3. EVALUATING ATMOSPHERIC RELEASES OF DIOXIN-LIKE COMPOUNDS FROM COMBUSTION SOURCES

3.1. INTRODUCTION

Since the late 1970's, it has become well established that the combustion of certain fuels containing both organic material and chlorides can form polychlorinated dibenzo-p-dioxins (CDDs) and polychlorinated dibenzofurans (CDFs). This discovery has prompted world-wide research to identify combustion sources, to characterize the conditions favoring the formation of CDD/Fs within the combustion process, and to characterize the emission of dioxin-like compounds to the air from the stack of the process.

The purpose of this chapter is to provide site-specific procedures for evaluating the emission of dioxin-like compounds from stationary combustion sources. The first step is to characterize stack emissions in terms of mass of CDD/F congener released, and then to partition that release into a vapor and a particle phase. Using atmospheric transport modeling, these releases are translated to ambient air vapor and particle phase concentrations, and wet and dry particulate deposition amounts, in the vicinity of the release. This chapter demonstrates these procedures on a hypothetical incinerator using an air dispersion model called the Industrial Source Complex 3, or ISC3. The short-term version of that model, ISCST3, is used in this document. A second purpose of this chapter, therefore, is to provide the background and justification for the model inputs and key parameters for ISCST3. The final results for this model simulation are vapor and particle phase concentrations, and particulate deposition amounts of the specific dioxin-like congeners, which are then used for the demonstration of the stack emission source category in Chapter 5 of this Volume.

This chapter is structured as follows:

- Section 3.2 describes the generation of CDD/F congener-specific emission factors. These factors are defined as the mass of congener emitted per mass of feed material combusted. Subsections within Section 3.2 discuss: 1) a hierarchy of preferred options for generating such emission factors, starting with site-specific stack testing for specific congeners and ending with engineering evaluations when no other data is available, 2) an approach to estimating congener-specific emission factors using congener profiles generated for a source when only total dioxin (sum of homologue group CDD and CDF concentrations) emissions are available; 3) an approach for estimating congener-specific emission rates from CDD and CDF homologue group emissions data if congener profiles are not available; 4) the emission factors for the example incinerator demonstrated in Chapter 5, and assuming a feed rate into the example incinerator, emissions expressed on a mass per time basis (which is required for transport modeling), 5) partitioning of emissions into a vapor and a particle phase for atmospheric transport modeling, and 6) a procedure to estimate the mass released and concentrations for a related emission of a combustor, that of ash.

- Section 3.3 describes a general air modeling procedure for evaluating the fate and transport of dioxin-like compounds emitted from stacks. The discussion presents a general review of dispersion theory, a general review of dry particle deposition, and a general review of the wet deposition algorithm employed in this analysis. EPA's ISCST3 air dispersion and deposition model is reviewed. Wherever pertinent, Section 3.3 describes the assumptions, equations, and parameter values that were used in the demonstration of methodologies in Chapter 5 of this Volume.
- Sections 3.2 and 3.3 summarized input data and assumptions (emission rates, vapor/particle partitioning assumptions, etc.) that were made for the demonstration of the methodologies for evaluating stack emissions in Chapter 5 of this Volume. Section 3.4 supplies all other key assumptions for the stack emission demonstration, such as stack height and exit temperatures, meteorological data, and others. This Section also provides the final results from the ISCST3 modeling, including vapor phase air concentrations at various distances in the predominant wind direction, and dry and wet deposition fluxes, also at various distances in the predominant wind direction.
- Section 3.5 closes out the chapter by summarizing critical aspects for making site specific evaluations of stack emission sources.

3.2. ESTIMATING THE EMISSIONS OF DIOXIN-LIKE COMPOUNDS FROM ANTHROPOGENIC COMBUSTION SOURCES

Estimating the emission factor is the first step in assessing a specific stack emission source of dioxin-like compound release. For this assessment, an emission factor is defined as the total mass (in vapor and particulate forms) of dioxin-like compound emitted per mass of feed material combusted. An emission factor is a representative value that attempts to relate the quantity of a pollutant released to the atmosphere with an activity associated with the release of that pollutant. Such factors facilitate estimation of emissions from various sources of air pollution. In most cases, these factors are averages of all available data of acceptable quality, and are generally assumed to be representative of long-term averages for all facilities in the same source category.

The general equation for emission estimation is:

$$E_{yr} = A_{yr} * EF \qquad (3\text{-}1)$$

where:

E_{yr} = emission dioxin/yr; e.g., g/yr

A_{yr} = annual activity level of the subject source; e.g. kg/yr

EF = emission factor, mass dioxin emitted/ unit of activity level; e.g., ng/kg

Inherent in Equation (3-1) is the assumption that long-term emissions of dioxin-like compounds from a facility is best represented by the mean emission factor. Emission factors are usually developed from measurements of dioxin releases that are associated with normal operating conditions, not upsets nor industrial accidents.

This assessment recommends the generation of emission factors for individual dioxin-like congeners for a site-specific assessment. Volume I, *Sources of Dioxin-Like Compounds in the United States*, contains congener-specific CDD/F emission factors for specific types or classes of combustion processes. The emission factors were developed from stack gas emission measurements at tested facilities, usually as a result of compliance testing under the Clean Air Act, or in conjunction with the issuance of a State operating permit. The actual facility-specific emission rates and the derivation of emission factors representative of classes of combustors are documented in Database of Sources of Environmental Releases of Dioxin-Like Compounds in the United States (EPA/600/C-01/012. March, 2001). This database includes congener-specific CDD and CDF emissions data extracted from original engineering test reports. It has been published independently from the Reassessment and is available on Compact Disk-Read only Memory (CD-ROM), without cost, from EPA's National Service Center for Environmental Publications (NSCEP) in Cincinnati, Ohio (telephone: 1-800-490-9198, or 513-489-8190; fax: 513-489-8695). Summary files from the database will be available for downloading from the Web page of the National Center for Environmental Assessment, www.epa.gov/ncea/dioxin.htm. Instructions on how to order and obtain the CD-ROM will also be available on the Web page. This compilation of emission factors is the result of entering raw data of stack emissions from engineering reports of tested facilities data into a series of spreads-sheets. Facilities are classified and sub-classified according to similarity of process, design, types of materials processes or combusted and air pollution control equipment. These emissions factors are current through 1995. However, because most combustion processes are generally configured as they were in 1995, EPA believes the database, in most respects, is current with state-of-the-art technologies. This also applies to air pollution control equipment. EPA will, however, provide a periodic update to the database. Currently, EPA is updating this database to be current with the year 2000. These updates should reflect changes in the improvements in the combustion-related technology and air pollution control equipment with the passage of time.

When evaluating potential human exposure to dioxin-like compounds using an Air Quality Model, EPA has traditionally converted the stack gas concentrations and emissions of CDD/F mixtures into an equivalent concentration of 2,3,7,8-TCDD, or TEQ (Cleverly, et al., 1989, 1991; EPA, 1987; Mukerjee and Cleverly, 1987), when deriving an emission factor. The fate, transport, and transfer parameters of 2,3,7,8-TCDD were applied to model the environmental fate of this TEQ mixture. For the site-specific procedures in this document, individual dioxin congeners are modeled from source to receptor. Only at the interface to human exposure, e.g., ingestion, inhalation, dermal absorption, etc., are the individual congeners recombined and converted into the toxic equivalence of 2,3,7,8-TCDD to be factored into the quantitative risk assessment.

Section 3.2.1 presents a strategy for development of emission factors for conducting a site-specific assessment. Section 3.2.2 describes an approach to estimating congener-specific emission factors when all that is available are homologue group emission factors. Section 3.2.3 summarizes the emission factors for the hypothetical incinerator demonstrated in Chapter 5. Section 3.2.4 presents an in-depth evaluation of the partitioning of emissions between a vapor and a particle phase for further atmospheric transport modeling. This discussion includes subsections on measurements of partitioning at the stack, measurements of partitioning in ambient air, and the theoretical approach used in this assessment for vapor/particle partitioning. Section 3.3.5 closes this section on emission factors by describing procedures to estimate the mass of ash (fly and bottom) produced and the concentration of dioxin-like compounds on ash.

3.2.1. A Strategy for Generating Emission Factors

The following is a hierarchial listing of data collection options for emission factors:

A. *For facilities that are built and operational*, it is preferred that direct stack measurements be used, using EPA recommended congener-specific stack monitoring and analytical protocols (e.g., EPA Method 23 for stack and EPA Method 1613 revision b for laboratory analysis). Stack monitoring provides concentrations and mass release rates of the pollutant, actual volume of stack gas and temperature. Care should be taken to ensure that the emissions characterization reflects a wide range of operating conditions and also accounts for deterioration in emissions output of the facility over its useful life. Procedures to convert data expressed in concentrations or mass release rates to an emission factor are as follows:

1. Test data of emissions are first placed into common units of measurement. English units are converted into metric, and the concentration term (mass of pollutant per unit volume of combustion gas emitted from the stack) should be corrected to the standard temperature and pressure on a dry gas basis, and standard percent carbon dioxide or oxygen within the combustion gas (e.g.,12% CO_2 or 7% O_2). These adjustments may be necessary if more than one test occurred for stack emissions.
2. The next step involves converting the mass emission concentration of the specific dioxin-like congener in units of nanogram per normal cubic meter (at standard temperature and pressure) of combustion gas corrected to 12% carbon dioxide into an equivalent emission factor in units of grams of pollutant emitted from the stack per kilogram of combustible material or feed (g [CDD/F]/kg feed) that was incinerated at the facility during the duration of stack sampling. This is solved in (Equation 3-2) below. In Equation (3-2), it is important that both the concentration of the dioxin-like compound (C_{fg}) and the volume of combustion gas (V_{fg}) be calibrated to the identical oxygen percent, temperature, and pressure.

$$EF = C_{fg} \text{ x } V_{fg} \text{ x } A$$

$$EF = \left\{\frac{\text{ng dioxin}}{\text{dscm (STP)}}\right\} \text{ x } \left\{\frac{\text{dscm (STP)}}{\text{hr}}\right\} \text{ x } \left\{\frac{\text{hr}}{\text{kg combusted}}\right\} \qquad (3\text{-}2)$$

where:

EF = congener-specific CDD/F emission factor, ng dioxin/kg
C_{fg} = concentration in flue gas, ng dioxin/dscm
V_{fg} = volume of combustion gas/unit of time, dscm/hr
A = combustion activity level, kg/hr

3. As a final step, the average emission factor of each congener is derived by summing the emission factors and dividing by the number of data points used. The average should represent an approximation of long-term emissions (i.e., annual emissions). Many air dispersion models require that emission factors (ng/kg) be translated into units of amount of the pollutant emitted per second of time (ng/s). Therefore the average emission factor must be adjusted accordingly by adjusting the units in Equation (3-2) to a time-scale of one second.

B. *For facilities that have been constructed, but not yet operational, or are in the planning stages of development, the following procedure is recommended:*

1. Refer to the *Database of Sources of Environmental Releases of Dioxin-like Compounds in the United States* (EPA, 2001). This database contains CDD/F emission factors for a variety of combustion sources through 1995:
    a) municipal solid waste incinerators
    b) medical waste incinerators
    c) cement kilns burning hazardous waste
    d) cement kilns not burning hazardous waste
    e) dedicated hazardous waste incinerators
    f) industrial wood burning
    g) residential wood burning
    h) coal and oil-fired utility boilers
    I) secondary aluminum smelters
    j) iron ore sintering
    k) secondary lead smelting
    l) secondary copper smelting
    m) kraft black liquor boilers
    n) sewage sludge incinerators
    o) boilers/industrial furnaces burning hazardous waste
2. Review the listing of air emission sources and combustor types. From this listing, select the closest analogy to the subject technology in terms of design-type, kinds and types of materials processed or combusted, and air pollution control device. Care should be taken to assure that the subject source type and design, controls, and raw material input are those of the source(s) analyzed to produced the emission factor. This fact should be considered, as well as the age of the information and the user’s knowledge of technology advances.
3. After selecting the similar technology, go to the area of the *Dioxin Source Database* where average and congener-specific CDD/F emissions factors have been computed.

D. *If no data exist in the National Database that is relevant to a specific facility, then the Compilation of Air Pollution Emission Factors,* Fifth Edition (EPA, 1997; and subsequent updates), should be used. This compilation was put together and is periodically updated by EPA's Office of Air Quality Planning and Standards (OAQPS), and is commonly referred to as AP-42. Care should be taken to select emission factors which were developed for technologies that best match the facility under consideration. The basic limitation of these of these data is the fact that emission factors are not usually reflective of specific emission control equipment. The AP-42 emission factors can be found in one of six chapters:

Chapter 1, External Combustion Sources
Chapter 2, Solid Waste Disposal
Chapter 3, Stationary Internal Combustion Sources
Chapter 4, Evaporative Loss Sources
Chapter 5, Petroleum Industry
Chapter 6, Organic Chemical Process Industry

Emission factors presented in AP-42 are designed for estimating emissions from a large number of sources over a wide area. They are averages of values determined at one or more individual facilities. The individual values which are used to develop the average may vary considerably. The use of AP-42 emission factors to estimate emissions from any one facility should be done with great care.

3.2.2. Use of Homologue and Congener-Specific Profiles to Estimate Emission Factors

Situations may occur in which CDD/F emissions data of classes of combustor types are reported as either homologue-groups and/or total CDDs plus CDFs. These data may, however, be most relevant to a combustion source under evaluation. Congener-specific emissions data are needed for the analyses of the ambient air impacts and deposition flux of dioxin-like compounds using air dispersion and deposition models. This is because each specific congener will have different physico-chemical properties, and this will greatly affect the modeling result. This section presents guidance on estimating congener-specific emission rates from homologue-specific and total CDD/F emissions data.

The preferred approach is to convert CDD/F homologue and total CDD/F emissions to congener-specific emissions using congener profiles developed for each source. Congener profiles are the fractional distribution of CDD/F congeners in an environmental release, in an environmental sample, or in a biological sample. Congener-specific profiles have been developed for known anthropogenic source activity in the U.S. as part of this assessment, and these profiles can be reviewed at the end of each Chapter in Volume I, *Sources of Dioxin-Like Compounds in the United States*. The following subsection 3.2.2.1 provides guidance for the use of congener profiles to estimate congener-specific emission rates when only total CDD/F emissions data are available. In some cases no congener-specific profiles may exist for a source. Subsection 3.2.2.2 provides guidance for assuming a congener-specific emissions if at least homologue data are available.

3.2.2.1 *Using Congener Profiles to Convert Total CDD/F*

The assessor may have stack emissions data displayed as the sum of tetra through octa-CDD and CDF congener-groups, i.e., total CDDs plus CDFs. Congener-specific emissions data are needed for the most accurate assessment of potential air and deposition impacts near a source with the application of an air dispersion and deposition model. Congener-profiles derived from stack emissions data of similar combustion sources may assist this effort.

Congener profiles were determined by dividing the mean congener emission factor for the source class by the total tetra through octa-CDD and CDF emission factor for that class. All nondetects were treated as zero values. The result is an average fractional distribution (unitless) of each toxic CDD/F congener. Figure 3-1 is an example of the congener and homologue profile of typical emissions from sewage sludge incineration. In this example, the most prevalent congener in the emissions from sewage sludge incineration is OCDD. When the congener profile is plotted, OCDD is approximately 27% of the total CDD/F emissions. In this example, 2,3,7,8-TCDD is approximately 1% of total CDD/F emissions. Multiplication of the total CDD/F emission factor by the fractional distribution of each congener gives an estimate of the congener-specific emission factor for the source. For example, if it is assumed that the total CDD/F emission factor is 500 ng/kg of waste feed for a sewage sludge incinerator emissions, then the emission factor for OCDD is estimated from the congener profile to be 135 ng/kg (500 ng total CDD/F * 0.27). By this method, 2,3,7,8-TCDD would have an estimated emission factor of 5 ng/kg.

3.2.2.2 *Estimating Congener-Specific Emissions when no Congener Profiles are Available*

In some cases the congener profile may not available for a specific source of interest. This may be due to the general lack of emissions data for that particular source. However, the assessor may have information on homologue emissions from a combustion source. When only homologue emission factors are available, and no congener-specific profile exists for the source, then rough estimates of congener specific emission factors can still be made. First, an equal probability of occurrence of the specific congener is assumed based on relative proportionality. For example, 2,3,7,8-TCDD is one congener out of 22 possible congeners in the TCDD homologue. Therefore, the probability of occurrence is assumed to be the ratio of 1/22 or 0.045. Multiplication of a total TCDD emission factor by 0.045 gives an approximation of the emission factor for 2,3,7,8-TCDD. Table 3-1 lists the number of dioxin-like congeners within a homologue group and the total number of congeners within that homologue group.

3.2.3. Estimation of Emissions of Dioxin-Like Compounds from the Hypothetical Incinerator

The emission factors for the dioxin-like compounds from the stack of the hypothetical waste incinerator were derived from actual stack monitoring and emissions testing of an incinerator burning a complex mixture of organic waste. The concentrations of the specific CDD/F congeners in units of nanograms per dry standard cubic meter (at 20° C; 1 atm.; 7% O_2) were available, as was the volume of gas escaping from the stack and feed rates for the material being combusted during the stack tests. Using procedures described in Section 3.2.1, this data was converted to emission factors. Such factors for three test runs are shown in Table 3-2. The fourth column is the average of these emission factors converted to g/sec units, which are the appropriate units for the application of the ISCST3 model. The conversion assumed a constant feed rate of 200 metric tons of feed material per day (further details on the hypothetical incinerator are found in Section 3.5). Human exposures to the coplanar PCBs emitted from a combustion source is not demonstrated in Chapter 5. Therefore, an estimation of congener-specific emission factors of coplanar PCBs for the hypothetical incinerator are not provided.

In order to put the emissions from the hypothetical waste incinerator into perspective, they can be compared with emissions from other incineration sources that are similarly controlled, e.g., equipped with scrubbers and/or fabric filters. Such air pollution control devices can reduce the amount of dioxin that is formed within the system by >99% prior to the release from the stack. In this comparison, emissions typical of waste incineration were taken from Volume 2, Chapter 3. The following types of incineration processes were used: medical waste incineration; hazardous waste incineration; sewage sludge incineration; municipal solid waste incineration, and tire incineration. For comparisons, all emissions factors are expressed in units of nanograms I-TEQ emitted from the stack per kg of waste combusted, and are presented as arithmetic mean emission factors. This should not be confused as typical of the incineration source category, but specific only to sources having scrubbers and/or fabric filters. Volume I, Chapter 3 of this assessment gives an overview of dioxin emissions from incineration technologies equipped with a variety of pollution control systems. The emissions from the hypothetical incinerator is ranked with the other types of waste incinerators that are well controlled with some combination of a scrubber device and/or a fabric filter, as follows:

1. Medical waste incinerator: 70 ng I-TEQ/kg waste combusted
2 .Municipal solid waste incineration: 16 ng I-TEQ/kg waste combusted.
3. Sewage sludge incineration: 6.9 ng I-TEQ/kg sludge combusted
4. **Hypothetical waste incinerator: 4.5 ng I-TEQ/kg waste combusted**
5. Hazardous waste incineration: 3.8 ng I-TEQ/kg waste combusted.
6. Tire incineration: 0.3 ng I-TEQ/kg tires combusted.

From these comparisons it appears that the I-TEQ emission factor derived for the hypothetical incinerator lies well within the range of emission factors developed for well controlled sewage sludge and hazardous waste incinerators, but considerably lower than municipal solid waste and medical waste incinerators. The hypothetical incinerator was arbitrarily assigned a waste combustion rate of 200,000 kg waste/day (i.e., 200 tonnes/day). This charging rate conforms to a large medical waste incinerator, an average hazardous waste facility, and moderate sewage sludge and municipal waste incinerators.

3.2.4. Estimation of the Vapor Phase/Particle Phase Partitioning of Emissions of Dioxin-Like Compounds

The first step in the air modeling is the partitioning of total emissions into a vapor and a particle state. This section will review data on partitioning at the point of stack emission, in ambient air, and a theoretical approach to estimating the partitioning of dioxin- like compounds in ambient air. The true vapor/particle partitioning of dioxin under different conditions has not been directly measured, and therefore, is usually implied from these limited data or by theoretical means.

3.2.4.1. *Vapor Phase/Particulate Phase Inferences from Stack Measurements*

While the available literature is weak in this area, various investigators have made inferences on the vapor phase/particulate phase (V/P) partitioning from in-the-stack sampling of CDD/F emissions from combustion sources. Sampling systems which have been used basically consist of a particulate filter followed by a section designed to condense vapors in impinger glassware surrounded by an ice bath, and a resinous material suitable for absorbing vapor phase compounds. Depending on where the congener is distributed within the component parts of the sampling apparatus, the investigator reports the fraction associated with particulate, and the fraction found in the vapor absorbing material. In order to collect sufficient mass of particulate for accurate analytical determination of the concentration of the recovered congener at sub-part per trillion levels of detection, it is often necessary to sample in stack for periods of four hours or longer. This introduces the possibility of movement of the collected dioxin sample from one part of the sampling train to another through adsorption, desorption, particulate blow-off, or other such phenomena as the sampling train continues to be exposed to the hot combustion gases. No real-time sampling method currently exists to instantaneously measure the concentration and physical state of the various CDD/F congeners in the fluid turbulence of the hot combustion plasma characteristic of gases from combustion traveling up a cylindrical stack. For these reasons, V/P partitioning based on stack test data is highly uncertain. Additional laboratory research is needed that is specifically directed at identifying the physical state partitioning of individual CDD/F congeners at the exit to the stack under varying temperature profiles and conditions of particulate loading and acid gas concentration. Table 3-3 is a summary of the percent distribution of CDD/Fs between the vapor-phase (V) and the particulate phase (P) as interpreted by various stack sampling techniques employed in the measurement of the compounds during incinerator operations.

Cavallaro, et al. (1982) performed a series of stack tests on six municipal solid waste (MSW) incinerators in Italy. He was one of the first investigators to interpret the V/P ratio from where the CDD/F segregated with the sampling train, e.g., the particulate filter and resinous trap. From these data, the percent distribution of congener groups were estimated. Cavallaro observed that the CDD/F emissions from the stack of the tested incinerators seemed to predominate in vapor phase. He attributed this to the possibility that the relatively high temperatures of the combustion gases during sampling (700 to 900° C) may have promoted desorption of CDD/Fs from particulate, although the sampling probe was kept at a constant 150°C.

Benfenati, et al. (1986) describes the stack testing of a modular MSW incinerator in Italy having a combustion capacity of 1500 kg/hour. The purposes of the study were to analyze the concentration of TCDD and TCDF at various points of the incineration process, to estimate the vapor phase versus the particulate phase partitioning at various sampling points corresponding to changes in temperatures, and to estimate the TCDD/F control efficiency of the pollution control device (an electrostatic precipitator). Comparisons were made between the distribution of TCDD/F after the secondary furnace in a region where combustion gas temperature was about 330°C, and the distribution at the stack where combustion gas temperature was 230° C. Benfenati observed that approximately 85% of the TCDD was in the vapor phase at the exit to the furnace, and approximately 95% of the TCDD was in the vapor phase at the stack. It was concluded that most of the TCDD predominated in vapor phase at the point of release from the stack at the reported temperature of 230°C. However, Benfenati could not exclude the possibility that the TCDD was adsorbed onto ultra fine, submicron aerosol particles.

Tiernan, et al. (1984) reported on the distribution of CDD/Fs recovered in the stack sampling apparatus (EPA Modified Method 5) following the stack testing of a mass burn MSW incinerator operating in Japan. In the Modified Method 5 procedure, the sampling probe is maintained at a temperature of 120°C while the stack gases are isokinetically sampled. The facility was equipped with a dry scrubber combined with a fabric filter as the primary pollution control device. Tiernan observed congener-specific variability in the V/P partitioning inferred from the sampling method. However, greater than 55% of the CDD/Fs were estimated to be in vapor phase at the point of release to the stack. In an earlier stack test (Tiernan, et al., 1982) of an MSW incinerator equipped with an electrostatic precipitator, Tiernan found that 45% to 89% of the CDD/Fs were associated with particulate.

Clement, et al. (1985) stack tested a mass burn MSW incinerator operational in Canada for the emission of CDD/Fs. Three 24-hour stack samples were taken using the EPA Modified Method 5 train with a stack temperature of 230 - 250°C. The components of the sampling train were analyzed separately. Clement observed that more than 95% of the total CDD/Fs detected in the sampling train samples was found in the impingers used to condense vapor phase organic pollutants. Interpretation of this is difficult. However, it is implied from these data that most of the CDD/Fs prevailed in vapor phase.

Hagenmaier, et. al (1986) conducted field tests of two different stack test methods for the accuracy, precision, and comparability of CDD/F measurements. Both instruments were similarly constructed with a glass fiber filter for the capture of particulate-bound contaminants, a series of water or ice-cooled impingers to promote condensation of vapor phase contaminants, followed by an absorbing material to trap vapor phase pollutants. Eight parallel stack sampling experiments were carried out over a three week period using the sampling trains known as the German simple dilution method and the EPA Modified Method 5. Although the two methods reported quite similar total concentrations of CDD/Fs, the distribution of CDD/Fs between the heated glass filter, and ice-cooled impingers and the sorbent trap were remarkably different. In one train, referred to as Train A by Hagenmaier, the temperature in the filter housing was 140° C, and in the second train, Train B, the temperature was 90° C. The stack gas temperature in both cases was 230° C. Hagenmaier found that the percentage of CDD/Fs in the glass fiber filter was markedly greater in Train B than in Train A. Up to 93% of the PCDDs and 90% of the

PCDFs were detected in the particulate filter in Train B. By comparison, 73% and 58% of PCDDs and PCDFs, respectively, were detected in the particulate filter in Train A. Although Hagenmaier's data is used in Table 3-3, Hagenmaier theorized that this difference in the distribution of CDD/Fs in the two sampling trains was due to the differences in the temperature of the glass fiber filter housing.

EPA (1990a) conducted a field validation study for the EPA stack testing Method 23 (the Modified Method 5) for the collection and retention efficiency of CDD/Fs. A carbon-13 labelled congener was metered into the sampling probe just preceding the glass fiber filter using a dynamic spiking system. The validation procedure involved the isokinetic sampling in the stack of a large mass burn MSW incinerator. Sampling *in situ* in the stack while using a dynamic spiking system demonstrated that most of the isotope was recovered in the filter trap and front half of the sampling train designed to capture particulate, and a lower amount was recovered in the XAD resin designed to capture vapor phase organic compounds. In the particular tests in which the overall percent recovery of the dynamic spike were found to be acceptable, the XAD resin and condensor contained about 49% of the isotope, and 51% was associated with carbonaceous particulate.

3.2.4.2. *Discussion of Vapor/Particle Ratios Derived from Stack Testing Methods*

It is apparent that the stack sampling method gives inconclusive and contradictory evidence of the V/P partitioning of CDD/Fs at the stack of incinerators. Although most of the researchers report finding the greatest quantity of CDD/Fs captured within the resinous material having the physical/chemical properties of absorbing vapor phase organic compounds, a few studies have reported the opposite. What is unusual about the V/P distributions in Table 3-3 is the lack of complete consistency despite the similarity of sampling method. Although the stack gas temperatures may vary, the probe and housing to the sampling instrument is usually kept at a standard temperature while traversing the hot flue gas. A more consistent pattern of V/P should have emerged.

Hagenmaier, et al. (1986) has postulated that, depending on the temperature of the glass fiber particulate filter housing, the CDD/Fs might desorb (volatilize) from particulate matter trapped in the filter during the 4 hours of sampling time required of the stack sampling method. Therefore, Hagenmaier does not believe that the distribution of CDD/Fs between the particulate filter, the condensing impingers, and the vapor absorber gives a true indication of the V/P partitioning of these compounds at the stack.

Tests also have been devised by the EPA (1990a) to study the effect a change in temperature of the glass fiber filter housing might have on the distribution of CDD/Fs in the sampling train. During the sampling period, two sampling trains were used: one inlet to the electrostatic precipitator (ESP), and the other placed near the outlet to the ESP. Temperatures of the filter housing were raised from the standard 120° C to 215° C in both sampling trains. In agreement with the observations of Hagenmaier, et al. (1986), an increase in temperature generally resulted in a change in the distribution of the recovered 13-C labelled CDD/F congeners. However, the temperature effect was most apparent within the sampling train inlet to the ESP. In the inlet sampling train, the higher filter box temperature increased the relative percentage of CDD/Fs trapped in the impingers and XAD-2 resin. An amount estimated to be in the vapor phase, based on the segregation of the compounds within the component parts of inlet sampling train, is as follows (with a range listed from low to high temperature): TCDD = 20 - 55% vapor; HxCDD = 10 - 30% vapor; OCDD = 5 - 18% vapor; HxCDF = 18 - 58% vapor; OCDF = 5 - 18% vapor. In the outlet sampling train (characteristic of stack emissions), this dramatic shifting of the congeners from the filter to the XAD-2 did not occur with an increase in temperature. Interpretation of the vapor phase partitioning in the outlet sampling train from low to high temperatures was as follows: TCDD = 90 - 95% vapor; HxCDD = 85 - 90% vapor; HxCDF = 90 - 95% vapor; OCDD = 75 - 90% vapor; OCDF = 78 - 90% vapor. Both these interpretations were developed using a 500 ng CDD/F spiked congener. Notice that the vapor phase to particle phase ratio is significantly different between the inlet and outlet sampling trains: in the inlet train most of the CDD/F congeners seemed to predominate in the particle phase at the standard temperature of the filter housing, whereas in the outlet train most of the CDD/F congeners seemed to predominate in the vapor phase, as interpreted by the distribution within the apparatus.

The temperature-dependent partitioning has recently been observed by Janssens, et al. (1992) during field validation studies involving the sampling of operating incinerators in Belgium. Janssens observed that the fraction of CDD/Fs collected in the heated portion of the particulate glass filter (temperatures in the range of 250 to 300° C) showed an expected partitioning according to the vapor pressures of the compounds. It was found that a very low proportion of the CDD/Fs were found in the particle phase; nearly all the compounds were detected in the vapor phase. Moreover, Janssens observed that higher temperatures seemed to favor the vaporous state of the lower chlorinated congeners (compounds having one to five chlorines on the aromatic ring), and the particulate phase for higher chlorinated congeners (five to eight chlorines). This agrees well with the decrease in vapor pressures that occurs with an increase in chlorination, and an increase in vapor pressure that occurs with a decrease in chlorination of CDD/Fs. Adding to the theory of Hagenmaier, et al. (1986), Janssens believed that either the sampling apparatus was giving a true distribution of the V/P ratio of individual congeners, or that a significant portion of the congeners were reversibly sorbed onto particulate surfaces and could be eluded to vapor phase by the passage of the volume of sampled combustion gas over a lengthy time interval, neither of which could be proven by his study.

Benfenati, et al. (1986) has suggested that what may be reported as vapor phase may actually consist of nucleated aerosol particles having diameters less than 0.1 micrometers. The impingers in the sampling method are located a few centimeters behind the heated particulate glass fiber filter, and are bathed in an ice bath. The dramatic reduction in temperature within the impinger glassware may cause sublimation from vapor phase to nucleation of aerosol particles. Downstream of the impingers is the vapor absorbing material, usually XAD-2 resin. Although this has been shown to be an excellent trap for semi-volatile organic compounds, the retention of submicron size particles with CDD/Fs adsorbed onto the surfaces, or absorbed into the interior spaces, cannot be ruled out or excluded as a possible explanation for investigators reporting a preponderance of concentration both in the impingers and the vapor trap.

Complicating any meaningful interpretation of the data is the long duration of sampling time required in the stack measurement method. In order to reach a sub-ppt level of detection of CDD/Fs for reliable quantification of specific congeners, sampling proceeds until approximately a five gram mass of particulate is gathered in the particulate filter. This may require *in situ* placement of the sampling apparatus such that samples are taken isokinetically, and the stack interior diameter is traversed for four or more hours. Thus the sampling instrument is continuously exposed to the hot gas plasma over a long sampling moment. In addition the hot gases also contain precursor compounds, chlorides, oxides of sulfur and HCl which may have an effect on the success of accurately sampling CDD/Fs. Although Janssens, et al. (1992), Hagenmaier, et al. (1986), and EPA (1990a) have all but excluded the possibility that sampling under these conditions creates results by producing CDD/Fs or destroying CDD/Fs somewhere within the sampling train, the possibility that the method creates an illusion of the true V/P ratio cannot be excluded.

The above discussions have indicated the variability in the data and the uncertainty with the stack results of vapor/particle partitioning. For these reasons, these data will not be used to infer the V/P distribution of CDD/Fs at the point of release from the stack.

3.2.4.3. *Vapor/Particle Partitioning of CDD/Fs from Ambient Air Sampling*

The measurement of CDD/Fs in air under ambient conditions has only been achieved since the late 1980's. The ambient air sampler which is most often used to estimate particulate and gaseous fractions consists of a glass or quartz fiber filter followed by a sorbent trap such as polyurethane foam (PUF), XAD resins, or a combination of the two. These are active samplers which utilize electric pumps to draw air through the collector at approximately 0.2 - 0.6 m^3/min. This provides sample volumes of 300 - 600 m^3 in a 24-h period, although longer sampling times are not uncommon. The phase distribution is estimated from the segregation of compounds on the filter and sorbent trap, which are assumed to capture compounds that are particulate and gaseous, respectively. PUF is capable of collecting many semivolatile compounds with high efficiency (Bidleman, 1987; Hart and Pankow, 1994; Pankow, 1989; Tashiro et al., 1989; Wagel, et al., 1989), although its usefulness is limited by the vapor pressure of the compound. Examples of compounds for which PUF can be used are the tetrachloro- and higher CDD/Fs, and three-ring and heavier PAHs and PCBs having three or more chlorines. The more volatile members of these classes as well as chlorobenzenes and chlorophenols are collected with greater efficiency by XAD and similar resins (Bidleman, 1987; Hart and Pankow, 1994; Hornbuckle et al., 1993; Patton et al., 1992; Zaranski et al., 1991). The glass fiber filters used in air samplers are rated to collect particles of diameters $\geq$0.3 micrometer, with 99.9% collection efficiency.

Filtration samplers are subject to artifacts which include loss of organic compounds from the particles on the filter by volatilization ("blow-off") (Eatough et al., 1993; Gundel et al., 1995; Lane et al., 1988; Lewis et al., 1991; Subramanyam et al., 1994) and sorption of gaseous compounds to the particle mass collected on the filter and to the filter itself (Cotham and Bidleman, 1992; Hart and Pankow, 1994; McDow et al., 1990; Turpin et al., 1994). The possibility of blow-off losses are recognized and discussed extensively in the literature, but there is disagreement as to how seriously this artifact will bias estimated particle/gas distributions.

Because sampling of CDD/Fs is not instantaneous (i.e., real time measurement), but requires 24+hour air sampling to assure a level of detection of about 0.03 pg/m^3, the V/P ratios described in this section should be considered as “operationally defined”. Operationally defined are relative and not absolute vapor phase and particle bound phase partitioning behavior within the design contraints of the measurment method. The following is a review of ambient air sampling data on the relative V/P partitioning of CDD/F congeners at ambient temperatures. Table 3-4 provides a summary of the particle percentages (vapor percentage = 100 - particle percentage) inferred from these reports.

Oehme, et al. (1986) first described a method sensitive enough for the congener-specific measurement of CDD/Fs at 0.1 pg/m^3 levels of detection in ambient air. Such low levels of detection introduced the possibility of taking ambient air samples in the vicinity of known combustion sources of CDD/Fs to reliably establish an association with stack emissions. Oehme tested the performance and reliability of an ambient air sampler consisting of a glass fiber filter followed by a polyurethane foam plug. Ambient air was sampled over a predetermined period after first spiking the filter with a known concentration of $^{13}C_{12}$ labelled CDD/F standards. This experiment was designed to determine the percent of the initial spiked labelled standard that could be recovered from the sampler after sampling 1000 m^3 of ambient air. The percent recovery of the standard was a measure of the collection and retention efficiency of the sampler. After collecting a sample, the particulate filter and the PUF plugs were extracted and analyzed separately. This was done in order to establish the particle phase and vapor phase partitioning of the CDD/F congeners. Oehme demonstrated that the sampling method was capable of a high degree of reliability in sampling sub-part per trillion concentrations of CDD/Fs as indicated by highly satisfactory recovery of the isotopically labelled standards in the apparatus, e.g., 88 - 102% recoveries. From the results of separately analyzing the filter and the PUF, Oehme postulated on the typical distribution of CDD/Fs between vapor and particles in ambient air. They suggested that TCDF and PeCDF were mainly present in the vapor phase, and HxCDD, HxCDF as well as the less volatile isomers of HpCDF, HpCDD, OCDF, and OCDD, were mainly present in the particle phase. Oehme took over 60 ambient air samples with this device in rural, suburban, and urban areas of Europe.

Eitzer and Hites (1989) reported on the measurement of CDD/Fs in the ambient atmosphere of Bloomington, Indiana while using a similarly configured ambient air sampling method, the General Metals Works PS-1 sampler. Ambient air is drawn through a glass fiber filter followed by a polyurethane foam plug (PUF). This was a long-term study designed to investigate the daily and seasonal variability of the compounds in the ambient air as measured at a single location, and to examine the vapor-phase, particulate-phase partitioning of the chlorinated congeners under ambient conditions. Samples were taken at four different sites over a 2-3 day sampling period until 1500 to 2400 m^3 of ambient air volume had passed through the apparatus. Sampling was conducted monthly from August, 1985 through July, 1986. The quantitative method produced a limit of detection of the individual chlorinated congeners in the range of ~1 femtogram/m^3. Eitzer and Hites (1989) operationally defined the vapor-phase/particle-bound phase of the chlorinated congeners as any compounds found in the PUF plug and the glass fiber filter, respectively. The V/P ratio was subject to certain restrictions of the sampling method, which the authors identified as: 1. Particles smaller than 0.1 microns would pass through the filter paper of the glass fiber particulate filter and be absorbed into the polyurethane foam; 2. Diurnal temperature variation could cause particle-bound CDD/Fs collected and retained in the filter to vaporize and be "blown-off" to the PUF plug by the passage of the sampled air stream; 3. At these relatively large sampling volumes of ambient air, it is possible that some breakthrough on the PUF plug occurs, and a portion of the CDD/F sample is lost. The investigators were able to rule-out the latter condition through the addition of a XAD-2 resin trap after the PUF. This was one of the first reports on the congener-specific V/P partitioning in the ambient air under variable average ambient temperatures. Although they could find no seasonal effect on the total concentrations of CDD/Fs, seasonal change in temperature did affect the V/P ratio. It was noted that during the warm summer months the V/P ratio was as great as 2:1, and during the cold winter months the V/P ratio could be <0.5. Thus, at warm temperatures most of the lower chlorinated congeners, e.g., mono through penta-chlorinated CDD/Fs, were mostly found in the vapor phase and the hexa - octachlorinated congeners were mostly particulate-bound. The colder winter temperatures produced the effect of causing the lower chlorinated species to partition more onto airborne particles. The higher chlorinated congeners, e.g., hexa-, hepta-, and octa-CDD/Fs, mostly were found to be particle-bound at both the warm and cold temperatures. These quantitative results of the V/P ratio of individual congeners at three ambient air temperatures (3° C, 16 - 20° C, and >28° C) was again reported by Hites (1991), as shown in Table 3-4. Through these analyses, Eitzer and Hites (1989) and Hites (1991) found two dependant variables controlled the V/P ratio in ambient air: 1. the ambient air temperature; and 2. the vapor pressures of the CDD/F congeners. The authors concluded that because the lower chlorinated compounds have higher vapor pressures, they will be found mostly in the vapor phase, and because the higher chlorinated congeners have lower vapor pressures, they will prevail in the ambient air bound to particulate matter.

Wagel, et al. (1989) reported on the performance of the General Metals Works PS-1 sampler for the collection and retention of CDD/Fs while sampling ambient air. This sampler configuration consists of a quartz glass fiber filter followed by a polyurethane foam (PUF) plug, and the investigators added an XAD-2 resin cartridge after the PUF. The addition of the XAD was a check on whether breakthrough of any CDD/F congeners occurred from the PUF during sampling. The PS-1 is the sampler most often used in the U.S. to quantify CDD/Fs in air under ambient conditions. The protocol of this research was to use two samplers co-located. The particulate filter of one sampler was spiked with $^{13}C_{12}$-labelled CDD/F congeners while the second sampler was used to provide background measurements of native (non-labelled) CDD/Fs.

Both units were operated to sample ambient air for 24-hours. The average ambient temperature during the sampling period was 24° C. Following the sampling the filter and PUF were removed and extracted according to published procedures (Wagel, et al., 1989). Performance of the PS-1 sampler was reported as percent recovery of the labeled standards initially spiked onto the particulate filter. The percent recovery was calculated by subtracting the background contributions from the total detected spike concentration and dividing by the concentration of the labeled standard initially added to the filter. The percent recoveries were reported in a range of from 85% to 124%, with an average recovery of 102%. This indicated a high degree of reliability in collecting and retaining CDD/Fs in the sampler during the 24-hr sampling period.

A second series of experiments were conducted to investigate the distribution of CDD/Fs within the sampling apparatus, e.g., the particulate filter versus the PUF plug, by extracting and analyzing the filter and PUF separately. Subject to the caveats previously discussed, the investigators made observations regarding the V/P ratio of CDD/F congeners. It was observed that CDD/Fs having 7-8 chlorines were mostly detected in the particulate filter, and lower chlorinated species were mostly detected in the PUF. Wagel, et al. (1989) suggested that it was possible that the lower chlorinated congeners volatilized from the particulate filter (somewhat affected by the rate of flow of the sampled air volume), and then were retained by the PUF. Furthermore, Wagel, et al. (1989) warned that if results of separately analyzing the filter and PUF are used to derive a vapor phase and particle phase partitioning of the CDD/Fs under ambient conditions, then this may give erroneously high estimates of the amount present in vapor phase.

Harless and Lewis (1992) have quantitatively evaluated the performance of the General Metals Works PS-1 sampler for the trace-level measurement of CDD/Fs in ambient air, adding to the growing evidence that results are actual measurements and not an artifact of the sampling method. In this study, three samplers were used in the same general vicinity, and were operated for a 24-hour period until an air volume of 350 - 400 m^3 had passed through the system. The quartz glass fiber particulate filters of two of the samplers were then spiked with $^{13}C_{12}$ labeled CDD/F congener with a known concentration after the 24-hour sampling period. The three samplers were then operated another 24-hours. The samplers were then shut down, and the filters and PUF plugs were removed and extracted and analyzed for CDD/Fs separately according to prescribed procedures. A separate series of experiments involved precleaning the glass fiber particulate filters, and adding the isotopically labeled CDD/F spike to the filter prior to sampling for seven days until about 2660 m^3 of ambient air had been sampled. Results of this study confirmed the accuracy and reliability of the PS-1 sampler for collecting and retaining

CDD/Fs at sub-ppt concentrations in ambient air. Performance was defined as the percent of the initial concentration of the labelled isotope recovered in the sampling apparatus following the operation over the predetermined sampling period. The average efficiency of recovery of the 0.8 ng $^{13}C_{12}$-1,2,3,4,-TCDD isotope that was spiked onto the filter prior to sampling was 91%, and similar efficiencies were observed for the recovery of the other labeled CDD/Fs. Additionally, Harless and Lewis (1992) used the spiking system to observe the distribution of CDD/Fs in the filter and the PUF after sampling 400 m^3 of ambient air. It was observed that most of the hepta-, and octa-CDD/Fs were retained by the glass fiber filter, indicating that these compounds were retained and not blown off the filter, and most of the tetra-, penta-, and hexa-CDD/Fs volatilized and were collected by the PUF plug. When partitioning was observed on a congener-specific basis, significant differences were observed in the V/P ratio, as shown in Table 3-4.

Hunt and Maisel (1990) reported on the ambient air measurement of CDD/Fs in a northeastern U.S. urban coastal environment during the fall and winter seasons. Isomer-specific sampling was conducted with the General Metal Works PS-1 sampler in and around Bridgeport, Connecticut from November, 1987 through January, 1988. Nine sampling sessions consisting of a total of 43 ambient air samples were taken in this study. Each sampling session was conducted either over a 24-hour or 72-hour period until about 350 m^3 and 600 m^3 of air volume had passed through the sampler. Hunt and Maisel (1990) reported on the typical vapor phase/particle bound partitioning of individual congeners during cold ambient air temperatures. The V/P ratio was based on the results of separately analyzing the PUF plugs and the glass fiber particulate filters for the presence of CDD/Fs. From these data, the investigators concluded that greater than 92% of all the congeners of CDD/Fs were particulate bound (operationally defined as detected in the particulate filter). The 2,3,7,8-TCDD isomer was not detected in any of the 43 collected samples (reported limit of detection was 5-20 fg/m^3). The particulate bound distribution (reported as a percent of the detected concentration) for some of the other congeners were as follows: 2,3,7,8-TCDF = 93%; 1,2,3,7,8-PeCDF = 94%; 2,3,4,7,8-PeCDF = 99%; 1,2,3,4,7,8-HxCDF = 97%; 1,2,3,4,6,7,8-HpCDF = 100%; 1,2,3,6,7,8-HxCDD = 96%; and the 1,2,3,4,6,7,8-HpCDD = 92%. The vapor phase/ particle bound distribution observed in this study is probably controlled by the cold January temperatures from which these observations were derived (average temperature = -5° C).

At a later date, Hunt and Maisel (1992) conducted ambient air monitoring of CDD/Fs in multiple locations in the warm climate of southern California for the State of California Air Resources Board (CARB). Ambient air samplers, e.g., the General Metal Works PS-1 sampler, were primarily placed in areas of high population density that contained known combustion sources of CDD/Fs, but sites were also sampled that were considered removed from the influences of any local sources. The purpose of the study was to evaluate the congener-specific spacial distribution of CDD/Fs in ambient air near environmental sources of the compounds, and in remote locations, in order to provide a baseline to evaluate population exposures within the region. Monitoring sites were established at eight locations in the South Coast Air Basin in and around the city of Los Angeles. Nine discrete sample sets were collected from December, 1987 through March, 1989. The authors defined a sample set as consisting of five to seven stations at which one or two co-located samplers were operated. Microscale meteorological data was collected during sampling to include wind speed, wind direction, barometric pressure, and temperature. One sampling site was chosen to investigate the distribution of CDD/Fs in ambient air where average ambient temperatures ranged from 16-20°C. This was done by the usual procedure of separately analyzing the filter and the PUF and making the assumption that what is detected in the glass fiber filter is particulate bound, and what is trapped in the PUF is in vapor phase. The authors noted that under these conditions, the V/P partitioning is operationally defined by the ambient air sampling system, and therefore may not be a true indication of the partitioning in the atmosphere. The majority of the hexa through octa CDD/F congeners were detected in the filter, and the authors observed that they were mainly associated with particulate matter. The authors found these observations were consistent with the V/P ratio observed by Eitzer and Hites (1989) in warm climate conditions. In addition, the authors noted that these observations give further evidence that vapor pressures of the specific CDD/F compounds and ambient air temperatures strongly influence the V/P partitioning. Therefore the tetra- and penta-CDD/Fs are expected to predominate in vapor phase during warm seasons. However, during the cold temperatures of the winter season these congeners are expected to be primarily associated with particulate matter in the ambient air.

Bobet, et. al. (1990) reported the results of an ambient air monitoring network operated by Environment Canada to temporally measure CDD/Fs in the ambient air in southwestern Ontario, Canada. The intent of the study was to monitor possible environmental impacts of a large refuse-derived fuel municipal waste combustor operational in the City of Detroit, Michigan. The ambient air monitoring network consisted on two stations, one in Windsor, Ontario, and the other located in the Walpol Island Indian Reservation 18 km to the northeast of Windsor. The former site was considered in an urban area near the expected point of maximum impact from the stack emissions from the MWC, and the other site was considered rural, and away from the influence of any stationary combustion source. CDD/F samples were collected once every 24 days using an high-volume ambient air sampler consisting of a Teflon-coated glass fiber particulate filter and a PUF adsorbent trap. Ambient air was sampled over a 24-hour period from July, 1987 to August, 1988 with a total sample volume of 800 - 1000 m^3 of air. From August on, the samplers were operated over a 48-hour period, and 1600 - 2000 m^3 of air passed through the sampler. Mean total concentrations of CDD/Fs were compared between the urban and rural sites, and Bobet observed that concentrations measured at the urban site were 4 - 20 times greater than at the rural site. Additionally, the V/P partitioning of CDD/Fs (as operationally defined by detection in the PUF verses detection in the filter) was investigated at both sampling stations. Bobet stated that the V/P may be influenced by "blow-off" of particulate from the filter to the PUF, and/or the passage of particulate matter <0.1 microns from the filter to the PUF, and if this is the case, then the vapor phase partitioning may be too great as interpreted by the method. Under these circumstances the authors suggested that the V/P partitioning should be considered as roughly representative of the vapor/particulate phases in the ambient air. On a total concentration basis, and on a total of 12 separate ambient air samples, the investigators found the following average percent vapor phase versus percent particle phase partitioning of the CDD/F homologues at the Windsor, Ontario station: TCDD = not detected; PeCDD = 100% V/ 0% P; HxCDD = 35% V/ 65% P; HpCDD = 18% V/ 82% P; OCDD = 0% V/100% P; TCDF = 80% V/20% P; PeCDF = 29% V/ 71% P; HxCDF = 0% V/100% P; HpCDF = 0% V/ 100% P; OCDF = 0% V/ 100% P. At the rural Walpole Island station, no TCDD, PeCDD or TCDF - OCDF were detected in any of the 5 separate ambient air samples. All of the detected HxCDD, HpCDD and OCDD was found in the particulate filter indicating a V/P distribution of 0% V/ 100% P for these compounds. The authors did not report the average ambient air temperature at the two stations.

Welsch-Paulsch et al. (1995) presented results of an experiment in Bayreuth, Germany in which grass was grown in a greenhouse and outdoors on soils having different concentrations of CDD/Fs. The purpose of the experiment was to determine the pathways by which these compounds accumulate in the grass. The principal finding of this study was that dry gaseous deposition, rather than particle deposition or soil-to-plant transfer, explained the concentrations of CDD/Fs in the grass. A subset of these data included measurements of CDD/Fs in the particle and gas phases using a glass fiber filter - XAD resin sampler. Samples were collected over two-week integration times during July - August 1991 when the average air temperature was 18°C. The particulate percentages determined in the study showed a predominance of tetra- and penta-CDD/Fs in the gas phase, approximately equal percentages of the hexa-CDD/Fs in the gas phase and associated with particles, and most of the hepta- and octa-CDD/Fs in the particle phase.

3.2.4.4. *Discussion of the Vapor/Particle Partitioning in Ambient Air Sampling Studies*

The studies that have been reviewed here indicate the following:

- The high-volume ambient air sampler consisting of a glass fiber particulate filter and polyurethane foam absorbent trap is a reliable method for the collection and retention of CDD/Fs in ambient air.
- Current analytical methods assure detection limits, on a congener specific basis, of about 1 - 10 fg/m^3.
- Experiments involving the recovery of isotopically labeled CDD/Fs within the sampler after 24-hours operation indicate that the sampler does not create artifacts representative of either sample losses or the synthesis of dioxin.
- Because the sampler is not artificially heated or cooled, but is allowed to operate at existing ambient air temperatures during sampling sessions, the method can be used to imply the vapor phase and particle bound partitioning of CDD/Fs in ambient air. This is accomplished by separately extracting and analyzing the glass fiber filter and the polyurethane foam for the presence of CDD/F congeners.
- However, the V/P ratio interpreted from these results is operationally defined. This will only give an approximate indication of the V/P ratio since mass transfer between the particulate matter on the filter and the vapor trap cannot be ruled out. The glass fiber filter will collect particles $\geq$ 0.1 microns in diameter, and therefore it is possible that aerosol particles with smaller diameters will pass through the filter and be trapped in the polyurethane foam plug. If this is the case, the percent observed in vapor phase will be overestimated. The method involves ambient air sampling at a relatively high sample volume, around 300-400 m^3 of air, over a 24-hour period. It is possible that a portion of the CDD/Fs that are sorbed to particulate matter captured by the filter may be volatilized by changes in ambient temperature, and carried with the air flow to the PUF sorbent trap (blow-off effect). If this were to occur, the observed vapor-phase fraction of the CDD/Fs would be an over-estimate (or equivalently, the observed particulate fraction would be underestimated). Unfortunately there are no empirical data that have demonstrated that any of these effects may actually occur.

3.2.4.5. *Junge-Pankow Model of Particle/Gas Distribution in Ambient Air*

A relationship first proposed by Junge (1977) and later reviewed and critically evaluated by Pankow (1987) is the most widely used model for estimating the adsorption of semivolatile compounds to aerosols:

$$\phi = \frac{c\ \Theta}{p^\circ_L + c\ \Theta} \tag{3-3}$$

where:

ϕ = fraction of the compound adsorbed to aerosol particles
p°_L = saturation liquid phase vapor pressure of the pure compound at ambient temperature, Pa
Θ = the particle surface area per unit volume of air, cm^2 aerosol/cm^3 air
c = a constant which is related to the difference between the heat of desorption from the particle surface, Q_d, and the heat of vaporization of the compound, Q_v. The value of c is often estimated at 17.2 Pa-cm

Pankow (1987) argued that different values of Q_d - Q_v (and therefore c) may be appropriate for different classes of compounds.

Although Junge (1977) did not specify the physical state of the sorbing compound in Equation (3-3), field and laboratory studies of the particle/gas distribution of PAHs and organochlorine compounds indicate that the process is better described by using the vapor pressure of the subcooled liquid rather than the solid-phase vapor pressure (p^o_S) (Bidleman et al., 1986; Cotham and Bidleman, 1992; Foreman and Bidleman, 1987). The two vapor pressures are related by:

$$\ln \frac{p^\circ_L}{p^\circ_S} = \frac{\Delta\ S_f\ (\ T_m\ -\ T\ )}{RT} \tag{3-4}$$

where:

p°_L = liquid sub-cooled vapor pressure of the pure compund, Pa
p°_S = crystalline solid phase vapor pressure of the pure compound, Pa
ΔS_f = the entropy of fusion, J/mol-K
T_m = the melting point of the compound, K
T = is the ambient temperature, K
R = ideal gas constant, 8.314 J/mol-K.

Values of ΔS_f have been summarized for CDD/Fs (Rordorf, 1989) and other semivolatile compounds (Hinckley et al., 1990). In the absence of an experimental value, an average $\Delta S_f/R = 6.79$ is often used (Hinckley et al., 1990), and it is used in this assessment. Liquid-phase vapor pressures have also been estimated for PCBs, PAHs, CDD/Fs and organochlorine pesticides by capillary gas chromatography (Falconer and Bidleman, 1994; Eitzer and Hites, 1988; Eitzer and Hites, 1989; Hinckley et al., 1990; Yamasaki et al., 1984). The hypothesis that p^o_L controls sorption to aerosols is especially significant for CDD/Fs, as many of these compounds have high melting points and thus large differences between p^o_L and p^o_S.

Estimates of θ are given by Bidleman (1988), based on a study by Whitby (1978) of the size distribution of accumulation mode aerosols. Whitby also estimated the average total volume of particles per unit volume of air (V_T = cm^3 aerosol/cm^3 air). Values of θ and V_T are given in Table 3-5. From V_T and an assumed particle density of 1.4 g/cm^3, the average TSP concentrations in urban and average background air are 98 and 42 µg/m^3. These can be compared to average monitored TSP concentrations of 79 and 30 µg/m^3 in 46 U.S. cities and 20 rural locations in 1975 (Shah et al., 1986). Similar calculations using values of θ yield estimates of the aerosol specific surface area (A_{tsp}) of 11 m^2/g in urban air and 3.6 m^2/g in average background air (Bidleman, 1988). Measurements of A_{tsp} from particles collected on glass fiber filters were 1.9 - 3.1 m^2/g in Pittsburgh, Pennsylvania (Corn et al., 1971) and 2.3 - 8.7 m^2/g in Portland, Oregon (Sheffield and Pankow, 1994). The latter authors noted that particles tended to agglomerate to a greater extent on teflon membrane filters than on glass fiber filters, and that experimentally determined specific surface areas were higher on the glass fiber filters. This suggests that values of A_{tsp} measured on filtered particles may be biased on the low side, although more data are needed in this regard.

The particulate fraction can also be expressed by:

$$\phi = \frac{C_p\ (\ TSP\ )}{C_g + C_p\ (\ TSP\ )} \tag{3-5}$$

where:

ϕ = fraction of the compound adsorbed to aerosol particles

C_p = the concentration of semivolatile compounds associated with aerosols, ng/µg particles

C_g = the gas-phase concentration, ng/m^3

TSP = the total suspended particle concentration, $\mu g/m^3$

Equation (3-5) is a general relationship that applies to any experimental or model estimate of C_g and C_p. Combining Equations (3-3) and (3-5) yields:

$$Log \frac{C_p}{C_g} = Log\ K_p = Log \frac{c\ \theta}{TSP} - Log\ p^\circ_L \tag{3-6}$$

Here and in other work (Falconer et al., 1995; Kamens et al., 1995; Hart and Pankow, 1994; Pankow and Bidleman, 1992) C_p/C_g is referred to as the particle/gas partition coefficient, K_p ($m^3/\mu g$). Its inverse, $C_g/C_p = 1/K_p$, has also been used for these correlations (Cotham and Bidleman, 1992). According to Equation (3-6), the expected slope of log K_p vs. log p^o_L is -1 and the intercept is related to the specific surface area of the aerosol A_{tsp} (m^2/g) = $10^8\theta/TSP$. Plots of log K_p vs. log p^o_L for partitioning data obtained with filtration air samplers are usually well correlated and follow the general relationship:

$$Log\ K_p = m\ Log\ p^\circ_L + b \tag{3-7}$$

It is often the case that $m \neq -1$ because of kinetic limitations and/or sampling artifacts. In these situations the intercept b is partially dependent on the slope and cannot be used to estimate θ (Pankow and Bidleman, 1992).

3.2.4.6. *Modeling the Vapor/Particle (V/P) Distribution of CDD/Fs*

A portion of the semivolatile compounds found in ambient air appears to be freely exchangeable between the particulate and gaseous phases. A second portion, the "non-exchangeable" fraction, may be irreversibly sorbed or occluded by the aerosols and not in equilibrium with the corresponding gas phase (Bidleman, 1988; Pankow, 1988; Pankow and Bidleman, 1991, 1992). In this procedure methodology document, it is assumed that all compounds emitted from combustion sources are freely exchangeable unless information exists otherwise.

The first step in the modeling of the V/P distribution is to determine the sub-cooled liquid vapor pressure for the CDD/Fs. Eitzer and Hites (1988,1989) used a capillary GC method to determine liquid-phase vapor pressures for 63 CDD/F congeners. These measured values will be used to develop the V/P partitioning for the dioxin-like compounds in this assessment. The $p°_L$ given in these references are measurements at 25°C. This section will outline a procedure for calculating the $p°_L$ at different temperatures. The V/P calculations of this assessment assume an ambient temperature of 20 °C, necessitating a conversion of $p°_L$ from 25 to 20°C. Finally, this section will also show the calculation of the $p°_L$ based on the crystalline solid phase vapor pressures, $p°_S$. These calculated $p°_L$ will be compared against the measured $p°_L$.

Table 3-6 lists the crystalline solid vapor pressure, p^o_S, at 25ºC for the seventeen CDD/F congeners having dioxin-like toxicity. These values of p^o_S were judged as the most appropriate from available reportings in the literature in Chapter 2 of Volume I. They were used in conjunction with Equation (3-4) above to calculate $p°_L$ at 25°C, also shown in Table 3-6. Finally, Table 3-6 gives the p^o_L values at 25ºC, which were reported in Eitzer and Hites (1988, 1989).

As seen in Table 3-6, the calculated $p°_L$ were generally less the measured $p°_L$. On the average, the calculated $p°_L$ was 60% of the measured $p°_L$. This assessment will use the measured $p°_L$, which is thought to be preferable to using the modeled values.

These vapor pressures can be corrected to ambient, or any, temperature by the following procedure. The relationship between the liquid sub-cooled vapor pressure and temperature (°K) is (Hinckley, et al., 1990):

$$Log\ p°_L = \frac{-\ Q_v}{2.303\ R\ T} + b \tag{3-8}$$

where:

$p°_L$ = sub-cooled liquid vapor pressure of the pure compund, Pa
Q_v = the latent heat of vaporization, J/mol
R = ideal gas constant, 8.314 J/mol-K
T = temperature, K
b = intercept (related to entropy of vaporization)

The capillary GC method of Eitzer and Hites (1988) provides the temperature coefficient of vapor pressure, expressed by them as the ratio of the heats of vaporization for CDD/Fs to p,p'-DDT: Qv (CDD/Fs)/Qv (DDT). The authors determined these ratios for 14 CDD/F congeners, including 13 of the ones listed in Table 3-6. For the remaining 4 congeners, it was assumed that Qv (CDD/Fs)/Qv (DDT) were the same as for other members of the same homolog group (e.g., the ratio for 2,3,7,8-TCDD was the same as for 1,2,3,4-TCDD). OCDF was assumed to have the same ratio as OCDD. The value of -Qv/2.303R for p,p'-DDT is -4640 (Hinckley, et al., 1990). This was used with the information given by Eitzer and Hites (1988) to estimate the temperature coefficients of vapor pressure for the CDD/Fs. For example, Eitzer and Hites (1988) give the ratio Qv (2,3,7,8-TCDF)/Qv(DDT) = 0.947. Thus the value of -Qv/2.303R for 2,3,7,8-TCDF = -4640(0.947) = -4394. This quantity can be used as the slope of Equation (3-6) for this congener: log $p°_L$ (2,3,7,8-TCDF) = -4394/T = b.

The next step in the procedure is to estimate the constant, b, of Equation (3-8). This can be accomplished given the slope (as just calculated), and a known (or calculated) $p°_L$, and the temperature associated with that $p°_L$. For example, the measured $p°_L$ of 2378-TCDF at 25 °C, is $1.23*10^{-4}$ Pa (Eitzer and Hites, 1988). Substituting -4394, T = 298 °K, and log p^o_L = -3.910 into Equation (3-6) yields a value for b, 10.83. Therefore, one now has an equation for the vapor pressure of 2378-TCDF as a function of temperature: Log p^o_L (2,3,7,8-TCDF) = 10.83 - 4394/T. In this manner, values of b were derived for all the 17 dioxin-like congeners, and these are shown in Table 3-6. It is importantly noted that all these b were developed from the measured values of the $p°_L$, not the modeled values calculated from the crystalline solid vapor pressure, p^o_S. Therefore, extrapolations to 20 °C are defined as extrapolations from the measured and not the modeled $p°_L$.

At this point, it is now possible to calculate the $p°_L$ as a function of temperature for all the congeners. For estimating the vapor particle partitioning of dioxins, it was assumed that the ambient temperature was 20 °C. The final column in Table 3-6 lists the calculated $p°_L$ at 20°C. Comparing the $p°_L$ at 25 and 20°C, reducing the temperature by 5°C causes the $p°_L$ to be reduced by about a factor of 2.

The Junge-Pankow model, Equation (3-3), was used to estimate particulate percentages for airsheds characterized as clean continental background, average background, background plus local sources, and urban. The particle surface area parameters (θ-values) representative of each airshed were those in Table 3-5. Liquid sub-cooled vapor pressures at 20°C, as derived above, were used, and c = 17.2 Pa-cm was assumed. As an example, the particulate fraction of 1,2,3,7,8-PCDF at 20°C in average background air ($\theta = 1.5 \times 10^{-6}$) is calculated as follows:

a) $p^o_L = 1.98*10^{-5}$ (from Table 3-6)
b) $c\theta = 17.2(1.5 \times 10^{-6}) = 2.58 \times 10^{-5}$

c) $\phi = c\theta/(p^o_L + c\theta) = 2.58 \times 10^{-5}/(1.98*10^{-5} + 2.58 \times 10^{-5}) = 0.57$

Table 3-7 shows the percentage of CDD/Fs predicted to be in the particle phase at 20°C for the seventeen congeners having dioxin-like toxicity.

3.2.4.7. *Comparison of Measured and Modeled Vapor/Particle Distributions for CDD/Fs*

Two factors complicate the comparison of field measurements and predictions of the Junge-Pankow model. One is the problem of sampling artifacts that are inherent with filter-sorbent devices. Parallel collections of PAHs made with filtration samplers and denuders suggest that the more volatile members of a chemical class will be partially lost from the particles on the filter during sampling -- the "blow-off" effect (Gundel et al., 1995; Lewis et al., 1991; Subramanyam et al., 1994). A second difficulty is that very few field measurements of <u>both</u> particulate and gaseous CDD/Fs have been made and presented in such a way that they can be related to model predictions.

The study by Eitzer and Hites (1989) is the best data set for particle/gas partitioning, since a large number of CDD/F congeners were measured on both the glass fiber filter and PUF trap. In their paper, the particle/gas ratios of individual congeners were reported as averages for the entire year, and the average ratios were related to the liquid-phase vapor pressures of the congeners at 25°C. Although their study showed conclusively that vapor pressure controls the distribution of CDD/Fs between the aerosol and gas phases, there is a problem with their method of data treatment. The particle/gas ratio varied greatly with temperature and the average ratio for the year may or may not have been represented by the situation at 25°C.

In his thesis, Eitzer (1989) also presented the particle/gas distributions as functions of the sampling temperature through the equation:

$$Log\ K_p = \frac{Q_d}{2.303\ R\ T} + b \tag{3-9}$$

where the heat of desorption, Qd, of individual congeners and the intercept b were estimated by plotting K_p vs. 1/T for all the sampling events. In this form the data allow the particle/gas distributions to be related to event-to-event differences in ambient air temperature.

To relate Eitzer's (1989) data to vapor pressure, his parameters of Equation (3-9) were used to calculate log K_p for individual congeners at 20° C. The K_p values at 20°C were then plotted against the liquid-phase vapor pressures at 20°C according to Equation (3-9) to yield:

$$Log\ K_p \ = \ -\ 0.719\ Log\ p°_L \ -\ 5.53 \qquad r^2 \ = \ 0.962 \tag{3-10}$$

The plot of Equation (3-10) for the 17 dioxin-like CDD/Fs is shown in Figure 3-2a. As seen, there is an excellent correlation between log K_p and log p^o_L. It should be noted that although Equation (3-10) was obtained from values of K_p and p^o_L at 20°C, it applies at <u>any</u> temperature since the variation in partitioning with temperature is accounted for by the temperature effect on vapor pressure. The particulate fraction is related to K_p by:

$$\phi \ = \ \frac{K_p\ [\ TSP\ ]}{1\ +\ K_p\ [\ TSP\ ]} \tag{3-11}$$

which follows from Equation (3-5) and the definition of K_p. Comparison of the Eitzer-Hites partitioning data to predictions of the model was done as follows:

a) Field estimates of the particulate fraction (ϕ) were calculated from values of K_p at 20°C by Equation (3-11), scaling to TSP = 60 $\mu g/m^3$ (corresponding to, "background plus local sources", Table 3-5).
b) Model estimates were calculated from Equation (3-3), using $\theta = 3.5 \times 10^{-6}$ (corresponding to, "background plus local sources", Table 3-5).

Plots of measured and modeled particulate percentages vs. log p^o_L at 20°C are shown in Figure 3-2b. Although the Eitzer-Hites partitioning data show a strong dependence on vapor pressure, their measurements fall below the model predictions.

A similar approach was used to evaluate particle/gas distributions for a subset of the other ambient air investigations reviewed earlier. The partitioning data of Hites (1991), Hunt and Maisel (1990, 1992) and Welsch-Paulsch et al. (1995) are given on a homolog basis in Table 3-4. However, because these studies were done at different ambient temperatures, the particulate percentages cannot be directly compared. Therefore, all field data had to be adjusted to a common temperature of 20°C by establishing relationships between the particle/gas distributions and vapor pressure:

a) Values of K_p were calculated from the particulate percentages in Table 3-4 for CDD/Fs which were found to a measurable extent in both the particle and gas phases (i.e., K_p could not be calculated for the 0% and 100% particulate data points). Since these studies were carried out in semi-rural locations, the "background plus local sources" air regime seemed to be the most appropriate, and a value of TSP = 60 $\mu g/m^3$ was assumed in calculating K_p by Equation (3-11).

b) The resulting log K_p values were examined for outliers (only one point was omitted, from the Hites (1991) data set), then regressed against log p^o_L at the ambient sampling temperature (Equations 3-7 and 3-8). The vapor pressure of each homologue group was taken to be the central value for the congeners in that group. Regression parameters of Equation (3-7) are given in Table 3-8 for the various field studies.

c) Values of K_p for each homologue group at 20°C were calculated from the vapor pressure at 20° C, using the regression parameters in Table 3-8.

d) Particulate percentages at 20°C were calculated from K_p by Equation (3-11), assuming TSP = 60 $\mu g/m^3$.

Thus, although the actual field measurements were done under a variety of temperatures, they were normalized to 20°C for comparison. Figure 3-3 shows the particulate percentages from four field studies in comparison to those predicted by the Junge-Pankow model for Whitby's "background plus local sources" air regime. These comparisons are also given in Table 3-9. All of the field data fall substantially below the model curve. For example, the particle-bound percentages of tetrachlorodioxins and furans, which are predicted to be 43-65% at 20°, averaged only 11-18% with the filter-sorbent sampler.

3.2.4.8. *Discussion of Monitored and Modeled Results for CDD/Fs*

The above comparisons show substantial differences between filtration sampling and the Junge-Pankow model for estimating particulate percentages of CDD/Fs. Reasons for these discrepancies may be related to both sampling artifacts and model uncertainties. Blow-off losses during collection are likely to reduce the filter-retained fraction. This artifact is expected to be the most serious for long sampling times, especially if the day-to-night temperature changes are large. However, the Welsch-Paulsch samples, which were collected over two-week integration times, show only slightly lower particulate values than those of other workers which were obtained over 24-36 h sampling periods. Aside from the Eitzer-Hites data, the measurements of CDD/F vapor/particle distribution in Table 3-4 were based on only a few samples and it is difficult to judge their representativeness. Daily measurements of phase distributions for PAHs and PCBs in Chicago show up to an order of magnitude variation in K_p values, even when normalized for vapor pressure (Cotham and Bidleman, 1995). These variations may be caused by sampling artifacts and kinetic effects, and also by daily differences in aerosol properties.

Limitations of the Junge-Pankow model include uncertainties in the parameters c and θ. Pankow (1987) suggested that optimal values of c might be chosen for different classes of compounds. His reasoning was that the excess heat of desorption (Q_d-Q_v) appeared to be a smaller term for organochlorine compounds than for PAHs. However, this conclusion was based on the very limited field data available at the time Pankow's article was written. It is difficult to extract Q_d information from field data, by plots of Equation (3-7), because such plots involve combining particle/gas distributions for individual air samples which are collected over a range of ambient temperatures, humidities and aerosol properties. Confidence intervals around the Q_d values obtained from such plots are typically large (Pankow, 1991). Moreover, significant differences in Q_d values are obtained by analyzing Equation (3-7) plots by simple linear regression versus regression assuming a constant y-intercept for all compounds (Pankow, 1991). A better approach is to determine Q_d in the laboratory by measuring K_p under equilibrium conditions and at different temperatures, but few of these experiments have been carried out (Cotham and Bidleman, 1992; Falconer and Bidleman, 1994; Storey and Pankow, 1992). The authors of this assessment believe that there is insufficient information at this time to warrant recommending different values of the c-parameter for different compound classes.

The θ-parameter is also subject to uncertainty. It is likely that Whitby's values of θ do not reflect the true surface area distribution, since they were based on the average size spectrum of aerosols and assumed spherical particles. Other limitations of the model are the inability to consider the kinetics of adsorption/desorption (Kamens et al., 1995; Rounds, et al., 1993) and humidity effects (Pankow et al., 1993).

In conclusion, neither the filter-sorbent sampler nor the Junge-Pankow model necessarily give the "correct" vapor/particle distributions. Evidence based on limited field data suggest that the model overestimates the particulate fraction of CDD/Fs relative to the filtration sampler, but it can just as well be stated that the sampler underestimates the particulate fraction relative to the model. Further work needed to improve the state of knowledge of CDD/F partitioning between the aerosol and gas phases includes:

a) Comparative monitoring with filter-sorbent samplers and other speciating devices such as denuders (Coutant et al., 1992; Eatough et al., 1993; Krieger and Hites, 1994; Lane et al., 1988; Lewis et al., 1991; Gundel et al., 1995; Subramanyam et al., 1994; Tang et al., 1994) and diffusion separators (Hornbuckle et al.,1995; Turpin et al., 1993).

b) Laboratory experiments to investigate the kinetics and thermodynamics of the sorption of CDD/Fs and other semivolatile compounds sorption aerosols.

c) Improvements in modeling particle/gas distributions in ambient air.

Despite the differences in the monitored and modeled results, the Junge-Pankow model is the recommended approach for estimating the particle/gas distribution of CDD/Fs at the present time. In addition to reproducing the general trend in partitioning with vapor pressure (Figures 3-2 and 3-3), the Junge-Pankow equation was used in an air-to-beef model validation which is described in Chapter 7. That exercise used the Junge-Pankow model for partitioning dioxins in the air. A key finding of that work was that the transfer of vapor-phase dioxins to plants and subsequently to animals dominated the terrestrial food chain. Also, vapor/particle partition data on other semi-volatile organic compounds are compared in Chapter 7 to model predictions, and the match for these compounds is, in most cases (especially for PAHs), superior to that of the CDD/Fs.

3.2.4.9. *Discussion of Vapor/Particle Partitioning*

This subsection has reviewed stack testing data, ambient air sampling data, and theory rooted in basic physical chemistry that either imply, directly deduce or theoretically calculate the V/P partitioning in the ambient air. From this review it is generally concluded that:

1. Although the sampling methods in use today to characterize stack emissions from combustion sources accurately determine stack gas concentrations of CDD/Fs, these methods do not provide a credible basis for assuming the vapor phase and particle bound partitioning at the point of release. There is no consistent pattern to the interpretation of V/P based on where the CDD/F segregates in the instrument, e.g., the glass fiber filter or the XAD resin. Factors that mostly contributing to this are: (a) The relatively long residence time spent *in situ* during the sampling of stack gases; (b) The fact that the particulate filter housing is kept at a constant temperature, and, (c) The fact that a condensing section (consisting of glass tubing surrounded

by an ice or chilled water bath) is usually located between the particulate trap and the vapor trap to force condensation of vapor-phase organic constituents in the gases.

2. On the other hand, the ambient air sampling methods do give an approximate indication of the V/P ratio that seems to be responsive to changes in temperature, and degree of chlorination of the CDD/Fs. This is in accordance with what would be expected from their individual vapor pressures. There is no artificial heating or cooling of any component of the sampler. The sampler is exposed to actual temperature, pressure, and humidity of the ambient air. This removes the possibility that the vapor phase-particle bound partitioning, operationally defined as the compound segregating to the particulate trap and vapor trap, is actually an artifact induced by artificial heating and cooling within the system. Therefore the methods present a realistic picture of partitioning under variable ambient conditions. However, the method has certain limitations that currently prevent deriving a true measurement of V/P partitioning in the ambient air. Among these limitations are:

a. The glass fiber filter designed to capture and retain particulate matter has filter pours down to 0.1 µm diameter. Particles less than this diameter will pass through the filter and be retained in the polyurethane foam vapor trap downstream. If this is the case, the amount of CDD/Fs observed to be particle bound would be underestimated, and the amount observed to be in vapor phase would be overestimated.

b. The relatively high sampling volume passed through the system (200 to 400 m^3 of air per 24 hours) may redistribute the more volatile congeners from the filter to the absorbent trap by a process known as 'blow-off'.

3. Until sampling methods are improved and modified such that they give results that indicate the true V/P ratio of CDD/Fs in ambient air, the theoretical construct described by Bidleman (1988; and detailed above) is used to calculate the V/P ratio for purposes of air dispersion and deposition modeling of emissions from the hypothetical case demonstrated in Chapter 5. Key advantages to the theoretical approach are that the theoretical construct relies on current adsorption theory, considers the molecular weight and the degree of halogenation of the congeners, uses the boiling points and vapor pressures of the congeners, and uses the availability of surface area for adsorption of atmospheric particles that correspond to a variety of ambient air shed classifications having variable particulate matter densities.

3.2.5. Estimation of the Concentration of Dioxin-Like Compounds in Incineration Ash

The ash that is collected by the particulate matter control device preceding the stack is known conventionally as fly ash. Fly ash is the airborne combustion residue from burning the fuel. Bottom ash is the ash residue that results from the combustion of the organic solids within the combustion chamber, and usually is collected below a grate system used to convey combustible fuels into the fire zone, or is collected at the bottom of the combustion chamber. In general, there are many factors that may influence the formation of particulate matter known as fly ash from the incineration of organic wastes. Among these factors are: the heating value of the incinerated material (BTU/kg), the percent moisture in the fuel, the furnace temperature and combustion efficiency, and the efficiency of particulate matter capture by the air pollution control device (Brunner, 1984; OTA, 1989). Fly ash, and not the bottom ash, contains most, if not all, the dioxin-like congeners. This can be explained by the synthesis of dioxin that occurs on the reactive surface of fly ash. Therefore, the following estimation of the ash generation rate, and the concentration of dioxin-like compounds in the ash particles, will focus solely on fly ash to the exclusion of bottom ash. Because bottom ash is mostly free of these contaminants, and is about 10 to 100 times the mass of fly ash, the mixing of fly ash with bottom ash will dilute the concentration of dioxin by about a factor of 10 - 100.

Estimation of the mass of fly ash generated, and concentration of dioxin-like compounds can be determined by the following (if no actual data exists):

1. Determine the mass of fly ash generated per day at the facility. This can be estimated from the percent control of particulate matter (PM) of the air pollution control device (APCD) installed at the facility. For example, if a combustor emits 0.5 kg of particulate matter per hour of operation, then 12 kg of PM is released from the stack in one day. If PM is controlled by 99%, then this rate of emission represents one percent of the fly ash generated by the combustion process. The amount of fly ash that is collected by the APCD would be 100 times the amount emitted, or 1200 kg/day.

2. Estimate the congener-specific concentration of CDD/Fs contained in the collected fly ash. This is done by assuming that what is prevented from exiting the stack is contained in the fly ash collected by the pollution control device. If, for example, 10 picograms CDD/F is emitted per gram of PM from the facility per day, and the APCD reduces emissions by 99%, then 100 times more CDD/F concentration, or 1000 picograms CDD/F per gram fly ash, would be in the collected fly ash. If the concentration of dioxin in emitted fly ash and the percent control of dioxin are known, then the concentration of dioxin in the mass of collected fly ash can be estimated. It is important to make such estimations in order to evaluate the potential environmental impact of ash management practices before the operation of the facility, and to select appropriate disposal practices to preclude future adverse conditions from arising.

3. Now estimate total mass, including fly and bottom ash, and final concentrations. If bottom ash mass is estimated at ten times fly ash, than the total ash generated in this example would be 1200 + 1200*10 = 13,200 kg/day. If fly and bottom ash were mixed for disposal, which is common, than the average concentration of the total ash would be one-tenth that estimated for fly ash.

The hypothetical example in Chapter 5 does not assess impacts associated with ash disposal. Section 4.3.5 of Chapter 4 describes procedures for estimating impacts from ash disposal given ash concentrations and mass generated.

3.3. AIR DISPERSION/DEPOSITION MODELING OF THE STACK GAS EMISSIONS OF DIOXIN-LIKE COMPOUNDS

It has been customary for EPA to use air dispersion/deposition models to estimate the atmospheric transport, the deposition flux, and the ambient air concentrations of specific pollutants attributable to smokestack emissions from an industrial combustion source. Air dispersion models are mathematical constructs that approximate the physical and chemical processes occurring in the atmosphere that directly influence the dispersion of gaseous and particulate emissions from smokestacks of stationary combustion sources. These models are computer programs encompassing a series of partial differential and algebraic equations to calculate the dispersion and deposition of the emissions. Concentration and deposition isopleths of the pollutants discharged from the stack are computed at specified distances from the smokestack. These quantities are used to estimate the magnitude of potential exposures to the human receptor.

Numerous dispersion/deposition models have been developed. This document focuses on the Industrial Source Complex 3 Short Term, ISCST3, dispersion model recently developed by EPA to provide modeling outputs useful in the analysis of wet/dry deposition and ambient air concentrations of stack emitted contaminants in all terrain settings (EPA, 1995). The ISC3 was developed as a general replacement to the COMPDEP model first described in EPA (1990b). Modeling enhancements of ISCST3 include more refined small particle dry and wet deposition algorithms than used by the COMPDEP model. The ISCST3 was used to generate the results for the hypothetical incinerator of this assessment. However, the use of ISCST3 is this assessment is not intended to imply that ISCST3 is the only acceptable model to use in the analysis of ambient air concentrations, and wet and dry deposition of dioxin-like compounds.

Subsection 3.3.1 below presents an overview of the dispersion and deposition algorithms in the ISCST3 model. Subsection 3.3.2 discusses dry deposition fluxes, including pertinent assumptions made in the application of the ISCST3 model for the hypothetical combustor demonstrated in Chapter 5. Subsection 3.3.3 discusses particle size distributions for emitted particles. Subsection 3.3.4 discusses wet deposition, again noting key assumptions for the hypothetical combustor. Subsection 3.3.5. closes the section with guidance indicating that the ISCST3 model should be run with two simultaneous modes of operation: one mode provides estimates of particulate concentrations in air and wet/dry particle deposition flux; the other mode provides for the estimation of vapor phase concentrations of dioxin-like compounds in ambient air.

3.3.1. Basic Physical Principles Used to Estimate Atmospheric Dispersion/Deposition of Stack Emissions

Air dispersion/deposition models mathematically simulate the basic physical processes in the atmosphere to estimate the ground-level air concentrations and deposition flux of contaminants known to be released from the stacks/vents of stationary combustion sources. These processes include advection, turbulent diffusion, and removal of atmospheric particles. Advection describes the physical movement of the air contaminants by the horizontal movement of wind. Turbulent diffusion is the "spreading" of the emissions plume with distance from the stack due to multi-directional fluctuations in air movement. Removal refers to mechanisms which remove emissions from the atmosphere. This can be caused by the force of gravity exerted on the particle mass, Brownian movement of aerosol particles, and scavenging of particles. Scavenging is the removal of particles or vapors by precipitation.

ISCST3 contains modifications of the Industrial Source Complex model (Short-Term version; ISCLT, as described in EPA, 1986b), and COMPLEX I to incorporate algorithms to estimate dispersion, and resulting ambient air concentrations and wet and dry deposition flux. COMPLEX I is a second level screening model applicable to stationary combustion sources located in complex and rolling topography (EPA, 1986a). The ISCST model was developed by EPA to provide estimates of air concentrations and deposition rates of the stack emissions of contaminants from industrial sources located in varied terrain (e.g., from simple to complex terrain). Simple and complex terrain are defined as topography that is either below or above the effective stack height of the source (Turner, 1986). To account for pollutant deposition, the concentration algorithms in COMPLEX 1 were replaced with those from the Multiple Point Source Algorithm with Terrain Adjustments Including Deposition and Sedimentation (MPTER-DS) model (Rao and Sutterfield, 1982). The MPTER-DS algorithms incorporate the gradient transfer theory described by Rao and Sutterfield (1982), and are extensions of the traditional

Gaussian plume algorithms. The dispersion algorithms contained in the ISCST were incorporated to analyze ground-level receptors located below the height of the emission plume (EPA, 1986b). For a steady-state Gaussian plume, the hourly concentrations at downwind distance x (meters) and crosswind distance y (meters) are given by:

$$\chi = \frac{QKVD}{2\pi\mu_s\sigma_y\sigma_z}\exp\left[-0.5\left(\frac{y}{\sigma_y}\right)^2\right] \tag{3-12}$$

where:

χ = the ambient air concentration of the contaminent, µg/m^3
Q = contaminant emissions rate, g/s
K = units conversion factor
V = vertical term - accounts for the vertical distribution of the Gaussian plume, dimensionless
D = plume depletion term relating removal by physical or chemical processes, dimensionless
σ_y, σ_z = standard deviation of lateral and vertical concentration distribution, m
μ_s = mean wind speed at release height, m/s
y = crosswind distance from source to receptor, m

ISCST3 uses the generalized Briggs (1975, 1979) equation to estimate plume-rise and downwind dispersion as a function of wind speed and atmospheric stability. A wind-profile exponent law is used to adjust the observed mean wind speed from the measurement height to the emission height for the plume rise and pollutant concentration calculations. The Pasquill-Gifford curves are used to calculate lateral and vertical plume spread (EPA, 1986a). These curves are based on Pasquill's definitions of atmospheric stability classes, e.g., extremely unstable, moderately unstable, slightly unstable, neutral, slightly stable, and moderately stable, that correspond to various intensities of solar radiation and wind speeds (Seinfeld, 1986). The incorporation of these two basic models into ISCST3 permits analysis of a source located in all types of terrain.

3.3.2. Estimation of Dry Surface Deposition Flux

The dry deposition of particle-bound contaminants is a physical atmospheric removal process that is simulated by the ISCST3 model. Dry deposition refers to the transfer of airborne particulate matter to the Earth's surface (including water, soil, and vegetation) whereby it is removed from the atmosphere. Although the dry gaseous deposition of vapor-phase contaminants is currently considered in the ISCST3 model, this feature has not been calibrated for the estimation of the deposition flux of dioxin-like compounds into vegetation. Until the algorithm has been verified to make reasonably accurate estimates of gaseous deposition of dioxin-like compounds, this guidance will not incorporate examples of it’s site-specific application. The focus of the following discussion is directed to the operation of the ISCST3 model to estimate the dry deposition of dioxin-contaminated particles.

The general processes controlling the transfer of particulate from some height above the surface through the surface layer down to the immediate vicinity of the surface are the forces of gravity and turbulent diffusion, followed by diffusion through the laminar sub-layer (defined as a thickness of 10^{-1} to 10^{-2} cm) to the surface (Seinfeld, 1986). The term “deposition flux” is mass concentration of a contaminant sorbed to atmospheric particulates that is delivered to the surface per unit of time by the physical forces of gravity, atmospheric turbulence, and diffusion (Kapahi, 1991). Deposition flux is represented mathematically by F_d. The dry deposition flux, F_d, is defined as the product of the ambient air concentration of the chemical contaminant, C_o, times a deposition velocity(m s^{-1}) of the contaminated particles as in Equation (3-13).

$$F_d = V_d C_o \tag{3-13}$$

where:

F_d = dry deposition flux of contaminants sorbed to particles, µg/m^2-sec
V_d = the particulate depostion velocity, m/sec
C_o = concentration of pollutant on settling particles, µg/m^3

In general, Chamberlain and Chadwick (1953) first defined the depositon velocity, V_d, as the quotient of the deposition flux, F_d, divided by the airborne concentration, C_o:

$$V_d = - \frac{F_d}{C_o} \qquad (3\text{-}14)$$

The value for F_d in Equation (3-14) has a minus sign because the downward flux is negative, whereas the deposition velocity is positive (Sehmel,1980). By this relationship, Chamberlain and Chadwick (1953) first introduced the concept of plume depletion, i.e., as the emission plume is dispersed with downwind distance from the stack, the deposition flux decreases with distance from the source.

The basic dynamics of the physics of modeling dry deposition have not changed significantly since Sehmel's (1980) comprehensive scientific review. The factors that most influence the predicted deposition flux can be divided as being either meteorological influences, or the influences of the properties of the pollutant under analysis. Meteorological influences include the friction velocity, represented as $\mu_ø$, and the aerodynamic surface roughness, represented as z_o. These terms are used to describe the wind speed profile above the Earth's surface. In most cases, the analyst uses a graphical procedure to determine values for $\mu_ø$ and z_o. If the logarithm of wind speed is plotted for near neutral atmospheric stability as a function of height from the surface, then the values for the constant z_o is fitted to a straight line on a semi-logarithmic scale. This can be described mathematically by Equation (3-15). In most cases, the friction velocity is a percentage of the wind speed.

$$\mu = \left(\frac{\mu*}{\lambda}\right) \ln \left(\frac{z + z_o}{z_o}\right) \qquad (3\text{-}15)$$

where:

μ = the measured wind speed, cm/sec

μ_* = the friction velocity, cm/sec

z = the measured height above the surface, cm

z_o = surface roughness length, cm

λ = von Karman's constant, approx. = 0.4

As a general rule, particles greater than 30 micrometers (µm) in diameter will be removed from the atmosphere primarily by the force of gravity, whereas particles less than 30 µm will be removed primarily by atmospheric turbulence. The deposition flux for the smaller particles is influenced by many factors, including: the distribution of particles by diameter and density; the atmospheric turbulence; the friction of the ground surface and the height of the stack release of emissions. Deposition flux is also affected by the partitioning properties of the pollutant. These properties will determine how much of the pollutant is sorbed to the particle and how much is in the vapor phase. A detailed list of the many factors that can affect dry deposition is shown in Table 3-10.

The ISCST3 estimates dry deposition flux based on empirical associations developed by Sehmel (1980) and Sehmel and Hodgson (1978) relating the deposition flux to the deposition velocity of particles. The downward motion represented by deposition velocity is controlled by the gravitational settling velocity, atmospheric resistance, surface resistance and the atmospheric surface friction layer. This model assumes that a fraction of the particulate comes into contact with the ground surface by the combined processes of gravitational settling, atmospheric turbulence, and Brownian diffusion. The ISCST3 model contains enhancements to calculate dry deposition flux using a dry deposition model developed by Pleim et al. (1984). The Pleim et al. (1984) algorithms represent Sehmel's (1980) empirical relationships for transfer resistances as a function of particle size, density, surface roughness, and friction velocity. In the Pleim et al. (1984) model, integrated resistances to mass transfer are computed within two layers. In the first layer, which extends from one centimeter to one meter above the surface, atmospheric turbulence dominates mass transfer. This is a fully turbulent region where vertical fluxes are nearly constant, and is referred to as the aerodynamic resistance. In the second layer, which lies within one centimeter of the surface, the resistance to mass transfer is derived from particle deposition measurements that were taken in a wind tunnel over various surfaces using mono-dispersed particles (Sehmel,1980; Sehmel and Hodgson,1978). The general approach used by ISCST3 in the resistance methods for estimating the dry deposition velocity of particles is given by:

$$v_d = \frac{1}{r_a + r_d + I_a I_d I_s} + V_g \qquad (3\text{-}16)$$

where:

V_d = the depositon velocity, cm/s

V_g = the gravitaional settling velocity, cm/s
r_a = the aerodynamic resistance, s/cm
r_d = the deposition layer resistance, s/cm

Despite what is currently known about the physical and chemical processes that influence the final deposition flux of particles released from a stationary combustion source, a more thorough understanding of the influence of particle size on deposition velocity is needed. In Sehmel's (1980) review of settling velocities corresponding to particle diameter it was noted that the range of values spanned several orders of magnitude. This complicates efforts to make generalizations of V_d by particle diameter for air modeling purposes. Although dry particle deposition velocities have been estimated from both field studies and laboratory experiments, derived velocities are limited and highly uncertain. This is due largely to the complex and variable array of factors that can influence the rate of deposition (which are summarized in Table 3-10).

In the general classification of particles, particles < 2.5 micrometers (µm) in diameter are referred to a "fine particles", and those > 2.5 µm are "coarse particles". Sehmel (1980) offers the most current review of dry deposition settling velocities for a variety of depositing materials having a broad range of particle diameters. This summary appears in Table 3-11.

For the example application of the ISCST3 model in Chapter 5, particles less than 2 µm were represented by a 1 µm size and were calculated by ISCST3 to deposit at a velocity of $<10^{-2}$ cm/sec. Particles between 2 and 10 µm were represented by a 6.78 µm size and were calculated to deposit at a velocity of < 0.5 cm/sec. Finally, particles greater than 10 µm were represented by a 20 µm size and were calculated to deposit at a velocity of >2.0 < 5.0 cm/sec, although the variable ambient conditions resulted in more variable calculations. The derivation of these particle size representations is given in the next section.

3.3.3. Estimation of the Particle Size Distribution in the Stack Emissions

A distribution of particle size and diameter of the particulate stack emissions must be known before the ISCST3 program can predict deposition flux of the dioxin-like congeners. The diameters of small particles comprising particulate matter in stack emissions are usually measured in units of one millionth of a meter (micrometer, commonly called micron, abbreviated by the letters µm). Unfortunately, few studies have been conducted that describe the distribution of particulate matter entrained in the emissions from various combustion technologies broken down and fractionated by particle diameter. The characterization of particulate matter by particle diameter will differ from one combustion process to another, and is greatly dependent on such factors as: 1) the efficiency of various air pollution control devices to the remove particles over a broad range of diameters from the gas stream , 2) the composition of the feed/fuel, 3) the design of the combustion chamber, 4) the amount of air used to sustain combustion, and 5) the temperature of combustion. Table 3-12 gives an example of a particle diameter distribution as measured at a stack of an incinerator, and was adopted from USEPA (1980). This example distribution will be assumed for the hypothetical incinerator.

Although the ISCST3 model can simulate up to 10 particle size categories, only three particle sizes are assumed for the model runs of the demonstration in this assessment. These three sizes are generalized from the data in Table 3-12:

• **Category 1:** ≤ 2 µm • **Category 2:** > 2 to ≤ 10 µm • **Category 3:** > 10 µm

After selecting the particle size distribution, it is necessary to calculate the mass emission rate of the particulate-bound congeners of CDD/Fs by particle size category. This is accomplished by calculating the proportion of surface area (available for adsorption of CDD/Fs) for a given particle diameter. The ratio of the surface area to volume is proportional to the ratio of the surface area to weight for a particle with a given radius. Multiplying this proportion times the weight fraction of particles of a specific diameter (µm) gives a value that approximates the amount of surface area available for chemical adsorption. The surface area to volume ratio can be described as follows:

(a) Assume aerodynamic spherical particles.

(b) Specific surface area of a spherical particle with radius,r:

$$S = 4\ \pi r^2$$

(c) Volume of spherical particle with radius, r:

$$V = 4/3\ \pi r^3$$

(d) The ratio of surface area to volume is:

$$S/V = 4\ \pi r^2 / (4/3\ \pi r^3)$$

$$S/V = 3/r$$

Dividing the surface area for each particle category by the total available surface area for all particles gives an estimation of the fraction of total area on any size particle. Multiplication of the emission rate of the dioxin-like congener times the fraction of available surface area will estimate the emission rate of the pollutant per particle size. The fraction of total surface area was computed for the three particle size categories. The fraction of total surface areas for the ranges of particle diameters are summed with each particle size category to represent a single fraction of total surface area for the given particle size category, as follows:

- Particulate category 1: fraction of total surface area = 0.875
- Particulate category 2: fraction of total surface area = 0.095
- Particulate category 3: fraction of total surface area = 0.030

Thus by these assumptions, 87.5% of the emission rate of the dioxin-like congener is calculated to be associated with particles less than ≤ 2 µm in diameter, 9.5% of the emission is associated with the particle size of > 2 to ≤ 10 µm, and only 3% of the emission is associated with particles greater than 10 µm. To assist in deposition modeling of the emissions from the hypothetical incinerator, the particle size distribution is further simplified by assuming a median particle diameter to represent each broad particle size category, as follows:

- Particulate category 1 = 1 µm particle diameter
- Particulate category 2 = 6.78 µm particle diameter
- Particulate category 3 = 20 µm particle diameter

3.3.4. Estimation of Wet Deposition Flux

Wet deposition occurs by precipitation (rain, hail, snow) physically washing out the chemically contaminated particulate and vapors from the atmosphere. Vapor scavenging is not yet well understood and is not addressed in the ISCST3 model. The remainder of this discussion refers only to the wet deposition of particles.

Wet deposition flux depends primarily on the fraction of the time precipitation occurs and the fraction of material removed by precipitation per unit of time by particle size. Based on these relationships, scavenging coefficients were developed by Jindal and Heinold (1991) for varying types and intensities of precipitation relative to different particle diameters by incorporating the observations of Radke, et al. (1980) in a study of scavenging of aerosol particles by precipitation. The principal assumptions made in computing wet deposition flux are: (1) The intensity of precipitation is constant over the entire path between the source and the receptor; (2) The precipitation originates at a level above the top of the emission plume so that the precipitation passes vertically through the entire plume; (3) The flux is computed on the bases of fraction of the hour precipitation occurs as determined by hourly precipitation measurements compiled by the National Weather Service. The remaining fraction is subject only to dry deposition processes. Thus no dry deposition occurs during hours of steady precipitation, and dry deposition occurs between the periods of precipitation.

Wet deposition flux is estimated by ISCST3 using a scavenging ratio approach. In this approach, the flux of contaminant to the surface (F_w) is the product of the savenging ratio times the contaminant concentration, as in the following equation.

$$F_w = \Lambda \chi \tag{3-17}$$

where:

F_w = wet deposition flux, g/m^2-sec

Λ = scavenging ratio, sec^{-1}

χ = contaminant air concentration value calculated from the Gaussian plume equation, g/m^3

The scavenging ratio (Λ) is calculated as the product of the scavenging coefficient and precipitation rate (Scire et al., 1990), as follows:

$$\Lambda = \lambda R \tag{3-18}$$

where:

Λ = scavenging ratio, sec^{-1}

λ = scavenging coefficient, (sec-mm/hr)$^{-1}$

R = precipitation rate, mm/hr

The scavenging coefficient depends on the size distribution for particles and the nature or form of precipitation, i.e., liquid or frozen.

Across the plume, the total flux to the surface must be approximately equal to the mass lost from the plume. ISCST3 contains a plume wet deposition depletion equation as follows:

$$Q(x) = Q_o e^{-\Lambda x/u} = Q_o e^{-\Lambda t} \tag{3-19}$$

where:

Q(x) = wet plume depletion factor, dimensionless

Λ = precipitation scavenging ratio, sec^{-1}

t = x/u = the plume travel time, sec

The relationship between the scavenging coefficient, Λ, and the particle size and precipitation intensity was derived from the review of wet deposition studies of aerosol particles by Jindal and Heinold (1991). Table 3-13 displays the scavenging coefficients assigned to the generalized particle size categories and forms of precipitation (liquid rainfall, frozen) used for computing estimates of wet deposition in the application of the ISCST3 for the demonstration scenarios in Chapter 5.

3.3.5. Using ISCST3 to Model Emissions of Particles and Vapors

The ISCST3 model had to be run in two modes in order to provide estimates of ambient air concentrations of vapor-phase and particle-bound dioxins, combined with estimates of wet/dry particle deposition flux. The short-term ISCST3 model can accommodate these estimates in a single run. The user may select any or all of the output types, e.g, air concentration, wet deposition, dry deposition and combined wet and dry deposition, to be generated in a single model run. Instructions for this appear in the User's Guide for the Industrial Source Complex Models (ISC3) (EPA, 1995). To facilitate the modeling exercise, the modeler should assume a "unit emissions release rate" of CDD/Fs from the stack, e.g., 1 g CDD/F congener per second (1 g/s). Results from these unit runs can easily be transformed to final outputs given assumptions on CDD/F emissions in vapor and particle forms. Two assumptions are required. One assumption is the total emission rate of the compound, in units of mass/time (g/s), and the second is the vapor/particle partitioning of this total emission. The two modes are:

- **Mode 1: To estimate vapor-phase concentration of the contaminant in ambient air.**

The first mode assumes that the emissions of dioxin-like compounds are gaseous, e.g., with the wet/dry deposition switches turned to the "off" position. This is to isolate the ambient air concentration of the contaminant in vapor-phase from the calculation of wet and dry particle deposition flux. This inactivates a plume depletion equation that subtracts out losses in ambient air concentration due to particle deposition. What remains is the Gaussian dispersion algorithm to calculate air concentrations.

With the "unitized" emission rate, one can reconstruct the actual predicted ambient air concentration (µg/m^3) of vapors by multiplying the "actual" vapor-phase emission rate (g/s) by the "unitized" modeling result. For example, let the actual stack gas emission rate of total (vapor plus particle components) contaminant be 1x10^{-5} g/s, and the V/P ratio (expected under ambient conditions) be 60%V/40%P. Then the "actual" emission rate of the vapor-phase portion of the contaminant is calculated to be 6x10^{-6} g/s (1x10^{-5} g/s * 0.6). If the "unitized" ambient air concentration at the ground-level receptor is estimated by the ISCST3 model to be 1x10^{-8} µg/m^3 (i.e., this concentration is predicted with a unit emission rate of 1 g/s), then the "actual" predicted air concentration at that receptor can be estimated as:

$$(6\text{x}10^{-6}\ \text{g/s} \div 1\ \text{g/s}) * 1\text{x}10^{-8}\ \mu\text{g/m}^3 = 6\text{x}10^{-14}\mu\text{g/m}^3$$

- **Mode 2: To estimate wet and dry particle deposition flux, and the ambient air concentration of the contaminant that is particle-bound**.

ISCST3 should be run with the wet/dry particle deposition switches turned to the "on" position, and using a "unit emission rate" of 1 g/s. This second run is considered a simulation of particle-bound contaminant only. Outputs of this run include unitized deposition rate and unitized ambient air concentrations of particles.

Like the vapor-phase run, the "actual" deposition flux (g/m^{-2} -yr) and "actual" particle-phase airborne concentrations can then be determined by multiplying the "actual" emission rate (g/s) of the particle-bound portion of the total contaminant emissions by the "unitized" modeling result at the ground receptor. For example, let the "actual" emission rate of the particle-bound portion of the contaminant be 4x10^{-6} g/s, and the "unitized" dry deposition flux at the ground receptor be 1x10^{-5} g/m^2-yr. Then the "actual" predicted dry deposition flux is 4x10^{-11} g/m^2 (4x10^{-6} g/s ÷ 1 g/s * 1x10^{-5} g/m^2-yr). Using this same procedure, this second run provides the airborne concentration of contaminants bound to particles (µg/m^3).

There are two meteorological preprossesors used by ISCST3 model program to access local conditions necessary to compute model concentrations in both modes of operation: PCRAMMET (Catalano et al., 1987) and MPRM (Irwin and Paumier, 1990). These files contain hourly data for the wind speed, wind direction, stability class, mixing height, ambient air temperature, precipitation, and surface friction velocity.

Inhalation exposures are estimated as the sum of vapor and particle phase concentrations. Air-to-plant transfers require the vapor phase concentrations for vapor transfers and the particle-phase depositions. The air-to-soil algorithm requires particle phase depositions.

3.4. RESULTS OF THE AIR DISPERSION MODELING OF CONGENER-SPECIFIC EMISSIONS FROM THE HYPOTHETICAL ORGANIC WASTE INCINERATOR

The preceding subsections have presented general procedures for conducting air modeling of the emissions of dioxin-like compounds from the stack to the ground, starting with estimation of emission factors, vapor/particle partitioning at the stack, and proceeding to atmospheric dispersion and deposition using EPA's ISCST3 model. Where appropriate, previous subsections have also included discussion on the assumptions and the selection of parameters for the hypothetical incinerator which is demonstrated in Chapter 5. For example, Section 3.2.3 provided the emission factors that were used in this demonstration. This section will provide all other details of the hypothetical incinerator and provide the final results of the ISCST3 model simulations.

To reiterate, the purpose of the hypothetical construct is to help readers understand how to apply these principles to the air dispersion modeling and analysis of dioxin emissions from the source. Therefore, generalizations should not be made on the basis of this example regarding the magnitude of the emissions release and associated environmental impact.

A completely hypothetical incinerator was devised to serve as the example. Accordingly, a hypothetical, but realistic, incineration technology, facility size, stack height, and geographical location was selected. The hypothetical incineration facility has an assumed total daily capacity of 200 metric tons of organic waste materials. The emission rates of specific congeners of PCDD/Fs were derived from the stack testing and monitoring of emissions from a modern incinerator of this size. These emissions are expressed in units of g/sec, and are shown for the hypothetical incinerator in Table 3-14.

In constructing the hypothetical case, the following was defined: stack height; stack diameter; exit velocity of the gaseous emissions from the stack; and temperature of the exhaust gases characteristic of incineration facilities of this size. In order to access historical meteorological data for air modeling purposes, the hypothetical facility was located in a specific geographical area having specific meteorological conditions. To simplify the ambient air modeling and deposition, the hypothetical organic waste incinerator was assumed to exist in a simple terrain setting (e.g., flat terrain). By definition, simple terrain refers to an area where the terrain features are all lower in elevation than the top of the stack of the stationary source under analysis.

The dispersion and deposition computations performed by the ISCST3 model require data on wind speed, wind direction, wind profile above the surface, and hourly precipitation data.

When performing a regulatory analysis, e.g., to set air quality permit conditions, EPA's *Guideline on Air Quality Models* (EPA, 1986a) recommends the use of five consecutive years of representative meteorological data. However, in this example analysis of only one year of meteorological data was used as compiled at the Denver-Stapleton International Airport by the National Weather Service (NWS), because this was not intended as a regulatory analysis. Hourly measurements of wind speed, wind direction, temperature, and precipitation were used as a basis of computing annual average ground-level concentrations of dioxin in ambient air, and as a basis for the estimation of the dry and wet deposition flux. The Pasquill-Gifford (P-G) stability categories, were used as defined in the Modeling Guidelines. The specifications of stability categories depending on wind speed, cloud cover and mixing heights were established by Pasquill (1961), and later modified by Turner (1964). Reference is made here to Tables 9-3 and 9-4 on pages 9-21,22 of the Modeling Guidelines which gives a method for estimating P-G Stability Categories for daytime and nighttime conditions based on surface roughness and the wind speed profiles distributed in the United States.

To summarize, inputs for the ISCST3 model included hourly meteorological data, source characteristics and receptor features. Hourly meteorological data requirements are the mean wind speed, the direction from which the wind is blowing, the wind-profile exponent, the ambient air temperature, the Pasquill stability category, the vertical potential temperature gradient with height, the mixing layer height, and the frequency distribution of hourly precipitation. Source input data requirements included the congener-specific mass emission rate partitioned by vapor and particulate; the physical stack measurements, e.g., diameter, base elevation of the stack, and exit velocity and temperature of the stack gas, and settling parameters for particulate matter for both dry and wet deposition. Table 3-14 is a review of the congener-specific emissions data, and Table 3-15 is a review of the modeling parameters used in the air quality modeling of the hypothetical incinerator.

The output of the ISCST3 model for both surface deposition and ambient air impacts is a concentration array for 160 ground-level receptors around the incinerator, e.g., 10 receptor points along each of the 16 wind directions every 22.5° on the polar azimuth. Vapor and particle phase concentrations are in units of grams per cubic meter of air (g/m^3), and particle-bound depositions are in units of grams per square meter of surface area per year (g/m^2-yr). Results for both ambient air and surface deposition were estimated at concentric radial distances from the incinerator of 0.2, 0.5, 0.8, 0.9, 1.0, 2.0, 5.0, 10, 20, 30, 40, and 50 kilometers. The maximum annual average ground-level vapor and particle-phase air concentrations of all modeled congeners is estimated to occur 900 meters from the center of the stack. Tables 3-16 and 3-17 display the annual average vapor-phase and particle-phase air concentrations of dioxin-like congeners at various distances in the direction of the maximum impact. Tables 3-18 and 3-19 display the dry and wet deposition fluxes of dioxin-like compounds at various distances in the direction of maximum impact. The maximum annual average dry deposition flux occurs 800 meters from the center of the stack, although there is no significant difference from the 900 m distance where the maximum annual average ambient air concentration occurs. The maximum annual average wet deposition occurs 200 meters from the center of the stack, which is what is expected from the algorithm (refer to subsection 3.3.4. Estimation of Wet Deposition Flux).

3.5. REVIEW OF PROCEDURES FOR ESTIMATING SITE-SPECIFIC IMPACTS FROM A STACK EMISSION SOURCE

This chapter has detailed a procedure for evaluating site-specific impacts from stack emission sources. For purposes of demonstration, a hypothetical incinerator was defined, and using the ISCST3 model, estimates of vapor-phase concentrations and particle phase depositions at points around the stack were made. Three major points for estimating impacts of dioxin-like compounds using the ISCST3 or other models are as follows:

1. Characterize the emissions on a congener-specific basis: Although much of the information available on stack emission sources in on a TEQ or a homologue group basis, and not a congener-specific basis, the approach in this assessment, and the recommendation made here, is to conduct site-specific assessments using specific congener emissions. This is because fate and transport parameters, and bioconcentration/biotransfer parameters, are different for the various congeners. Assuming one set of such parameters for TEQ emissions can lead to a different estimated exposure media TEQ concentration than assuming congener-specific parameters and then, given estimated congener-specific concentrations, calculating TEQ exposure media concentrations with the TEF scheme. Emission factors were used in this assessment to describe source and site-specific emissions. These are defined as the mass of contaminant emitted per mass of feed material combusted. Procedures to convert other emission data, such as mass per time emitted or concentration emitted, are presented.

2. Estimate the vapor/particle partitioning for atmospheric transport and deposition modeling: Vapors are dispersed assuming Gaussian plume dispersion algorithms, and particles are transported and deposited via wet and dry deposition. The principal output of the atmospheric transport model, ISCST3, used for further exposure analysis are the vapor and particle phase concentrations, and the wet and dry deposition totals at sites of exposure. There is some thought that the partitioning between the vapor and particle phases at the stack differs from the partitioning in ambient air. Such a difference might be due to the difference in temperature at the stack versus temperature of ambient air. If so, then deposition and dispersion trends in the close vicinity of the stack may differ from such trends further from the stack. Currently the data to support such a hypothesis is lacking; the earlier review of stack vapor/particle partitioning was inconclusive. Also, modeling approaches for such differences are unavailable. Instead, the approach in this chapter is to assume one partitioning scheme (separate V/P partitioning for individual congeners) for atmospheric transport and dispersion modeling. The scheme adopted in this assessment is based on a theoretical approach described by Bidleman (1988).

3. Conduct atmospheric dispersion and deposition modeling: The ISCST3 model is used in this assessment to estimate vapor and particle-phase concentrations, and wet and dry deposition totals for points around the stack emission source. Key inputs are vapor phase and particulate phase emission rates (rather than emission factor units, atmospheric transport models require emission rates in units of mass/time, or g/sec), stack descriptors (stack height, exit temperature, etc.), atmospheric transport parameters (particle size distributions, dry deposition velocity), meteorological data (hourly rainfall, windspeeds, etc.), and terrain descriptions. Procedures to translate the final model outputs of concentrations and deposition fluxes into exposure media concentrations is given in Chapter 4, Section 4.4.

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Table 3-1. The number of dioxin-like and total congeners within dioxin, furan, and coplanar PCB homologue groups.

Homologue Group	n: Number of Dioxin-Like Congeners	N: Number of Total Congeners	1/N
I. Dioxins			
Tetra-CDD	1	22	0.022
Penta-CDD	1	14	0.071
Hexa-CDD	3	10	0.100
Hepta-CDD	1	2	0.500
Octa-CDD	1	1	1.000
II. Furans			
Tetra-CDF	1	38	0.026
Penta-CDF	2	28	0.036
Hexa-CDF	4	16	0.063
Hepta-CDF	2	4	0.250
Octa-CDF	1	1	1.000
III. Mono-ortho coplanar PCBs			
Tetrachloro-PCBs	1	42	0.024
Pentachloro-PCBs	5	46	0.022
Hexachloro-PCBs	4	42	0.024
Heptachloro-PCBs	3	24	0.042

Table 3-2. Emission factors and average emissions used for the hypothetical incinerator.

Congener	Emission Factors, ng/kg			Emissions, g/sec
	Test 1	Test 2	Test 3	
2378-TCDD	0.052	0.031	0.037	$9.3*10^{-11}$
Other TCDD	0.826	0.870	0.913	$2.0*10^{-9}$
12378-PCDD	0.148	0.056	0.048	$1.9*10^{-10}$
Other PCDD	1.390	0.322	0.783	$1.9*10^{-9}$
123478-PCDD	0.104	0.165	0.056	$2.5*10^{-10}$
123678-PCDD	0.157	0.187	0.130	$3.6*10^{-10}$
123789-PCDD	0.148	0.165	0.117	$3.3*10^{-9}$
Other HxCDD	2.440	0.670	1.040	$3.2*10^{-9}$
1234678-HpCDD	2.350	0.957	0.957	$3.3*10^{-9}$
Other HpCDD	4.040	1.650	2.170	$6.0*10^{-9}$
OCDD	4.260	1.390	30130	$6.7*10^{-9}$
2378-TCDF	3.300	2.390	2.170	$6.0*10^{-9}$
Other TCDF	20.00	15.70	14.30	$3.8*10^{-8}$
12378-PCDF	0.435	0.165	0.226	$6.3*10^{-10}$
23478-PCDF	0.243	0.139	0.122	$3.9*10^{-10}$
Other PCDF	6.280	4.480	3.480	$1.1*10^{-8}$
123478-HxCDF	0.478	0.365	0.357	$9.2*10^{-10}$
123678-HxCDF	0.478	0.343	0.313	$8.7*10^{-10}$
123789-HxCDF	0.357	0.165	0.226	$5.7*10^{-10}$
234678-HxCDF	0.243	0.117	0.074	$3.3*10^{-10}$
Other HxCDF	1.490	0.313	0.943	$2.1*10^{-9}$
1234678-HpCDF	0.243	0.565	0.696	$1.2*10^{-9}$
1234789-HpCDF	0.391	0.096	0.165	$5.0*10^{-10}$
Other HpCDF	241.0	2.380	2.180	$5.4*10^{-9}$
OCDF	1.579	0.478	0.971	$2.2*10^{-9}$

Table 3-3. Percent distribution of dioxins and furans between vapor-phase (V) and particulate-phase (P) as interpreted by various stack sampling methods (4-D = tetraCDD; 4-F = tetraCDF).

Citation	V/P	4-D	5-D	6-D	7-D	8-D	4-F	5-F	6-F	7-F	8-F
Cavellaro et al., 1982	V	95	91	94	99	89	NR	NR	NR	NR	96
	P	5	9	6	1	11	NR	NR	NR	NR	4
Cavallaro et al, 1982	V	9	38	69	57	14	59	NR	NR	NR	60
	P	91	62	31	43	86	41	NR	NR	NR	40
Cavallaro et al., 1982	V	99	99	99	99	99	99	NR	NR	NR	99
	P	1	1	1	1	1	1	NR	NR	NR	1
Cavellaro et al., 1982	V	85	92	99	98	99	99	NR	NR	NR	99
	P	15	8	1	2	1	1	NR	NR	NR	1
Cavellaro et al., 1982	V	97	90	63	82	59	80	NR	NR	NR	97
	P	3	10	37	18	42	20	NR	NR	NR	3
Cavellaro et al., 1982	V	100	99	99	100	99	100	NR	NR	NR	100
	P	0	1	1	0	1	0	NR	NR	NR	0
Benfenati et al., 1986	V	94	NR	NR	NR	NR	NR	NR	NR	NR	NR
	P	6	NR	NR	NR	NR	NR	NR	NR	NR	NR
Tiernan et al, 1984	V	75	68	67	55	64	75	70	64	69	86
	P	25	32	33	45	36	25	30	36	31	14
Tiernan et al, 1984	V	95	90	88	85	98	86	98	89	88	98
	P	5	10	12	15	2	14	2	11	12	2
Tiernan et al, 1984	V	91	91	89	77	56	92	89	91	72	65
	P	9	9	11	23	44	8	11	9	28	35
Tiernan et al, 1984	V	17	22	45	84	85	7	10	22	63	77
	P	83	78	55	16	15	93	90	78	37	23
Clement et. al., 1985	V	98	92	96	93	73	97	96	98	98	94
	P	2	8	4	7	27	3	4	2	2	6
Clement et. al., 1985	V	84	55	54	72	20	95	73	70	52	68
	P	16	45	46	28	80	5	27	30	48	32

Table 3-3. Cont'd.

Citation	V/P	4-D	5-D	6-D	7-D	8-D	4-F	5-F	6-F	7-F	8-F
Clement et. al., 1985	V	100	99	98	93	95	100	100	99	99	98
	P	0	1	2	7	5	0	0	1	1	2
Hagenmaier et al., 1986	V	62	42	25	20	20	68	55	40	25	0
	P	38	58	75	80	80	32	45	60	75	100
Battelle 1988	V	90	NR	NR	NR	NR	NR	NR	NR	NR	NR
	P	10	NR	NR	NR	NR	NR	NR	NR	NR	NR
US EPA, 1990a	V	56	42	30	26	18	62	56	45	37	21
	P	44	58	70	74	82	38	44	55	63	79
Radian 1986	V	16	16	16	20	16	16	14	17	16	17
	P	84	84	84	80	84	84	84	83	84	83
AVERAGE	**V**	**76**	**70**	**71**	**73**	**63**	**76**	**66**	**64**	**62**	**73**
	P	**24**	**30**	**29**	**27**	**37**	**24**	**34**	**36**	**38**	**27**

Table 3-4. Review of air monitoring data on the percentage of measured dioxins and furans which are in the particle phase (4-D = tetraCDD; 4-F = tetraCDF).

Reference	4-D	5-D	6-D	7-D	8-D	4-F	5-F	6-F	7-F	8-F
1, T=20°C	23	37	66	87	96	14	31	64	87	91
2, T=3°C	40	87	100	100	100	100	60	88	100	98
2, T=18°C	8	28	45	88	100	ND	28	30	93	100
2, t=28°C	5	13	45	60	100	ND	0	38	78	98
3	21	20	24	70	85	23	26	29	59	94
3	3	5	12	64	90	7	12	15	43	91
4, T=18°C	NR	NR	92	100	78	14	42	73	100	100
4, T=18°C	NR	NR	100	100	100	5	43	100	100	NR
5	ND	0	65	82	100	20	71	100	100	100
5	ND	ND	100	100	100	ND	ND	ND	ND	ND
6, T=18°C	10	28	45	77	93	9	22	48	77	89
AVERAGE	16	27	63	84	95	24	32	59	84	96

Notes: - For references, 1 = Eitzer & Hites (1989) and Eitzer (1989). Average distribution at 20°C based on plots of log Kp vs 1/T from their data; see Section 3.2.4.7. and Figure 3-2a).; 2 = Hites, 1991; 3 = Harless & Lewis, 1992; 4 = Hunt, et al 1990; 5 = Bobet, et al 1990; 6 = Welsch-Pausch, et al, 1995;
- For dioxin columns, 4D = tetra dioxin congener group; 5F = penta furan congener group, etc.
- NR = not reported; ND = not detected; NR and NDs not included in average estimation
- Welsch-Pausch, et al (1995) does not include V/P data, but it was sent by authors
- Harless and Lewis (1992) do not calculate V/P, rather V/P calculated here is based on isotopically labeled CDD/F spiked onto the filter and recovered from the filter and PUF trap.

Table 3-5. Values of θ, V_T, and TSP in different air regimes.

Airshed type	θ cm^2 aresol/cm^3 air	V_T cm^3 aerosol/cm^3 air	TSP µg/m^3
Clean continental background	$4.2*10^{-7}$	$6.5*10^{-12}$	9
Average background	$1.5*10^{-6}$	$3.0*10^{-11}$	42
Background plus local sources	$3.5*10^{-6}$	$4.3*10^{-11}$	60
Urban	$1.1*10^{-5}$	$7.0*10^{-11}$	98

Sources: Bidleman (1988), Whitby (1978)

Table 3-6. Data for calculation of the liquid subcooled vapor pressure, p°_{L}, at 20 °C, and final p°_{L} for the dioxin-like congeners.

Congener	EPA p°_{S} (25°C)	EPA p°_{L} (25°C)	E-H p°_{L} (25°C)	Slope	Int.	E-H p°_{L} (20°C)
2378-TCDD	$2.00*10^{-7}$	$1.18*10^{-4}$	$1.14*10^{-4}$	-4417*	10.88	$6.34*10^{-5}$
12378-PCDD	$5.87*10^{-8}$	$7.87*10^{-6}$	$1.74*10^{-5}$	-4779	11.28	$9.30*10^{-6}$
123478-HxCDD	$5.07*10^{-9}$	$1.47*10^{-6}$	$3.96*10^{-6}$	-5058	11.57	$2.03*10^{-6}$
123678-HxCDD	$4.80*10^{-9}$	$1.80*10^{-6}$	$3.96*10^{-6}$	-5058	11.57	$2.03*10^{-6}$
123789-HxCDD	$6.53*10^{-9}$	$9.37*10^{-7}$	$3.96*10^{-6}$	-5058*	11.57	$2.03*10^{-6}$
1234678-HpCDD	$7.47*10^{-10}$	$1.73*10^{-7}$	$1.02*10^{-6}$	-5280*	11.73	$5.10*10^{-7}$
OCDD	$7.10*10^{-10}$	$1.02*10^{-7}$	$2.77*10^{-7}$	-5526	11.99	$1.34*10^{-7}$
2378-TCDF	$2.00*10^{-6}$	$2.00*10^{-4}$	$1.23*10^{-4}$	-4394	10.83	$6.81*10^{-5}$
12378-PCDF	$2.27*10^{-7}$	$2.16*10^{-5}$	$3.64*10^{-5}$	-4608	11.02	$1.98*10^{-5}$
23478-PCDF	$3.47*10^{-7}$	$1.71*10^{-5}$	$2.17*10^{-5}$	-4728	11.20	$1.17*10^{-5}$
123478-HxCDF	$3.20*10^{-8}$	$3.12*10^{-6}$	$8.09*10^{-6}$	-4877	11.27	$4.25*10^{-6}$
123678-HxCDF	$2.93*10^{-8}$	$3.35*10^{-6}$	$8.09*10^{-6}$	-4877	11.27	$4.25*10^{-6}$
123789-HxCDF	$3.73*10^{-8}$	$6.01*10^{-6}$	$4.99*10^{-6}$	-4983	11.42	$2.58*10^{-6}$
234678-HxCDF	$2.67*10^{-8}$	$3.50*10^{-6}$	$4.99*10^{-6}$	-4983	11.42	$2.58*10^{-6}$
1234678-HpCDF	$4.67*10^{-9}$	$5.71*10^{-7}$	$2.24*10^{-6}$	-5099	11.46	$1.14*10^{-6}$
1234789-HpCDF	$1.43*10^{-8}$	$1.27*10^{-6}$	$1.31*10^{-6}$	-5192	11.54	$6.58*10^{-7}$
OCDF	$5.00*10^{-10}$	$1.01*10^{-7}$	$2.60*10^{-7}$	-5526*	11.96	$1.24*10^{-7}$

Column 1: p°_{S}: crystalline solid phase vapor pressure at 25°C, Pa. Assigned based on analysis of available literature; see Volume II, Chapter 2
Column 2: p°_{L}: sub-cooled liquid vapor pressure at 25°C, Pa, calculated from p°_{S} in Column 1 and the use of Equation (3-2)
Column 3: p°_{L}: liquid sub-cooled vapor pressure at 25°C, as measured by Eitzer and Hites (1988, 1989)
Column 4: slope: the slope of Equation (3-6), equal to Q_v/2.303R
Column 5: b: intercept b of Equation (3-6)
Column 6: p°_{L}: liquid sub-cooled vapor pressure calculated at 20°C using the slope and intercept in Columns 4 and 5, and Equation (3-6)

* numbers without asterisks were based on ratios of Qv (CDD/Fs)/Qv (DDT) measured by Eitzer and Hitest (1989). Numbers with asterisks were assumed to be the same as for other members of the homologue group. OCDF was assumed to have the same ratio as OCDD.

Table 3-7. Particle fractions, ϕ, in four airsheds at 20°C for the dioxin-like congeners.

Congener	Clean Continental	Average Background	Background Plus Local Sources	Urban
2378-TCDD	0.10	0.29	0.49	0.75
12378-PCDD	0.44	0.74	0.87	0.95
123478-HxCDD	0.78	0.93	0.97	0.99
123678-HxCDD	0.78	0.93	0.97	0.99
123789-HxCDD	0.78	0.93	0.97	0.99
1234678-HpCDD	0.93	0.98	0.99	0.997
OCDD	0.98	0.995	0.998	0.999
2378-TCDF	0.09	0.27	0.47	0.73
12378-PCDF	0.27	0.57	0.75	0.91
23478-PCDF	0.38	0.69	0.84	0.94
123478-HxCDF	0.63	0.86	0.93	0.98
123678-HxCDF	0.63	0.86	0.93	0.98
123789-HxCDF	0.74	0.91	0.96	0.99
234678-HxCDF	0.74	0.91	0.96	0.99
1234678-HpCDF	0.86	0.96	0.98	0.99
1234789-HpCDF	0.92	0.98	0.99	0.997
OCDF	0.98	0.995	0.998	0.999

Table 3-8. Regression parameters slope m and intercept b for Equation (3-5), Log K_p = m Log $p°_L$ + b, based on field measurements of particle/gas distributions for CDD/Fs.

Reference	Slope, m	Intercept, b	r^2
Eitzer and Hites (1989), congeners	-0.775	-5.72	0.96
Hites (1991), homologues	-0.988	-6.87	0.87
Hunt and Maisel (1992), homologues	-0.620	-5.00	0.61
Weslch-Pausch, et al. (1995), homologues	-0.707	-5.73	0.99

Table 3-9. Comparison of monitored and modeled particulate percentage for CDD/F homologues at 20°C.

Homologue	Monitored (see below for study identification)				Modeled*
	1	2	3	4	
TCDD	23	10	19	10	49
PCDD	37	30	36	22	87
HxCDD	66	67	59	45	97
HpCDD	87	91	80	72	99
OCDD	96	98	91	90	99.8
TCDF	14	8	16	8	47
PCDF	31	24	31	18	79
HxCDF	63	64	57	43	93
HpCDF	87	90	79	71	99
OCDF	97	98	92	90	99.8

Study identification: 1 = Eitzer (1989); Eitzer and Hites (1989); 2 = Hites (1991);
3 = Hunt, et al. (1988); Hunt and Maisel (1992); 4 = Welsch-Pausch, et al. (1995)
* by Equation (3-1), $\theta = 3.5*10^{-6}$ cm^2 aerosol/cm^3 air, c = 17.2 Pa-cm

Table 3-10. Factors that influence the dry deposition removal rate in the atmosphere.

Micrometeorological Variables	Characteristics of Particles	Characteristics of Gases	Surface Variables
Aerodynamic roughness	Agglomeration	Chemical activity	Accommodation
Mass transfer of particles gases Heat transfer Momentum transfer Atmospheric stability Diffusion Friction velocity	Diameter Diffusion Effects Brownian Eddy Particle Momentum Heat Electrostatic effects	Diffusion effects Brownian Eddy Partial pressure in equilibrium with the surface Solubility	Edudates Trichomes Pubescence Wax Biotic surface Canopy growth Dormant Expanding
Inversion layer Pollutant concentration Relative humidity Seasonal variation Solar radiation Surface heating Temperature Terrain effects Turbulence Wind velocity Zero plane Displacement Effect Mass transfer of particles	Attraction Repulsion Gravity settling Hygroscopicity Impaction Interception Momentum Physical properties Resuspension Solubility Thermophoresis		Senescent Canopy structure Areal density Bark Bole Leaves Porosity Soils Stem Type Electrostatic properties Water Pollutant
Gases Heat transfer Momentum transfer			Penetration of canopy

Table 3-11. A summary of dry deposition velocities for particles.

Depositing Material	Particld Diameter (µm)	Deposition Surface	Deposition Velocity (cm/s)
Particles	0.03-30	grassland	10^{-3} - 40
Pollen	20 32-35 90-100	grassland grassland grassland	4.5 9.9 20
Natural aerosol Pb auto exhaust	1-10	grass shard	0.8

Source: Sehmel (1980).

Table 3-12. Generalized particle size distribution (µm), and proportion of available surface area, in particulate emissions from incineration.

Particle Diameter (µm)[a]	Particle Radius (µm)	Surface Area/ Volume	Fraction of Total Weight	Proportion Available Surface Area	Fraction of Total Surface Area
>15.0	7.50	0.400	0.128	0.0512	0.0149
12.5	6.25	0.480	0.105	0.0504	0.0146
8.1	4.05	0.741	0.104	0.0771	0.0224
5.5	2.75	1.091	0.073	0.0796	0.0231
3.6	1.80	1.667	0.103	0.1717	0.0499
2.0	1.00	3.000	0.105	0.3150	0.0915
1.1	0.55	5.455	0.082	0.4473	0.1290
0.7	0.40	7.500	0.076	0.5700	0.1656
<0.7	0.40	7.500	0.224	1.6800	0.4880

Total surface area: 3.4423 μm^2

Notes: a. Geometric mean diameter in a distribution. Distribution from EPA (1980).

Table 3-13. Unit wet deposition scavenging coefficients per particle diameter category (micrometers) used in the example ISCST3 analysis, expressed as 1/(sec-mm/hr).

Form of Precipitation	Particle Diameter Category (µm)		
	1	6.78	20
Liquid (rain)	0.43×10^{-4}	0.46×10^{-3}	0.66×10^{-3}
Frozen (snow)	0.14×10^{-4}	0.16×10^{-3}	0.22×10^{-3}

Table 3-14. Emission of CDD/Fs (g/sec) from the hypothetical incinerator.

Congener	Emission rate, g/sec	Vapor emissions, g/sec	Particulate emissions, g/sec	V/P ratio
2378-TCDD	$9.23 * 10^{-11}$	$4.71 * 10^{-11}$	$4.52 * 10^{-11}$	0.51/0.49
Other TCDD	$2.00 * 10^{-9}$	$1.02 * 10^{-9}$	$9.00 * 10^{-10}$	0.51/0.49
12378-PCDD	$1.93 * 10^{-10}$	$2.51 * 10^{-11}$	$1.68 * 10^{-10}$	0.13/0.87
Other PCDD	$1.91 * 10^{-9}$	$2.49 * 10^{-10}$	$1.66 * 10^{-9}$	0.13/0.87
123478-HxCDD	$2.50 * 10^{-10}$	$7.50 * 10^{-12}$	$2.43 * 10^{-10}$	0.03/0.97
123789-HxCDD	$3.63 * 10^{-10}$	$1.09 * 10^{-11}$	$3.52 * 10^{-10}$	0.03/0.97
123678-HxCDD	$3.30 * 10^{-10}$	$9.90 * 10^{-12}$	$3.20 * 10^{-10}$	0.03/0.97
Other HxCDDs	$3.19 * 10^{-9}$	$9.56 * 10^{-11}$	$3.09 * 10^{-9}$	0.03/0.97
1234678-HpCDD	$3.27 * 10^{-9}$	$3.27 * 10^{-11}$	$3.23 * 10^{-9}$	0.01/0.99
Other HpCDDs	$6.03 * 10^{-9}$	$6.03 * 10^{-11}$	$5.97 * 10^{-9}$	0.01/0.99
OCDD	$6.73 * 10^{-9}$	$1.35 * 10^{-11}$	$6.72 * 10^{-9}$	0.002/0.998
2378-TCDF	$6.03 * 10^{-9}$	$3.20 * 10^{-9}$	$2.84 * 10^{-9}$	0.53/0.47
Other TCDFs	$3.83 * 10^{-8}$	$2.03 * 10^{-8}$	$1.80 * 10^{-8}$	0.53/0.47
23478-PCDF	$6.33 * 10^{-10}$	$1.01 * 10^{-10}$	$5.32 * 10^{-10}$	0.16/0.84
12378-PCDF	$3.87 * 10^{-10}$	$9.67 * 10^{-11}$	$2.90 * 10^{-10}$	0.25/0.75
Other PCDFs	$1.09 * 10^{-8}$	$2.73 * 10^{-9}$	$8.19 * 10^{-9}$	0.25/0.75
123478-HxCDF	$9.20 * 10^{-10}$	$6.44 * 10^{-11}$	$8.56 * 10^{-10}$	0.07/0.93
123678-HxCDF	$8.70 * 10^{-10}$	$6.09 * 10^{-11}$	$8.09 * 10^{-10}$	0.07/0.93
123789-HxCDF	$5.73 * 10^{-10}$	$2.29 * 10^{-11}$	$5.50 * 10^{-10}$	0.04/0.96
234678-HxCDF	$3.33 * 10^{-10}$	$1.33 * 10^{-11}$	$3.20 * 10^{-10}$	0.04/0.96
Other HxCDFs	$2.10 * 10^{-9}$	$8.41 * 10^{-11}$	$2.02 * 10^{-9}$	0.04/0.96
1234678-HpCDF	$1.15 * 10^{-9}$	$2.31 * 10^{-11}$	$1.13 * 10^{-9}$	0.02/0.98
1234789-HpCDF	$5.00 * 10^{-10}$	$5.00 * 10^{-12}$	$4.95 * 10^{-10}$	0.01/0.99
Other HpCDFs	$5.35 * 10^{-9}$	$5.35 * 10^{-11}$	$5.29 * 10^{-9}$	0.01/0.99
OCDF	$2.23 * 10^{-9}$	$4.47 * 10^{-12}$	$2.23 * 10^{-9}$	0.002/0.998

Table 3-15. Modeling parameters used in the ISCST3 modeling of CDD/F emissions from the hypothetical incinerator.

Description	Value
General	Modeled after actual organic waste incinerator
Rate of organic waste combustion	200 metric tons per day
Air pollution control system	dry scrubber combined with a baghouse (fabric filters) resulting in 99% reduction of CDDs/CDFs
Model Options: Terrain adjustments	Yes
Stack downwash	No
Gradual Plume Rise	Yes
Buoyancy induced dispersion	Yes
Gravitational settling/deposition	Yes
Wet deposition	Yes
Calm winds processing option	Yes
Building wake effects	No
Stack height	30.48 m
Stack diameter	1.52 m
Anemometer height	10 m
Terrain	simple
Stack temperatre	400 °K
Stack exit velocity	8.9 m/sec
Source elevation	0 m
Z minutes	10 m
Exponents for power law wind increase with height:	0.07, 0.07, 0.10, 0.15, 0.35, 0.55
Particle size categories for dry/wet deposition analysis	
Category 1	$\leq$ 2 μm represented by 1.0 μm diameter
Category 2	>2 - $\leq$ 10 μm represented by 6.78 μm
Category 3	>10 μm represented by 20.0 μm
Particle density	1.4 g/cm^3
Fraction of CDD/F particle bound emission by particle size category:	
Category 1	0.88
Category 2	0.09
Category 3	0.03
Dry deposition velocities predicted by the CARB algorithm:	
1.0 μm	$7.11 * 10^{-3}$ cm/sec
6.78 μm	$2.87 * 10^{-1}$ cm/sec
20.0 μm	2.47 cm/sec
Wet deposition scavenging coefficients	Table 3-13
National Weather Service data	Denver-Stapleton Airport: 1989
Grid System	Polar

Table 3-16. Predicted average vapor-phase concentrations of CDD/Fs (pg/m^3; columns are downwind distance in km).

Congener	0.2	0.5	0.8	0.9	1	2	5	10	20	30	40	50
2378-TCDD	$4.34*10^{-7}$	$7.02*10^{-6}$	$9.14*10^{-6}$	$9.19*10^{-6}$	$9.10*10^{-6}$	$6.06*10^{-6}$	$2.94*10^{-6}$	$1.10*10^{-6}$	$4.57*10^{-7}$	$2.73*10^{-7}$	$1.91*10^{-7}$	$1.45*10^{-7}$
Other TCDD	$9.40*10^{-6}$	$1.52*10^{-4}$	$1.98*10^{-4}$	$1.99*10^{-4}$	$1.97*10^{-4}$	$1.31*10^{-4}$	$5.40*10^{-5}$	$2.37*10^{-5}$	$9.90*10^{-6}$	$5.92*10^{-6}$	$4.13*10^{-6}$	$3.14*10^{-6}$
12378-PCDD	$2.32*10^{-7}$	$3.75*10^{-6}$	$4.88*10^{-6}$	$4.91*10^{-6}$	$4.86*10^{-6}$	$3.23*10^{-6}$	$1.33*10^{-6}$	$5.85*10^{-7}$	$2.44*10^{-7}$	$1.46*10^{-7}$	$1.02*10^{-7}$	$7.74*10^{-8}$
Other PCDD	$2.29*10^{-6}$	$3.71*10^{-5}$	$4.83*10^{-5}$	$4.86*10^{-5}$	$4.81*10^{-5}$	$3.20*10^{-5}$	$1.32*10^{-5}$	$5.79*10^{-6}$	$2.42*10^{-6}$	$1.44*10^{-6}$	$1.01*10^{-6}$	$7.66*10^{-7}$
123478-HxCDD	$6.92*10^{-8}$	$1.12*10^{-6}$	$1.46*10^{-6}$	$1.46*10^{-6}$	$1.45*10^{-6}$	$9.65*10^{-7}$	$3.97*10^{-7}$	$1.74*10^{-7}$	$7.28*10^{-8}$	$4.35*10^{-8}$	$3.04*10^{-8}$	$2.31*10^{-8}$
123789-HxCDD	$1.00*10^{-7}$	$1.63*10^{-6}$	$2.11*10^{-6}$	$2.13*10^{-6}$	$2.11*10^{-6}$	$1.40*10^{-6}$	$5.77*10^{-7}$	$2.54*10^{-7}$	$1.06*10^{-7}$	$6.32*10^{-8}$	$4.41*10^{-8}$	$3.36*10^{-8}$
123678-HxCDD	$9.13*10^{-8}$	$1.48*10^{-6}$	$1.92*10^{-6}$	$1.93*10^{-6}$	$1.91*10^{-6}$	$1.27*10^{-6}$	$5.24*10^{-7}$	$2.30*10^{-7}$	$9.61*10^{-8}$	$5.74*10^{-8}$	$4.01*10^{-8}$	$3.05*10^{-8}$
Other HxCDD	$8.81*10^{-7}$	$1.43*10^{-5}$	$1.85*10^{-5}$	$1.87*10^{-5}$	$1.85*10^{-5}$	$1.23*10^{-5}$	$5.06*10^{-6}$	$2.22*10^{-6}$	$9.28*10^{-7}$	$5.54*10^{-7}$	$3.87*10^{-7}$	$2.94*10^{-7}$
1234678-HpCDD	$3.01*10^{-7}$	$4.87*10^{-6}$	$6.34*10^{-6}$	$6.38*10^{-6}$	$6.31*10^{-6}$	$4.20*10^{-6}$	$1.73*10^{-6}$	$7.60*10^{-7}$	$3.17*10^{-7}$	$1.89*10^{-7}$	$1.32*10^{-7}$	$1.01*10^{-7}$
Other HpCDD	$5.56*10^{-7}$	$9.00*10^{-6}$	$1.17*10^{-5}$	$1.18*10^{-5}$	$1.17*10^{-5}$	$7.76*10^{-6}$	$3.19*10^{-6}$	$1.40*10^{-6}$	$5.86*10^{-7}$	$3.50*10^{-7}$	$2.44*10^{-7}$	$1.86*10^{-7}$
OCDD	$1.24*10^{-7}$	$2.01*10^{-6}$	$2.61*10^{-6}$	$2.63*10^{-6}$	$2.60*10^{-6}$	$1.73*10^{-6}$	$7.13*10^{-7}$	$3.13*10^{-7}$	$1.31*10^{-7}$	$7.81*10^{-8}$	$5.45*10^{-8}$	$4.15*10^{-8}$
2378-TCDF	$2.95*10^{-5}$	$4.77*10^{-4}$	$6.20*10^{-4}$	$6.24*10^{-4}$	$6.18*10^{-4}$	$4.11*10^{-4}$	$1.69*10^{-4}$	$7.44*10^{-5}$	$3.10*10^{-5}$	$1.85*10^{-5}$	$1.30*10^{-5}$	$9.85*10^{-6}$
Other TCDF	$1.87*10^{-4}$	$3.03*10^{-3}$	$3.94*10^{-3}$	$3.97*10^{-3}$	$3.93*10^{-3}$	$2.61*10^{-3}$	$1.08*10^{-3}$	$4.73*10^{-4}$	$1.97*10^{-4}$	$1.18*10^{-4}$	$8.23*10^{-5}$	$6.26*10^{-5}$
23478-PCDF	$9.34*10^{-7}$	$1.51*10^{-5}$	$1.97*10^{-5}$	$1.98*10^{-5}$	$1.96*10^{-5}$	$1.30*10^{-5}$	$5.36*10^{-6}$	$2.36*10^{-6}$	$9.84*10^{-7}$	$5.88*10^{-7}$	$4.10*10^{-7}$	$3.12*10^{-7}$
12378-PCDF	$8.91*10^{-7}$	$1.44*10^{-5}$	$1.88*10^{-5}$	$1.89*10^{-5}$	$1.87*10^{-5}$	$1.24*10^{-5}$	$5.12*10^{-6}$	$2.25*10^{-6}$	$9.39*10^{-7}$	$5.61*10^{-7}$	$3.92*10^{-7}$	$2.98*10^{-7}$
Other PCDF	$2.52*10^{-5}$	$4.07*10^{-4}$	$5.29*10^{-4}$	$5.33*10^{-4}$	$5.27*10^{-4}$	$3.51*10^{-4}$	$1.44*10^{-4}$	$6.35*10^{-5}$	$2.65*10^{-5}$	$1.58*10^{-5}$	$1.10*10^{-5}$	$8.40*10^{-6}$
123478-HxCDF	$5.94*10^{-7}$	$9.60*10^{-6}$	$1.25*10^{-5}$	$1.26*10^{-5}$	$1.24*10^{-5}$	$8.29*10^{-6}$	$3.41*10^{-6}$	$1.50*10^{-6}$	$6.25*10^{-7}$	$3.74*10^{-7}$	$2.61*10^{-7}$	$1.98*10^{-7}$
123678-HxCDF	$5.61*10^{-7}$	$9.08*10^{-6}$	$1.18*10^{-5}$	$1.19*10^{-5}$	$1.18*10^{-5}$	$7.84*10^{-6}$	$3.22*10^{-6}$	$1.42*10^{-6}$	$5.91*10^{-7}$	$3.53*10^{-7}$	$2.47*10^{-7}$	$1.88*10^{-7}$
123789-HxCDF	$2.11*10^{-7}$	$3.42*10^{-6}$	$4.45*10^{-6}$	$4.48*10^{-6}$	$4.43*10^{-6}$	$2.95*10^{-6}$	$1.21*10^{-6}$	$5.33*10^{-7}$	$2.23*10^{-7}$	$1.33*10^{-7}$	$9.29*10^{-8}$	$7.06*10^{-8}$
234678-HxCDF	$1.23*10^{-7}$	$1.99*10^{-6}$	$2.59*10^{-6}$	$2.60*10^{-6}$	$2.58*10^{-6}$	$1.72*10^{-6}$	$7.06*10^{-7}$	$3.10*10^{-7}$	$1.29*10^{-7}$	$7.73*10^{-8}$	$5.40*10^{-8}$	$4.11*10^{-8}$
Other HxCDF	$7.76*10^{-7}$	$1.25*10^{-5}$	$1.63*10^{-5}$	$1.64*10^{-5}$	$1.63*10^{-5}$	$1.08*10^{-5}$	$4.45*10^{-6}$	$1.96*10^{-6}$	$8.17*10^{-7}$	$4.88*10^{-7}$	$3.41*10^{-7}$	$2.59*10^{-7}$
1234678-HpCDF	$2.13*10^{-7}$	$3.44*10^{-6}$	$4.47*10^{-6}$	$4.50*10^{-6}$	$4.46*10^{-6}$	$2.97*10^{-6}$	$1.22*10^{-6}$	$5.37*10^{-7}$	$2.24*10^{-7}$	$1.34*10^{-7}$	$9.34*10^{-8}$	$7.10*10^{-8}$
1234789-HpCDF	$4.61*10^{-8}$	$7.46*10^{-7}$	$9.70*10^{-7}$	$9.76*10^{-7}$	$9.66*10^{-7}$	$6.43*10^{-7}$	$2.65*10^{-7}$	$1.16*10^{-7}$	$4.86*10^{-8}$	$2.90*10^{-8}$	$2.03*10^{-8}$	$1.54*10^{-8}$
Other HpCDF	$4.93*10^{-7}$	$7.97*10^{-6}$	$1.04*10^{-5}$	$1.04*10^{-5}$	$1.03*10^{-5}$	$6.88*10^{-6}$	$2.83*10^{-6}$	$1.24*10^{-6}$	$5.19*10^{-7}$	$3.10*10^{-7}$	$2.17*10^{-7}$	$1.65*10^{-7}$
OCDF	$4.12*10^{-8}$	$6.66*10^{-7}$	$8.67*10^{-7}$	$8.72*10^{-7}$	$8.63*10^{-7}$	$5.75*10^{-7}$	$2.36*10^{-7}$	$1.04*10^{-7}$	$4.34*10^{-8}$	$2.59*10^{-8}$	$1.81*10^{-8}$	$1.38*10^{-8}$

Table 3-17. Predicted average particle-phase concentrations of CDD/Fs (pg/m^3 ; columns are downwind distance in km).

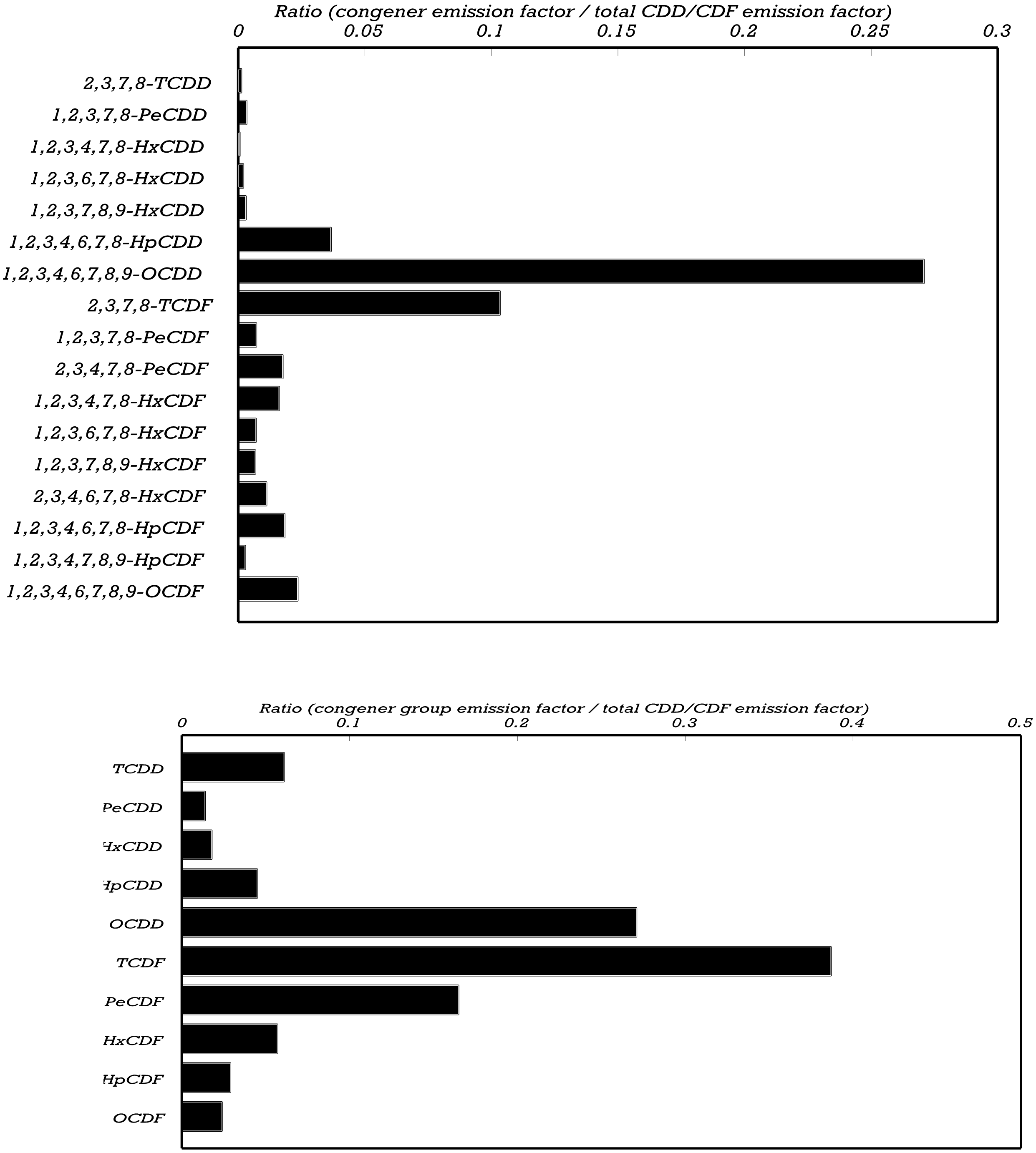
Congener	0.2	0.5	0.8	0.9	1	2	5	10	20	30	40	50
2378-TCDD	$4.16*10^{-7}$	$6.71*10^{-6}$	$8.70*10^{-6}$	$8.75*10^{-6}$	$8.66*10^{-6}$	$5.76*10^{-6}$	$2.36*10^{-6}$	$1.03*10^{-6}$	$4.22*10^{-7}$	$2.49*10^{-7}$	$1.72*10^{-7}$	$1.29*10^{-7}$
Other TCDD	$8.28*10^{-6}$	$1.33*10^{-4}$	$1.73*10^{-4}$	$1.74*10^{-4}$	$1.72*10^{-4}$	$1.14*10^{-4}$	$4.69*10^{-5}$	$2.04*10^{-5}$	$8.40*10^{-6}$	$4.95*10^{-6}$	$3.42*10^{-6}$	$2.57*10^{-6}$
12378-PCDD	$1.55*10^{-6}$	$2.49*10^{-5}$	$3.24*10^{-5}$	$3.25*10^{-5}$	$3.22*10^{-5}$	$2.14*10^{-5}$	$8.76*10^{-6}$	$3.82*10^{-6}$	$1.57*10^{-6}$	$9.25*10^{-7}$	$6.39*10^{-7}$	$4.81*10^{-7}$
Other PCDD	$1.53*10^{-5}$	$2.47*10^{-4}$	$3.20*10^{-4}$	$3.22*10^{-4}$	$3.19*10^{-4}$	$2.12*10^{-4}$	$8.67*10^{-5}$	$3.78*10^{-5}$	$1.55*10^{-5}$	$9.16*10^{-6}$	$6.33*10^{-6}$	$4.76*10^{-6}$
123478-HxCDD	$2.23*10^{-6}$	$3.59*10^{-5}$	$4.66*10^{-5}$	$4.69*10^{-5}$	$4.64*10^{-5}$	$3.08*10^{-5}$	$1.26*10^{-5}$	$5.50*10^{-6}$	$2.26*10^{-6}$	$1.33*10^{-6}$	$9.22*10^{-7}$	$6.94*10^{-7}$
123789-HxCDD	$3.24*10^{-6}$	$5.22*10^{-5}$	$6.78*10^{-5}$	$6.82*10^{-5}$	$6.75*10^{-5}$	$4.48*10^{-5}$	$1.84*10^{-5}$	$8.00*10^{-6}$	$3.2*10^{-6}$	$1.94*10^{-6}$	$1.34*10^{-6}$	$1.01*10^{-6}$
123678-HxCDD	$2.94*10^{-6}$	$4.74*10^{-5}$	$6.16*10^{-5}$	$6.19*10^{-5}$	$6.13*10^{-5}$	$4.07*10^{-5}$	$1.67*10^{-5}$	$7.27*10^{-6}$	$2.99*10^{-6}$	$1.76*10^{-6}$	$1.22*10^{-6}$	$9.15*10^{-7}$
Other HxCDD	$2.84*10^{-5}$	$4.58*10^{-4}$	$5.95*10^{-4}$	$5.98*10^{-4}$	$5.92*10^{-4}$	$3.93*10^{-4}$	$1.61*10^{-4}$	$7.02*10^{-5}$	$2.88*10^{-5}$	$1.70*10^{-5}$	$1.17*10^{-5}$	$8.84*10^{-6}$
1234678-HpCDD	$2.98*10^{-5}$	$4.79*10^{-4}$	$6.22*10^{-4}$	$6.26*10^{-4}$	$6.19*10^{-4}$	$4.11*10^{-4}$	$1.69*10^{-4}$	$7.34*10^{-5}$	$3.02*10^{-5}$	$1.78*10^{-5}$	$1.23*10^{-5}$	$9.25*10^{-6}$
Other HpCDD	$5.50*10^{-5}$	$8.85*10^{-4}$	$1.15*10^{-3}$	$1.16*10^{-3}$	$1.14*10^{-3}$	$7.60*10^{-4}$	$3.11*10^{-4}$	$1.36*10^{-4}$	$5.57*10^{-5}$	$3.29*10^{-5}$	$2.27*10^{-5}$	$1.71*10^{-5}$
OCDD	$6.18*10^{-5}$	$9.96*10^{-4}$	$1.29*10^{-3}$	$1.30*10^{-3}$	$1.29*10^{-3}$	$8.55*10^{-4}$	$3.50*10^{-4}$	$1.53*10^{-4}$	$6.27*10^{-5}$	$3.70*10^{-5}$	$2.55*10^{-5}$	$1.92*10^{-5}$
2378-TCDF	$2.61*10^{-5}$	$4.20*10^{-4}$	$5.45*10^{-4}$	$5.49*10^{-4}$	$5.43*10^{-4}$	$3.61*10^{-4}$	$1.48*10^{-4}$	$6.44*10^{-5}$	$2.65*10^{-5}$	$1.56*10^{-5}$	$1.08*10^{-5}$	$8.11*10^{-6}$
Other TCDF	$1.66*10^{-4}$	$2.67*10^{-3}$	$3.47*10^{-3}$	$3.49*10^{-3}$	$3.45*10^{-3}$	$2.2*10^{-3}$	$9.39*10^{-4}$	$4.09*10^{-4}$	$1.68*10^{-4}$	$9.91*10^{-5}$	$6.85*10^{-5}$	$5.15*10^{-5}$
23478-PCDF	$4.89*10^{-6}$	$7.89*10^{-5}$	$1.02*10^{-4}$	$1.03*10^{-4}$	$1.02*10^{-4}$	$6.77*10^{-5}$	$2.77*10^{-5}$	$1.21*10^{-5}$	$4.96*10^{-6}$	$2.93*10^{-6}$	$2.02*10^{-6}$	$1.52*10^{-6}$
12378-PCDF	$2.67*10^{-6}$	$4.30*10^{-5}$	$5.58*10^{-5}$	$5.61*10^{-5}$	$5.55*10^{-5}$	$3.69*10^{-5}$	$1.51*10^{-5}$	$6.58*10^{-6}$	$2.71*10^{-6}$	$1.60*10^{-6}$	$1.10*10^{-6}$	$8.29*10^{-7}$
Other PCDF	$7.53*10^{-5}$	$1.21*10^{-3}$	$1.57*10^{-3}$	$1.58*10^{-3}$	$1.57*10^{-3}$	$1.04*10^{-3}$	$4.27*10^{-4}$	$1.86*10^{-4}$	$7.64*10^{-5}$	$4.50*10^{-5}$	$3.11*10^{-5}$	$2.34*10^{-5}$
123478-HxCDF	$7.87*10^{-6}$	$1.27*10^{-4}$	$1.65*10^{-4}$	$1.66*10^{-4}$	$1.64*10^{-4}$	$1.09*10^{-4}$	$4.46*10^{-5}$	$1.94*10^{-5}$	$7.98*10^{-6}$	$4.71*10^{-6}$	$3.25*10^{-6}$	$2.45*10^{-6}$
123678-HxCDF	$7.44*10^{-6}$	$1.20*10^{-4}$	$1.56*10^{-4}$	$1.57*10^{-4}$	$1.55*10^{-4}$	$1.03*10^{-4}$	$4.22*10^{-5}$	$1.84*10^{-5}$	$7.55*10^{-6}$	$4.45*10^{-6}$	$3.07*10^{-6}$	$2.31*10^{-6}$
123789-HxCDF	$5.06*10^{-6}$	$8.16*10^{-5}$	$1.06*10^{-4}$	$1.06*10^{-4}$	$1.05*10^{-4}$	$7.00*10^{-5}$	$2.87*10^{-5}$	$1.25*10^{-5}$	$5.14*10^{-6}$	$3.03*10^{-6}$	$2.09*10^{-6}$	$1.57*10^{-6}$
234678-HxCDF	$2.94*10^{-6}$	$4.74*10^{-5}$	$6.16*10^{-5}$	$6.19*10^{-5}$	$6.12*10^{-5}$	$4.07*10^{-5}$	$1.67*10^{-5}$	$7.26*10^{-6}$	$2.99*10^{-6}$	$1.76*10^{-6}$	$1.22*10^{-6}$	$9.15*10^{-7}$
Other HxCDF	$1.84*10^{-5}$	$2.99*10^{-4}$	$3.88*10^{-4}$	$3.91*10^{-4}$	$3.86*10^{-4}$	$2.57*10^{-4}$	$1.05*10^{-4}$	$4.58*10^{-5}$	$1.88*10^{-5}$	$1.11*10^{-5}$	$7.67*10^{-6}$	$5.77*10^{-6}$
1234678-HpCDF	$1.04*10^{-5}$	$1.68*10^{-4}$	$2.17*10^{-4}$	$2.19*10^{-4}$	$2.16*10^{-4}$	$1.44*10^{-4}$	$5.89*10^{-5}$	$2.57*10^{-5}$	$1.05*10^{-5}$	$6.22*10^{-6}$	$4.30*10^{-6}$	$3.23*10^{-6}$
1234789-HpCDF	$4.55*10^{-6}$	$7.37*10^{-5}$	$9.52*10^{-5}$	$9.58*10^{-5}$	$9.47*10^{-5}$	$6.30*10^{-5}$	$2.58*10^{-5}$	$1.12*10^{-5}$	$4.62*10^{-6}$	$2.72*10^{-6}$	$1.88*10^{-6}$	$1.42*10^{-6}$
Other HpCDF	$4.87*10^{-5}$	$7.85*10^{-4}$	$1.05*10^{-3}$	$1.02*10^{-3}$	$1.01*10^{-3}$	$6.73*10^{-4}$	$2.76*10^{-4}$	$1.20*10^{-4}$	$4.94*10^{-5}$	$2.91*10^{-5}$	$2.01*10^{-5}$	$1.51*10^{-5}$
OCDF	$2.05*10^{-5}$	$3.30*10^{-4}$	$4.29*10^{-4}$	$4.31*10^{-4}$	$4.27*10^{-4}$	$2.84*10^{-4}$	$1.16*10^{-4}$	$5.06*10^{-5}$	$2.08*10^{-5}$	$1.23*10^{-5}$	$8.47*10^{-6}$	$6.37*10^{-6}$

Table 3-18. Predicted annual dry deposition of particle-bound CDD/Fs (pg/m^2-yr; columns are downwind distance in km).

Congener	0.2	0.5	0.8	0.9	1	2	5	10	20	30	40	50
2378-TCDD	0.028	0.444	0.584	0.578	0.561	0.315	0.097	0.035	0.010	0.005	0.003	0.002
Other TCDD	0.558	8.84	11.6	11.5	11.2	6.26	1.93	0.666	0.207	0.099	0.063	0.045
12378-PCDD	0.104	1.65	2.17	2.15	2.09	1.17	0.360	0.124	0.039	0.019	0.012	0.008
Other PCDD	1.03	16.3	21.5	21.3	20.6	11.6	3.56	1.23	0.393	0.183	0.117	0.083
123478-HxCDD	0.150	2.38	3.13	3.10	3.01	1.69	0.519	0.179	0.059	0.027	0.017	0.012
123789-HxCDD	0.219	3.46	4.55	4.50	4.37	2.45	0.754	0.261	0.081	0.039	0.024	0.018
123678-HxCDD	0.198	3.14	4.13	4.09	3.97	2.23	0.685	0.237	0.074	0.035	0.024	0.016
Other HxCDD	1.92	30.4	39.9	39.5	38.3	21.5	6.61	2.29	0.711	0.340	0.216	0.155
1234678-HpCDD	2.01	31.8	41.7	41.3	40.1	22.5	6.92	2.39	0.744	0.356	0.226	0.162
Other HpCDD	3.70	58.7	77.1	76.3	74.1	41.6	12.8	4.42	1.37	0.657	0.418	0.299
OCDD	4.17	66.0	86.7	85.9	83.3	46.8	14.4	4.97	1.55	0.739	4.70	0.336
2378-TCDF	1.76	27.8	36.6	36.2	35.2	19.7	6.07	2.10	0.652	0.312	0.198	0.142
Other TCDF	11.2	177.0	232.0	230.0	223.0	125.0	38.6	13.3	4.12	1.98	1.26	0.903
23478-PCDF	0.330	5.22	6.86	6.80	6.60	3.70	1.14	0.394	0.122	0.059	0.037	0.027
12378-PCDF	0.182	2.85	3.74	3.71	3.60	2.02	0.621	0.215	0.067	0.032	0.020	0.015
Other PCDF	5.07	80.4	106.0	105.0	101.0	57.0	17.5	6.06	1.88	0.900	0.573	0.409
123478-HxCDF	0.530	8.40	11.0	10.9	10.6	5.95	1.83	0.633	0.197	0.094	0.060	0.043
123678-HxCDF	.0502	7.95	10.4	10.3	10.0	5.63	1.73	0.599	0.186	0.089	0.057	0.041
123789-HxCDF	0.341	5.40	7.10	7.03	6.82	3.83	1.18	0.407	0.127	0.061	0.039	0.028
234678-HxCDF	0.198	3.14	4.13	4.09	3.97	2.23	0.685	0.237	0.074	0.035	0.022	0.016
Other HxCDF	1.25	19.8	26.0	25.8	25.0	14.1	4.32	1.49	0.464	0.222	0.141	0.101
1234678-HpCDF	0.701	11.1	14.6	14.4	14.0	7.87	2.42	0.836	0.260	0.124	0.079	0.057
1234789-HpCDF	0.307	4.86	6.39	6.33	6.14	3.45	1.06	0.366	0.114	0.054	0.035	0.025
Other HpCDF	3.28	52.0	68.3	67.6	65.6	36.8	11.3	3.92	1.22	0.582	0.371	0.265
OCDF	1.38	21.9	28.8	28.5	27.6	15.5	0.477	0.165	0.051	0.245	0.156	0.111

Table 3-19. Predicted annual wet deposition of particle-bound CDDs/Fs (pg/m^2-yr; columns are downwind distance in km).

Congener	0.2	0.5	0.8	0.9	1	2	5	10	20	30	40	50
2378-TCDD	1.80	0.684	0.406	0.356	0.315	0.143	0.046	0.019	0.007	0.004	0.003	0.002
Other TCDD	35.9	13.6	8.07	7.07	6.27	2.81	0918	0.369	0.144	0.081	0.054	0.036
12378-PCDD	6.71	2.54	1.51	1.32	1.17	0.525	0.172	0.069	0.027	0.015	0.010	0.007
Other PCDD	66.4	25.2	14.9	13.1	11.6	5.19	1.70	0.683	0.266	0.150	0.100	0.067
123478-HxCDD	9.67	3.66	2.18	1.91	1.69	0.757	0.247	0.099	0.039	0.022	0.015	0.010
123789-HxCDD	14.1	5.33	3.16	2.77	2.46	1.10	0.359	0.144	0.056	0.032	0.021	0.014
123678-HxCDD	12.8	4.84	2.87	2.52	2.23	0.999	0.327	0.131	0.051	0.029	0.019	0.013
Other HxCDD	123.0	46.7	27.7	24.3	21.5	9.64	3.15	1.27	0.495	0.278	0.185	0.124
1234678-HpCDD	129.0	48.9	29.0	25.4	22.5	10.1	3.30	1.33	0.517	0.291	0.194	0.129
Other HpCDD	238.0	90.3	53.6	46.9	41.6	18.6	6.09	2.45	0.956	0.538	0.358	0.239
OCDD	268.0	102.0	60.3	52.8	46.8	21.0	6.85	2.76	10.8	0.605	0.403	0.269
2378-TCDF	113.0	42.8	25.4	22.3	19.8	8.85	2.89	1.16	0.454	0.255	0.170	0.113
Other TCDF	719.0	272.0	162.0	142.0	126.0	56.2	18.4	7.39	2.88	1.62	1.08	0.721
23478-PCDF	21.2	8.04	4.77	4.18	3.71	1.66	0.543	0.218	0.085	0.048	0.032	0.021
12378-PCDF	11.6	4.38	2.60	2.28	2.02	0.905	0.296	0.119	0.046	0.026	0.017	0.012
Other PCDF	326.0	124.0	73.4	64.3	57.0	25.5	8.35	3.36	1.31	0.737	0.491	0.327
123478-HxCDF	34.1	12.9	7.67	6.73	5.96	2.67	0.873	0.351	0.137	0.077	0.051	0.034
123678-HxCDF	32.3	12.2	7.26	6.36	5.64	2.52	0.825	0.332	0.129	0.073	0.049	0.032
123789-HxCDF	22.0	8.32	4.94	4.33	3.84	1.72	0.561	0.226	0.088	0.049	0.033	0.022
234678-HxCDF	12.8	4.84	2.87	2.52	2.23	0.998	0.326	0.131	0.051	0.029	0.019	0.013
Other HxCDF	80.5	30.5	18.1	15.9	14.1	6.30	2.06	0.828	0.323	0.182	0.121	0.081
1234678-HpCDF	45.1	17.1	10.1	8.88	7.88	3.53	1.15	0.463	0.181	0.102	0.068	0.045
1234789-HpCDF	19.7	7.48	4.44	3.89	3.45	1.54	0.505	0.203	0.079	0.045	0.029	0.020
Other HpCDF	211.0	80.0	47.5	41.6	36.9	16.5	5.40	2.17	0.847	0.476	0.318	0.212
OCDF	88.9	33.7	20.0	17.5	15.5	6.95	2.27	0.914	0.357	0.201	0.134	0.089



Source: Mean concentrations from Green et al. (1995); nondetects set equal to zero.

Figure 3-1. Example of a congener and a homologue profile from a sewage sludge incinerator

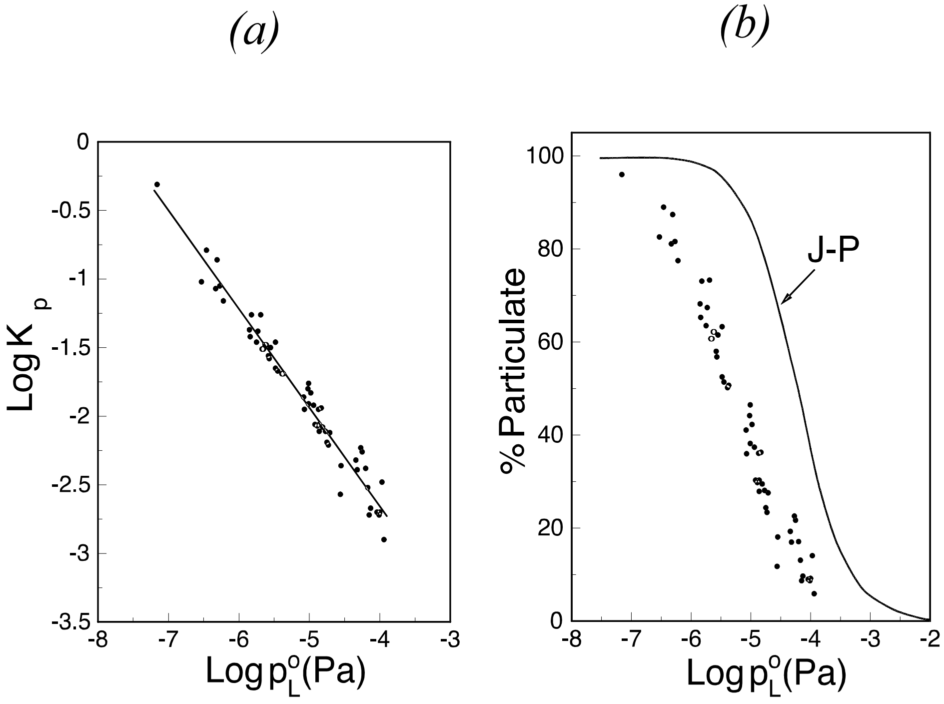
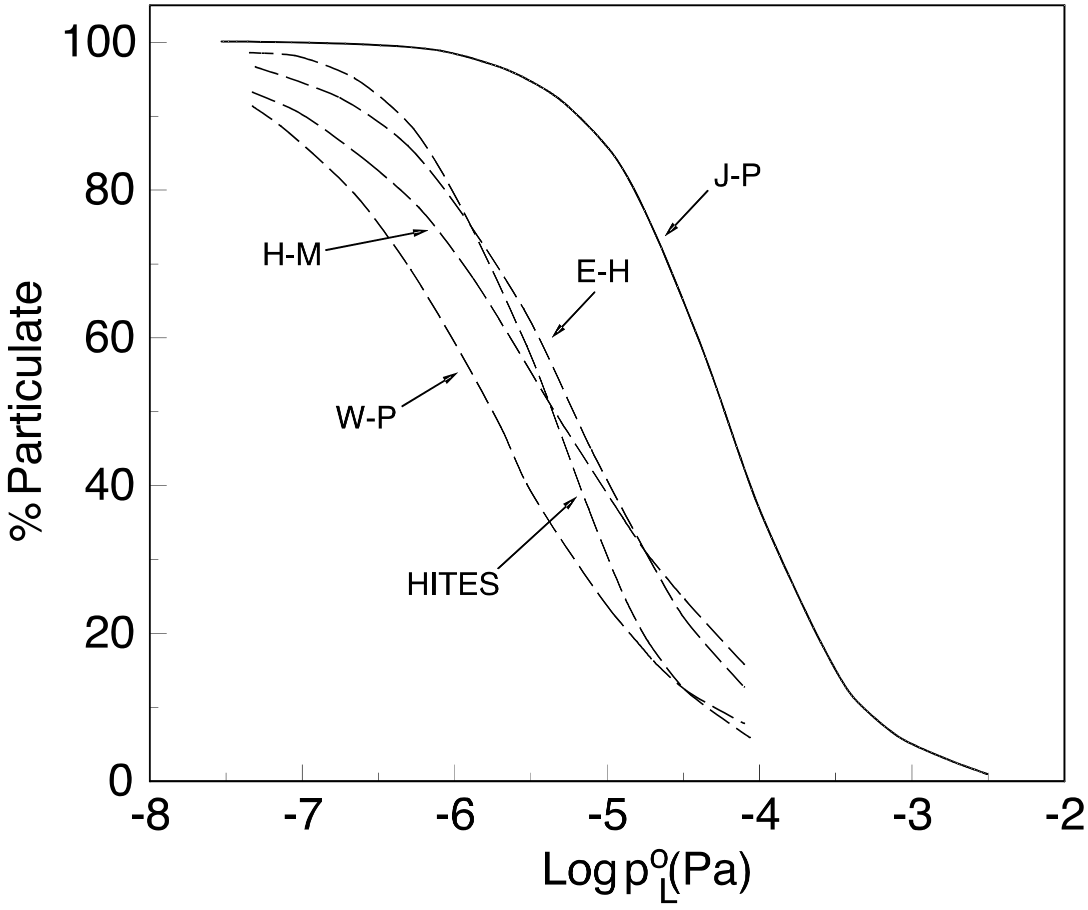


Figure 3-2. The relationships between the log of liquid sub-cooled vapor pressure, p_L°,0 and the particle-gas partition coefficient, K_p, (figure (a)), and between p_L° and modeled (as indicated by "J-P" in figure (b)) and measured percent particulate-phase in the ambient air (measurements from Eitzer & Hites (1989)).



KEY: E-H = Eitzer and Hites (1989); HITES = Hites (1991)
H-M = Hunt and Maisel (1990); Hunt and Maisel (1992)
W-P = Welsch-Pausch, et al. (1995)

Figure 3-3. Comparison of measured particulate percentages of PCDD/F on a homolog basis to predictions of the Junge-Pankow model as a function of the sub-cooled liquid vapor pressure, $p°_L$, of the homolog groups.