of the appropriate internal standard added to the sample prior to extraction (ng)

H_n^1 and H_n^2	=	The peak heights of the noise for both of the quantitation ions of the isomer of interest
H_{is}^1 and H_{is}^2	=	The peak heights of both the quantitation ions of the appropriate internal standards
D	=	Dilution factor - the total volume of the sample aliquot in clean solvent divided by the volume of the sample aliquot that was diluted (unitless)
V	=	Volume of sample extracted (L)
RF_n	=	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:

$$EDL = \frac{2.5 \cdot Q_{\beta} \cdot (F \cdot H) \cdot D}{W \cdot A_{\beta} \cdot RRF_{\sigma}} \quad \text{Equation 2-8}$$

where

EDL	=	Estimated detection limit
2.5	=	Minimum response required for a GC signal
Q_{β}	=	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_{σ}	=	The mean analyte relative response factor from the initial calibration

- Practical Quantitation Limit (PQL) is 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).

- Target Detection Limit (TDL) is a quantitation level constructed similar to the PQL.
- Reporting Limit (RL) is a quantitation level constructed similar to the PQL.
- Estimated Quantitation Limit (EQL) is a quantitation level constructed similar to the PQL.
- Sample Quantitation Limit (SQL) is 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.
- Contract Required Quantitation Limit (CRQL)/Contract Required Detection Limit (CRDL) is a quantitation pre-set by contract, which may incorporate U.S. EPA (1986b) 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 Use In the Risk Assessment of Data Reported As Non-Detect

In collecting data for use in risk assessments or in setting regulatory compliance levels, the 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. Because measurements made below analytical detection and quantitation levels are associated with increased measurement uncertainty, an understanding of these levels is important to the comprehension of the impact they may have when they are applied.

As a result 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. For the second question, the answer is “somewhere between true zero and the quantitation level applied.” For samples obtained during the trial burn that report compounds at below the detection limit, earlier U.S. EPA

(1994i) guidance has recommended that emission rates for non-detects be developed using one-half of the “detection limit” and applied in conducting the risk assessment. However, which detection limit should be used has not been explicitly defined or presented in quantitative terms.

To increase consistency and reproducibility in dealing with non-detects, U.S. EPA OSW recommends application of the MDL-derived RDL to quantify non-detects for COPCs analyzed with non-isotope dilution methods, and application of the method-defined EDL to quantify non-detects for COPCs analyzed with isotope dilution methods. Procedures for these applications are as follows:

Non-isotope Dilution Methods: Non-detects for COPCs analyzed with non-isotope dilution methods should be quantified for use in the risk assessment using an MDL-derived RDL. Commonly used non-isotope dilution methods include SW-846 Method 8260 (volatiles), SW-846 Method 8270 (semivolatiles),

1. Require the laboratory to report the actual MDL for every non-detect compound analyzed, in addition to the commonly used reporting limit, such as an EDL, EQL, or PQL. The MDL should be derived in a manner consistent with 40 CFR Part 136 Appendix B. This would also apply for 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 for quantitative application in the risk assessment. This would be obtained by multiplying the MDL, as reported by the laboratory, times 2.623 (interim factor) (U.S. EPA 1995i).
3. Adjust the RDL, as appropriate, to account for sample-specific volumetric treatments (e.g., splits and dilutions) that differ from those utilized in the Part 136 MDL determinations.

Isotope Dilution Methods (SW-846 Methods 8290, 1624, 1625; and CARB 429, etc.): Non-detects for COPCs analyzed with isotope dilution methods should be quantified for use in the risk assessment using the EDL as defined by the analytical method without the use of empirical factors or other mathematical manipulations specific to the laboratory (e.g., EDL as defined in SW-846). Commonly used isotope dilution methods include SW-846 Methods 8290, 1624, and 1625.

It should be noted that the MDL definition used in 40 CFR Part 136 (see Section 2.4.1) addresses errors of the first type, false negatives. The 99 percent confidence limit stating that the MDL has only a 1 percent chance the detects will be misidentified as negative, when the compound of concern was present. Errors of the second type, false positives are not addressed. By not addressing false positives, or errors of the second type, the statistically defined default value become 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 conservative approach, and biased toward not missing any compounds of potential concern that may be present. The use of 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: (1) the uniform fill-in (UFI) method, in which each LOD value is replaced with a randomly generated data point by using a uniform distribution; (2) the log fill-in LFI method which is the same as UFI, except for using a logarithmic distribution; (3) the normal fill-in (NFI) method which is the same as UFI, except for using a log-normal distribution; and (4) the maximum likelihood estimation (MLE) techniques (Cohen and Ryan 1989; Rao et al. 1991). If determined to be applicable by the permitting authority, a Monte Carlo simulation may also be used to determine a “statistical” value for each non-detect concentration.

2.4.4 U.S. EPA OSW-Recommendations on Quantifying Non-Detects

Use of non-detects in risk assessments is dependent on the analytical method used to produce the data. In most cases, U.S. EPA will estimate 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 the method-defined EDL for isotope dilution methods. U.S. EPA OSW believes that these methods are reasonable and conservative, and that they represent a scientifically sound approach that allows maximum protection of the environment while recognizing the uncertainty associated with analytical measurements at very low concentrations in a real world sample matrix. It is also recognized 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 state permitting authorities have expressed the desire to obtain and use non-routine data (e.g., uncensored data) of defensible quality in the risk assessment as a way to deal with non-detect issues.

While this guidance does not address what forms or how such data may be used, the decision to use non-routine data in a risk assessment is not precluded just because it is different; nor does this guidance automatically approve the use of non-routine data. A permitting authority that chooses to use non-routine data should carefully identify and evaluate the limitations associated with non-routine data and clearly document this discussion in the uncertainty section of the risk assessment report.

For collection of data to be used in a risk assessment, U.S. EPA OSW recommends comprehensive sampling using typical sampling and analytical methods for VOCs, SVOCs, metals, PCDDs, PCDFs, total organics, and other appropriate constituents as necessary based on the type of waste that will be burned by the unit. A pretrial burn risk assessment can help to ensure that the desired quantitation limit (and, therefore, DREs and COPC stack gas emission rates) will be achieved during the trial burn test.

2.4.5 Estimated Maximum Possible Concentration (EMPC)

The EMPC, as defined in SW-846 Methods 8280A and 8290, is in most cases only used with the isotope dilution methods as stated. An EMPC is calculated for dioxin isomers that are characterized by 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 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. U.S. EPA OSW recommends that EMPC values be used as detections without any further manipulation (e.g., dividing by 2). However, because EMPCs are worst case estimates of stack gas concentrations, permitting authorities and facilities should consider techniques to minimize EMPCs when reporting trial and risk burn results, especially when the EMPC values result in risk estimates above regulatory levels of concern. Some techniques that may be applied 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.

RECOMMENDED INFORMATION FOR RISK ASSESSMENT REPORT

- Actual MDLs for all non-detect results
- Description of the method applied to quantify the concentration of non-detects

2.5 CONCENTRATIONS DETECTED IN BLANKS

Blank samples are intended to provide a measure of any contamination that may have been introduced into a sample either in the field while the samples were being collected, in transport to the laboratory, or in the laboratory during sample preparation or analysis. Blank samples are analyzed in the same manner as the site samples from the trail burn. In order to prevent the inclusion of non-site related compounds in the risk assessment, the concentrations of compounds detected in blanks should be compared 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 of 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 should 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 of Method Blank - A laboratory reagent of 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 processes 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 should be compared with the results with which the blanks are associated. However, if the association between blanks and data can not be made, blank data should be compared to the results from the entire sample data set.

U.S. EPA (1989e) makes a division in comparison 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 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 treated as a non-detect in that particular sample.

In some limited cases, it may be appropriate to consider blanks which contain compounds that are not considered by U.S. EPA to be common laboratory contaminants as identified above. In these limited cases, sample results are not 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 is treated as a non-detect in that particular sample.

Permitting authorities should carefully consider the evaluation of blank data in the overall context of the risk assessment and permitting process. U.S. EPA OSW expects that issues related to non-laboratory contaminant blanks to be minimal because data collection and analysis efforts in support of trial and risk burns are expected to be of high quality in strict conformance to QA/QC plans and SOPs. The trial and risk

burn data should be carefully evaluated to ensure that the level of contamination present in the blanks does not compromise the integrity of the data for purposes of risk assessment, or result in retesting in order to properly address data quality issues.

When considering blank contamination in the COPC selection process, permitting authorities should 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 and 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 reports emissions rates both as measured, and as blank corrected, in situations where there is a significant difference between the two values.