7. MODEL COMPARISONS AND MODEL VALIDATIONS

7.1. INTRODUCTION

This chapter is comprised of two principle sets of exercises aimed at lending credibility to the models selected for use in this site-specific methodology. One set compares alternate approaches to modeling the fate and transport of dioxins, which users can consider in place of the models selected. The comparisons involve generating results with both sets of models, and then seeing how the results compare. Assuming the models selected in this document and the alternates have some inherent credibility, the model results should compare favorably. In most cases, they do compare well, but there are a few where model comparisons are not satisfactory. If the two sets of models compare favorably, one would expect that this lends credibility to both sets of models, and hopefully some confidence in the use of the models selected for this document.

The fate, transport, and transfer models presented in this document can also attain a measure of credibility if it can be shown that estimations of environmental and exposure media concentrations are consistent with those found in the literature. Some of those comparisons can use the exposure media concentrations generated in the demonstration scenarios because the source strength terms of the demonstrations were crafted to be meaningful. Specifically, the background scenario was demonstrated with both air concentrations and soil concentrations that are from an actual rural background setting that is justified as being generally typical for rural settings. The soil contamination source category was demonstrated with a bounded area of high soil concentrations of 1 ppb. This was also supported by literature showing this that sites of high soil contamination contained dioxin-like compounds in the ppb range. Other comparisons are more site-specific: for a specific site, the source strength is known and input into the model, and the model predictions of environmental media concentrations are compared with site-specific measurements of these concentrations.

Tests of this latter case can be termed “validation” exercises. In this document, the word “validation” refers to an exercise in which the following holds true:

1. <u>An impacted media concentration is known</u>. A concentration of a contaminant in a media that can be predicted by the fate models, such as a concentration in soil, vegetation, water, sediment, biota, or ambient air, is known through a site-specific monitoring program. Model predictions of these concentrations have often been termed the “dependent” model results in a validation exercise.

2. The source causing this impact is known. The source term information has often been called the "independent" model input in a validation exercise. For example, if the concentration of a contaminant in ambient air represents the known dependent quantity, than the independent, or source, term could be the emissions from one or more tall stacks nearby. Specifically, source term information would translate to the level of emissions (in units of mass/time such as g/sec) of the particular contaminant from the identified stacks. The model validation exercise would take these known emissions, put them into an air dispersion model along with other parameters (i.e., stack heights, exit velocities, site-specific meteorological data, etc.), and predict ambient air concentrations. In other model validation exercises, however, the source is likely not going to be the incinerator emissions. For example, if underground vegetables were the impacted media, than the independent source term could be the concentration in the soil in which the vegetables were growing. One could also start with ambient air concentrations in a model validation exercise involving underground vegetables. In this case, the air concentrations would be used to predict the soil concentrations, and these soil concentrations would be used to predict the vegetable concentrations. In any case, the source term needs to be known and the model user needs to be reasonably certain, or at the very least, the model user needs to assume, that the source directly impacts the effected media.

3. All other model parameters are assigned values using the best available information. Site-specific information is the most appropriate to use, if it is available. Chemical-specific parameters, such as the bioconcentration/biotransfer parameters, can either rely on site-specific information or are inherent properties of the chemical. An example of the former are the soil (or sediment)/water partition coefficients: Kd, Kdsed, and Kdssed. These parameters are calculated as the product of the organic carbon partition, Koc, which is an inherent chemical property, and the organic carbon content of the sorbing media (soil, sediment, or suspended sediment), which is site-specific. Examples of inherent properties are the bioconcentration parameters which are used to predict, for example, biota concentrations (vegetation, animal fat) as a function of the concentration in the contacting media (soil, vegetation).

4. Model predictions of the impacted media are compared with observations. Once all the parameters are assigned values, the model is run and model predictions of the dependent media concentration are compared to the real world observations of this concentration. This is the final step in a model validation exercise.

Model validation needs to be distinguished from model “calibration”. Calibration exercises require real world measurements of independent source terms and dependent media impacts, as do validation exercises. What distinguishes the two exercises is that a calibration exercise is conducted in order to determine values for one or more key model input parameters by “forcing” the model to duplicate the observed data by adjusting the value of this key input parameter until this duplication is reached. As described in step 3 above, all model parameters are assigned values in a validation exercise; none are adjusted in order for model predictions to fit the observed data. An example of a model calibration exercise is the calibration of the air-to-leaf transfer factor for the vapor phase, B_{vpa}. The exercise is described in detail in Chapter 4. Briefly, air concentrations of these compounds in experimental conditions were known, as were the final concentrations in grass harvested after three weeks of growth. All other model parameters necessary for the prediction of the concentration of the dioxins and furans in the grass, including the physical parameters (mass of grass harvested, fresh to dry weight conversion, etc.), vapor/particle partitioning in the air, and particle deposition algorithm parameters, were assigned values based on site-specific measurements or the literature. The B_{vpa} was then adjusted until the model predictions of grass concentrations matched the observed grass concentrations.

Finally, it should be understood that model testing is an ongoing process. The model comparisons and validations described in this chapter are, by no means, expected to establish model validity beyond any doubt. Users of this methodology are encouraged to subject the models to any number of tests, validation or otherwise, as they use the models described in this document to conduct site-specific assessments for dioxin-like compounds

7.2. MODEL COMPARISON EXERCISES

7.2.1. Evaluation of Alternative Air-to-Leaf Modeling Approaches

The first section below describes the field data that was used in this model testing exercise. The second section describes the two alternative empirical models of air-to-plant impacts of the dioxin-like compounds. One was developed only for the impact of vapor phase dioxins, and does not have an explicit particle phase impact model. It will be compared to the vapor transfer model of this methodology. The other model assumes that plants “scavange” a fixed volume of air of dioxins; grass concentrations are very simply modeled as the total (vapor+particle) air concentration times a “scavenging” coefficient. The third section presents the results of this exercise. These first three section are paraphrased from Lorber and Pinsky (1999), where further details on this exercise can be found. Finally, the fourth section reviews a very similar model comparison exercise published in the literature in which the model of this methodology, along with these same two alternative models, are applied to different field data.

7.2.1.1. The Field Data

Jones and Duarte-Davidson (1997) present the results of an extensive monitoring study of dioxin concentrations in air and grass, as well as deposition fluxes, from three sites over three time periods between 1992 and 1993 in the United Kingdom. The three sites include a rural background site, an urban site, and an industrial site. The study was originally funded as a monitoring program to evaluate the environmental levels of dioxin-like compounds in a contaminated industrial area in Bolsover, UK (Sandalls, et al, 1996). By also including an urban site and a rural background site in their study, the authors were able to use the data to better understand the processes of air-to-plant transfer of the dioxins. The regional background site was located about 6 km upwind of the industrial complex in Bolsover, the urban site was about 2 km in the town of Bolsover, and the industrial sampling location was located just outside the industrial complex, about 100 m away.

Jones and Duarte-Davidson (1997) present two sets of data which are appropriate for air-to-plant model validation and model comparison purposes. Specifically, they presented concurrently measured concentrations of dioxin and furan congeners, and homologue groups, for air and grass sampled for two of the sites, the industrial and rural background site, for one of the sampling periods, Sep. 14 - Oct. 30, 1993. They also presented the results of their deposition collection for those two sites/sampling periods. Although other data sets of this kind were collected during the program, only these two sets were presented. Specifically, the following observed data were available for one sampling period each at the rural background and industrial sites: 1) average total air concentrations of 17 dioxin congeners and 8 homologue groups for a 6+-week period (9/14/93-10/30/93), 2) average concentrations of these compounds in grass grown during this period, 3) average deposition rates, in units of pg/m^2-day for these compounds, and 4) grass yields, in g/m^2. The air, grass, and deposition data are provided in Table 7-1. Further details on the sampling design, monitoring program, analytical methods, and other aspects of the study can be found in Jones and Duarte-Davidson (1997).

7.2.1.2. Model Descriptions and Application to the Field Data

The vapor transfer approach was parameterized and applied to 2,3,7,8-TCDD by Smith, et al. (1995a) and Trapp and Matthies (1995). The steady state solution for their vapor transfer velocity approach is given as:

$$C_{vpa} = \frac{F_v}{k_v\ Y_j} \qquad (7\text{-}1)$$

where:

C_{vpa} = plant concentration due to vapor-phase transfer, pg/g dry weight
F_v = deposition of vapor-phase congener, pg/m^2-day
k_v = first-order dissipation constant, day^{-1}
Y_j = yield of crop j, g/m^2

The non-steady state solution has an additional term in the numerator, 1-e$^{(-kv\ t)}$, where t is the time to harvest. This non-steady state term was used for the particle phase solution in the model validation exercise. However, given that the k_v was assigned a relatively large value by both researchers for 2,3,7,8-TCDD vapors depositing onto plants (a large k_v corresponds to a short half-life), and the growing period for grasses is 45+ days in the field data set applied, this additional term approaches 1.0, and it can therefore be neglected in the vapor phase solution.

The two articles evaluated diverge at this point. The Trapp and Matthies (1995) approach is actually a comprehensive approach involving root uptake impacts. They summarize the literature to conclude that vapor phase impacts for lipophilic compound such as dioxin dominate the plant contamination and hence, they do not model particle phase impacts. They also present their solution in a more generalized fashion by having a volume term in the denominator of Equation (7-1) above instead of a plant yield term; the volume term is easily converted to a mass (or yield) term with a plant density factor. Their solution for F_v is:

$$F_v = A\ g\ C_{va}\ 86400 \qquad (7\text{-}2)$$

where:

F_v = deposition of vapor-phase congener, pg/m^2-day
A = leaf area index, m^2 leaf area/m^2 ground area
g = conductance, m/sec
C_{va} = vapor phase air concentration, pg/m^3
86400 = converts sec to days

Trapp and Matthies (1995) state that g has a range of 0.0001 m/sec to 0.005 m/sec, where the upper boundary conductance is appropriate for a plant species with relatively permeable cuticles and the compounds are very lipophilic, and the lower boundary conductance is where uptake is mainly via stomata and the compounds are less lipophilic. For 2,3,7,8-TCDD, Trapp and Matthies (1995) assume a g of 0.001 m/sec. For the leaf area term, they have assumed a value of 5 for the condition they describe as “meadow”. Without further information on refinement of these terms for the experimental conditions of the Jones and Duarte-Davidson (1997) settings, a g of 0.001 m/sec and an A of 5 will be assumed for this exercise.

Smith, et al. (1995a) estimate the F_v as a multiplication of the vapor phase air concentration, C_{va} (pg/m^3), the transfer velocity, V_t, (cm/sec), and the plant interception (fraction, unitless). They state that the transfer velocity is represented as the inverse of the sum of the resistances to transfer to the plant surface as:

$$V_t = \frac{1}{R_a + R_b + R_c} \tag{7-3}$$

where:

V_t = transfer velocity, cm/sec
R_a = atmospheric resistance, sec/cm, a function of vertical turbulent transport
R_b = surface boundary layer resistance, sec/cm, a function of molecular diffusivity
R_c = plant canopy/leaf resistance, sec/cm, a function of vegetative density, stomatal uptake, surface effects, humidity, and so on

They have assigned values of $R_a = 0.4$ sec/cm, $R_b = 0.38$ sec/cm, and $R_c = 0.5$ sec/cm, leading to an overall V_t of 0.78 cm/sec. They assumed a crop interception fraction of 1.00.

Both research efforts have, therefore, arrived at fairly similar quantities in front of the air concentration term (C_{va}), despite having slightly different theoretical frameworks. Trapp and Matthies (1995) arrive at the quantity of 0.005 m/sec (A g = 5 * 0.001 m/sec), and Smith, et al. (1995a) arrive at 0.0078 m/sec (INT * V_t = 1 * 0.0078 m/sec).

Both also have used the same experimental work of McCrady and Maggard (1993) as part of their derivation of the k_v. Trapp and Matthies (1995) assumed that the overall k term was a function of losses by photodegradation, volatilization, and dilution from plant growth. They used the photodegradation k term of 0.3744 day^{-1} taken from McCrady and Maggard (1993), but then multiplied it by 0.30 assuming that the plant was in full sunlight only 30% of the time. They calculated a volatilization rate term of 0.012 day^{-1}, and assumed a dilution term of 0.035 day^{-1}, leading to an overall k_v term of 0.159 day^{-1}. Smith, et al. (1995a) took the full photodegradation plus volatilization rates determined by McCrady and Maggard (1993), without any correction for time in sunlight, to arrive at a k of 0.495 day^{-1}. They did not consider dilution by plant growth.

McLachlan (1995) developed a simple "scavenging" approach to predict grass concentrations of dioxins from air concentrations of dioxins. He suggests that grass scavenges the equivalent of 9 m^3 or air per gram of grass, and that corn scavenges 4.5 m^3 of air. The important assumption in this approach is that plants can scavenge vapors and particles equivalently; therefore, vapor/particle partitioning is unnecessary, and grass concentrations are very simply modeled as:

$$C_{gi} = SC\ C_{ai} \tag{7-4}$$

where:

C_{gi} = grass concentration of congener i, pg/g dry weight basis
SC = scavenging coefficient, m^3/g
C_{ai} = total (vapor + particle) phase air concentration of congener i, pg/m^3

With this as background, it is now possible to describe how the three models will be applied to the field data. For simplicity, the three models will be referred to as the EPA model, the scavenging model, and the vapor deposition model. In applying the EPA model, total dioxin concentrations were first partitioned into a vapor and a particle phase following the procedures outlined in Chapter 3. In that chapter, particle fractions, ϕ (the vapor fractions are solved as, 1 - ϕ), are developed for an ambient air temperature of 20 °C for airsheds described as, "clean continental", "background", "background plus local conditions", and "urban". For this application, these ϕ were rederived for 10 °C, the air temperature more typical of September and October in the UK, and the "average background" and "urban" ϕ were used for the rural and industrial sites, respectively. According to the modeling procedures of this assessment, described in detail in Chapter 4, vapor dioxins "transfer" to the grass; grass concentrations due to air-borne vapors are modeled simply as the air concentration times an air-to-leaf transfer factor, B_{vpa}. Chapter 4 describes the derivation of this empirical transfer factor. Particle-phase dioxins deposit onto grass, under both wet and dry conditions. Jones and Duarte-Davidson (1997) do not provide the rainfall data for the sampling period necessary to estimate wet deposition. For simplicity, wet deposition will not be modeled. Dry deposition, as outlined in Chapter 4, Section 4.3.4, will be modeled as a function of the particle phase concentration times a deposition velocity, which will be assumed to be 0.20 cm/sec. This deposition mixes in a reservoir of grass, described by the grass yields, which were provided in Jones and Duarte-Davidson (1997) as 89 and 42 g dry weight/m^2 for the rural and industrial sites, respectively. As outlined in Chapter 4, Section 4.3.4, interception fractions for grasses corresponding to these yields are solved for as 0.23 (for 89 g/m^2) and 0.11 (42 g/m^2). The first-order weathering constant will be assigned a value of 0.0495 day^{-1}, corresponding to a half-life of 14 days. This value has also been used in the literature and otherwise in this document.

For testing of the scavenging model, the measured air concentrations in the rural and industrial site will be multiplied by the scavenging coefficient of 9.0. For testing of the vapor deposition model, the total air concentration of 2,3,7,8-TCDD will be partitioned into the particle and vapor phase for these field data, again assuming “average background” for the rural site and “urban” for the industrial site. The vapor portion of the air concentration will be used in the vapor deposition model. The model predictions of the vapor component of the grass concentration will be compared against the vapor component of grass concentration as predicted by the models of this assessment and the measured grass concentration.

There were 25 modeled/measured concentration pairs in the rural site data set, including the 17 individual congeners and the 8 homologue groups. In order to obtain independent data points for model testing, the measured air and grass concentrations of the individual congeners were subtracted from the homologue group concentrations; individual congener concentrations are, by definition, contained within the homologue group concentrations. Doing this subtraction should have resulted in 25 independent measured/modeled pairs for model testing. However, it was found that, for HpCDD, HxCDF, and HpCDF, subtraction of the congener air concentrations from these homologue group air concentrations resulted in negative concentrations. There was obviously some measurement error in this data set. The air:grass pairs for these three homologue groups were, therefore, not considered for further model testing. Without these three readings, the air and grass data at the rural site were quite correlated; the correlation coefficient of the remaining 22 data pairs was 0.92.

Similar measurement error resulted in the deletion of 4 air:grass pairs in the industrial data set. The air concentrations of the homologue groups HpCDD and HpCDF also were lower than the sum of the individual congener concentrations. The grass concentrations of 1,2,3,7,8-PCDD and 1,2,3,7,8-PCDF were given as non-detected, but the air concentrations of these congeners in the urban settings were similar to the air concentrations in the rural settings, and significant grass concentrations were noted in the rural setting.

Even with these four pairs deleted, the industrial site data was not as consistent as the rural data. The correlation coefficient for the remaining 21 data pairs was 0.66. An examination of the data highlights some of the differences between the two data sets. In some instances, air concentrations that were similar in the rural and industrial sites led to grass concentrations that were more impacted in the industrial site. For example, the air concentration of 2,3,7,8-TCDD in the rural setting was 0.01 pg/m^3, while it was 70% higher than that in the industrial setting at 0.017 pg/m^3. However, the grass concentration in the industrial site was about 4 times as high as in the rural setting, 2.8 pg/g in the industrial site versus 0.72 pg/g in the rural site. Similar observations can be made for 4 other congeners. On the other hand, there were several instances where similar rural and industrial air concentrations resulted in lower grass concentrations in the industrial as compared to the rural setting. Similar OCDD concentrations of 2.5 pg/m^3 in the two settings resulted in a grass concentration of 94 pg/g in the rural setting but only 43 pg/g in the industrial site setting. This trend can be found in 13 other instances. Also, the industrial data contained three data points that appeared to be flawed.

In summary, then, 22 air:grass pairs for the rural data set and 21 air:grass pairs for the industrial site were retained for model testing

Model goodness-of-fit tests were run for the rural site only, not on the industrial site, simply because the rural site data was better correlated. The absolute and signed difference between the natural logs of the measured and modeled grass concentrations provided the goodness-of-fit measure. The signed error, or bias, measures the systematic tendency of the model to under or overpredict; a bias near 0 suggests that the model underpredicts and overpredicts by about the same amount. The absolute error calculation describes model variation; how close the model predictions come to the observations, regardless of whether the model over or underpredicted. A value close to 0 suggests a very good match between predictions and observations. Log concentrations were used because there were a wide range in grass concentrations, from sub-ppt concentrations for the lower chlorinated dioxins to concentrations near 100 ppt for the homologue groups.

7.2.1.3. Results and Discussion of the Air-to-Leaf Model Comparison Exercise

Results of this model comparison are shown in Figures 7-1 through 7-4, and Table 7-2.

Figures 7-1 and 7-2 compare the measured grass concentrations with the EPA and the Scavenging Model for the rural and urban site, respectively. The natural log of the observed concentrations are shown on the x-axis and the predicted concentrations on the y-axis. The dashed line shows where predicted equals observed; points above the line show overpredictions by the models while points below the line show model underpredictions. As seen in Figure 7-1, model predictions of rural grass concentrations using the EPA Model matched the observed concentrations better than the Scavenging model, but both models underpredicted concentrations. The predicted total toxic equivalent (I-TEQ) concentration of the EPA model was 3.7 pg/g, compared to the observed I-TEQ concentration of 6.0 pg/g. The bias was -0.66, giving a bias factor of exp [-0.66] = 0.51 and suggesting that the EPA model underpredicted by about a factor of 2.0. The absolute error was close to the bias at 0.68, again indicating that the EPA model mostly underpredicted plant concentrations; of 22 observation:prediction pairs, the EPA model underpredicted concentrations 21 times.

Figure 7-1 shows that the Scavenging Model underpredicted grass concentration at the rural site more than the EPA model. The modeled I-TEQ concentration was 1.85 pg/g, less than one-third the measured I-TEQ concentration of 6.0 pg/g. The absolute error was 1.325, and the bias was its negative counterpart, -1.325. This means that the model underpredicted concentrations in all instances, and that this underprediction was by an average factor of 3.8 ($e^{1.325}$) .

Figure 7-2 shows the EPA and the Scavenging Model predicting essentially the same concentration for nearly every data point, and both underpredicted grass concentrations significantly. The TEQ concentrations predicted by the EPA and the Scavenging Models were 3.26 and 2.94 pg/g, respectively, while the observed TEQ concentration was 7.35 pg/g. The bias and absolute differences for both models on this data set also mirrored each other. For the EPA Model, the bias and absolute differences were -1.01 and 1.09, and for the Scavenging Model, the bias and absolute difference were nearly the same at -1.07 and 1.15. These results indicate that both models underpredicted by about the same factor of 3.

One reason for this similarity in performance is that the EPA model reduced to principally a particle-phase deposition model; nearly all the dioxin was in the particle phase for the “urban” setting at 10 °C. Like the Scavenging Model, therefore, plant concentrations were mostly a linear function of total air concentrations for the application of the EPA Model at the industrial site.

As described earlier, the data at the industrial site was not nearly as well correlated as the data at the rural site - the correlation between air and grass data at the industrial site was 0.66 compared to 0.92 at the rural site. One factor likely to have influenced this is the fact that the soil at the industrial site was much higher for some of the dioxins as compared to the rural site. While the soil concentrations were not reported by Jones and Duarte-Davidson (1997), Sandalls

(1996) reported exceedingly high concentrations of TCDD (up to 9400 ppt, and several hundred ppt even 4-5 km from the major air source identified in the Bolsover area), and elevations in 2,3,7,8-TCDD, PCDD and TCDF in soils near the industrial site. Not ironically, these same four compounds, along with 1,2,3,6,7,8-HxCDD, were identified earlier as the compounds which had high grass concentrations at the industrial site despite air concentrations that were comparable to air concentrations of the same compounds at the rural site. If these five air:grass pairs are subtracted from the industrial site data set, the correlation between air and grass data now is much improved: it is at 0.80, up from 0.66. Also, the absolute error for both the Scavenging and the EPA Model for this smaller observed:predicted test improve to 0.61, indicating that modeled grass concentrations are now within exp [0.61] = 1.85 of measurements concentrations, rather than within a factor of 3.0. Obviously, the grass concentrations of these five compounds appear to have been influenced by high soil concentrations, and the ability of the models to reproduce these concentrations is limited because they are air-to-grass models and not air/soil-to-grass models. While it has been demonstrated that there is essentially no translocation from soil to above-ground plants (although pumpkins, cucumbers, squash, and other members of the cucumber family have been shown to translocate dioxins for an unknown reason (Hulster, et al., 1994)), there may have been some rainsplash impact or soil-to-air-to-plant impacts such as from wind erosion or soil volatilization for these compounds at the industrial site.

On the other hand, it was also true that air concentrations reasonably similar at the industrial and rural site led to lower grass concentrations at the industrial site for all the other dioxin and furan compounds. This is a trend that can possibly be explained and modeled by the EPA Model of this evaluation. For an urban setting, more of the dioxins are modeled to partition into the particle phase. As will be described below when discussing the calibration of the Scavenging Model, vapor phase dioxins have been shown to have a greater impact to plants compared to particle phase dioxins. Therefore, equivalent total air concentrations in a rural and an urban setting would lead to higher vegetation concentrations in the rural setting, because dioxins partition more into the vapor phase in such a setting, both in reality and as modeled by the EPA Model.

Table 7-2 shows the comparison of the measured grass concentration of 2,3,7,8-TCDD with the modeled vapor transfer concentration using the EPA vapor transfer model and the two Vapor Deposition Models. It is clear from this table that the vapor deposition algorithm, as parameterized by Smith et al. (1995) and Trapp and Mattheis (1995), predicts concentrations that are 2 to 4 times lower than predictions made by the vapor transfer algorithms of the EPA Model, and even lower still than observed grass concentrations. As will be described below, vapor phase deposition velocity and the decay rate of the dioxins on the plant are two parameters likely to have been assigned inappropriate values for this exercise, and also likely to be difficult to assign in any application of the vapor deposition approach.

Whereas the scavenging ratio of 9.0 may have been appropriate for the field data used by McLachlan (1995) in the development of this approach, it is by far too low for this particular data set. A calibration exercise was performed on the 22 rural air/grass data points. In this exercise, the least squares fit of the difference between predicted and measured log grass concentrations was sought. The best fit was found at the constant scavenging coefficient of 36.4. With this value, the goodness-of-fit measures improve substantially: the bias goes to 0 (by definition of the least squares fit) from -1.325, and an absolute error goes to 0.417 (predictions are within a factor of 1.5, sometimes higher, sometimes lower) from 1.325 (predictions are always lower by about a factor of 4.0).

A critical assumption of the scavenging approach is that vapor and particle-phase dioxins are scavenged equivalently from the air. Therefore, a constant scavenging coefficient can be applied to total air concentration to predict total grass concentration. The error terms for the best-fit scavenging ratio suggest this might be reasonable. However, this assumption is not supported by the data in this field site. Figure 7-3 shows the scavenging ratios calculated for the 22 air:grass data points of the rural field site graphed as a function of the degree of chlorination. For example, there are four data points plotted for 4 on the x-axis: 2,3,7,8-TCDD, 2,3,7,8-TCDF, the TCDD homologue group, and the TCDF homologue group. The scavenging ratios are simply calculated as the grass concentration (in pg/g dry weight) divided by the air concentration (in pg/m^3) at the rural field site (with subtractions of congener concentrations from homologue group concentrations). As seen in the figure, there is a clear trend in that the scavenging ratio appears to generally decrease from the tetra to the hepta degrees of chlorination, with perhaps an increase at the octa degree of chlorination. It also suggests more of a trend for the dioxins as compared to the furans: there may be a higher scavenging ratio, in general, for the dioxins.

The experiments on Welsh Ray Grass (Welsch-Pausch, et al., 1995) used to calibrate the EPA's air-to-leaf transfer factor (Lorber, 1995) provided a reason for this trend: when blocking out the particle deposition impacts to potted grass, the authors found that the grass concentrations of the tetra through hexa chlorinated dioxins and furans were similar to concentrations in potted grass where particle depositions were not blocked out. The authors concluded that the plant concentrations for these dioxin/furan homologue groups were dominated by vapor-phase dioxins, even though the total air concentration itself was not necessarily dominated by the vapor phase. Therefore, given these experimental results, it follows that the lower chlorinated congeners would have a larger overall scavenging coefficient. The field data certainly shows that trend; Figure 7-3 shows larger scavenging coefficients for the lower chlorinated dioxins and furans.

Figure 7-4 compares measured and modeled deposition amounts for the rural and industrial site combined. It is clear that the modeled rates of deposition were consistently higher than the measured rates. There was a high degree of correlation between measured and modeled rates, however, with a correlation coefficient of 0.99. The absolute error and bias were 1.16 and 1.11, respectively, suggesting that the model predictions were about 3.2 times higher than observed. This would indicate a systematic bias, either that the model tended to overpredict depositions or that the measurements tended to under-represent depositions.

If the model tended to overpredict deposition, this may have been due to inappropriate parameter assignment: too rapid a velocity of deposition, or too much dioxins assumed to be in particle phase. Measured deposition velocities can be calculated from the data of Jones and Duarte-Davidson (1997) in Table 7-1 simply as the deposition flux divided by the air concentration (with proper conversions). Average velocities calculated this way were 0.06 cm/s for the rural site and 0.08 cm/s for the industrial site and only one calculated deposition velocity was greater than the 0.20 cm/s velocity assigned for this modeling exercise. The predicted depositions would be lower still if measured particle phase fractions were used instead of modeled fractions since, measured particle-particle fractions of dioxins tend to be lower than modeled using the Junge model for vapor/particle partitioning. For this particular field site, measured vapor/particle fractions were not available to evaluate this possibility.

On the other hand, it could be the case that the deposition collectors are underestimating depositions. Jones and Duarte-Davidson (1997) suggest two possible causes for the upturned frisbees to be underestimating deposition: 1) they are smooth and therefore less efficient at capturing particles as compared to leafy vegetation or ground surfaces, and 2) dioxins in wet deposition can be adsorbed onto the sampler surface and presumably, not be available to be measured.

In any case, it can be concluded that the deposition model, which was the simple product of the particle-phase reservoir times a deposition velocity of 0.20 cm/s, resulted in the deposition amounts that about 3 times higher than were measured in the rural and industrial sites of this data set.

In the introduction to Section 7.2.1, this exercise was described as both a model validation and model comparison exercise. It can be concluded that the EPA model was reasonably successful in this validation with the rural site field data, but less successful on the industrial site data. On the other hand, both the vapor transfer and scavenging models could not be successfully validated on this field data. In the case of the vapor transfer model, the likely shortcoming was in the assignment of the parameters, vapor deposition velocity and degradation of vapor phase 2,3,7,8-TCDD deposited on the grass. In the case of the scavenging coefficient, the value of 9.0 suggested in its development (McLachlan, 1995) was too low. One can calibrate both models such that the fit between observed and predicted grass concentrations is favorable. These calibrated models can then be applied to other field data sets in order to see if the calibrated values are “valid”.   The deposition portion of the EPA model was found to consistently overpredict deposition, which could be due to either inappropriate parameter assignments, or the tendency of the upturned frisbee to underestimate deposition amounts.

7.2.1.4.   Literature Comparisons of Air-to-Plant Modeling Approaches

Douben, et al. (1997) presents an exercise comparing the three air-to-plant approaches that were compared in the previous section: the approach in this document, the scavenging approach, and the vapor deposition approach. Their exercise used, as observed air data, concentrations from a semi-rural site in the United Kingdom (UK). This was not the same as the rural site in the Jones and Duarte-Davidson (1977) study. Since this data set had several non-detects, the authors supplemented it with data from a rural site showing similar detected concentrations in Germany; the final observed air concentrations were crafted from these two data sets. The observed grass data came from a different site in the UK. Comparing model performance on a set of data from a single site, as was done in the previous section, is preferable to “crafting” observed air and grass data. Still, if the data can be considered representative, than using data from different sites may not be invalid; developing representative air and beef profiles was done for the air-to-plant-to-beef model validation described in Section 7.3.11 below. The application of the approach of this document used an earlier vapor transfer factor, from Lorber (1995), which also had an earlier vapor/particle partitioning scheme. They used the vapor deposition approach described and parameterized by Smith, et al. (1995) for all dioxin congeners, not just 2,3,7,8-TCDD - the vapor deposition velocity (0.78 cm/sec) and plant degradation (0.495 day^{-1}, corresponding to a half-life of 1.4 days) parameters were assigned the same the same for all congeners.   For the vapor deposition algorithm, they used measured vapor fractions (from the site in Germany) as compared to use of the modeled vapor fractions in the exercise above. Finally, they used the scavenging approach promoted by McLachlan (1995) including the assignment of a scavenging coefficient of 9 for all congeners.

In general, they showed some of the similar trends that were described above. The models of this assessment had the highest predicted grass concentration; this was also the trend in the exercise described above. However, these predictions were higher than the grass observations of the crafted air/grass data set in Douben, et al. (1997), sometimes by upwards of a factor of 10. The vapor transfer approach was the lowest predictor, but in their case, predictions were usually within an order of magnitude, sometimes within a factor of 2. The scavenging approach performed the best on their data set. Similar to the conclusion in Jones and Duarte-Davidson (1997), Douben, et al. (1997) concludes the following regarding vapor and particle atmospheric scavenging (p. 342 in Douben, et al. (1997)): "However, an implication of the good predictions obtained across the range of PCDD/Fs with the scavenging model is that airborne PCDD/Fs which may be present either in the vapour- or particulate-phase appear to transfer with similar efficiencies to pasture grass and may remain associated with the grass after deposition." However, even in the crafted air and grass profile, there is similar evidence as described above in that the scavenging coefficient increases as the degree of chlorination decreases, at least clearly so for the tetra congeners. From their data, calculated scavenging coefficients are: 57 for TCDD/Fs (n=2), 9 for PCDD/Fs (n=3), 5 for HxCDD/Fs (n=7), 11 for HpCDD (n=3), and 11 for OCDD/Fs (n=2).

Currado and Harrad (1998) evaluated two of the three modeling approaches described in the previous section to a data set including air concentrations, deposition amounts, and grass concentrations of 20 individual PCB congeners from an urban site in Birmingham, UK. The two models they tested were the EPA air-to-leaf model (which they further developed for CDD/Fs to include a soil-to-plant algorithm as described in Harrad and Smith (1997), although they only used the air-to-plant algorithm for this application to PCBs), and the Scavenging Model. For the EPA model, they partitioned the PCBs into particle and vapor phases using the Junge-Pankow model advocated in this assessment, corrected for air temperature, and then transferred the vapor-phase and deposited the particle-phase PCBs onto the grass. The vapor phase transfer factors were determined as a function of the PCB log Kow and H, as described in Lorber, et al. (1994), including an empirical reduction factor of 40. For the test of the Scavenging Model, they simply plotted total (vapor + particle) air concentrations against measured air concentrations, and investigated the correlation between the two. According to the Scavenging Model approach, the total air concentration times a constant (equal to the volume of air being "scavenged" of PCB to produce the grass concentration), which is the same constant for all PCBs, should equal the grass concentration.

Using the EPA framework, they found very good agreement between predicted and measured grass concentration for the PCBs: observed/predicted ratios ranged from 0.34 to 1.97, with a mean of 0.93 and a correlation coefficient of 0.46. They also found good agreement observed and predicted vapor/particle partitioning (observed/predicted particle fraction ratios ranged from 0.17 to 2.15, mean of 0.89 and correlation coefficient of 0.59) and observed and predicted particle deposition fluxes (observed/predicted ratios from 0.33 to 4.19, mean of 1.33, and correlation coefficient of 1.09).

On the other hand, they did not get as good results with the Scavenging Coefficient model. They did find that this would work for the penta- and hexachlorobiphenyls - their grass scavenged the PeCBs and HxCBs present in 22 m^3 of air, but there was not a similar relationship found for tri- and tetrachlorobiphenyls. Although the authors didn't investigate further, there may be a relationship between portion of the PCBs in the particle-phase, there would be more in the particle phase as the degree of chlorination increases (as it is with CDD/Fs), and the capabilities of the Scavenging Approach.

7.2.2. An Alternate Modeling Approach for Estimating Water Concentrations Given a Steady Input Load from Overland Sources

A study to evaluate the bioaccumulation of 2,3,7,8-TCDD in fish in Lake Ontario included an extensive modeling exercise (EPA, 1990a). The model used was WASP4 (Ambrose, et al., 1988). This is a substantially more complicated model than used in this assessment. The underlying principal for the WASP4 model is a conservation of mass. Contaminant source terms, described in mass/time units, enter what are termed control volumes, or segments. The contaminant partitions between sorbed, bound, and dissolved phases; it is not required to specify whether the contaminant enters via soil erosion, water runoff, surface deposition, or otherwise. Contaminants are, however, assumed to enter via the surface or as part of inflows to the water body, in contrast to ground water recharge. The mass transported into a segment is either transported out of the segment, accumulates in the segment, or is transformed by chemical or biological reactions.

As noted, 2,3,7,8-TCDD input into the Lake Ontario application partitions within the water column into a sorbed compartment, a dissolved compartment, and a bound compartment. This bound compartment is further described as non-settling organic matter. Three analogous compartments receive 2,3,7,8-TCDD in the bottom sediment layer. Several exchanges between the six compartments and contaminant losses within each compartment are modeled. For example, losses from water column compartments include downstream transport, volatilization and photolysis; the loss mechanism from the bottom sediment layer is sedimentation. Exchanges between compartments consider partitioning, diffusion, and sediment settling and resuspension.

This model requires substantial parameterization. Once values were selected for the Lake Ontario application, an evaluation was made on the impact of different levels of 2,3,7,8-TCDD input. Dynamic and steady state results were discussed. Principally examined for the steady state results were the concentrations of bottom sediment sorbed 2,3,7,8-TCDD and water column dissolved (soluble) phase 2,3,7,8-TCDD. A given level of steady 2,3,7,8-TCDD input, in kg/yr, resulted in a steady state concentration sorbed to bottom sediment and dissolved in the water column.

The premise in both the Lake Ontario steady state application of WASP4 and the water concentration algorithms in this assessment is that contaminants continue to enter water bodies over time unabated. Ground water entry of contaminants is not considered in either approach. Although a direct modeling comparison cannot be done, it is possible to slightly adjust the algorithms of this assessment to evaluate how results from a simple partitioning approach would compare with results from the complex fate and transport approach of the WASP4 steady state application.

Assume a surface water body is initially free of contaminant and at time t equals 1 day, a strongly hydrophobic contaminant, such as the dioxin-like compounds of this assessment, begins to enter a lake. Assuming the contaminant enters via soil particles, as in the approach of this assessment, it will then partition between those soil particles and surrounding water. The soil particles will slowly move toward the bottom of the lake at a rate described by a particle settling velocity. A settling velocity of 1 m/day is assumed in the Lake Ontario simulations. The amount of time it takes to settle to the bottom once entering from the surface equals the lake depth divided by this settling time. The Lake Ontario depth was 86 m. Therefore, it might take 86 days to settle. This, of course, neglects resuspension of settled particulates. With this simplistic framework, a steady state amount coming into the lake after 86 days is matched by an amount depositing onto the lake bottom; the amount of contaminant within the water column has reached steady state. Water concentrations can then be estimated assuming equilibrium partitioning.

Results of sediment and water column steady state concentrations are described for any loading of 2,3,7,8-TCDD in the WASP4 steady state application; those loadings are described in kg/yr. Loadings in kg/yr are easily correlated to a steady state water column amount, given the above analysis. For example, a loading of 1.0 kg/yr could translate to a within water column steady state amount of 0.24 kg (1.0 kg/yr * (86 d)/(365 d/yr)).

This steady water column amount partitions between suspended sediment and surrounding water. First, the total concentration (sorbed + soluble) simply equals:

$$C_{tot} = 1000 \frac{LD}{VOL} \qquad (7\text{-}5)$$

where:

C_{tot} = total concentration, mg/L
LD = water column steady state amount of contaminant, kg
VOL = lake volume, m^3
1000 = converts kg to mg and m^3 to L

The dissolved phase portion of total is given by:

$$C_{wat} = \frac{C_{tot}}{1 + (Kd_{ssed}\ TSS\ 10^{-6})} \qquad (7\text{-}6)$$

where:

C_{wat} = soluble phase water concentration, mg/L
C_{tot} = total concentration, mg/L
Kd_{ssed} = partition coefficient between suspended sediment and surrounding water, L/kg
= $Koc*OC_{ssed}$
Koc = organic carbon partition coefficient, L/kg
OC_{ssed} = fraction organic carbon of suspended sediments
TSS = total suspended sediments, mg/L
10^{-6} = converts mg/kg to mg/mg

Parameters in this equation for the Lake Ontario WASP4 application include VOL, Koc, OC_{ssed}, and TSS. Lake Ontario volume was given as 1.68 x 10^{12} m^3, Koc was estimated for the WASP4 application as 3,162,000, OC_{ssed} was estimated at 0.03, and TSS was estimated 1.2 mg/L. For a steady load of 1 kg/yr and a resulting LD of 0.24 kg, the steady state water column 2,3,7,8-TCDD concentration, using the simplistic approach described above, is estimated as 0.13 pg/L (ppq). The steady state water column concentration estimated by WASP4 given the same parameters and a load of 1 kg/yr is roughly 0.20 pg/L. An uncertainty analysis done with these WASP4 results concluded that 95% confidence limits around this prediction are 0.03 and 0.40 pg/L.

This would seem to imply that the simple partitioning approach used in this assessment compares favorably with the more complex fate and transport modeling assessment using WASP4, for Lake Ontario.

7.2.3. Estimating Fish Tissue Concentrations Based on Water Column Concentrations Rather than Bottom Sediment Concentrations

EPA prepared a document titled, "Interim Report on Data and Methods for Assessment of 2,3,7,8-Tetrachlorodibenzo-p-Dioxin Risks to Aquatic Life and Associated Wildlife" (EPA, 1993). That document provides details on the two key bioaccumulation parameters used for the methodologies of this document, the Biota Sediment Accumulation Factor, BSAF, used for the soil and stack emission source categories, and the Biota Suspended Solids Accumulation Factor, BSSAF, used for the effluent discharge source category. That document also discussed several water column based bioaccumulation factors, which are the focus of this section. A later publication prepared by the same group at EPA titled, “Great Lakes Water Quality Initiative Technical Support Document for the Procedure to Determine Bioaccumulation Factors” (EPA, 1995a), also describes water and sediment based bioaccumulation factors.

Before discussing these factors, it is noted that food chain modeling is a well developed alternate approach for estimating fish tissue concentrations of bioaccumulating contaminants (Thomann, 1989), which has also been applied to 2,3,7,8-TCDD (Parkerton, 1991). This approach is significantly more complex than the bioaccumulation/biotransfer approach of this methodology. It involves detailed site-specific characterizations, specifically the identification and transfer modeling between trophic levels of a food chain in a water body. Food chain modeling is a mechanistic approach, while the transfer approaches of this methodology are empirical. No judgement is rendered as to the relative merit of food chain models versus use of bioaccumulation coefficients. If detailed site-specific data is available, and given time and resources, assessors should consider food chain modeling for estimating fish tissue concentrations.

One water column measure which has been classically used is termed the Bioconcentration Factor, or BCF. Bioconcentration refers to the net accumulation of a chemical from exposure via water only, and BCFs are most often obtained in laboratory conditions. BCFs are defined as the ratio of the chemical concentration in organism (mass of chemical divided by wet weight of organism tissue) to that in water.

Another water column measure of the potential for a contaminant to accumulate in fish tissue is termed the Bioaccumulation Factor, or BAF. Bioaccumulation refers to the net accumulation of a chemical from exposure via food and sediments as well as water. Similar to the BCF, BAFs are defined as the ratio of the chemical concentration in the organism to that in the water.

For chemicals that are not strongly hydrophobic (unlike the dioxin-like compounds), the distinction between bioconcentration and bioaccumulation is small. Whereas food intake is generally a few percent of body weight per day, water passing over gills will equal hundreds to thousands times the organism weight per day, depending on species, activity, temperature, and other factors. Given this, the concentration of chemical in food must be 3 or more orders of magnitude greater than that in water before food can substantially contribute to uptake. EPA (1993) estimates that food intake becomes a critical contributor to the accumulation of contaminants in fish tissue for contaminants with log Kow of 5 and greater.

Since the dioxin-like compounds fall into this category, the remainder of this section will focus on the Bioaccumulation Factor. EPA (1993) defines steady-state lipid-based BAFs for total chemical in water and freely dissolved chemical in water (i.e., chemical which is truly in a dissolved phase and not bound to dissolved or suspended particulate organic materials) as:

$$ssBAF_l^t = \frac{C_{lipid}}{C_w^t} \qquad (7\text{-}7a)$$

$$ssBAF_l^d = \frac{C_{lipid}}{C_w^d} \qquad (7\text{-}7b)$$

where:

$ssBAF_l^t$ = steady-state lipid-based BAF for total chemical in water, unitless

C_{lipid} = the mass of contaminant in fish lipid tissue divided by the mass of fish lipid tissue, mg/kg

C_w^t = the mass of total contaminant in water divided by the mass of water in the water body, mg/kg (note: 1 L water nearly equals 1 kg, therefore, 1 mg/L can be assumed to equal 1 mg/kg)

$ssBAF_l^d$ = steady-state lipid-based BAF for freely dissolved chemical in water, unitless

C_w^d = the mass of freely dissolved contaminant in water divided by the mass of water in the water body, mg/kg

EPA (1993) then develops relationships between $ssBAF_l^d$ and $ssBAF_l^t$, based on dissolved and particulate organic carbon reservoirs in the water column, and partition coefficients for these reservoirs. This is meaningful in complex modeling where these two reservoirs of organic carbon can be accounted for, such as in the WASP4 model. Alternately, EPA (1993) defines the TBF_{oc}, a total binding factor to organic carbon, which empirically considers the reservoir of dissolved organic material (i.e., increases total binding and reduces truly dissolved phase concentrations) when such a reservoir is not explicitly modeled. The modeling frameworks in this assessment have only one compartment of suspended material to which contaminants sorb, with one associated organic carbon content. A second reservoir to which contaminants bind, the reservoir of dissolved organic material, is not modeled.

EPA (1993) developed a $ssBAF_l^t$ and a $ssBAF_l^d$ for lake trout, 2,3,7,8-TCDD, and for Lake Ontario 1987 contamination conditions. The WASP4 model was used to model three hypothetical loading conditions that might have resulted in fish tissue concentrations observed in 1987: steady state loading, a steady state loading followed by a 90% reduction in annual loads for 20 years (i.e., 1968-1987), a steady state loading followed by a 100% reduction (i.e., no loading) for 20 years. The BSAF for lake trout estimated for 1987 data is given in EPA (1990a) as 0.07. The BSAF is determined from measured bottom sediment concentrations and fish tissue concentrations; an assumption of historical loading is not necessary for BSAF development. Details of the Lake Ontario study, including initial modeling efforts with the WASP4 model can be found in EPA (1990a). Slight refinements to the WASP4 runs were later made (cited in EPA, 1993 as an unpublished report: Endicott, D.D., W.L. Richardson, T.F. Parkerton, and D.M. DiToro. 1990. A steady-state mass balance and bioaccumulation model for toxic chemicals in Lake Ontario: Report to the Lake Ontario Fate of Toxics Committee. U.S. EPA, Environmental Research Laboratory, Duluth, MN: 121 pp). The BAFs determined in these later runs will be tested using the models of this assessment.

In order to do this exercise, all critical model parameters used to develop the BAFs for this WASP4 modeling exercise will be used in the model framework of this assessment. The most critical parameter is the organic carbon partition coefficients, Koc, assumed for 2,3,7,8-TCDD. BAFs were determined assuming Koc of 10^7 and 10^8. Since the models of this assessment assume steady loading into water bodies, only the BAFs developed under "steady state" loading conditions will be used. As noted, the WASP4 model considers binding to more than one suspended compartment. The increased binding can be modeled using a TBF_{oc}, which was assumed to be 1.5 for Lake Ontario by Cook. For the models of this assessment, this factor will be applied to Koc - it effectively increases Koc by 50%. The concentration of suspended solids in Lake Ontario and used in the WASP4 modeling exercise was 1.2 mg/L. The other critical parameters are the fraction organic carbon contents of the suspended solids and the bottom sediments, OC_{ssed} and OC_{sed}, respectively. Assigned values to these parameters, based on Lake Ontario data, in the WASP4 exercise and in this exercise were 0.15 (15%) and 0.03 (3%), respectively.

Since the purpose of this exercise is to evaluate how the modeling approaches of this document perform using the BSAF or the alternate BAF approach, duplicating the source strength terms used in the WASP4 modeling exercise is not necessary. The pertinent question is, with a given source strength, how would both approaches predict fish tissue concentrations. For simplicity, the background demonstration scenario described in Chapter 5 will be adopted for use here. In this scenario, the soil within the watershed is assumed to at a uniform concentration. For the exercise here, a uniform concentration of 1.0 ppt for 2,3,7,8-TCDD will be assumed.

In summary, the parameters for this exercise including the steady state BAFs are:

Test 1: Koc = $1.5*10^{7}$; $ssBAF_{l}^{d} = 1.9x10^{6}$; $ssBAF_{l}^{t} = 5.16x10^{5}$; BSAF = 0.07
Test 2: Koc = $1.5*10^{8}$; $ssBAF_{l}^{d} = 1.9x10^{7}$; $ssBAF_{l}^{t} = 6.78x10^{5}$; BSAF = 0.07

The 1.5 in the Kocs was the TBF_{oc} noted above. The BAFs specific to each Koc were the ones developed also specific to those Koc in the WASP4 modeling exercises. For both tests: soil concentration of 2,3,7,8-TCDD = 1.0 ng/kg (ppt), total suspended solids (TSS) = 1.2 mg/L, the organic carbon content of suspended sediments (OC_{ssed}) = 0.15, and the organic carbon content of bottom sediments (OC_{sed}) = 0.03. Whole fish tissue concentrations are estimated as $C_{lipid} * f_{lipid}$, where f_{lipid} is 0.07.

The whole fish tissue concentration for the BSAF approach in Test 1 was estimated to be 0.61 ppt. Using the $ssBAF_{l}^{t}$ and $ssBAF_{l}^{d}$, the whole fish tissue concentrations were estimated very nearly to be the same at 0.867 ppt for $ssBAF_{l}^{t}$ and 0.863 ppt for $ssBAF_{l}^{d}$. The test results did not change substantially for Test 2. The BSAF approach led to a fish tissue concentration of 0.62 ppt, and the concentration was identical for BAFs at 0.869 ppt.

While it appears that the water column based approaches estimate fish tissue concentrations identical to each other and very close to estimates made based on bottom sediment concentrations, in fact the performance of the models differ when parameters are changed in these tests. More incoming 2,3,7,8-TCDD can be modeled to remain in the water column with an increase in the reservoir of total suspended solids, the TSS parameter initialized in above tests at 1.2 mg/L. Continuing with Test 1 parameters above, increasing TSS from 1.2 mg/L to 10 mg/L has the following changes to fish tissue concentrations: 0.54 ppt for the BSAF test, 4.85 ppt for the $ssBAF_{lt}$ test and 0.76 ppt for the $ssBAF_{l}^{d}$ test. Decreasing the organic carbon content of the suspended solids will have the effect of reducing the amount of incoming 2,3,7,8-TCDD simulated to remain in the water column, while increasing the amount modeled to reside in bottom sediments (because a mass balance of 2,3,7,8-TCDD is maintained), and also increases the dissolved phase concentration. Changing the TSS back to 1.2 mg/L and reducing the organic carbon content of suspended solids from 0.15 to 0.05 results in the following changes to fish concentrations: 0.62 ppt for the BSAF test, 0.45 ppt for the $ssBAF_l^t$ test and 0.88 ppt for the $ssBAF_l^d$ test. These two tests have demonstrated the variability in fish tissue concentrations when key water column parameters are altered. Fish concentrations would also differ if the key bottom sediment parameter, the organic carbon content of bottom sediments, was different. Returning to original Test 1 parameters and reducing the organic carbon content of bottom sediments from 0.03 to 0.01 results in the following changes to fish concentrations: 1.73 ppt for the BSAF test, 2.45 ppt for the $ssBAF_l^t$ test and 2.44 ppt for the $ssBAF_l^d$ test.

The predictions for all tests might be considered reasonably close, given the uncertainties in the bioaccumulation and water modeling parameters. The one test described above where the BSAF and BAF approaches led to the most differences was the one which increased suspended material contents from 1.2 mg/L to 10 mg/L. In that case, nearly a ten-fold difference was noted in fish concentrations with the $ssBAF_l^t$ as compared to the BSAF or the $ssBAF_l^d$.

An important consideration in using the water column based approaches is that the BAFs developed by Cook (or that could be developed otherwise) are based on modeled rather than measured water column concentrations, and measured lake trout tissue concentrations. In that sense, the BAFs were calibrated for Lake Ontario conditions and specific to the WASP4 modeling exercise. Therefore, using these BAFs in the modeling framework of this assessment is, strictly speaking, invalid. Further, the values of the BAFs varied depending on the assumptions on historical loadings into Lake Ontario. As noted above, three loading conditions were tested. The steady state BAFs were given above. For the 20 year - 90% reduction tests, the following BAFs were determined: BAF_l^d was 3.03×10^6 for Koc = 10^7 and 2.86×10^7 for Koc = 10^8, and BAF_l^t was 8.26×10^5 for Koc = 10^7 and 1.02×10^6 for Koc = 10^8. For the 20 year - 100% reduction tests, the following BAFs were determined: BAF_l^d was 3.86×10^6 for Koc = 10^7 and 3.40×10^7 for Koc = 10^8, and BAF_l^t was 1.05×10^6 for Koc = 10^7 and 1.21×10^6 for Koc = 10^8. The BSAF developed for lake trout for Lake Ontario was developed using measurements of both fish tissue and bottom sediment concentrations.

Both the BSAF and BAF are most appropriately developed using site specific data (coupled with a modeling exercise for BAF). Inasmuch as that can be impractical or difficult for many sites, efforts are underway to determine the general applicability of BSAFs and BAFs determined for one site to other sites. EPA (1993) proposes that BAF_ls for different congeners can be roughly estimated as the BAF_l for 2,3,7,8-TCDD multiplied by the ratio of the BSAF for the congener and the BSAF for 2,3,7,8-TCDD. Such an estimate will incorporate differences in uptake, metabolism and chemical partitioning but not differences caused by chemical loss processes such as volatilization and photolysis. This approach for estimating BAF_ls for other congeners does allow for some generality since sediment and fish tissue data for other congeners and water bodies is available.

Another bioaccumulation term discussed in one literature article for dioxin is termed the Regulatory Bioaccumulation Multiplier, or RBM (Sherman, et al., 1992). Multiplication of this term and a "nominal water concentration" estimates a 3% lipid fish concentration. A nominal water concentration equals an amount of a contaminant, 2,3,7,8-TCDD in this application, added or entering a water body over time, divided by a flow volume over that same time. Assuming a fish lipid content of 3%, an RBM of 5000 was recommended based on examination of laboratory flow through data, simulated field data, and actual field data (EPA's Lake Ontario study and data downstream of pulp and paper mills). Dividing the 5000 by 0.03 gives $1.67*10^5$, and this number is now analogous to the $ssBAF_l^t$ developed by EPA (1993) described above, and in the same range as the $5.2\text{-}6.8*10^5$ range for $ssBAF_l^t$.

7.2.4. Other Modeling Approaches and Considerations for Air Concentrations Resulting from Soil Volatilization

Volatilization was modeled for the soil contamination source category, using an approach given in Hwang, et al. (1986), developed for PCB flux from soils. Another model often used to estimate volatilization from soil was presented by Jury and coworkers in a series of papers in the early 1980s (Jury, et al., 1983, 1984a,b). The full solution to Jury’s model is complex and not amenable to spreadsheet programming structure. It was available for use in this exercise in an EPA model known as EMSOFT (EPA, 1997a). There is a steady state, simplified solution to the Jury model which is used in EPA’s Superfund Soil Screening Methodology (EPA, 1996). Both of these Jury approaches account for movement of the organic contaminant in the vapor phase via diffusion and the dissolved phase via solute movement, and they also account for changes in volatilization rate over time: volatilization decreases with time after an initially assumed soil concentration in the surface soil depletes and deeper residues volatilize to a lesser extent (the Hwang model also accounts for a decrease in the volatilization rate over time).

If one assumes that the contaminant moves through the soil column in only the vapor phase, a simplification of the fundamental equations used by Jury offers another option for modeling soil volatilization. The steady-state vapor diffusion equation was used by Farmer, et al. (1980a) in modeling hexachlorobenzene vapor diffusion in a laboratory soil column, and also by Johnson and Lindberg (1995) in modeling mercury volatilization from soil. It will be applied here to 2,3,7,8-TCDD.

The two Jury models and the vapor phase diffusion model are compared with the Hwang approach, as applied in this document for 2,3,7,8-TCDD. Following now are more complete descriptions of the Hwang model, the Jury models and the vapor diffusion model. The parameters used for all models are shown in Table 1.

I. Hwang Model: Farmer, et al. (1980b) applied a basic diffusion equation to the problem of soil volatilization of pesticides. This diffusion equation does not consider movement of the contaminant with soil water or degradation in the soil column:

$$\frac{\partial^2 C_T}{\partial z^2} - \frac{1}{D}\frac{\partial C_T}{\partial t} = 0 \qquad (7\text{-}8)$$

where:

C_T = mass of chemical per unit soil volume, g/cm^3
z = soil depth, cm
D = apparent diffusion coefficient for contaminant in soil, cm^2/sec
t = time, sec

Hwang, et al. (1986) redefined this basic equation to consider instead the gas phase, C_G, which they assumed was in local equilibrium with soil concentration, Cs. Their steady state equation was:

$$\frac{\partial^2 C_G}{\partial z^2} - [1 + \frac{BD\ Kd}{\Phi\ K_H}]\frac{1}{Dei}\frac{\partial C_G}{\partial t} = 0 \qquad (7\text{-}9)$$

where:

C_G = concentration of chemical in the gas phase, g/cm^3
BD = soil bulk density, g/cm^3

Kd = soil/water partition coefficient, cm^3/g
= Koc * foc
Koc = organic carbon partition coefficient, cm^3/g
foc = fraction organic carbon in soil, unitless
ϕ = soil porosity, cm^3/cm^3, or unitless
K_H = dimensionless Henry's Constant
= H/RT (= 41 H, substituting R and T below)
H = Henry's Constant, atm-m^3/mol
R = universal gas constant, $8.21*10^{-5}$ atm-m^3/mol-°K
T = standard temperature, 20 °K
Dei = effective diffusivity of contaminant in soil, cm^2/sec
z = distance from surface soil, cm
t = time, sec

Hwang, et al.(1986) assumed that PCBs in soil were in equilibrium between the sorbed and the gaseous phase as follows:

$$C_G = \frac{K_H\ Cs}{Kd} \tag{7-10}$$

where:

C_G = concentration of chemical in the gas phase, g/cm^3
K_H = dimensionless Henry's Constant (= 41H, as defined above)
Cs = soil concentration, g/g (unitless form here for units consistency)
Kd = soil/water partition coefficient, cm^3/g (= foc*Koc, as defined above)

They also assumed that the effective diffusion was related to the diffusion coefficient of the contaminant in air as:

$$Dei = D_G^{air}\ \Phi^{1/3} \tag{7-11}$$

where:

Dei = effective diffusion coefficient, cm^2/sec
D_g^{air} = diffusion coefficient for contaminant in air, cm^2/sec
ϕ = soil porosity, cm^3/cm^3, or unitless

Hwang, et al. (1986) solved this equation for two cases: when the contaminated soil was bare to the atmosphere and where the contaminated soil was covered with a layer of clean soil. Obviously, the option chosen for this methodology, and for this examination of alternate volatilization methods, was the bare soil contamination. Their initial and boundary conditions were: 1) the concentration of the contaminant in the air at the soil surface is 0 continually, and 2) the concentration in the soil air just below the surface and at an infinite depth remains constant and is a function of the soil concentration and contaminant properties - this function is given as Equation (7-10) above.

The flux rate that occurs after a time period t is given as:

$$J_s\ (t) = \frac{(\Phi)\ (D_{ei})\ (Cs)\ (H)\ (41)\ (10^{-6})}{Kds\ [\ (\pi)\ (I)\ (t)\ ]^{0.5}} \tag{7-12}$$

where:

J_s = average volatilization flux rate of contaminant from soil, g/cm^2-s
ϕ = soil porosity, cm^3/cm^3, unitless
D_{ei} = effective diffusivity of contaminant in air, cm^2/s
Cs = contaminant concentration in soil, ppm or mg/kg
H = Henry's Constant of contaminant, atm-m^3/mol
Kds = soil/water partition coefficient, cm^3/g
t = time, sec
I = interim undefined term for calculation, cm^2/s
= $[\ D_{ei}\ \phi\ ] / [\ \phi + P_{soil}\ (1-\phi)\ [Kds/(41\ H)]\ ]$
P_{soil} = particle bulk density of soil, g/cm^3

The average flux rate during the exposure period is given as 2 * J_s(ED), where ED is the exposure duration in seconds.

It is noted in Hwang, et al. (1986) that this procedure would tend to overestimate emissions and resulting exposures in situations involving small spills which would not involve deep contamination. It is also noted that the average flux rate is inversely proportional to the square root of the duration of exposure - the longer the duration of exposure, the lower will be the average flux rate. Whereas this solution assumes an unlimited reservoir of contaminant, it is an unsteady state solution (unlike most other solution strategies) and is essentially an average flux rate over an amount of time defined by the exposure duration. Inherent in the solution was the consideration that residues dissipate by volatilization at the surface layers, resulting in contaminants diffusing upwards from deeper soil layers over time. With this longer path of diffusion, volatilized amounts decrease, and hence the average flux over time also decreases.

The parameters required for the Hwang model are provided in Table 7-3, and these include the initial soil concentration of 2,3,7,8-TCDD, C_0, the soil parameters P_{soil}, foc, ϕ, and BD, the exposure duration (or total time during which volatilization occurs starting from time t = 0 at the initial soil concentration, C_0), and the chemical-specific parameters D_g^{air}, Koc, and H.

<u>II. Jury Model:</u> This model assumes: 1) uniform soil properties throughout the soil column to an infinite depth, 2) there is a stagnant air boundary layer at the soil surface across which diffusion occurs and the chemical concentration at the top of this boundary layer is zero, 3) linear equilibrium liquid-solid and liquid-air partitioning is valid, and 4) degradation follows first-order kinetics. With these conditions, the mass conservation equation is:

$$\frac{\partial C_T}{\partial t} + \frac{\partial J_s}{\partial z} + \mu C_T = 0 \qquad (7\text{-}13)$$

where:

C_T = mass of chemical per unit soil volume, g/cm^3
J_s = chemical mass flux per unit soil are per unit time, g/cm^2-sec
μ = net degradation rate, 1/sec
t = time, sec
z = soil depth, cm

The volumetric total soil concentration, C_T, is given as:

$$C_T = BD\ Cs + \theta\ C_L + a\ C_G \tag{7-14}$$

where:

C_T = mass of chemical per unit soil volume, g/cm^3
Cs = concentration of chemical on soil, g/g (expressed in unitless form here for units consistency)
BD = soil bulk density, g/cm^3
C_L = concentration of chemical in the liquid phase, g/cm^3
θ = volumetric soil water content, cm^3/cm^3, or unitless
C_G = concentration of chemical in the gas phase, g/cm^3
a = volumetric soil air content, cm^3/cm^3, or unitless

The terms BD, θ, and a are in front of the concentration terms to convert them to volumetric units, to be consistent with the volumetric definition of C_T. It should be noted that for 2,3,7,8-TCDD, which is very tightly sorbed to soil, C_G and C_L become very small and C_T can be calculated as Cs BD. The mass flux, J_s, can be written as:

$$J_s = -D_G \frac{\partial C_G}{\partial z} - D_L \frac{\partial C_L}{\partial z} + J_w C_L \tag{7-15}$$

where:

J_s = chemical mass flux per unit soil are per unit time, g/cm^2-sec
D_G = soil-gas diffusion coefficient, cm^2/sec
C_G = concentration of chemical in the gas phase, g/cm^3
D_L = soil-liquid diffusion coefficient, cm^2/sec
C_L = concentration of chemical in the liquid phase, g/cm^3
J_w = water flux, cm/sec
z = soil depth, cm

D_G and D_L are given by appropriate forms of the Millington-Quirk equations:

$$D_G = \frac{a^{10/3}}{\Phi^2} D_G^{air} \tag{7-16a}$$

$$D_L = \frac{\theta^{10/3}}{\Phi^2} D_L^{water} \tag{7-16b}$$

where:

D_G = soil-gas diffusion coefficient, cm^2/sec
a = volumetric soil air content, cm^3/cm^3, or unitless
ϕ = soil porosity, cm^3/cm^3, or unitless
D_g^{air} = chemical gaseous diffusion coefficient in air, cm^2/sec
D_L = soil-liquid diffusion coefficient, cm^2/sec
D_L^{water} = chemical liquid diffusion coefficient in water, cm^2/sec
θ = volumetric soil water content, cm^3/cm^3, or unitless

Soil porosity is defined as the amount of void space in the soil, and can be calculated as, 1 - (soil bulk density)/(soil particle density). A common value used for soil bulk density, in the absence of site-specific data, is 1.5 g/cm^3. Soil particle density is not site-specific, rather it is an inherent soil property. It has been estimated to be between 2.6 and 2.7 g/cm^3, and is often assigned a value of 2.65 g/cm^3. Therefore, soil porosity is calculated at 0.434 (ie., 1 - 1.5/2.65). This porosity is comprised of air and water; that is, soil porosity, ϕ = volumetric soil water content, θ + volumetric soil air content, a, using the terms defined above. For a soil that is sometimes wet and sometimes dry, an average soil water content would range between field capacity, around 0.30 for typical soils, and wilting point, around 0.15. This exercise will assume a water content of 0.23 and a porosity of 0.43, leaving air content to be calculated at 0.20.

This solution requires the partitioning of the chemical into sorbed (Cs), liquid (Cl) , and gas (Cg) phases. The soil concentration is initially given, and liquid and gas phases are then solved as:

$$C_L = \frac{Cs}{Kds} \tag{7-17}$$

where:

C_L = liquid phase concentration, g/cm^3 soil water
Cs = soil concentration, g/g (unitless form here for units consistency)
Kds = soil/water partition coefficient, cm^3/g (= Koc*foc, as above)
C_G = concentration of chemical in the gas phase, g/cm^3
K_H = dimensionless Henry's Constant (= 41 H, as above)

Like the Hwang model, initial and boundary conditions are required for the solution to this model. The key initial condition is that the total concentration is constant to some depth, and that below this depth, the concentration is zero. The upper boundary condition is represented by a stagnant boundary layer condition, and the lower boundary conditions is that the total concentration is 0 at infinite depth. With these initial and boundary conditions, Equation (7-13) is solved using the Laplace transform method. This is not amenable to spreadsheet calculations. The EPA model, EMSOFT, was coded in fortran using original code supplied by Jury for his equations, and it performs this transformation. EMSOFT calculates water flux under user-specified water flux conditions, entering a positive flux amount (meaning a net leaching rate at that amount), 0 (no net leaching or evapotranspiration), or a negative flux amount (meaning a net evapotransiration rate) in units of cm/day. For this exercise, the solution at water flux = 0 will be assumed.

The parameters required for EMSOFT are provided in Table 7-3, and these include the initial soil concentration of 2,3,7,8-TCDD, C_0, the soil parameters foc, θ, ϕ, a, and BD, the water flux assumption, the depth of constant soil concentration, the exposure duration (or total time during which volatilization occurs starting from time t = 0 at the initial soil concentration, C_0), the boundary layer thickness, and the chemical-specific parameters D_g^{air}, D_l^{water}, Koc, H, and the 2,3,7,8-TCDD soil half-life. Of various output options in EMSOFT, average volatilization rate was selected.

$$C_G = K_H C_L \tag{7-18}$$

III. Steady-State Solution to the Jury Model: This steady-state, simplified solution to the Jury model was used in Superfund's soil screening model. The simplifying assumptions (in addition to other assumptions of the Jury approach) which allowed for this solution were: 1) there is no stagnant boundary layer, 2) there is no water evapotranspiration or leaching (equivalent to the selection of 0 water flux in the full Jury model described above), 3) the chemical is at a uniform concentration from the soil surface until depth d_z, and 4) there is no degradation of the chemical over time. The volatilization flux rate, J_s, at any given time after t=0 when the uniform soil concentration is C_{T0}, is given by:

$$J_s\ (t) \ = \ C_{T0}\ \left(\frac{D_E}{\pi t} \right)^{1/2} \left(1 - \exp\left(\frac{-d_z^2}{4 D_E\ t} \right) \right) \tag{7-19}$$

where:

J_s = volatilization flux, g/cm^2-sec

C_{T0} = initial total concentration on a volumetric basis, g/cm^3

D_E = effective soil diffusion coefficient, cm^2/sec

d_z = depth of uniform soil concentration at t=0

t = time, sec

Equation (7-19) was derived specifically for the case where there is a finite reservoir of contaminant to volatilize; i.e., where the depth of contamination, d_z, is meaningful. At infinite depth, this term drops out. With a combination of large enough d_z and small enough D_E, the exponential term quickly approaches 0, so the parenthetical approaches 1 and can be neglected in the solution. Mayer, et al. (1974) suggests that the infinite reservoir solution is violated for a finite reservoir when t (time) exceeds $(d_z^2)/(14.4 * D_E)$. With dioxin parameters, D_E is calculated to be $2*10^{-10}$. Therefore, time t calculates out to over 1000 years with d_z equal to 10 cm before the infinite solution becomes violated. Needless to say, the infinite reservoir steady state solution can be used for dioxin, and the exponential term can be neglected. The total soil concentration, or concentration expressed as mass divided by a volume of (soil+soil pore space), is required for this solution, rather than just the soil concentration expressed as mass of contaminant divided by mass of soil to which it is adsorbed. As discussed above, total soil concentration is the sum of the concentrations in soil, soil air, and soil water, and for 2,3,7,8-TCDD and similarly very tightly sorbed contaminants, the total volumetric soil concentration can be estimated as BD * Cs. The effective soil diffusion is given by:

$$D_E = \frac{D_G^{air}\ K_H\ a^{10/3}/\Phi^2 + D_L^{water}\ \theta^{10/3}/\Phi^2}{BD\ Kds + \theta + aK_H} \qquad (7\text{-}20)$$

where:

D_E	=	effective soil diffusion coefficient, cm^2/sec
D_g^{air}	=	chemical air-gas diffusion coefficient, cm^2/sec
D_l^{water}	=	chemical liquid diffusion coefficient in water, cm^2/sec
θ	=	volumetric water content, cm^3/cm^3, or unitless
a	=	soil air content, cm^3/cm^3, or unitless
ϕ	=	soil porosity, cm^3/cm^3, or unitless
BD	=	soil bulk density, g/cm^3
Kd	=	soil/water partition coefficient, cm^3/g (= Koc * foc, as above)
K_H	=	dimensionless form of the Henry's Constant (= 41H, as above)

As can be seen in this formulation, Equation (7-19), the maximum volatilization flux decreases as time increases. Again, the Jury algorithm considers the depletion of the surface residues as a function of time. The Superfund Soil Screening Guidance document (EPA, 1996) suggests that this formulation, Equation (7-19), be run several times over the exposure duration in order to determine the average flux. However, assuming the infinite reservoir solution which neglects the exponential term in Equation (7-19) (and like the Hwang model), the average flux can more easily be calculated as, 2 * J_s (t), where t is the full duration of volatilization flux. That is what is assumed for this exercise.

The parameters required for this simplified solution to the Jury model are provided in Table 7-3, and these include the initial soil concentration of 2,3,7,8-TCDD, C_0 , the soil parameters foc, θ, ϕ, a, and BD, the exposure duration, and the chemical-specific parameters D_g^{air}, D_l^{water}, Koc, and H.

IV. State-State, Infinite Reservoir, Vapor-Phase Diffusion Only: If the liquid phase in the mass flux Equation (7-15) above is neglected, than the flux through soil can be very simply calculated as:

$$J_s = -D_G \frac{C_{G1} - C_{G0}}{d_z} \qquad (7\text{-}21)$$

where:

J_s = chemical mass flux per unit soil are per unit time, g/cm^2-sec
D_G = effective soil diffusion coefficient, cm^2/sec
= $(a^{10/3}/\phi^2)\ D_g^{air}$; a, ϕ, and D_g^{air} defined as above
C_{G1} = concentration of the contaminant in soil air-filled pore space, g/cm^3
C_{G0} = concentration of the contaminant in air at the soil-air interface, g/cm^3
d_z = depth over which a constant concentration is assumed, cm

Maximum vapor phase diffusion occurs when C_{G0}, the concentration of the contaminant in air at the soil-air interface (essentially just above the soil surface), is set to 0.0, which is done for this solution. This assumes, essentially, that wind is sufficiently high to cause a 0 concentration directly above the soil. The concentration in air-filled pore space, C_{G1}, is simply solved as, (K_H Cs)/Kds, as described above. The depth of the soil column will be assumed to be 10 cm in this example.

The parameters required for this simplified vapor diffusion solution are provided in Table 1, and these include the initial soil concentration of 2,3,7,8-TCDD, C_0, the soil parameters foc, ϕ, a, and BD, and the chemical-specific parameters D_g^{air}, Koc, and H.

V. Results of Alternate Soil Volatilization Model Testing: The results of this simple test are shown in Table 7-4. This model comparison test showed that the Hwang model predicted an average flux over 30 years roughly four times higher than the average flux predicted by the full Jury model, and about three times higher than the simplified Jury model used in the Superfund Soil Screening methodology. The close match between the full Jury model coded in Fortran in EMSOFT and the simplified Jury solution coded into the spreadsheet was evidence that both models were correctly coded and used (or that they were both incorrect in the same way, which is unlikely). The exact reason for this three- to four-fold difference in the Jury versus the Hwang models was not investigated, and could lie in differences in assumed boundary conditions (Hwang, et al. (1986) discusses differences in boundary conditions between his and Jury's models). In any case, it is judged that both models predict comparable volatilization fluxes. On the other hand, the vapor diffusion model predicted volatilization rates that were 100 times less than the Jury models and about 250 times lower than the Hwang models. The reason for this discrepancy could not be ascertained.

The Jury model was run altering the boundary layer assumption and the half-life assumption. The simplified Jury solution assumes no boundary layer to offer resistence to volatilization. That was one key reason that the simplified model predicted higher concentrations than the full Jury model. When the boundary layer assumption was reduced from 0.5 cm to 0.01 cm, the volatilization rate predicted by EMSOFT increased slightly from $2.8*10^{-19}$ to $3.0*10^{-19}$ g/cm^2-sec. Another simplification of the Soil Screening Methodology solution was that no soil degradation was assumed. The full Jury model in EMSOFT does allow for consideration of soil degradation. When the half-life was assigned a value of 25 years, which was what has been assumed for dioxins which had deposited in soils from distant sources in this document (depositing by air from incinerators or overland by erosion from contaminated soil sites), the average volatilization dropped slightly from $2.8*10^{-19}$ to $2.2*10^{-19}$ g/cm^2-sec.

These differences between the Hwang and Jury models are insignificant considering that the compounds modeled by this methodology - the dioxins, furans, and PCBs, are all relatively tightly bound and resist degradation in soil, so that losses in the 10^{-19} g/cm^2-sec range represent a minisicule part of the entire soil reservoir.

VI. Alternate Approaches for Dispersion of Soil-Emitted Dioxins: Near-field and far-field dispersion models are used to estimate air concentrations resulting from soil emissions, including volatilization and wind erosion, for the soil contamination source category. The near-field model can be used to estimate concentrations which occur on-site whereas the far-field model can be used to estimate off-site air concentrations. An alternate approach to estimating on-site dispersion given a volatilization flux is the "box-model" approach. This simple approach can be visualized as follows: air above soil is contained within a structure which has two walls, say a north and south wall, and a ceiling - wind blows through the building in an east-west direction mixing the volatilized flux. This is expressed mathematically as:

$$C_{air} = \frac{FLUX\ AREA\ 10^6}{b\ U_{mix}\ Z} \qquad (7\text{-}22)$$

where:

C_{air} = total concentration of contaminant in air, µg/m^3
FLUX = average volatilization + wind erosion flux rate of contaminant from soil, g/cm^2-sec
AREA = area over which flux occurs, cm^2
b = side length perpendicular to wind direction, m
U_{mix} = mean annual wind speed corresponding to mixing zone height, m/sec; estimated as ½*Um, where Um is average wind speed
z = mixing zone height, m
10^6 = converts g to µg

Before testing the box-model equation, results for the approach used in this assessment are summarized. The key factors impacting air concentration calculations for the soil contamination source category include characteristics of the contaminant (Henry's Constant, etc.), the duration of exposure, the area over which contamination occurs, and whether the near field or far field dispersion algorithms are used. For the demonstration of the soil contamination scenario, Scenario 3, the contaminated soil area was 40,000 m^2 (10 acres). The exposure duration was 30 years. The flux of 2,3,7,8-TCDD was 1.11x10^{-18} g/cm^2-sec. The air concentration estimated for Scenario 3 where the exposure site was 150 meters from the site of soil contamination was 0.0043 pg/m^3. This calculation used the far field dispersion algorithm. When the flux rate is input into the near field algorithms, the air concentrations is a little over ten times higher at 0.045 pg/m^3.

The values used to evaluate the box model approach were the fluxes, as given above, the mixing zone wind speed, 2 m/sec, which is half the average wind speed assumed in this assessment, the areas noted above, the side length, estimated as the square root of the area, and a mixing zone height estimated initially at 2 m. The box-model air concentration is estimated at 0.55 pg/m^3. This is 10 times higher than the near-field dispersion modeling and 100 times higher than the far-field solution.

An uncertain parameter for both modeling approaches is the area of soil contamination. The mixing zone height for the box model is also a parameter of uncertainty. Users of the box model approach have often assumed a conservative 2 m height approximating the height of exposed individuals. However, others have claimed this is far too low a mixing height, suggesting 10 meters or even an atmospheric height closer to 100 meters. Higher mixing zone heights would have brought the box model estimations more in line with estimations made in this assessment. The closest analogous parameter in the dispersion model to the mixing zone height is the height of exposed individual, which is more unambiguously the breathing zone height of 2 m.

One key assumption concerning the exposure site air concentrations resulting from a distant area of soil contamination should be questioned. The current approach assumes that air-borne contaminates originate at the site of contamination and are transported to the site of exposure. On the other hand, this assessment also assumes that exposure site soil becomes contaminated over time due to erosion. It is at least plausible that volatilization and wind erosion from soils other than the area of elevated contamination would contribute to air-borne contamination, and concentrations to which individuals are exposed to at sites of exposure near sites of contamination.

This was tested by using the near field algorithms and assuming soil concentrations predicted to occur at the exposure site. In more detail, the soil contamination demonstration scenario included a 10 ha field at 1 ppb 150 m from the exposure site, also at 10 ha. The soil concentrations estimated to occur at the exposure site were 0.39 ppb for a 2-cm no-till depth and 0.06 ppb for a 20 cm tilled depth. The near field algorithms for volatilization, wind erosion, and dispersion were run starting with these concentrations, and resulting concentrations were compared with those estimated to occur only from volatilization and wind erosion from the contaminated site followed by transport to the exposure site. The air concentration estimated to occur from untilled soil is about 4.3 times higher than that estimated to occur from the off-site area and transported; the air concentration estimated to occur from tilled soil is 25% less than estimated to occur from volatilization and transport.

This might imply that exposure site air concentrations are being underestimated if air concentrations at the site of exposure are assumed to only originate at the site of contamination, and not also at the site of exposure, or even from other areas. This exercise implies that the underestimation might be less than a factor of 5.0. Of course, this conclusion is contingent on the off-site impact algorithms which have estimated that a 0.39 or a 0.07 ppb soil concentration will result 150 meters from an area whose concentration is 1.00 ppb.

7.2.5. Alternate Models for Estimating Plant Concentrations from Soil Concentrations

The models of this assessment separate above and below ground vegetation for estimating concentrations. Root concentrations (roots are below ground vegetation) are a function of soil water concentrations and a Root Concentration Factor, RCF. Above ground vegetation, which in this assessment include above ground fruits and vegetables, pasture grass, and cattle feed, are modeled as a function of vapor phase transfers and wet plus dry particle depositions. This section examines one alternate approach for above ground vegetation; alternate approaches for below ground vegetation could not be found.

One approach to modeling plant concentrations would be with passive uptake via evapotranspiration. The assumption here is that soluble phase contaminants move passively with transpiring water. This approach has been applied for contaminants which are soluble in water. However, nearly all the evidence suggests that this would not be appropriate for the dioxin-like compounds. Specifically, the evidence suggests that residues do not translocate to within portions of either above or below ground vegetation. Such would be case for soluble contaminants moving passively with transpiring water. This conventional wisdom was, however, challenged with recent experiments by Hulster, et al. (1994) on vegetation of the cucumber family. Their results were most striking for zucchini, which showed uniform plant concentrations from inner to outer portions of the zucchini fruit, and the highest whole fruit concentrations they had ever measured, despite careful experimental conditions which physically isolated the fruit from the soil. Pumpkins also showed high plant contamination, with more expected plant concentrations measured for the cucumber. Assuming the vegetation of this assessment - fruit/vegetables for human consumption and vegetation of the beef/dairy food chain - do not behave as in the Hulster, et al. (1994) experiments, than translocation to inner plant parts is not expected.

The specific issue of uptake and translocation via transpiration was investigated using soybean and corn plants grown hydroponically in carefully constructed growth chambers (McCrady, et al., 1990). Roots and the hydroponic growth solution were separated from the shoots and leaves of these plants using two separate chambers, one inverted over the other. Separate air-flow systems for each chamber included traps for volatile organics. Mass balance on the tritiated TCDD experiments was able to recover 98% in the soybean experiment and 86% for the corn experiment. Most of the recovered material was found in the roots; 75% for soybeans and 67% for corn, with the second highest recovery was on the inside surface of the root chamber, around 15% for both experiments. Recovered TCDD was also found, in order of decreasing percentage, in the growth solution, root chamber air, shoot chamber air, and shoots. The recovery from the shoots was negligible at 0.004% and 0.001% of the total TCDD for the soybean and corn, respectively. McCrady, et al. (1990) concluded that transpiration stream transport of 2,3,7,8-TCDD to plant shoots is an insignificant mechanism of plant contamination, and that volatilization of TCDD is an important transport mechanism that can result in significant quantities of airborne TCDD being absorbed by plant shoots.

Briggs, et al. (1982) provide another way to evaluate the translocation of contaminants from roots to above ground vegetation. Experiments with barley roots in growth solution led to the development of an empirical parameter describing the efficiency of transport of organic chemicals to plant shoots from root uptake. This parameter is called the Transpiration Stream Concentration Factor (TSCF) and is defined as (concentration in transpiration stream)/(concentration in external solution). The empirical formula presented for this factor is:

$$TSCF \;=\; 0.784\; e^{-[\log Kow \;-\; 1.78\,]^2\,/\,2.44} \qquad (7\text{-}23)$$

Given a log Kow for 2,3,7,8-TCDD of 6.8, TSCF is solved for as roughly 2 * 10^{-5}. Assuming that the concentration of external solution concentration for the experimental conditions of Briggs' experiments is equivalent to the concentration in soil water in a field situation, then the TSCF for 2,3,7,8-TCDD implies that the transpiration stream water of a plant is over 5 orders of magnitude lower than the soil water concentration. Like McCrady's experiments, this also shows the insignificance of translocation of residues from roots to shoots.

The one approach that was found that might have been used in the place of the algorithms for above ground vegetation, is simpler and more general in nature. It was developed from field data on above ground vegetation concentrations correlated to soil concentrations of contaminants and the octanol water partition coefficient (Travis and Arms, 1988). This correlation led to an empirical bioconcentration factor for vegetation, B_v, regressed against the contaminant log Kow, and defined by the authors as the concentration in above ground plant parts divided by the concentration in soil:

$$\log B_v \;=\; 1.588 \;-\; 0.578\;\log K_{ow} \qquad n \;=\; 29,\; r \;=\; 0.73 \qquad (7\text{-}24)$$

With 2,3,7,8-TCDD log Kow equal to 6.8, the B_v translates to a value of 0.0041. Note that this B_v is defined identically to the plant:soil contaminant concentration ratios that are discussed in Section 7.3.10 below which compares the model's estimations of these ratios with those found under experimental conditions. As discussed in that section, plant:soil ratios calculated using the soil contamination algorithms were in the range of 10^{-5} for bulky vegetables and 10^{-3} for leafy vegetation. It is not clear how to compare the B_v of 0.0041 to these ratios without retrieving the studies which Travis and Arms (1988) used, although this value is clearly higher than the fruit/vegetable ratio and consistent with the grass/feed ratios. The studies used by Travis and Arms were not retrieved. An examination of the chemicals used by Travis and Arms show that 25 of 29 used are pesticides, which suggests that plant concentrations may be those of agricultural crops, which might make it a closer kin to bulky vegetables rather than leafy vegetation. If so, a comparison of the above-ground vegetable 10^{-5} ratio with this 0.0056 ratio would be appropriate. An examination of the chemicals also reveals that 10 of the 29 are moderately to very soluble (log Kow less than 4.00), while others are similarly insoluble as the dioxin-like compounds (including DDT, TCDD, Aroclor 1254, and others; 15 with log Kow greater than 5.0). Developing such an empirical relationship which mixes chemicals whose mode of action is passively with water (which would be the case with aldicarb and simazine, among others on the list) with those whose mode is through vapor transfers or particle depositions (TCDD, and so on) does not appear to be technically valid. Nonetheless, the fact that the Travis and Arms B_v is much higher than the plant:soil ratio for vegetables generated for the soil contamination source category demonstration is noted. Also, there is no provision in the Travis and Arms approach to distinguish between bulky and leafy vegetation, and this appears to be an important consideration for the dioxin-like compounds.

7.2.6. Alternate Modeling Approaches for Estimating Beef and Milk Concentrations

Webster and Connett (1990) compared five models which estimated the 2,3,7,8-TCDD content of cow's milk from 2,3,7,8-TCDD air contamination. The five models were described in Michaels (1989), Connett and Webster (1987), Stevens and Gerbec (1988), Travis and Hattemer-Frey (1987), and McKone and Ryan (1989). Ironically, a sixth model by Fries and Paustenbach (1990), noted by Webster and Connett as available but received too late for inclusion in their article, formed the basis for the approach taken in this assessment.

All five models compared by Webster and Connett have the same basic framework. Particulate-bound 2,3,7,8-TCDD deposits onto the ground and vegetation (cattle feed and pasture grass). Algorithms to estimate resulting vegetation and soil concentrations in these models are the same ones used in this approach, although parameter assignments are different. A daily dosage of 2,3,7,8-TCDD to the cattle is calculated and converted to a concentration in whole milk using a "biotransfer factor". This same structure was used to estimate concentrations in beef, using a beef biotransfer factor different than the milk biotransfer factor. Mathematically, this is expressed as:

$$C_{m,b} = F_{m,b} \; Dose \qquad (7\text{-}25)$$

where:

$C_{m,b}$ = concentration in whole milk/beef, mg/kg
$F_{m,b}$ = milk/beef biotransfer factor, day/kg
= $(BCF_{mf,bf} * f_{m,b})/Q$
$BCF_{mf,bf}$ = experimentally-derived unitless bioconcentration factor defined as the concentration in milk fat/beef fat divided by the concentration in the experimental vehicle (cattle feed, e.g.); similar to BCF of this assessment
$f_{m,b}$ = fat content of milk/beef, unitless
Q = daily mass intake of cattle in experiment, kg
Dose = total daily dose of 2,3,7,8-TCDD, mg/day
= sum $(a_j * c_j * Q_j)$
a_j = relative bioavailability on intake vehicle j (soil, air, vegetation, etc)
c_j = concentration of 2,3,7,8-TCDD in vehicle j, mg/kg (or equivalent units)
Q_j = mass of vehicle j intake, kg (or equivalent units)

Further details on the models can be found in their primary references and in Webster and Connett's comparison. Some highlights, including comparisons of the five approaches to the approach taken in this assessment, are:

1) Two of the approaches, that of Stevens and Gerbec (1988), and McKone and Ryan (1989), consider inhalation of contaminated air by cattle to contribute to their daily dose of 2,3,7,8-TCDD. One of the approaches, that of Travis and Hattemer-Frey (1987), considers ingestion of contaminated water by cattle. A later assessment by Travis and Hattemer-Frey (1991) has all the components of their earlier assessment, and adds cattle inhalation exposures. This assessment does not consider cattle inhalation of contaminated air nor ingestion of contaminated water in estimating beef and milk concentrations. However, these intakes were shown to be insignificant when estimated by these researchers. Stevens and Gerbec estimate inhalation contributions to be less than 0.05% (0.0005 in fractional terms) of total daily dose, or an essentially insignificant amount. Travis and Hattemer-Frey (1991) estimate inhalation to contribute between 0.3 and 1.0% to milk and beef concentrations, respectively. McKone and Ryan (1989) did not provide sufficient information to easily determine the relative contribution

of inhalation on estimation of cattle beef and milk concentrations by their estimations. Travis and Hattemer-Frey (1987, 1991) estimate water contributions to be less than 0.01% (0.0001) of total daily cattle dose of 2,3,7,8-TCDD.

2) None of the approaches considered vapor phase transfers from air to plant, although Webster and Connett recommended its inclusion in their article. The later assessment by Travis and Hattemer-Frey (1991) on 2,3,7,8-TCDD did include vapor phase transfers into vegetation consumed by cattle. According to results of the example scenarios in this assessment, these transfers appear to be particularly critical, and this was also the conclusion of Travis and Hattemer-Frey based on their modeling results.

3) Two of the assessments, that of Stevens and Gerbec (1988) and Fries and Paustenbach (1990) considered a period of residue-free grain only diet for a period of time before slaughter for purposes of fattening the cattle. Stevens and Gerbec (1988) assumed that the residues in cattle would depurate during the last 130 days of their lives on this regime. Assuming a half-life of 2,3,7,8-TCDD in cattle of 115 days, they showed a 54% reduction in beef concentrations due to this practice. Fries and Paustenbach (1990) note that cattle can gain as much as 60-70% in body weight, so dilution can also result in lower beef concentrations at slaughter. Based on these findings, a "feedlot fattening" factor of 0.50 was used in the air-to-beef model validation exercise that is described in Section 7.3.12. The procedures to estimate a reduction in concentration used by these researchers is straightforward. Assuming first order kinetics sufficiently describes reduction in concentrations during a period prior to slaughter, the fractional reduction during such a period is given as, $1 - \exp(-k_d t)$, where k_d is the depuration rate constant, in days^{-1}, and t is the depuration period, in days. The rate constant can be estimated from the depuration half-life, HL, as 0.693/HL. The 115 day half-life assumed by Stevens and Gerbec (1988) corresponds to a rate constant of 0.006 day^{-1}, and assuming a 130 day depuration period, the fractional reduction is easily calculated as 0.54 (i.e., $1 - \exp(-k_d t)$). The amount remaining after 130 days is estimated as the initial amount multiplied by 0.46 (i.e., $\exp(-k_d t)$).

4) Two of the assessments did not assume any cattle ingestion of contaminated soil, and two of the assessments estimated the contribution to milk concentrations due to ingestion of contaminated soil was minor at 1 and 2%. Only one of the assessments, Travis and Hattemer-Frey (1987), estimated any significant impact due to soil ingestion, attributing 19% of the concentration due to ingestion of contaminated soil. Their later assessment (Travis and Hattemer-Frey (1991)) estimated soil to contribute 29 and 20% of beef and milk concentration estimations, respectively. They estimated this high a contribution by contaminated soil even though they assumed that contaminated soil comprised 1% of the total dry matter intake by cattle.

Fries and Paustenbach (1990) recognized the importance of cattle soil ingestion, evaluating scenarios where cattle soil ingestion ranged from 1 to 8% of total cattle dry matter intake.

The example scenarios in Chapter 5 assumed that beef cattle ingestion of contaminated soil was 4% of their total dry matter intake, and 2% of a dairy cattle's intake was contaminated soil. The percentage of beef and milk concentrations of 2,3,7,8-TCDD attributed to soil, feed, and pasture grass, when soil contamination is the source and when stack emissions are the source, was examined in Section 6.3.3.6 in Chapter 6. It is noted there that soil ingestion appears significantly more critical for soil contamination as compared to stack emissions. Soil ingestion by beef and dairy cattle explain around 90% of final beef and milk concentration for soil sources. On the other hand, soil ingestion explained only around 5% of final beef and milk concentration for the stack emission source.

The earlier literature noting only 1-2% impact by soil ingestion were more analogous to the stack emission source category than the soil source category, in that impacts were estimated starting from air-borne contaminants depositing onto soils and vegetation. One difference in the assessments estimating the 1-2% impact with this assessment indicating about 5% impact was that the other assessments assumed less soil ingestion, 0.5% in Stevens and Gerbec (1988) and 1-3% in Travis and Hattemer-Frey (1987) and McKone and Ryan (1989).

The critical focus of the Webster and Connett (1990) comparison, is the milk fat bioconcentration factor, BCF_{mf}. As shown in Equation (7-25), the biotransfer factor, F_m, is estimated using experimental data which yields a milk fat bioconcentration factor, BCF_{mf}. Experiments most relied upon by these modelers are those described in Jensen, et al. (1981), and Jensen and Hummel (1982). A key difference in the early modeling approaches is the interpretation of these two and other studies and the resulting assignment of BCF_{mf}, with values ranging from 5 to 25. Webster and Connett (1990) discuss issues of experimental interpretation.

Parameter assignments and assumptions (cattle soil ingestion versus no ingestion, etc.) obviously all impact estimations and can be a critical source of variation and uncertainty in estimates of beef and milk concentrations. The uncertainty associated with the modeling framework described above was explored by McKone and Ryan (1989) using Monte Carlo techniques. They found that the 90% confidence range for human exposure to 2,3,7,8-TCDD, where the source was air contamination and the human exposure route was through milk, spanned two to three orders of magnitude.

The approach taken by all five researchers centers on the milk biotransfer factor, abbreviated F_m in Webster and Connett (1990) and in units of day/kg. Beef bioaccumulation was modeled in the same way using a beef biotransfer factor, F_b. Travis and Arms (1988) developed this concept to the fullest, taking several data sets from the literature on a variety of contaminants and animals, to derive empirical formulas for F_b and F_m, which they termed B_b and B_m, as a function of contaminant octanol water partition coefficient, Kow:

$$\log B_b = \log Kow - 7.6 \tag{7-26a}$$

$$\log B_m = \log Kow - 8.1 \tag{7-26b}$$

Given a log Kow of 6.8 for 2,3,7,8-TCDD (assumed in this assessment), B_b is solved for as 0.16 and B_m is solved for as 0.05. Travis and Hattemer-Frey (1991) used 0.80 and 0.03 for 2,3,7,8-TCDD B_b and B_m.

Simple transformations can show how the earlier approaches, summarized above in Equation (7-25), and the approach of Fries and Paustenbach (1990) (which is the approach used in this assessment), are the same. First, the concentration of dioxin-like compounds in the fat of beef and milk is given in this assessment by (also see Chapter 4):

$$C_{fat} = BCF\ DF_s\ B_s\ AC_s + BCF\ DF_g\ AC_g + BCF\ DF_f\ AC_f \tag{7-27}$$

where:

C_{fat} = concentration in beef fat or milk fat, mg/kg

BCF = bioconcentration ratio of contaminant as determined from cattle vegetative intake (pasture grass or feed), unitless

DF_s = fraction of cattle diet that is soil, unitless

B_s = bioavailability of contaminant on the soil vehicle relative to the vegetative vehicle, unitless

AC_s = average contaminant soil concentration, mg/kg

DF_g = fraction of cattle diet that is pasture grass, unitless

AC_g = average concentration of contaminant on pasture grass, mg/kg

DF_f = fraction of cattle diet that is feed, unitless

AC_f = average concentration of contaminant in feed, mg/kg.

Transformation steps are: 1) factor out the BCF from Equation (7-27) , 2) multiply Equation (7-27) by unity expressed as Q/Q, where Q equals total dry matter intake by cattle; 3) the multiplication of Q by the diet fraction terms, DF_s, DF_g, and DF_f, gives the values for soil dry matter intake, Q_s, grass - Q_g, and feed - Q_f, 4) with BCF factored out, and Q*DFs replaced by Q_s, etc., the parenthetical now reads, (Qs*Bs*ACs + Qg*ACg + Qf*ACf) - this is the "Dose" term defined earlier in Equation (7-25), 5) finally, multiply the right hand side of Equation (7-27) by fat content, say f_m for milk, which would transform the right and hence left hand side of that equation to whole product concentration. Transformed Equation (7-27) is analogous to Equation (7-25):

$$C = \frac{BCF\, f_m}{Q} \left[\, Q_s\, B_s\, AC_s \;+\; Q_g\, AC_g \;+\; Q_f\, AC_f \,\right] \tag{7-28}$$

While this analysis has shown how the biotransfer approach can be transformed into the bioconcentration approach of this methodology, one has to be careful with the assignment of the biotransfer and bioconcentration parameters. The following analysis shows why the Travis and Arms (1988) empirical algorithms shown above in Equations (7-26a) and (7-26b) are not appropriate for dioxin-like compounds.

McLachlan, et al. (1990) kept an inventory of the dioxins ingested by a lactating cow as well as the dioxins being emitted through the milk. This was the data used to develop the bioconcentration factors for the dioxins used in this assessment. The volume of milk generated by the cow was also given, allowing for the calculation of the biotransfer factor. The experimental biotransfer factor for milk derived from McLachlan's data is compared against the factor which can be estimated using the log Kow of the individual dioxin congeners (the congener log Kow are listed below in the issue regarding TEQ parameters) combined with the Travis and Arms (1988) biotransfer equation:

Congener	Travis and Arms B_m	McLachlan B_m
2378-TCDD	0.03	0.01
12378-PCDD	0.03	0.01
123478-HxCDD	0.49	0.006
123678-HxCDD	0.16	0.005
123789-HxCDD	0.16	0.005
1234678-HpCDD	1.26	0.001
OCDD	0.31	0.001

2378-TCDF	0.03	0.003
23478-PCDF	0.07	0.009
12378-PCDF	0.05	0.002
123478-HxCDF	0.16	0.007
123678-HxCDF	0.16	0.006
123789-HxCDF	0.16	0.006
234678-HxCDF	0.16	0.005
1234678-HpCDF	0.63	0.001
1234678-HpCDF	0.63	0.003
OCDF	5.00	0.001

It is clear that the Travis and Arms' biotransfer relationship will greatly overestimate the transfer of dioxins into milk, given the data of McLachlan. It would appear from McLachlan's data that as the log Kow increases, the biotransfer decreases, which is the opposite of the trend implied from the Travis and Arms' relationship.

The Travis and Arms trend is explainable, however, given the data from which Travis and Arms developed their relationship. In their literature article, they supplied the log Kow and the experimentally derived biotransfer factor for all the data points they used to derive their empirical relationship. For determining a milk biotransfer factor, they had 28 data points, and only 6 of them were for chemicals with log Kow greater than 6.00. The range of log Kows for data they had was 2.8 to 6.5. The dioxin-like compounds, on the other hand, have log Kow that range from 6.5 to 8.0. In this 2.8-6.5 log Kow range, it would appear that as log Kow increases, the tendency to bioaccumulate in milk increases. Interestingly, of the 6 data points Travis and Arms had for chemicals with log Kow over 6.00, their actual data point leads to a higher biotransfer point than is calculated with their derived empirical relationships:

Chemical	log Kow[1]	B_m from the data[2]	B_m calculated[3]
Aroclor 1254	6.47	0.01	0.02
Chlordane	6.00	0.0004	0.008
DDD	6.02	0.003	0.008
fenvalerate	6.20	0.0008	0.01
mirex	6.89	0.009	0.06
TCDD	6.15	0.01	0.01

[1] as used by Travis and Arms
[2] the actual data point claimed by Travis and Arms (1988)
[3] as calculated with Equation (7-26b)

As discussed above, it would appear that the trend of higher bioaccumulation with higher log Kow is true for the range of log Kow used by Travis and Arms - 2.8 to 6.5. However, for the dioxin congeners where log Kow is higher at 6.5 to 8.0, the trend is the opposite - the biotransfer decreases as the log Kow increases. This could be due to greater rates of metabolism for organic compounds of higher log Kow, or just for the dioxins, leading to lower concentrations in the animal food products. In any case, it is clear that the Travis and Arms' biotransfer factor equations for beef and milk are not appropriate for the dioxin-like compounds, and perhaps as a general rule, for other organic compounds with log Kow 6.5 or higher.

Douben, et al. (1997) compares three approaches for air-to-plant-to-milk modeling. One of the approaches is the one of this document. The second employs the “carryover” factor, which is very similar to the biotransfer factor defined above. Whereas the biotransfer factor is defined as the concentration in milk (mg/L, e.g.) divided by the mass of dioxin ingested (mg/day), the carryover factor is defined as the mass of compound excreted in milk (mg/day) divided by the mass of dioxin ingested (mg/day). Douben, et al. (1997) assigns values to the carryover factor based on the data of McLachlan, et al. (1990). The third approach is the “scavenging” approach developed by McLachlan (1995) and described above for the transfer of dioxins from air to grass. McLachlan (1995) developed the concept further to show that the concentration in milk can be estimated as a function of the total mass of dioxins ingested by the dairy cow (equal to the dry weight of vegetation consumed times the scavenging coefficient times the air concentration) times the absorption fraction (the amount absorbed by the dairy cow) divided by the mass of milk excreted each day:

$$C_{milk} = \frac{CA_j \; (\; SC_g \; M_g + \; SC_s \; M_s \;) \; ABS_j}{LAC} \tag{7-29}$$

where:

C_{milk} = milk concentration, ng/kg (ppt; 1 liter = 1kg)
CA_j = concentration of congener j in air, ng/m^3
SC_g = scavenging coefficient for grass, m^3/g
M_g = mass of grass ingested, g/day
SC_{cs} = scavenging coefficient for corn silage, m^3/g
M_{cs} = mass of corn silage ingested, g/day
ABS_j = absorption fraction for congener j

LAC = lactation rate, kg/day

Assuming 9 kg dry weight of grass and 4 kg dry weight of corn silage ingested per day, and scavenging coefficients for grass and silage to be 9 and 4.5 m^3/g, respectively, Douben, et al (1997) reduced the parenthetical above to a constant of 100,000 m^3/day (actually calculates to 99,000). They were able to test the model assuming a lactation rate of 0.6 kg/day and using absorption efficiencies provided in McLachlan (1995). While differences in specific congener/model predictions were noted, Douben, et al. (1997) generally found comparable predictions for milk TEQ concentrations - all were within a factor of 5 of observed concentrations.

One critical theoretical assumption not explored in these modeling comparison exercises is whether 2,3,7,8-TCDD and other congeners bioaccumulate equally in beef fat and milk fat - are the BCF_{mf} and BCF_{bf} equal? Fries and Paustenbach (1990) emphasize that differences in observed concentrations in beef and milk are critically a function of the differences in the diets of cattle raised for beef versus those raised for milk. They assumed that the beef and milk bioconcentration factor was equal for their example calculations. The key difference Fries and Paustenbach cite is the tendency for beef cattle to graze while lactating cattle are more often barn fed. Grazing cattle intake more contaminated soil than barn fed cattle. Fries and Paustenbach derived F for higher chlorinated dioxin-like compounds from experimental data, noting that the F value is less with higher chlorination. Webster and Connett (1990) made the analogous observation, saying that 2,3,7,8-TCDD equivalents transferred from air to milk less efficiently than 2,3,7,8-TCDD. This is also consistent with the data of McLachlan, et al (1990), which is used in this assessment for assignment of BCFs to dioxin-like compounds.

Besides different diets between beef cattle and lactating cows is that lactation provides a mechanism for dioxin excretion from the body, which theoretically would lead to body fat concentrations in lactating cows being less than body fat concentrations in non-lactating cattle which don't have this excretion mechanism. However, researchers have observed that the dioxin concentrations in the fat of milk and of body fat in non-lactating cattle are similar. McLachlan (1994) attributes this to the fact that cattle are most often slaughtered while they are still growing and increasing their body fat reservoir. Therefore, dioxins appear to reach steady state in the fat of non-lactating cattle at concentrations similar to those found in cow's milk.

Some conclusions from this analysis of these efforts for estimating bioconcentration in beef and milk are:

- Although the biotransfer and carryover frameworks look different than the framework used in this assessment, they are actually the same with a simple mathematical transformation;
- All of these approaches are empirical; that is, values for the critical dioxin-specific parameters (scavenging coefficients, carryover factors, bioconcentration factors, biotransfer factors) are developed from field data. When they are developed by different researchers on different field data, they will (of course) not predict equally. However, and as evidenced by the results of Douben, et al. (1997), they all appear to predict milk TEQ concentrations about equally.
- A caution is noted, nonetheless, with the use of the Travis and Arms (1988) empirical algorithm for the assignment of biotransfer factors for the dioxin compounds: as described above, this empirical relationship does not hold for the dioxin-like compounds, which have higher log Kow than the log Kow of the compounds used by Travis and Arms (1988) to develop their relationship. Provided above are biotransfer factors for dioxins developed from the same data used to develop the bioconcentration factors of this methodology.
- The possible dosage to cattle of 2,3,7,8-TCDD via contaminated air or water was considered in earlier assessments, but was not found to be a significant pathway, and was not considered in this assessment;
- Earlier assessments (before 1990) did not consider vapor phase transfers to vegetation consumed by cattle; key studies in the literature as well as the results of the demonstration scenarios suggest that this transfer is particularly critical;
- Even though the structure of the analysis has been consistent from the earlier to the current approaches, different assumptions on parameter values greatly impacts modeling results. The critical bioconcentration factor, earlier termed BCF_m (for milk) and termed simply BCF in this assessment, has been estimated to be between 5 and 25 for 2,3,7,8-TCDD in different assessments. This assessment uses a BCF value of 5.76 for 2,3,7,8-TCDD. Using Monte Carlo techniques on this model structure for estimating human exposure to milk resulting from air contamination of 2,3,7,8-TCDD, McKone and Ryan (1989) showed a 90% confidence interval spanning 2 to 3 orders of magnitude.

7.2.7. An Alternate Approach to Vapor/Particle Partitioning in the Air

Chapter 3 described the application of the Junge (1977) and Pankow (1987) model for partitioning air-borne dioxin-like compounds into vapor and particle phases. The governing equation for this model is:

$$\phi = \frac{c\ \Theta}{p^{\circ}_{L} + c\ \Theta} \qquad (7\text{-}30)$$

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

A disadvantage to using this model is that the parameters Θ and c in this equation must be estimated as they cannot be measured directly. There is also uncertainty is the saturation liquid vapor pressure, p°_{L}, which must be estimated from the solid-phase vapor pressure, p^{o}_{S}. Assignment of these parameters and the development of the vapor/particle partitioning algorithm is provided in Chapter 3.

A second model was developed in the latter part of the 1990s and is now widely used to characterize the partitioning of semivolatile organic compounds to aerosol particles (Finizio et al. 1997, Harner and Bidelman, 1998; Pankow, 1998). The derivation of this model begins with this alternate equation for the particle fraction, ϕ:

$$\phi = \frac{C_p\ (\ TSP\ )}{C_g + C_p\ (\ TSP\ )} \qquad (7\text{-}31)$$

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, µg/m^3

Defining the ratio of the particle phase to the gas phase (C_p/C_g) as K_p, a particle-gas partition coefficient, and dividing all terms on the right side of the equation by C_g, Equation (7-31) can be rewritten as:

$$\phi = \frac{K_p\ (\ TSP\ )}{1\ +\ K_p\ (\ TSP\ )} \qquad (7\text{-}32)$$

Once deriving K_p, ϕ can be solved for in this equation. K_p can be measured in the field, but alternately it has been related to the octanol air partition coefficient, Koa (Finizio et al., 1997):

$$K_p = 10^{-9}\ K_{oa}\ f_{om}\ (\gamma_{oct}/\gamma_{om})(M_{oct}/M_{om})/\rho_{oct} \qquad (7\text{-}33)$$

where:

K_p = particle-gas partition coefficient, m^3/ng
K_{oa} = octanol air partition coefficient, dimensionless
f_{om} = fraction of organic matter in the aerosol involved in partitioning
$\gamma_{oct,\ om}$ = activity coefficients in octanol and aerosol organic matter
$M_{oct,\ om}$ = molecular weights of octanol (130 g/mol) and the organic matter
ρ_{oct} = density of octanol, 820 kg/m^3

Simplifying assumptions that have been made for this formulation include that γ_{oct}/γ_{om} and M_{oct}/M_{om} are equal to 1 (Bidleman and Harner, 2000), leading to:

$$Log\ K_p = Log\ K_{oa} + Log\ f_{om} - 11.91 \qquad (7\text{-}34)$$

Bidleman and Harner (2000) make the further simplification that urban aerosols contain 15% carbon, present as compounds with the average molecular formula of octanol (74% carbon), thus leading to an assignment of 0.20 for f_{om}, and this equation:

$$Log\ K_p = Log\ K_{oa} - 12.61 \quad (7\text{-}35)$$

The octanol air partition coefficient is directly measurable at ambient temperatures and has been reported for several classes of semivolatile organic compounds, including PCBs (Harner and Bidleman, 1996; Komp and McLachlan, 1997), PAHs (Harner and Bidleman, 1998), polychloronaphthalenes (Harner and Bidleman, 1998), and other compounds (Harner and MacKay, 1995). However, measurements of K_{oa} for dioxin-like dioxin, furan, and PCB congeners could not be found in the literature. Alternately, K_{oa} can be estimated from the ratio of the octanol water partition coefficient and the Henry's Constant, as:

$$K_{oa} = \frac{K_{ow}\ R\ T}{H} \quad (7\text{-}36)$$

where:

K_{oa} = octanol air partition coefficient, dimensionless
K_{ow} = octanol water partition coefficient, dimensionless
R = universal gas constant, 8.2×10^{-5} atm-m^3/mole-K
T = ambient temperature, K
H = Henry's Constant, atm-m^3/mole

Lee and Jones (1999) discuss the difference between the K_{oa} calculated in this manner and measured values. For PCBs, they cite literature showing that measurements of K_{oa} were 1.4 to 4.7 times higher than modeled K_{oa}. Using a relationship derived for PCBs, they attempted a correction for the dioxin-like compounds. For this section, Equation (7-36) will be used to model the K_{oa} for dioxin-like compounds.

Another approach taken by some to develop a more site-specific relationship between K_{oa} and K_p is to measure the gas and particle fractions for a given site and compound, and then directly assign values for K_p (as C_p/C_g). Then, these site-specific K_p can be correlated to reported or estimated K_{oa} using the general formula:

$$Log\ K_p = m\ Log\ K_{oa} + b \qquad (7\text{-}37)$$

Kaupp and McLachlan (1999) took measurements of polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs), napthalenes (PCNs), and polycyclic aromatic hydrocarbons (PAHs) over the course of a year in southern Bavaria. They investigated the relationship between K_p and the saturation liquid vapor pressure, $p°_L$, as well as the relationship between K_p and K_{oa}, using the generalized logarithmic equation shown above. They found a good correlation between K_p and $p°_L$ when they grouped PCDD/Fs and PCBs (r^2 = 0.93) and separately when they grouped PAHs and PCNs (r^2 = 0.98), but not when they grouped all four sets of compounds together. On the other hand, they found a reasonable correlation existed for the whole group of four compound classes when they correlated K_p and K_{oa} (r^2 = 0.76). The linear relationship they found was:

$$Log\ K_p = 0.6368\ Log\ K_{oa} - 8.9111 \qquad (7\text{-}38)$$

Given values of K_{oa}, K_p can be solved for using Equations (7-38) or (7-35). In order to compare this approach for assigning vapor/particle partitioning with the one chosen for this document (the Junge-Pankow model based on the saturation liquid vapor pressure), these two versions of the particle-gas partition coefficient, K_p, will be generated from K_{oa}. In both cases, the octanol air partition coefficient, K_{oa}, will be assigned values based on Equation (7-36) since measured values the dioxin-like compounds could not be found in the literature. Then, the two sets of K_ps will be used to predict values of the particle phase fraction, ϕ, as given in Equation (7-32). As described in Chapter 3, four values for the atmospheric particle concentration, the parameter TSP of Equation (7-32), describe four conditions termed, “clean continental”, “background”, “background plus local sources”, and “urban”. For this exercise, the value selected for urban conditions, 98 $\mu g/m^3$, will be used. Finally, the two sets of ϕ for the 17 dioxin and furan congeners generated here using K_{oa} will be compared with the ϕ generated in this methodology document using the Junge-Pankow model. This comparison is shown in Table 7-5.

As shown there, while the trend is generally similar between the two models (higher particle fraction as the degree of chlorination increases), there is a large discrepancy between the predictive methods. The calculation of the particulate fraction, ϕ, using the Junge-Pankow model, results in much larger values as compared to the procedure described in this section using the octanol air partition coefficient. A similar discrepancy is found when calculating ϕ for other atmospheric conditions and lower values of the particle density term, TSP - background plus local conditions, background, and clean continental. There is not much difference in using a theoretical relationship between K_{oa} and K_p given above in Equation (7-35) or the empirical relationship shown as Equation (7-38).

The same discrepancy between the Junge-Pankow model and the K_{oa} model was found in two studies which both measured the concentration and partitioning of dioxin-like compounds in air and then tried to predict the particulate fraction using the same two models described in this section (Lee and Jones, 1999; Oh et al., 2001). Not only did both studies find that the octanol air partition coefficient method predicted a much smaller fraction to occur in the particulate phase for all congeners and homologue groups modeled, but they also both concluded that the octanol air partition coefficient method fit the measured data better. Chapter 3 discussed the general trend that the Junge-Pankow model based on $p°_L$ would lead to greater particulate fractions than measured, but it also discussed issues identified for the measurement of dioxin-like compounds - that “blow-off” and other causes could cause the filter-PUF derived measurements to be overestimates of the vapor phase fraction (equivalently, they would underestimate the particle phase).

In any case, this methodology document recommends use of the Junge-Pankow model for vapor/particle partitioning and, in particular, derives a set of particle-phase fractions for four atmospheric conditions for the dioxin-like compounds. The results of this analysis are shown in Table 3-7 of Chapter 3. Further, these results are used in several model validation exercises in this chapter, including air-to-leaf modeling, air-to-soil modeling, and air-to-leaf-to-beef modeling. Users may, of course, use other modeling approaches for the dioxin-like compounds, including the alternate vapor/particle model based on the octanol air partition coefficient described in this section.

7.3. MODEL VALIDATION EXERCISES

7.3.1. The Impact of Dioxin Soil Contamination to Nearby Soils

Contaminated soils from a bounded area of soil contamination are assumed to migrate via erosion and impact the soils of a nearby exposure site. This section examines the model algorithms for estimating impacts to nearby soils from a contaminated soil source.

Contaminated soils erode onto a nearby site of exposure and mix into a depth of either 2 cm for untilled conditions or 20 cm for tilled conditions. The 2-cm depth was chosen as the mixing depth for both depositing residues in the stack emission source category and for residues migrating from a contaminated site to a nearby impacted site in the soil contamination source category. This 2-cm depth replaced the 1-cm depth which was the value selected for earlier versions of this dioxin exposure reassessment (EPA, 1992a; EPA, 1994). Principal justification for this assumption came from a report showing soil concentration profiles taken at 2 cm increments to be generally uniform for background undisturbed soils to a depth of 5 cm, with dropoffs in concentrations below this (Brzuzy and Hites, 1995). For two sandy profiles, the peaks were found at greater than 30 cm. The authors speculated that their findings are the result of depositions corresponding to the rise of dioxins in the environment starting 50 or so years ago. A mixing depth of 5 cm may be more appropriate for the algorithms of this assessment if a source being evaluated has been emitting for that length of time. However, exposure durations and source emissions for the categories of this assessment are likely to be emitting for substantially less than the past 50 years, justifying the selection of 2 cm for the untilled mixing depth.

A *contaminant concentration ratio* is defined for purposes of this discussion as the ratio of soil concentration at the site of exposure to the soil concentration at the site of contamination. For example Scenario 3, soil eroded from a 40,000 m^2 (10-acre) contaminated site was assumed to partially deposit onto a 40,000 m^2 exposure site. The contaminant concentration ratio was 0.39 for the 2-cm depth of mixing at the site of exposure and 0.06 for the 20-cm mixing depth.

Data to rigorously validate the approach taken in this assessment to model the impacts of soil erosion from a site of contamination to a nearby site is unavailable. However, there have been documented evidence of migration of 2,3,7,8-TCDD away from industrial sites with soil contamination of 2,3,7,8-TCDD, resulting in off-site soil contamination. Off-site soil concentrations of concern were identified in 7 of 100 Tier 1 and Tier 2 sites of the National Dioxin Study (EPA, 1987). The study noted that in most cases, 2,3,7,8-TCDD had not migrated off-site. Most, but not all, Tier 1 and 2 sites did have some off-site soil sampling without detection. It should be noted, however, that soil detection limits for most of these 100 Tier 1 and 2 sites were at 1 ppb; this would have precluded finding concentrations less than 1 ppb in some of the off-site soil sampling, particularly important for many of the sites where on-site detections were in the low ppb range. Summary data from the 7 sites noted above is provided in Table 7-6. Contaminant concentration ratios cannot be evaluated by this summary because of lack of detail provided in the National Dioxin Study.

Further detail on the 1984 sampling at the Dow Chemical site in Midland is provided in Nestrick, et al. (1986). An evaluation of the information in that reference is more informative than the Dow Chemical summary in Table 7-6. The entire site is 607 hectares. On-site sampling included areas identified as chlorophenolic production areas, a waste incinerator area, and "background" areas. Background areas were within the 607 ha site but away from production areas. Two of the on-site areas were further identified as areas with Localized Elevated Levels (LELs). These two areas comprise less than 0.5% of the total site area, but had the three highest occurrences of 2,3,7,8-TCDD at 25, 34, and 52 ppb. Including these three high occurrences in the total of 33 samples taken on-site at sites of concern (i.e., not including the background sites) leads to an average concentration of 4.3 ppb; excluding them leads to an average of 1.0 ppb. The average of 11 background samples (including two ND assumed to be 0.0) was 0.15 ppb. A contaminant concentration ratio of 0.035 is calculated assuming an average concentration for contaminated soil of 4.3 ppb (0.15/4.3 = 0.035), and a ratio of 0.15 is calculated if the average soil contamination concentration is more like 1.0 ppb rather than 4.3 ppb.

This ratio of 0.035 is about one-tenth as much as the 0.39 ratio estimated assuming the shallow 2-cm depth of contamination, although the ratio of 0.15 is similar to the 0.39 ratio of Scenario 3. The depth of 20 cm led to a modeled ratio of 0.06, which is more in line with the Dow contaminant ratio of 0.035. The 2-cm depth ratios are probably more pertinent for comparison, however, since it is unlikely that there were tillage operations (or other soil practices which would distribute residues) in background areas of the 607 ha Dow site.

It appears reasonable that the no-till contaminant ratio of 0.39 is higher than the Dow ratios for several reasons. First, the contaminated areas sampled were those likely to be of concern and comprising only a small percentage of the total 607 hectare site. That might question the representativeness of 4.3 ppb as average soil contamination in impacted areas; the three highest concentrations came from specifically identified LELs comprising only 0.5% of the 607 ha site area. Second, a map provided in Nestrick, et al. (1986) including a distance scale clearly shows that all of the background samples were much further than 150 meters from the contaminated sample points, with several sample points hundreds to over a thousand meters from the contaminated sample points. The contaminant concentration ratio of example Scenario 3, 0.39, was estimated with a distance of 150 meters. Third, the example scenarios had specific assumptions about erosion which may or may not have been appropriate for application to the Dow site.

Ideally validation of the soil erosion model would involve direct application at the Dow site and comparison of predicted values to measured values. This was not feasible due to lack of information regarding the Dow site. Instead, this analysis has shown that the model predictions of contaminant concentration ratios differ logically from observed ratios at the Dow site.

7.3.2. Soil Concentrations and Concurrent Concentrations in Bottom Sediments and Fish

The Connecticut Department of Environmental Protection (CDEP, 1992; MRI, 1992) established a program in 1986 for monitoring TCDD, TCDF, and other dioxin-like isomers of comparable toxicity in several environmental matrices near resource recovery facilities (RRFs). Matrices monitored include ambient air, residues and leachate from the ash disposal sites, surficial soils, surface water surficial bottom sediments, and whole fish. The purpose of the program is to evaluate the impact of RRFs. Eight locations were evaluated through 1990, with one location serving as a baseline or reference site. Of the seven remaining locations, RRFs began operation in 1983 (1 RRF), 1987 (3), 1988 (1), and 1990 (2). This section will examine the soil, sediment, and fish data from that program.

The soil concentrations throughout all eight sites might be characterized as typical of background concentrations mainly because the concentrations of 2,3,7,8-TCDD measured through 1990 averaged 0.56 ppt (n = 77; assuming non-detects were ½ detection limit), with roughly a 50% non-detect rate (at a detection limit which has varied by data set, but has been around 0.1 ppt). In studies measuring soil concentrations of 2,3,7,8-TCDD in background or rural settings, either none was found, or concentrations were found in the low ppt range - this seems to also characterize the Connecticut data. For example, the soil concentration of 2,3,7,8-TCDD of 0.37 used in the background demonstration scenarios in Chapter 5 was measured at a rural background site located 28 miles from Columbus, Ohio. In a statistical analysis of the Connecticut data collected through 1988, the average soil concentration for 2,3,7,8-TCDD as 0.44 ppt (n = 42; CDEP, 1992; same procedures for estimating average concentrations), which is lower than the 0.56 ppt concentration for all samples through 1990. Concentrations of 2,3,7,8-TCDF taken after 1988, however, are lower than those taken in 1987 and 1988: the average including samples through 1988 was 8.20 ppt (n = 41; CDEP, 1992); while through 1990 was 6.77 (n = 77; CDEP, 1992). (Unlike the concentrations for 2,3,7,8-TCDD, this 2,3,7,8-TCDF concentration in the Connecticut data is higher than the background site near Columbus, Ohio: 0.64 ppt in Columbus versus 6.8-8.2 ppt in Connecticut.) This simple examination of averages over time does not seem to indicate statistically significant change, if any. As well, in a statistical analysis of the data (principal component analysis of the concentration levels of all isomers in soil, fish, and sediment to attempt to identify stratification of the data by year) for four of the RRFs through 1990, MRI (1992) concluded that the RRFs had no apparent effect on the levels of the dioxin-like compounds in the three matrices.

The purpose of developing the argument that levels in soil are low and perhaps typical of background conditions, although that is questionable for 2,3,7,8-TCDF, is to be able to compare the soil to sediment, and sediment to fish ratios that arise from this data with those that were generated in example Scenarios 1 and 2 in Chapter 5. Those scenarios were crafted to be typical of “background” settings. It is noted that the comparison of soil-to-sediment ratios and the sediment-to-fish ratios in this exercise is not, strictly speaking, a validation exercise since the Connecticut circumstances were not duplicated.

Information and results from the CDEP program for the soil, sediment, and fish matrices are presented in Tables 7-7 through 7-9. The data and supporting documentation was supplied by CDEP (1992). Table 7-7 provides a summary of the eight sites in the CDEP program for which data was available. One "reference" or "control" site includes two areas, which for 1988 was at Union, Connecticut, and for 1990 was at Stafford, Connecticut. No nearby potential sources of dioxin release (industrial, commercial) were identified for these two reference sites. One of the sites, the Hartford site, is near the Connecticut River. All water bodies sampled were coves with direct links to the river. Industrial and commercial enterprises which use the river are speculated to have resulted in the generally higher fish concentrations noted in the Hartford site, as compared to the other sites. Twenty-one water bodies have been sampled, including harbors, channels, impoundments, reservoirs, coves, ponds, rivers, and lakes. Six species of fish have been sampled, including carp, channel and white catfish, white sucker, brown bullhead, and yellow perch. All but the yellow perch are bottom feeders. The yellow perch was sampled mostly when a sufficient sample of bottom feeder could not be obtained. Samples of bottom feeders were sought because it was felt that they would have the highest tissue concentrations due to their association with bottom sediments, and therefore be the best markers for impact and change over time (C. Fredette, CDEP, personal communication). The soil sampling program was not extensive; samples were only taken near ambient air monitoring stations, and only 77 samples were taken through 1990. It certainly cannot be claimed that the samples are statistically representative of soils which drain into the water bodies. However, given the consistency in concentrations noted and their low values, the supposition is made that concentrations are adequately representative of soils which impact the water bodies. Maps of the sites were obtained from CDEP to evaluate the distance from the soil sampling sites to the nearest water bodies. Nearly all soil sampling sites were within 3 miles of the nearest water body, and most were near to and less than one mile away.

Table 7-8 lists the frequency of non-detects for all data through 1990, and incomplete information on detection limits. For determining average concentrations in sampled matrices, non-detects were assumed to equal ½ the detection limit. The detection limits for these matrices varied over time with different data sets. The detection limits noted were those cited for 1987 and 1988 data (from a draft Monitoring Progress Report supplied by CDEP). That report did not list detection limits for three matrices noted. In parenthesis is noted the lowest concentration in the data sets, which would correspond to ½ the detection limit at the time the non-detect was measured. The purpose of presenting this data is simply to argue that assuming ½ the detection limit for computing averages will not greatly impact the averages. This can be demonstrated for the one matrix where this is most likely to be a concern - soil concentrations of 2,3,7,8-TCDD where a 50% non-detect rate was noted. If half the samples were assigned a value of 0.0 instead of perhaps 0.07 ppt (half the noted detection limit of 0.13 ppt), than the overall average would drop from 0.56 ppt to 0.52 ppt.

Table 7-9 summarizes the key results from the CDEP data. The C_{sed}:C_{soil} ratio is the ratio of sediment concentration to soil concentration for the eight sites for 2,3,7,8-TCDD - these are not organic carbon normalized concentration ratios. The second ratio noted is called the BSAF, because it is defined in the same way that the Biota Sediment Accumulation Factor is defined: the ratio of the lipid-normalized whole fish tissue concentration over the organic carbon normalized bottom sediment concentration. The BSAF is used to estimate fish tissue concentrations from bottom sediment concentrations in this assessment. The fish lipid contents and organic carbon contents for each site were supplied by CDEP (1992). The BSAFs for the entire data set and the four concentrations are based on averages of fish lipid and organic carbon contents from the entire data set.

Key observations from the demonstration scenarios and the results of the CDEP program are:

1) Demonstration scenarios 1 and 2 in Chapter 5 estimated the impact from basin-wide soil concentrations of the 17 dioxin congeners that have been found in a typical background setting. The difference in the scenarios was in exposure patterns and exposure site characteristics - the impacts to surface water sediments and fish were the same in both scenarios. The estimated concentrations of 2,3,7,8-TCDD, 2,3,7,8-TCDF, and 2,3,4,7,8-PCDF in bottom sediments were 0.99, 1.22, and 0.51, respectively, and the sediment to soil ratios for these three compounds were 2.55, 1.82, and 2.43. The differences in the sediment:soil ratios of these congeners is due to slightly different organic carbon partition coefficients assumed for the three congeners. These ratios compare to the overall 3.86, 2.59, and 1.58 estimated in the Connecticut data set for 2,3,7,8-TCDD, 2,3,7,8-TCDF, and 2,3,4,7,8-PCDF, respectively. The ratio for total toxic equivalents was 2.69, compared to the modeled 2.64. These ratios tend to support the model's approach.

One of the key model parameters in the soil to sediment algorithm which is uncertain is the soil enrichment ratio. It was assigned a value of 3.0, which means that concentrations in soil eroding from the field are three times higher than concentrations on the field. If the soil enrichment ratio is set to 1.0, it would lead to sediment:soil ratios less than 1.00. The close match of sediment:soil ratios with an enrichment ratio of 3.0 does not necessarily validate the model's approach to evaluating surface water impacts from low basin-wide soil concentrations, however. The model assumes that all surface water impacts are from erosion of basin soils. However, sediment concentrations in water bodies are also a function of direct atmospheric depositions onto water bodies and other direct, industrial related, discharges into water bodies. Such depositions may originate from sources other than soil contamination, such as air emissions from cars or industry. The impact of industrial sources to the sediments in the CDEP data is unclear. As noted, evidence collected so far does not indicate an impact from incinerator emissions. The Hartford site has been cited as being impacted with industrial use of the nearby Connecticut River. However, the sediment concentrations of the water bodies at this site are not higher than other sites - in fact, the sediment concentrations from the Bridgeport, Bristol, Preston, and even the background Union/Stafford sites are comparable or higher. In any case, deposition of air-borne contaminants are likely to impact bottom sediments to some degree, and the soil contamination models of this assessment do not include such an impact (the stack emission source category does include this impact for emissions reaching water bodies).

In summary, the CDEP data appears to indicate that bottom sediment concentrations exceed surface soil concentrations by more than a factor of 2.0 in environmental settings that mostly do not appear to be impacted by industrial activities. The models also predict a similar enrichment of sediment concentrations, mainly due to the use of soil enrichment ratio of 3.0

2) The overall BSAF ratios for the three dioxin compounds and the I-TEQ ratio, ranging from 0.24-0.86, are higher than the BSAF used in the demonstration scenario of 0.09 for 2,3,7,8-TCDD and 0.144 for 2,3,4,7,8-PCDF. Higher BSAF in the CDEP data are expected because the fish species sampled were bottom feeders, except for the yellow perch. The selected BSAF of 0.09 is mainly supported by Lake Ontario data (EPA, 1990a), which was on brown and lake trout, smallmouth bass, and white and yellow perch, all column feeders. Bottom feeders are expected to have more exposure to the contaminants because of their direct contact with sediments. This implies that use of the BSAF for site-specific assessments should consider the dietary pattern of exposed individuals. If a significant portion of local fish consumption includes bottom feeders (such as catfish), then perhaps a BSAF greater the 0.09 used for the demonstration scenarios is warranted.

3) Of the six sites for which BSAFs were individually determined for 2,3,7,8-TCDD, the highest BSAF was from the Hartford site at 0.97. The claim is not made that it is substantially or significantly different from BSAFs at the other sites - it is simply a point of interest for comment. The Hartford site has been previously identified as likely to have been impacted by activity on Connecticut River - all the fish are taken from coves directly connected to the river. Although the bottom sediment concentrations at this site are not different from other sites, one hypothesis is that the water column is more impacted for this site as compared to other sites.

In Chapter 4, Section 4.3.4, a key issue identified for the validity of the BSAF approach is the issue of past versus ongoing contamination. Generally, the hypothesis offered was that fish are likely to be more exposed with ongoing impacts to the water body as compared to a situation where impacts were principally historical. The effluent discharge source category is a case of ongoing impacts. The argument presented in Section 4.6. of Chapter 4 was that the BSSAF (biota suspended sediment accumulation factor) should be greater in numerical value than a BSAF whose value is derived from data on a water body whose impacts have been primarily historical. This was the case for the assignment of a 0.09 for the BSAF, which was based on data on column feeders in Lake Ontario, a lake whose impact has been speculated as primarily historical. Although the numerical difference between the Hartford BSAF, at 0.97, and the next largest BSAF at Bristol, at 0.78, is not that large, perhaps that difference is due to the fact that the fish are more exposed at Hartford due to ongoing impacts from the Connecticut River.

In summary, this section has evaluated data supplied by the Connecticut Department of Environmental Protection on fish, sediment, and soil data. It is the only data set that could be found where soil and sediment data were concurrently taken in areas evaluated as (mostly) not impacted by industrial activity. An examination of the sediment to surface soil concentration ratios, showing them generally to be in the range of 1.6 to 3.9, supports the soil contamination model of this assessment for estimating sediment impacts from uniform basin-wide soil concentrations, which showed sediment to surface soil concentration ratios ranging from 1.8 to 2.6. The BSAFs determined from the CDEP data are higher than the BSAFs used in the demonstration scenarios of this assessment. This was likely due to use of bottom feeders for fish concentration of the CDEP - bottom feeders are likely to have more exposure to dioxin-like compounds in water bodies than column feeders due to their association with contaminated bottom sediments.

7.3.3. Other Bottom Sediment Concentration Data

Assuming elevated sediment concentrations are a function of elevated surface soil concentrations is reasonable when the only source of water body contamination is soil contamination. However, comparing soil and sediment concentrations would not be appropriate if sediments and water were impacted by industrial discharges, which has often been cited as the cause for sediment and water impacts (see Bopp, et al., 1991; Norwood, et al., 1989; e.g.). Sediment concentrations of note have also been found in surface water bodies near urban settings, with car and industrial stack emissions cited as likely causes (Gotz and Schumacher, 1990; Rappe and Kjeller, 1987). Rappe, et al. (1989) collected samples from the Baltic Sea, which were described as background samples. They note that the pattern of tetra-CDF congener concentrations found in the Baltic Sea were typical of what they termed the "incineration patterns" - air and air particulate concentrations that were attributed to sources such as incineration, car exhausts, steel mills, etc. On the other hand, sediment samples collected between 4 and 30 km downstream from a pulp mill revealed a congener pattern typical of bleaching mills. The stack emission and effluent discharge source categories provide separate models for water body impacts. The capability of the effluent discharge model is estimating fish tissue concentrations is examined in Section 7.3.6 below. The remainder of this section examines some of the data available which is not attributed to industrial or urban sources.

Smith, et al. (1995b) evaluated sediment core data from the Hudson River National Estuary Research Reserve system located on the lower (southern) Hudson River. They also took soil cores near the estuaries studied. Using principal component analysis, as well as a mass balance approach, they concluded that the CDD/CDF concentrations in the river sediments were dominated by soil erosion (76% of total influx) and sewage-containing effluents (19%). In doing their mass balance exercise, they used an “organic enrichment factor” of 1.6. Their data was on homologue groups, not on individual congeners, so their data is not directly amenable to comparison to model simulations or other data discussed in this section.

Except for the CDEP data described in Section 7.3.2 above, and possibly this data on Hudson River sediments (Smith, et al., 1995b), data was not found linking sediment concentrations to soil concentrations, in an urban or more pertinent to this assessment, a rural setting. Some sampling has occurred in areas described as rural or background. Sediment sampling in Lake Orono in Central Minnesota in such a setting found no tetra- and penta-CDDs, although occurrences of total hexa-CDDs were found in the low ng/kg (ppt) level, occurrences of hepta-CDDs to a high of 110 ppt, and total OCDD concentrations ranged from 490-600 ppt for three samples (Reed, et al., 1990). A report on sampling of several estuaries in Eastern United States included a "reference" or relatively clean site, central Long Island Sound. There were no occurrences of 2,3,7,8-TCDD, although 2,3,7,8-TCDF was found at 15 ppt in this clean site. Other sites had identified industrial source inputs and higher noted concentrations (Norwood, et al., 1989). 2,3,7,8-TCDD was extensively found in sediments of Lake Ontario (EPA, 1990a). The average of samples from all depths of sediment collection from 49 stations including 55 samples was 68 ppt. The average of 30 surficial sediment samples was 110 ppt. A modeling exercise implied that an annual load of 2.1 kg/year into Lake Ontario corresponds to a concentration of 110 ppt. One identified source was the Hyde Park Landfill, located about 2000 feet from the Niagara River, which drains into Lake Ontario. Between 1954 and 1975, an estimated 0.7 to 1.6 tons of 2,3,7,8-TCDD were deposited in the landfill. A principal conclusion from the modeling exercise, however, was that a characterization of historical loadings of 2,3,7,8-TCDD into the lake was not available and would be necessary to evaluate the contributions by the Hyde Park Landfill.

7.3.4. Data on Water Concentrations of Dioxin-Like Compounds

Chapter 3 of Volume II summarizes available data on surface water concentrations of the PCDDs and PCDFs. Results summarized there are not directly amenable to comparison because the sources of contamination were unspecified except to note that, in some studies, a portion of the sampling occurred for water bodies known to be impacted by industrial discharges. The 104-mill pulp and paper mill study, which measured discharges of 2,3,7,8-TCDD and 2,3,7,8-TCDF into surface water bodies, was the only such study currently available which measured impacts to surface water bodies. Section 7.3.6 below discusses the use of this data to evaluate the effluent discharge source category. However, this study did not measure water concentrations, and no other studies could be found which measured both source strength and resulting surface water concentrations.

Nonetheless, the data on water concentrations of dioxin-like compounds does indicate that occurrences of PCDDs and PCDFs are generally not-detected or in the low pg/L (ppq) range; detection limits were generally at or near 1 pg/L. The one exception to this is occurrences in tens to hundreds of pg/L range for PCDFs in one of twenty community water systems sampled in New York (Meyer, et al., 1989). Concentrations exceeding 200 pg/L were found in the hepta- and octa-CDFs; concentrations between 2 and 85 pg/L were found in the tetra to hexa-CDFs for this impacted water system.

The highest water concentrations estimated in the demonstration scenarios in this assessment were the concentrations associated with the soil contamination demonstration. There**,** soil concentrations in a bounded area of soil contamination were 1 ppb for the three example compounds. Also, watershed soils were assumed to be at 0.00 in order to demonstrate the incremental impact from the bounded area only. Water concentrations for 2,3,7,8-TCDD, 2,3,4,7,8-PCDF, and 2,3,3',4,4',5,5'-HPCB were 0.012, 0.091 and 0.0016 pg/L, respectively. Water concentrations for the effluent discharge scenario, #6, were comparable to these at 0.018, 0.029, and 0.0029 pg/L for the three example compounds, respectively. For Scenarios 1 and 2, where watershed soil concentrations of 2,3,7,8-TCDD and 2,3,4,7,8-PCDF were set at 0.39 and 0.67 ng/kg (ppt), respectively, surface water concentrations were lower $8*10^{-3}$ pg/L (ppq) for 2,3,7,8-TCDD and $9*10^{-3}$ pg/L for 2,3,4,7,8-PCDF. For Scenarios 4 and 5 demonstrating stack emission depositions and where watershed soil concentrations of toxic equivalents, WHO_{98}-TEQ_{DF}, were estimated to be in the10^{-3} ppt range, surface water concentrations were in the 10^{-5} ppq range.

7.3.5. Data on Fish Concentrations in the Literature

This assessment estimated fish lipid concentrations of 2,3,7,8-TCDD for the various source categories to be: 1) background conditions - 3.0 ppt, 2) soil contamination - 4.3 ppt, 3) stack emission source category - 0.0003 ppt, and 4) effluent discharge source category - 6.4 ppt. The fish lipid content assumed was 0.07. Therefore, whole fish tissue concentrations are estimated at about one order of magnitude lower than these lipid concentrations. Data was not found to appropriately compare the stack emission source category results, and data on the effluent discharge source category is examined in the next section below. This section will examine some available data on fish concentrations in order to compare results from the first two categories with measured results.

The most appropriate study with which to make comparisons is the National Study of Chemical Residues in Fish (EPA, 1992b; hereafter abbreviated NSCRF). Fish tissue data on a variety of species and contaminants of concern in aquatic environments and fish from around the country were developed. Most important for current purposes, the sites were carefully characterized in terms of potential sources of fish contamination. There were 353 sites from which fish tissue data were available, of which 347 had data on 2,3,7,8-TCDD. Results from four site categories might be appropriate for comparison with concentrations estimated to occur from low, possibly background, soil concentrations of 2,3,7,8-TCDD. The four categories and number of sites per category were: the USGS water quality network NASQAN - 40 sites; Background (B) - 34 sites, Agricultural (A) - 17 sites, and Publicly Owned Treatment Works (POTW) - 8 sites. The average 2,3,7,8-TCDD whole fish tissue concentrations (lipid contents not provided) measured for these four categories were: NASQAN - 1.02 ppt; B - 0.56 ppt; A -

0.75 ppt, and POTW - 0.90 ppt. Background conditions were demonstrated in Chapter 5 using a soil concentration of 2,3,7,8-TCDD that was found in an actual background conditions - 0.37 ng/kg (ppt). The resulting fish tissue concentrations estimated for this soil concentration was 0.2 ppt (on a whole tissue basis assuming a fish lipid fraction of 0.07). Four of the site categories of the NSCRF might be considered representative of sources characterized as land areas of high soil concentrations of 2,3,7,8-TCDD. These were: Industrial/Urban site (IND/URB) - 105 sites, Refinery/Other Industry (R/I) - 20 sites, Wood Preservers (WP) - 11 sites, and Superfund Sites (NPL) - 7 sites. Average fish tissue concentrations measured for these site categories were: IND/URB - 4.04 ppt, R/I - 4.38 ppt, WP - 1.40 ppt, and NPL - 30.02 ppt. The source category of this assessment most similarly characterized to these would the category of soil contamination, where a bounded area of contaminated soil had 2,3,7,8-TCDD concentrations at 1.00 ppb. The resulting fish tissue concentration predicted was 0.3 ppt (assuming a fish lipid fraction of 0.07). The two remaining site categories of the NSCRF were Paper Mills Using Chlorine (PPC), and Other Paper Mills (PPNC). These data served as the basis for the comparison discussed below in the effluent discharge source category.

In general, the range of fish tissue concentrations measured for (perhaps) background conditions, 0.56 - 1.02 ppt, were comparable to the 0.21 ppt fish tissue concentration estimated assuming the background soil concentration of 0.37 ppt. The same may not be true, however, in the comparison of fish tissue concentrations ranging from 1 to 30 ppt associated with urban/industrial contamination. The fish tissue concentration modeled in the demonstration of the soil contamination source category was much lower at 0.3 ppt. However, it may not be entirely appropriate to compare the demonstration of the soil contamination source category with the urban/industrial sites of the NSCRF. For the demonstration scenario, the contaminated site was 4 ha within a 100,000 ha watershed which had concentrations of 2,3,7,8-TCDD set to 0.0. The fact that the background demonstration predicted a fish concentration 0.2 ppt, which was within a factor of 3 to 5 of observations from the NSCRF (or closer to values in the NSCRF if the fish lipid content was higher than 0.07), might be considered a limited validation of the models. This is not a validation exercise, strictly speaking, since specific field data were not input and compared.

One data point from that study of interest is the 30.02 ppt concentration found for the NPL site. This is two orders of magnitude higher than the 0.3 ppt estimated for the soil contamination source category. No insights can be gained from this difference because information was unavailable on the seven sites which were characterized as Superfund sites and which were expected to have been the cause of the 30.02 ppt fish concentration. It would be interesting to know the surface soil concentrations of the 7 NPL sites, the size of these sites including the receiving water body, and their proximity to the receiving water body - that information may be sufficient to conduct a partial model validation exercise.

Another comprehensive data base of fish concentrations of 2,3,7,8-TCDD is from EPA's National Dioxin Study (EPA, 1987; abbreviated NDS), which actually provided the motivation for the NSCRF when significant residues of 2,3,7,8-TCDD were found in fish in the NDS. Fish concentrations from the NDS are also listed and discussed in Kuehl, et al. (1989). Travis and Hattemer-Frey (1991) summarized the fish data from the NDS. Their summary is as follows. Data collected from 304 urban sites in the vicinity of population centers or areas with known commercial fishing activity, including the Great Lakes Region, showed concentrations to range from non-detected to 85 ng/kg (ppt). The geometric mean concentration was 0.3 ppt, and only 29% had detectable levels of 2,3,7,8-TCDD. The Great Lakes data had more contamination, with 80% detection rate and a geometric mean concentration of 3.8 ppt.

The NSCRF also collected data on 2,3,4,7,8-PCDF, the second example compound demonstrated. Briefly, the range of average fish tissue concentrations noted for the site categories evaluated as background above is 0.42-0.78 ppt, very similar to the 2,3,7,8-TCDD range of 0.56-1.02 ppt. The modeled fish tissue concentration of 2,3,4,7,8-PCDF for background conditions was about the same as that for 2,3,7,8-TCDD at 0.17 ppt. The range of 2,3,4,7,8-PCDF average fish concentrations for the sites of elevated soil concentration was 1.86-5.44 ppt, which, like the comparison above for 2,3,7,8-TCDD, is higher than the modeled 2,3,4,7,8-PCDF concentrations of 0.18 for the soil contamination source category with initial soil concentrations of 1.0 ppb.

The NSCRF also collected data on PCB concentrations in fish, although the results were expressed in terms of total tetra-, hepta-, and so on. The data indicates concentrations well into the part per billion range for this breakout, and even higher considering total PCBs. The average concentration of total heptachlorobiphenyls over all study sites was 96.7 μg/kg (ppb). The average concentration of total PCBs over all sites was estimated as 1897.88 ppb, and the average concentration of total PCBs for background sites was 46.9 ppb. The modeled concentration of the example heptachlorobiphenyl, 2,3,3',4,4',5,5'-HPCB, for the soil contamination source scenario, where the soil concentration was 1 ppb, was 7.6 ppt.

Data from the Great Lakes region indicate that PCB concentrations are significantly higher than CDD/F concentrations in this area. PCB concentrations from fish in Lake Ontario are in the tens to hundreds of ppb level (Niimi and Oliver, 1989), while 2,3,7,8-TCDD contamination in Lake Ontario was in the tens of ppt level (EPA, 1990a) - a three order of magnitude difference. Other data in Table B.10, Appendix B, Volume II, where concentrations were similarly in the tens to hundreds of ppb level were from Lake Michigan (Smith, et al. 1990) and Waukegan Harbor in Illinois (Huckins, et al., 1988). The single data point from that table for 2,3,3',4,4',5,5'-HPCB, the example PCB congener in Chapter 5, was for carp in Lake Michigan, and was 29 ppb (29,000 ppt).

While the modeled CDD/F fish concentrations for background settings seem reasonably in line with measured concentrations from similar settings, this assessment may have underestimated concentrations of 2,3,3',4,4',5,5'-HPCB. As noted, concentrations for fish in the Great Lakes Region were in the tens to hundreds of ppb range, while this assessment derived estimates in the low ppt range. It is inappropriate to make direct comparisons without also comparing source strengths. Concentrations of PCBs in bottom sediments ranged from the low ppb for the tri-PCBs, to the tens of ppb for the tetra through hexa-PCBs, back to the low ppb for the hepta and octa-PCBs, in Lake Ontario (Oliver and Niimi, 1988). Another literature source showing fish concentrations in Waukegan Harbor, IL, in the hundreds of ppb range, had sediment concentrations of specific congeners as low as 5 ppb to as high as 131 ppm. The concentration of 2,3,3',4,4',5,5'-HPCB in bottom sediments was estimated to be 1.6 ppt in the soil contamination scenario. Therefore, one reason PCB concentrations in fish estimated in this assessment are as much as four orders of magnitude lower than noted in the literature is because sediment concentrations estimated for the source categories in this assessment are also about four orders of magnitude lower. The BSAF for PCBs also was noted to be variable, with values below 1.0 to values over 20.0 (see Chapter 4, Section 4.3.4). The BSAF for the example PCB congener in this assessment was 2.0. Higher BSAFs would also increase PCB concentrations estimated for fish.

The fish concentration of 2,3,7,8-TCDD estimated for the stack emission source category was lowest at 0.00002 ppt. Data was unavailable to place this in any comparative framework. This is because the incinerator modeled was a well-controlled incinerator and the impacts modeled were incremental - they did not include a background load into the water body which would undoubtably drive fish concentrations in an area where there is a well-controlled incinerator.

7.3.6. Impact of Pulp and Paper Mill Effluent Discharges on Fish Tissue Concentrations

a. Description of Exercise and Model Parameters

This section describes a validation exercise of the effluent discharge algorithm. The description of this exercise as a “validation” exercise tentative, since much of the data used is of uncertain quality. Discharge rates of 2,3,7,8-TCDD (mass/time units) into surface water bodies from a subset of 104 pulp and paper mills, which were sampled on a one-time basis in 1988 for such discharges and other parameters (EPA, 1990b; hereafter referred to as the 104-mill study), represent the key observed source term for this exercise. Fish concentrations of 2,3,7,8-TCDD for fish sampled downstream of these sources as part of the National Study of Chemical Residues in Fish (EPA, 1992b; abbreviated NSCRF hereafter) represent the key predicted model result for this exercise.

The National Council of the Paper Industry for Air and Stream Improvement (abbreviated NCASI hereafter) has already performed this exercise, and a brief description of their efforts and results can be found in Sherman, et al. (1992). NCASI carefully matched NSCRF data to appropriate mills of the 104-mill study. In many cases, they found more than one fish sample to correspond to a given discharge. Also, they considered circumstances where more than one mill effluent discharge can be considered to have impacted the environment where fish were sampled. In these cases, discharge rates from the contributing mills were fed into the model as source terms.

In NCASI's careful examination of the available data, they only considered 47 of the 104 mills as appropriate for this type of model testing. From these 47 mills, 95 fish samples with detectable residues of 2,3,7,8-TCDD were identified. Some mills had only one fish sample corresponding to it while others had up to four fish samples. The following explains why 57 of the remaining mills were not considered for this exercise:

1. Downstream of 10 pulp and paper mills was an estuary. NCASI considered the model appropriate for riverine situations only and did not calculate fish concentrations for estuarine settings.

2. The measurement for 2,3,7,8-TCDD in the effluent was listed as non-detect, and no further data examination and modeling occurred. There were 13 mills in this category.

3. NCASI could not identify appropriate fish measurements in the NCSRF downstream of the mill, and did not model further. Seven mills were in this category.

4. Some of the mills in NCASI's exercise were only considered "proximate" mills adding to the source term associated with another mill and one or more fish concentrations. Five mills were described in this manner.

5. For the remaining 22 mills, no explanation was provided for their lack of inclusion in the validation exercise.

Details of the NCASI modeling assumptions were supplied to EPA by NCASI (personal communication, Steven Hinton, PhD., P.E., NCASI, Inc.; Department of Civil Engineering, Tufts University, Medford, MA, 02155) and adopted for this exercise. Several other source materials were used to develop the parameters for this exercise. First, Figure 7-5 shows the effluent discharge model and all the numerical quantities required, including the source term and the observed fish concentration, and model parameters associated with the mill discharge and the aquatic environment. Further description of the effluent discharge model can be found in Chapter 4. The model parameters and their source materials are now listed.

1) **Mill parameters including the 2,3,7,8-TCDD discharge rate, the effluent flow rate, the suspended solids content of the effluent flow, and the organic carbon content of the suspended solids in the effluent flow:** The 104-mill pulp and paper mill study (EPA, 1990b), a cooperative study between EPA and the paper industry, measured mass releases of 2,3,7,8-TCDD (actually effluent flow and concentrations, from which mass releases can be estimated), effluent flow, and total suspended solids content of the effluent flow (and other information such as releases of 2,3,7,8-TCDF, which were not needed for this exercise). For purposes of this validation exercise, actually only the total suspended solids content of effluent discharges was used from the primary reference of this study (EPA, 1990b). Data from the 104-mill study was also used in a modeling study, described more fully below, and in that reference, it was more conveniently organized and compiled. As such, effluent flow and 2,3,7,8-TCDD discharge rates came from a secondary reference. The organic carbon content of the solids in the effluent was assumed to be 0.36. This was the value used in the example scenario of Chapter 5, and was based on the fact that effluent solids are principally biosolids).

2) Receiving water body parameters including flow rate, suspended solids content, and organic carbon content of suspended solids. A modeling study conducted by EPA (EPA, 1990c) used a simple dilution and the EXAMS model to evaluate the impact from discharges of 2,3,7,8-TCDD and 2,3,7,8-TCDF from chlorine bleaching mills. Mills from the 104-mill study were the ones evaluated in this report. This study developed key receiving water parameters for these mills which are pertinent to the dilution model of this assessment, including harmonic mean flows at the point of effluent discharges, which were based on the nearest STORET sampling point, and suspended solids concentration of the receiving water body at this point. Details on how these key quantities were developed are included in that report and will not be discussed here. The organic carbon content of the suspended solids was assumed to be 0.05, which was also the content assumed for the example scenarios in Chapter 5.

3) Parameters associated with 2,3,7,8-TCDD, including the organic carbon partition coefficient, Koc, and the biota suspended sediment accumulation factor (abbreviated BSSAF). The Koc for 2,3,7,8-TCDD was the same 3.98×10^6 otherwise assumed in this assessment, and the BSSAF value was assumed to be 0.09, which is the same value as the BSAF, Biota (bottom) Sediment Accumulation Factor. Sections in Chapter 4 further discuss the Koc, BSAF, and BSSAF.

4) Fish data including the fraction lipid and the observed fish concentrations: The core reference for this information is the National Study of Chemical Residues in Fish (EPA, 1992b), as noted above. NCASI compiled the fish concentrations and associated lipid content of the samples as part of their modeling exercise, and these were used here as well.

Table 7-10 lists the parameters used for each identified mill and receiving water body, as well as the modeled and observed fish concentrations. Not included in this table are the parameters assumed for all model runs, including the organic carbon contents of the suspended solids terms, and the 2,3,7,-TCDD Koc and BSSAF.

b. Results and Discussion

One important point to discuss up front is that 38 of the 47 eligible mills discharged into surface water bodies that were characterized as "low", while the remaining 9 mills discharged into "high" receiving water bodies. This characterization refers to the flow rates of the receiving water bodies. The average harmonic mean flow rate of the 38 low water bodies was 5.3 * 10^8 L/hr, with a range of 10^7 to 10^9 L/hr, while for the other nine, the average flow was 2.6 * 10^{10} L/hr, with a narrow range of 1 to 4 * 10^{10} L/hr.

This distinction appears to be non-trivial for a few reasons. One, model predictions appear to more closely match observations for the smaller water bodies. The average of 38 mills and 74 fish for modeled and observed fish concentrations is 7 ppt and 15 ppt, respectively. The average of 9 mills and 21 fish associated with large receiving water bodies for modeled and observed fish concentrations is 0.1 and 5.3 ppt, respectively. However, some paired data (predicted versus observed fish concentration) showed over 3 orders of magnitude difference - 0.001 pg/g TCDD predicted versus 1.4 pg/g TCDD observed, for example. As evaluated by NCASI, another important feature of the larger receiving water bodies that they were the ones principally considered to have multiple discharges.

A final observation concerning the large receiving water bodies is that the suspended solids data is also significantly different than the low receiving water bodies. For the 38 water bodies associated with the small water bodies, the receiving water body solids content averaged 9 mg/L, while for the nine high receiving water bodies, the suspended solids content averaged 73 mg/L. This importance of the suspended solids content is principally seen for mills 39-42. The solids content of these water bodies ranged from 107 to 221 mg/L. The average modeled fish concentration for these mills was 0.005 ppt, while the average observed fish concentrations was 3.0 ppt. The impact is one of "dilution": discharged 2,3,7,8-TCDD mixes into a larger reservoir of suspended particles, leading to a low 2,3,7,8-TCDD concentration on suspended solids concentration and lower predicted fish tissue concentrations. This dilution effect may also be real, as the average observed fish concentrations for these circumstances of 3.0 ppt may indicate a significant difference with the average 15.0 ppt observed for the smaller receiving water bodies. Nonetheless, these high suspended solids data must be considered suspect; if the suspended solids concentration were, in fact, lower on average, than model predictions would have closer than 3 orders of magnitude away from measurements.

Considering all 47 mills and 95 fish observations, it was found that 73 and 87% of predictions within a factor of 10 and 20 of observed concentrations, respectively. The predicted and observed results of this exercise for these 47 mills is shown graphically in Figure 7-6, which also shows the bounds of + or - a factor of 10 difference in predictions and observations Of note and perhaps not ironically, the highest observed fish concentration of 143.3 ppt is matched by the highest predicted fish concentration of 89.2 ppt. .

While Figure 7-6 appears to show a poor match in predictions and observations, the data available must be carefully considered. Only one discharge measurement is made, and a limited number of fish at various points downstream were available for this exercise. It would certainly be more meaningful if several discharge measurements per mill were made and several fish measurements were made downstream of the discharge. To be more rigorous, several measurements of discharge would have to be made over time to best reflect an average discharge. Likewise, other mill-specific parameters are uncertain, such as receiving water body flow, suspended solids in the water body, and so on. Finally, and perhaps most importantly, the assumption of this exercise is that the mill discharges of 2,3,7,8-TCDD represent the only sources impacting the fish. This is most unlikely to be the case for the large receiving water bodies, which may be receiving other industrial point discharges or non-point sources (runoff, atmospheric deposition). Given the factor of 2 difference in average predicted and observed fish concentrations for the low receiving water bodies, one might cautiously conclude that the effluent discharge model of this assessment is generally valid for, at least, receiving rivers with flows in the range of 10^8 L/hr.

Given this last cautious statement, one can continue this exercise by attempting a calibration on an appropriate parameter(s) so that predictions better match observations. The appropriate parameter for calibration is the BSSAF. The choice of 0.09 for the 2,3,7,8-TCDD BSSAF was based on data from Lake Ontario (EPA, 1990a). Specifically, 0.09 was the BSAF -

lake bottom sediment to fish lipid accumulation factor - for measured fish and bottom sediments of Lake Ontario. As this is a lake and not a riverine situation, and inasmuch as 2,3,7,8-TCDD contamination of Lake Ontario sediments have been attributed to historical impacts and not ongoing causes, the 0.09 may be inappropriate. As well, a range of BSAFs for 2,3,7,8-TCDD were noted in the literature in Chapter 4 of this assessment, ranging from less than 0.05 to greater than 1.00. EPA (1993) suggests that data collection methods limit the usefulness of some of the available literature, particularly those showing very high BSAF, and in a similar examination of BSAF data, suggests a range of 2,3,7,8-TCDD BSAF from 0.03 to 0.3. In any case, this suggests that the BSSAF is a reasonable candidate for calibration in this exercise.

A different selection for BSSAF significantly improves model performance. If the BSSAF is increased to 0.20 (up from 0.09), the average predicted fish tissue concentration for the 38 mills discharging into the smaller water bodies increases as expected from 7.0 to 15.6 ppt, comparing better now to the average observed concentration of 15.0 ppt.

Conclusions from this exercise include:

1. For at least smaller receiving water bodies, those with harmonic mean flows on the order of 10^7 to 10^9 L/hr, the effluent discharge model is appropriate for assessing effluent discharge impacts to fish for 2,3,7,8-TCDD and perhaps other dioxin-like compounds.

2. There appears to be a distinction in model performance for the large and small receiving water bodies. The high suspended solids concentrations generated in an earlier modeling exercise for the larger water bodies is one cause for model underprediction; these solids concentrations should be further reviewed. Also, these water bodies were evaluated by NCASI as ones with multiple sources. Other sources not identified by NCASI could also have been the cause for higher measured fish concentrations as compared to model predictions. The NSCRF report (EPA, 1992b) contains an appendix giving a matrix indicating point source categories of discharges which may have affected fish concentration results. Pulp and paper mills with and without chlorine were listed as point sources for 125 episodes (an episode is a fish sampling site). In 37 of these episodes, other point sources were identified, including one or more of the following: refinery (refinery using the catalytic reforming process), NPL site (a Superfund site), or other industry (an industrial discharge other than a paper mill or refinery). Given other sources, it is in fact a benefit to the exercise that predictions were lower than observations.

3. The model more closely predicts fish concentrations for the smaller receiving water bodies when the BSSAF is calibrated from 0.09 to 0.20. Considering that 0.09 was a value for 2,3,7,8-TCDD developed with data from Lake Ontario, a standing water body with principally

historic and not ongoing 2,3,7,8-TCDD impacts, this setting is probably an inappropriate surrogate for ongoing discharges to a riverine situation. This would argue that a calibration is warranted.

7.3.7. Air Dispersion and Soil Concentration Modeling Around an Incinerator Known to be Emitting Large Amounts of Dioxins

The Columbus Municipal Solid Waste-to-Energy (CMSWTE) Incinerator in Columbus, OH, operated between June 1983 and December 1994, and processed an average of 1600 metric tons of solid waste per day during its operation. A stack test taken in 1992 (EERC, 1992) indicated that the annual emission rate of dioxin I-TEQs was 984 g. Measures were taken to reduce dioxin emissions by the operators of CMSWTE. A second stack test was taken in 1994 (EMC, 1994) to evaluate the effectiveness of these dioxin reduction measures. The rate of emission from this test was calculated at 267 g TEQ/yr, indicating about a 75% reduction in dioxin emissions. These rates of emission can be compared against United States estimates of total annual emissions from all known sources of dioxin release of 12 kg TEQ in 1987 and 3 kg in 1995; see Volume I of these Dioxin Exposure Reassessment documents.

An ambient air monitoring study undertaken by the Ohio Environmental Protection Agency (OEPA) included two rounds of sampling in 1994, one during a concurrent stack test, and one round in 1995 after the incinerator had shut down (OEPA, 1994; 1995). For both sampling events in 1994, the concentration was highest in the air monitor (1 of 6 total monitors; 5 operational for each sampling event) located in the downwind direction (southeast) from the CMSWTE. Also, the profile of dioxins in the air matched the stack emission profile much more closely than the other air samples, which had lower and more typical urban air concentrations. A soil monitoring study conducted during 1995 and 1996 included 34 soil samples taken on-site and up to 8 km in all directions from the plant (Lorber, et al., 1998). An evaluation of these soil data clearly showed an imprint from the CMSWTE, with concentrations decreasing as a function of distance from the stack, approaching a local background after about 3 km.

Complete descriptions of the stack, air, and soil measurements conducted around the CMSWTE are available in previous papers (EERC, 1992; EMC, 1994; Ohio EPA, 1994, 1995; Lorber, et al., 1998) and only summarized here.

The ISCST3 was run twice, once to obtain predicted concentrations over the 48-hour period corresponding to the two ambient air monitoring events in 1994, and once to obtain annual average wet and dry deposition of sorbed dioxins to input into a simple soil reservoir mixing model to predict dioxin concentrations. The objective of this exercise was to use current

EPA guidance on the use of ISCST3 for air dispersion/deposition modeling of dioxins (EPA, 1994;1995b), coupled with a soil concentration model, and after doing so, determine how well the model was able to reproduce observed air and soil concentrations. This might be described as a "model validation" exercise because it has these characteristics: 1) all available site-specific information - stack emission rates, meteorological data, stack parameters, and others - are input into the model, 2) all other parameters for which no site-specific data is available - soil half-lives, atmospheric particle densities and mass fractions, and others - are input into the model using best available information with no attempts at "calibration" in order to make the model results best match observations, and 3) model results including predicted air and soil concentrations are compared against corresponding monitored concentrations.

On the other hand, it is recognized that this exercise falls short of a rigorous model validation exercise for ISCST3. The observed ambient air data set includes only two monitoring dates, with five ambient measurements for one date and four for the other date. Actual stack measurements of emissions are available for one of those dates, so a comparison of measured and predicted air concentrations for the second date does not qualify as a "validation" exercise. It must be assumed that emissions were the same for this second air sampling date. This is admittedly a small data set and a resulting rigorous test for ISCST3 dispersion model testing. Also, ISCST3 (and similar gaussian dispersion models) is expected to perform better for longer averaging periods (e.g., annual) than for short term events. Expectations for the "success" or characterization of the "failure" of the ISCST3 dispersion algorithms have to be tempered by these considerations.

The input of the average predicted depositions of dioxins into a simple soil mixing model to predict soil concentrations, and then comparing those to observed soil concentrations, is an exercise that may come closer to being a "model validation" exercise. In that case, the ISCST3 is applied in an hourly short-term mode over one year's worth of meteorological data to predict average long-term depositions to soil. These depositions are input into a soil mixing model to predict soil concentrations, and then the model results are compared with observations of soil concentrations. Unlike 48-hour air measurements, soil impacts are "long-term", particularly since dioxins are known to accumulate in soils over time and not undergo very meaningful dissipation. Also, there are 34 soil measurements around the CMSWTE available, and this number allowed for a reasonable characterization of the elevation of dioxin concentrations near the facility and the decline of concentration with distance.

In any case, discrepancies between predictions and observations in both the air and soil model comparison exercises were examined in order to gain insight on the capability of the

ISCST3 model to predict ambient air and soil impacts of emitted dioxins, and to gain insight on potential issues for further study of atmospheric and soil fate for dioxins.

7.3.7.1. *Modeling Procedures*

ISCST3 Modeling: ISCST3 is a Gaussian plume model, which accepts a variety of source geometries and emissions schedules in order to compute ambient air concentrations and surface deposition fluxes at specified receptor points. Two applications of ISCST3 were conducted for this effort. In one, the air dispersion algorithms alone were run, and meteorological data requirements included hourly wind speed, wind direction and stability for describing dispersion. These runs were conducted for the purpose of predicting 48-hr air concentrations, to compare with the 48-hr ambient air measurements. For the other, the particle-phase deposition algorithms were employed and dioxins were depleted from the plume by an amount equal to that depositing as the plume moved outward from the CMSWTE. The key output from these runs were long-term average dry and wet deposition of particle-bound dioxins, which were used for predicting soil concentrations of dioxins, to compare with the soil measurements.

For the dispersion model test, there were, in fact, two separate tests of the air dispersion algorithm - each test had a different meteorological data set: an “airport” set and an “on-site” meteorological data set. The airport set includes surface data (wind speed, wind direction and atmospheric stability) from the Columbus, OH, airport and upper air data for the mixing height from Dayton, OH. airport (BEEline Software, Inc. ISCST3 driver diskette 1998). The airport data was applied only for the first of two air monitoring events. On-site data for both of the 1994 measurement periods include wind speed and wind direction (Ohio Environmental Protection Agency. private communication 1998). The Columbus stability and Dayton mixing height were used in the on-site set. The purpose of obtaining and testing two meteorological data sets was to be able to evaluate the importance and uncertainty associated with key input stream. Besides meteorological data, other required inputs for modeling dispersion alone included: (1) building configuration data, (2) emissions data, and (3) receptor data. These dispersion model runs omitted particle-phase deposition, plume depletion, and chemical decay in the air. The dioxins were modeled as if the entire emission were in the form of a conservative pollutant, with no differentiation in fate of the individual compounds as a function of vapor/particle partitioning behavior, or atmospheric degradation or transformations.

For the deposition application of ISCST3, wet and dry deposition of particle-bound dioxins were modeled and then input to a separate soil mixing model to predict soil concentrations. Therefore, additional meteorological data required were precipitation data. The prediction of depositions of particle-bound CDD/Fs with ISCST3 relies on particle-specific (particle diameter, e.g.) and dioxin-specific (vapor/particle partitioning, e.g.) parameters which are not required for dispersion modeling. The ISCST3 model estimates deposition flux values by multiplying the pollutant concentration in airborne particles by a deposition velocity. The deposition velocity is calculated considering gravitational settling velocities and atmospheric resistance. Annual average depositions were predicted using a single year of meteorological data from 1989; modeling from 1983 to 1994 would obviously have been preferable, but only one year of data was available. Meteorological data was provided by the National Climatic Data Center and from EPA's Support Center for Regulatory Air Modeling internet page (www.epa.gov/ttn/scram). The surface and precipitation data was collected at the Columbus, Ohio Weather Service Office. Atmospheric mixing heights were determined using upper air data collected at the Dayton, Ohio Weather Service Station. An examination of the meteorological data from 1989 compared with historical averages showed that the wind speed and direction were very similar to historical means, and the precipitation was slightly above normal for 1989 (111 cm for 1989 compared to an historical average for Columbus, OH, of 96 cm/yr). The ISCST3 was run in plume depletion mode, meaning that dioxins were depleted from the plume moving away from the incinerator by an amount equal to the dioxins depositing by dry and wet particle-phase deposition.

Like the air dispersion tests of ISCST3, two sets of outputs were generated for soil concentration modeling. There were two stack tests available, and it was unclear as to which would better characterize long term emissions of dioxins from CMSWTE. Both were used to predict soil concentrations. This is described in more detail in the next section below on Source Characterization.

The ISCST3 model was run on a "unitized" basis for both dispersion and deposition simulations, meaning that ambient air concentrations and deposition results were generated for an emission rate of 1 g/sec. For the dispersion-only runs, the individual total emission rates of all 25 CDD/Fs (17 congeners on non-zero toxicity and 8 homologue groups) were multiplied by the predicted unit concentration to give the predicted ambient concentrations at the receptor points. Deposition predictions for the CDD/Fs were generated using this two-step procedure: 1) the total amount of the CDD/F emitted was assumed to partition into vapor and particle fractions according to ambient conditions at 20 °C (in contrast to partitioning assuming conditions at the stack exit); this step allowed for an estimation of dioxin-specific particle-bound emission rates in g/sec, 2) then, these particle-bound mass emission rates were multiplied by the unitized dry and wet deposition rates predicted to occur at the receptor point to provide the compound-specific deposition rates.

All model parameters for both runs, with the exception of the details on receptor locations (air and soil monitoring locations around the CMSWTE) are provided in Table 7-11. Further detail on modeling algorithms for the ISCST3 can be found in EPA (1995b).

Source Term Characterization: Two stack tests were available to supply the critical source term for this exercise (EERC, 1992; EMC, 1994). The first was conducted in 1992 by the Ohio Environmental Protection Agency (OEPA) for purposes of permit renewal. High dioxin emissions at 6799 ng total/dscm concentration (total = sum of the homologue group concentrations; dscm = dry standard cubic meter) and 976 g TEQ/yr (when extrapolating the results from 1 stack to the 3 stacks at CMSWTE and assuming historical average operation times for the CMSWTE) mass emissions were found, leading to regulatory actions by the state and federal environmental agencies. Process modifications were undertaken for purposes of reducing dioxin emissions, and the CMSWTE was retested in March of 1994. Total concentrations were reduced to 3685 ng/dscm and the mass TEQ emissions were reduced by about 75% to 267 g TEQ/yr (estimated using the same historical CMSWTE operation practices).

This second stack test occurred during March 16-18 of 1994. This corresponds closely to the time that the OEPA was sampling the air for dioxins - on the 15-17th of March. Therefore, the air dispersion model tests for March used the March stack test results. Unfortunately, the CMSWTE was not stack-tested during the April air sampling events. It was necessary to use the March stack test results for the April dispersion model tests, and then, of course, to assume that the April emissions were similar to the March stack test emissions.

For deposition modeling, a decision also needed to be made regarding characterization of long-term emission rates. Rather than select either the 1992 or the 1994 stack emission test for this evaluation, or an average of the two, to represent long-term dioxin emission rates, results were generated for both emission tests to demonstrate the importance of this critical and uncertain term in the modeling procedure.

Soil Concentration Modeling: Wet and dry depositions are summed and become the source term for a simple reservoir mixing model for predicting soil concentration C_s, as:

$$C_s = \frac{F\,(1 - e^{-kt})}{k\,M} \tag{7-39}$$

where:

Cs = the soil concentration, pg/g
F = the annual total (wet + dry) deposition of dioxins as predicted by ISCST3, pg/m^2-yr
k = the first order annual soil dissipation rate, yr^{-1}
t = the time during which deposition occurs, yr
M = the soil mixing mass, g/m^2

The dissipation rate assumed here for all dioxin compounds was 0.02772 yr^{-1} (half-life of 25 years), a mid-range value selected to be between a value of 0.0693 (half-life of 10 years) often assumed for surficial dioxin residues (EPA, 1994) and 0.00693 (half-life of 100 years) speculated to be an upper range for subsurface dioxin residues (Paustenbach, et al., 1992). The best validation of this choice of half-lives for all dioxin congeners comes from McLachlan, et al. (1996), who reported on an analysis of soil taken from experimental plots which had been amended with sewage sludge in 1968 and sampled in 1972, 76, 81, 85, and 90. These archived samples were analyzed for all 17 dioxin-like CDD/Fs, and based on an analysis of results, McLachlan and coworkers concluded that half-lives were on the order of 20 years, with dioxin removal from the plots being mainly physical removal processes (overland runoff, wind erosion). Furthermore, their results suggested that all congeners had been removed at roughly the same rate, which is why they concluded that removal processes were mainly physical and very little in-situ degradation appeared to be occurring. A time of operation, t, of 11.5 years was used, corresponding to the time of operation of the CMSWTE. The soil mixing mass, M, equaled 112,500 g/m^2, which assumes a mid-range soil bulk density of 1.5 g/cm^3 and the soil sampling depth of 7.5 cm.

Description of the Measured Air and Soil Concentrations: Ambient air monitoring was conducted by the Ohio Environmental Protection Agency (OEPA) in 1994 to evaluate ambient air concentrations after process modifications reduced dioxin emissions from the CMSWTE. General Metal Works model PS-1 high volume samplers were used to collect 48-hr samples. Concentrations were, therefore, the sum of vapor + particle phase concentrations. Six monitors were in the city of Columbus between 1.8 and 3.0 km from the site, mostly in the historical downwind direction, northeast, but one in the upwind southwest direction. Two of the samplers were co-located (for purposes of quality control), so results from these two samplers were averaged to represent one sampling point A seventh sampler was located 45 km southwest of the facility in a rural “background” setting; results from this sampler were not used in this modeling study. Five samples (4 sampling locations; the co-located samples were averaged) were taken in March and 6 samples (5 locations) were taken in April, 1994. The March set, taken on the 15-17th of the month, occurred at nearly the precise time that the March 1994 stack testing occurred, on the 16-18th. The April sampling event occurred during April 19-21. Exact starting and stopping times of the air monitors were not available for this test. For purposes of air dispersion modeling, the starting and stopping times were assumed to be the mid-day of the beginning and ending days of each sampling periods. In all, there were 9 urban air sampling events taken during 1994 that comprise the “observed” air concentration data set used in this modeling study. Wind rose data for the March and April sampling periods were also available, and the provided insights into the expected impact patterns. A final round of air samples from the seven air monitors was taken in 1995 after the CMSWTE had shut down. The purpose of this data set was to evaluate the air quality now that the CMSWTE was no longer operating. Full details on the air monitoring studies, including analytical methodologies, quality control, and final results, are described in OEPA (1994, 1995).

A first phase of soil sampling was conducted by the United States Environmental Protection Agency (EPA) in December of 1995. Sampling in this round included 4 samples on the site of the incinerator, 18 samples within about 3 km of the incinerator in the city of Columbus, and 3 samples at a background site 45 km from the CMSWTE. This background site was the same as the air monitoring background site. The study design for this phase employed a stratified random selection process, involving sites in the four major quadrants around the incinerator (northeast, southwest, etc.) with an emphasis of sampling in the quadrant which was historically downwind from the incinerator, the northeast quadrant. The following conditions were sought during site selection: 1) level, undisturbed soils, 2) away from trees, 3) not adjacent to roads, 4) not near pressure treated wood, and 5) not known or suspected to have high dioxin concentrations for any other reason. All samples were collected using pre-cleaned equipment dedicated to each sampling location. Each sample site consisted of an area of 1.5 m x 1.5 m. A grid of 25 sections was established at each site and used for random selection of aliquot sample sites. Four random aliquots were collected for each sample. A “sample” for this study was, therefore, a composite of four aliquots. Aliquots were collected using a stainless steel tulip bulb planting device. This device removed a plug approximately 7.5 cm in diameter to a depth of about 7.5 cm.

A second phase of soil sampling was undertaken in August of 1996. Thirteen samples were taken from about 2 km away from the incinerator to about 8 km distant. The purpose of this second phase was to ascertain whether a background concentration for the city of Columbus could be determined. A similar selection criteria for sample sites was employed in this second phase.

Altogether, there were 4 soil samples on the incinerator property, 31 samples in the city of Columbus taken from right outside the incinerator to upwards of 8 km away, and 3 background samples taken 45 km away, for a total of 38 soil samples. This modeling used 34 of the samples - it did not have use for the 3 background samples, and 1 of the remaining samples was found to be contaminated by a local source not associated with the CMSWTE. Full details of the soil monitoring study can be found in Lorber, et al. (1998).

Figure 7-7 shows the location of the CMSWTE in relation to the 32 soil samples in Columbus and the 5 urban air sampling locations. Not shown in this figure are 3 of the 4 soil samples taken on the site of the incinerator, and the background site in which 3 soil samples were taken and the 1 background air sampler was located. This figure identifies the groupings of the soil samples, as described in the results section below.

<u>Subtracting Local Background Concentrations From Measured Concentrations:</u> The ISCST3 will predict only the increments of dioxin concentration in the air and soil that are due to emissions from the CMSWTE. Therefore, a procedure had to be developed to subtract a local "background" of dioxins from both the air and soil observed data.

The average of 6 air measurements taken in 1995 after the CMSWTE shut down was assumed to represent the background dioxin air concentrations for this site. The average total concentration from 1995 was 2870 fg/m^3, with a range of 2030 to 4760 fg/m^3. The 1995 average concentrations of each dioxin-like congener as well as those of the homologue groups were subtracted from each of the March and April 1994 corresponding measurements. When such a subtraction resulted in a concentration less than 0, the concentration was assumed to be 0 for purposes of this exercise.

An analysis of the observed soil data in Lorber, et al. (1998) showed that concentrations decrease to the local soil background at about 3 km from the CMSWTE, at a TEQ soil concentrations of 4.0 pg/g (ppt). The soil profile of CDD/Fs for this background provided in

Lorber, et al. (1998) was subtracted from each of the 34 observed soil measurements; when this subtraction resulted in a concentration less than 0, the concentration was set to 0.

<u>Procedures for Evaluating the Performance of the Models:</u> The paucity of the observed data, particularly the air measurements, makes a rigorous "goodness-of-fit" statistical comparison of predicted versus observed inappropriate. Rather, tabular summaries of predicted and observed concentrations are utilized, and simple qualitative discussions address the goodness-of-fit. For the air dispersion comparisons, predicted air concentration quantities associated with a 48-hour air monitoring event are compared with the appropriate observed quantities. For the deposition comparisons, soil samples are "clustered" and simple mean concentrations are generated for both modeled and observed concentrations. Four clusters which are displayed include: 1) "on-site" - 3 soil samples taken on the site on the CMSWTE, 2) "off-site" - 5 samples just off-site and in the historical downwind direction, northeast, within 500 meters of the incinerator, 3) "urban" - 14 samples taken from about 500 meters to about 3 kilometers, and 4) "urban background" - 12 samples taken from about 3 to about 8 kilometers. As discussed in Lorber, et al (1998), the high soil concentrations found in the on-site cluster were speculated to have resulted in ash drift from piles or trucks transporting the ash to nearby landfills rather than deposition. Therefore, a comparison of predicted and observed concentrations for this on-site cluster are displayed for information purposes only, not to be considered in the context of model testing. Otherwise, all observed soil samples, and clusters, can be considered to represent long-term deposition trends as the monitoring study protocols insured that they were in relatively flat, undisturbed locations away from any nearby potential dioxin sources (roadways, PCP treated wood, etc.). The predicted and observed concentration quantities which are displayed include: 1) homologue group concentrations, 2) total concentrations, which are sum of the 10 homologue group concentrations, and 3) TEQ concentrations. These terms were defined above.

In addition to tabular summaries, isoline figures were generated. These are lines of equal concentration around the CMSWTE, either air or soil concentrations, that were generated using ArcView® - a desktop GIS package. First the point data, measured or modeled concentrations, are brought into ArcView® as point coverages. Then, using the ArcView® kriging routing, surfaces of the concentrations are generated using the exponential function to estimate the semivariogram. For the air and soil concentration isoline generation, modeled concentrations were generated for 250 meter intervals to about 3 km in all directions, and these were input as point coverages into ArcView®. There were too few observed air concentration measurements, so isolines could not be generated for these. Instead, measured air concentrations were overlain on the predicted isolines. For soil concentration, there was judged to be sufficient coverage with 34 soil samples to generate "observed" isolines to compare with predicted isolines.

Finally, it is reiterated that all "observed" concentrations, both soil and air, were generated by subtracting out background concentrations in the procedure described above. Therefore, all tabular or figure notations of a "0" observed concentration means that, if subtracting out the background concentrations from the measured concentrations resulted in a negative concentration, the measured concentration was set to zero for purposes here.

7.3.7.2. *Results and Discussions*

Air Dispersion Modeling: Even before air dispersion modeling was undertaken, examination of the data revealed clear trends. Analyses of on-site wind roses for the March and April 1994 sampling dates reveal that there is one dioxin monitoring station likely to have been influenced by the CMSWTE. This station, termed SE-3 by the Ohio Environmental Protection Agency (OEPA) was about 2 km east of the source and was downwind from the source approximately 53% of the time during the sampling period in March 1994 and 78% of the time in April 1994 (OEPA, 1994). In contrast, none of the other 5 stations was downwind for time fractions approaching those of SE-3. The measurements confirmed that SE-3 was the most impacted of the samplers, with TEQ measurements of 168 fg TEQ/m^3 in March and 353 fg TEQ/m^3 in April. The average of the measurements from the other 5 samplers over the two dates (a total of 8 samples; one sampler was not operational for both events) was 52 fg TEQ/m^3, with a range of 10 to 98 fg TEQ/m^3 (note: background not subtracted out for these observations). Lorber, et al (1998) examined this trend further, showing also that the profile of CDD/Fs found in March and April in SE-3 matched the stack emission profile of CDD/Fs more closely than the other ambient air samples, which displayed profiles more typical of background air.

Table 7-12 compares the observed total concentrations at each reporting monitoring station with the model predictions for both meteorological data sets, the "on-site" and "airport" sets. As noted earlier, two important considerations for evaluating the comparison of predicted and measured air concentrations are: 1) having 4 and 5 air measurements for sample dates in March and April, respectively, is a small sample size, and 2) one can expect the ISCST3 to perform better for longer averaging times as compared to shorter averaging times. It would be fair to conclude that the paired comparisons of predicted and observed 48-hr air concentrations are severe tests of model performance, and Table 7-12 shows the large scatter expected from this test.

Still, some meaningful observations might be possible from Table 7-12. First, it does not appear that either of the meteorological data sets provides a superior fit to the data for the March sampling event. The on-site runs appeared to better identify SE-3 as the monitor of most impact, and also to identify the sampler SN-2 as having some impact, but not as much impact as SE-3. The airport meteorological set appeared to show a significant impact to SN-2, but not as much of an impact for SE-3. On the other hand, the simulations using on-site meteorological data identified SNW-1 as having the highest concentrations, while the simulations using the airport data correctly modeled this site perhaps more correctly as having little impact. Both meteorological data sets correctly identified SSW-4 as the monitor which showed no impact.

For the April sampling date, the on-site meteorological data correctly identified SE-3 and SSW-4 as monitors having some impact, with little or no impact for the other three monitors. However, SE-3 was not simulated to have the most impact, as was found.

The difference between using the on-site and air meteorological data was further examined using isoline figures. Six such isoline drawings, with observed concentrations overlain, are shown in Figure 7-8. These include TCDD, OCDD, and TEQ predicted/observed results from March for the on-site data and the airport data set. Observations from this figure include:

1) ISCST3 modeling runs using both meteorological data sets appear to have correctly identified the western quadrants (northwest and southwest) as being areas of little impact. The observed “0" concentration in the southwest quadrant (sampler SSW-4) is consistent with this trend, as are wind rose that are displayed and discussed in OEPA (1994). Both figures appear to have identified the northeast and southeast as areas of principal impact, with little impact due east. The two observed air measurements in the northeast quadrant (samplers SN-2 and SNW-1) do, in fact, suggest low impact due north with increasing impact as one moves in the northeast direction. The observed air measurement in the southeast quadrant (sampler SE-3) may, in fact, have missed areas of higher impact during the two days, which the model runs suggest are either further north or further south.

2) The discussion above comparing the measured point estimates with the modeled point estimates suggests that there may be significant differences in the way the two meteorological data sets simulated impacts. More specifically, the “airport” data simulation showed three times as much impact for sampler SN-2 compared to the “on-site” simulation: 20,833 fg/m ^{3} total (airport) vs. 6,606 fg/m^3 (on-site). On the other hand, the “on-site” simulation showed 7 times more impact for sampler SNW-1: 8943 fg/m ^{3} (on-site) vs. 1270 fg/m ^{3} (airport). Looking at Figure 7-8, however, the differences do not appear that meaningful. The on-site simulations

seemed to push the plume a little more northeast and southeast compared to the airport runs, which showed more impact due north and south. Sampler SN-2 was simulated to be in a zone of important impact according to the airport meteorological data set, while sampler SNW-1 was simulated to approach this zone more so with the on-site meteorological data set. These types of trends emphasize the potential problems and misinterpretations that can occur when one attempts a validation exercise with ISCST3 with short-term data and a limited number of air measurements.

3) The biggest discrepancy for the three dioxin quantities compared in Figure 2 is for OCDD. It appears as though much higher concentrations, ranging from 1 to almost 5 pg/m^3 in the northeast and southeast were modeled, while measurements of 0.5 pg/m^3 and less were observed. These high modeled OCDD concentrations were the main reason that the ISCST3 modeled much higher observed total concentrations than were measured (see Table 7-12). For the other quantities, TCDD and TEQ, while the location of high impacts may not have been perfectly identified, at least the magnitude of the high measurements were in the range of the high modeled concentrations. This important trend is discussed in more detail below.

As mentioned above, station SE-3 stands out in both the March and April sampling as having the highest impact of all stations. Thus, the data from this station have the best chance of avoiding the uncertainties introduced by background fluctuations. Predicted and observed homologue group concentrations for SE-3 for the both sampling dates are compared in Table 7-13. These results were generated using on-site meteorological data. Table 7-13 also shows the CMSWTE stack emission rate of these homologue groups.

Being only an exercise in air dispersion modeling (no wet/dry deposition; no stack speciation; no atmospheric chemical reactions), there is a perfect correlation between the homologue profile of the emissions and air concentration predictions for both March and April. The observed air concentrations clearly do not have this stack emission profile, however. Specifically, the speciation pattern from source to receptor has shifted in these ways: 1) the lower chlorinated tetra and penta CDD/Fs have greatly magnified in importance in the ambient air profile as compared to the stack profile, and 2) conversely, the hexa through octa homologues, with the exception of OCDF, have been reduced in importance in the ambient air profile as compared to the stack profile. Said another way, the model predicted lower concentrations for the lower chlorinated CDD/Fs than were measured, and higher concentrations for the higher chlorinated CDD/Fs. The total concentration predictions were, however, within about a factor of two of observations. Not that it has meaning with regard to fate and transport considerations, but the TEQ concentrations were comparable: 125 and 309 fg TEQ/m^3 measured during March and April compared with 142 and 156 fg TEQ/m^3 modeled for SE-3.

Three possible explanations are offered to explain why the model did not predict the measured shift in homologue profile between the stack and field:

1) It is known that CDD/Fs with fewer chlorines have higher vapor to particle (V/P) ratios; indeed, high temperatures in the stack could generate even higher V/P ratios (Eschenroeder, 1994). If stack sampling methods underestimate the amount of vapor pollutant being emitted, than the lower chlorinated dioxin emission rates are being underestimated - an error that would be exacerbated by the even higher V/P ratios in the high temperature stack gas. The PS-1 samplers capturing both vapor and particle-phase CDD/Fs in ambient air are well tested and not expected to have caused error in the characterization of total ambient air concentrations of dioxins. There has been some speculation that PS-1 samplers may overestimate the vapor fraction of dioxins, but this would not affect their characterization total concentrations (sum of vapor and particle phase concentrations; see Chapter 3 for a complete discussion of vapor/particle partitioning).

2) Running the air dispersion algorithms of ISCST3 alone did not account for particle deposition, yet some of the higher chlorinated CDD/Fs, expected to be sorbed to ambient air particles or fly ash, may have deposited by dry deposition prior to the air sampling locations. The results for the deposition modeling described below support this hypothesis, at least for the dioxins. It compares model predictions of soil concentration with measured soil concentrations. One clear trend was that the model consistently underpredicted the soil concentration of the hepta and octa dioxin homologue groups. This result, combined with the observation that the higher chlorinated dioxins were the most overpredicted in air concentrations in this paper, suggests that the plume is being depleted of higher chlorinated dioxins by deposition. However, this trend was not duplicated by the higher chlorinated furans. There, modeled soil concentrations were more nearly consistent with measured soil concentrations, with a small degree of overprediction.

3) Another possible physical explanation is that dechlorination may occur between the emission point and the ambient measuring station a kilometer or two downwind. Workers at Monsanto Laboratories (Orth, et. al., 1987) and at the Agro-Environmental Science Institute in Japan (Koshioka, et al., 1989) have observed photolysis of TCDD. Generally, polychlorinated organic compounds easily experience photochemical loss of chlorine atoms. If the higher chlorinated CDD/Fs dechlorinated to form lower chlorinated CDD/Fs in the atmosphere, than more lower chlorinated CDD/Fs would have arrived at the ambient air monitoring stations to cause the distinct ambient air profile.

<u>Deposition and Soil Concentration Modeling:</u> Table 7-14 provides results from this exercise, which are observed and predicted homologue and TEQ concentrations for 4 clusters of soil samples. These clusters were developed for purposes of displaying results from the soil monitoring study conducted around the CMSWTE (Lorber, et al., 1998), and generally correspond to increasing distance in all directions from the incinerator. As discussed above, the observed and predicted soil concentrations for soil samples taken on-site, the first cluster of Table 7-14, are shown for informational purposes only; it is not expected that the on-site soil samples represented long-term deposition trends. Some trends that may be observed from the results in Table 7-14 include:

1) Since emission rates between the 1994 and 1992 stack tests differed by about a factor of 4, subsequent predictions of soil concentration made with each stack emission rate also differed by this factor of 4. Generally, the 1994 stack test predictions appear to better match the observed soil concentrations compared to the 1992 stack test with all homologue groups except TCDD; the TCDD predictions using the 1992 stack test are a better match. Most of the time, however, both sets of predicted homologue group soil concentrations were higher than observed soil concentrations, sometimes by more than a factor of 10 when using the 1992 stack test.

The question that this study is unable to answer is which stack test is more likely to have been representative of long term emission trends from the CMSWTE. The 1994 test occurred specifically after measures had been taken to reduce dioxin emissions. Because of process changes made to the CMSWTE, it would be reasonable to assume that the 1994 test is not representative of long term emissions. On the other hand, the 1992 test was occurring during heavy rainfall, which soaked the refuse to be burned. Data on the refuse moisture content showed that the average moisture content of the refuse burned in 1992 was about 10% higher than in 1994 - it was about 38% during the 1992 test compared to 28% in 1994. Some have suggested that wetter refuse may result in higher dioxin emissions (personal Communication, K. Jones, Zephyr Consulting, Seattle, WA.), although this hypothesis is unproven and the moisture content of feed materials is not considered to be a principal factor in predicting dioxin emissions - factors such as feedstock content, combustion efficiency, pollution control device, and pollution control inlet gas temperature are more often cited as the critical factors.

2) Noteworthy for results with both stack tests is that much more OCDD is found in the soil than predicted, and the same is true but to a lesser, although still noticeable, extent with HpCDD; in other words, the model under-predicted the soil concentrations of these homologue groups. As noted above in the description of air dispersion results, the ISCST3 was found to greatly over-predicted OCDD and HpCDD ambient air concentrations. Taken together, these

trends suggest that OCDD and HpCDD deposited near the incinerator to a much greater extent than was modeled. Since both dioxin homologue groups exist in the atmosphere principally sorbed to particles, this may reflect inappropriate parameter assignments relating to particle phase deposition algorithms, or possibly inappropriate deposition algorithms in general. However, the model appears to *overpredict* OCDF and HpCDF, and like OCDD/HpCDD, OCDF and HpCDF are also tightly sorbed to airborne particles, so perhaps the model's treatment of particle fate may not be the cause of significant underprediction of OCDD.

3) With both stack test results, the model would appear to proportionally overpredict most congeners (not OCDD/HpCDD) to a greater degree the further downwind one gets. This suggests that more dioxin mass is being removed from the plume as it disperses downwind than ISCST3 is able to simulate. Removal mechanisms include particle and vapor phase deposition, plant capture, and atmospheric degradation (photolysis and photooxidation).

Figure 7-9 shows a series of 9 isoline maps crafted to additionally display the trends of the measured versus the modeled soil concentration. Each group of three isoline maps pertains to one CDD/F compound; there are three isoline figures each for TCDD, OCDD, and TEQ concentrations. The first in the sequence of three are isoline maps drawn from the measured data, and the next two are maps drawn from using the 1992 and then the 1994 stack test. Observations from Figure 7-9 include:

1) The shape of the isoline figures developed using the 1992 stack emission test will be the same as those developed using the 1994 stack emission test, because they were all developed from the same unitized simulation - the only difference will be the mass of particle-bound emissions as a function of the compound and stack test.

2) The observed maximum soil concentration appears to occur in the northeast quadrant about a kilometer away. The predicted maximum soil concentrations are also found in the northeast quadrant, but they are a bit closer, at about ½ kilometer away. Also, the isolines drawn from model simulations seem to suggest that the maximum will occur more due north of the CMSWTE as compared to isolines drawn from measured data.

3) As was noted above, these isolines suggest much higher OCDD concentrations, in the thousands of parts per trillion (or equivalently, parts per billion), are found near the CMSWTE, as compared to modeled OCDD concentrations, which are in the hundreds of parts per trillion. It is noted that smooth isolines could not be drawn from the observed OCDD data because of the inhomogeniety of the results. Specifically, of the 8 highest soil samples nearest the CMSWTE, 5 had observed concentrations of OCDD above 1900 pg/g, ranging from 1930 to 6651 pg/g, but the

other 3 measurements were less than 1000 pg/g, ranging from 309 to 731 pg/g. The observation that OCDD was elevated in soils well above 1000 pg/g is supported by the data, despite oddly shaped isolines. The observed TCDD concentrations in the vicinity of the CMSWTE appear in range from 40 to a peak of 160 ppt, which is close to the range of 50 - 200 ppt modeled when using the 1992 stack emission test. However, when using the 1994 stack emission, the elevation in TCDD is only suggested to be in the 5 - 20 ppt range. Although not meaningful with regard to fate and transport, per se, the 1994 stack test appears to better duplicate the observed range of elevated TEQ concentrations - between 20 and 50 ppt, while the 1992 stack test simulations suggest elevations as high as 200 ppt TEQ.

7.3.7.3. *Discussion and Concluding Remarks*

Caution was expressed in the opening paragraphs that this exercise should not be characterized as a “model validation” exercise, mainly because of the weaknesses and uncertainties in the data and model parameters. To reiterate, some of those weaknesses/uncertainties include: a) a very small number of observed air monitoring data points (and the lack of precise information on when the air monitors were turned on and off, which can be important for short term air dispersion testing), and a relatively small number of soil measurements, b) the lack of consideration of all possible plume depletion mechanisms in the dispersion and deposition modeling. For the deposition modeling, the plume depletion by particle-phase deposition was considered, but other plume depletion mechanisms include atmospheric degradation of either vapor or particle phase dioxins, vapor phase deposition, and vapor- and particle-phase vegetative capture, c) a reasonable but still possibly flawed means to subtract “background” from measured air and soil concentrations. It is possible, for example, that air monitoring locations have their own, very localized, “background”. Therefore, averaging all 5 air concentration measurements from 1995 to represent “background” to subtract equally from all measurements in 1994 may not be appropriate, d) uncertainties in dioxin-specific fate parameters including vapor/particle partitioning of the CDD/Fs and soil half-lives, and e) uncertainties and/or lack of representativeness in the important source term, the rate of dioxin emissions from the stack, and the equally important meteorological data used to drive the model simulations.

These latter uncertainties in source term and meteorological data were evaluated by using different data sets. Specifically, two meteorological data sets were used in the dispersion modeling exercise - an “on-site” meteorological data set supplied by Ohio EPA (who took the air samples), and a publicly available data set from a nearby airport. Two possible stack tests were used to characterize long term emission rates for deposition and soil concentration modeling. As discussed above, there were no clear "superior" choices in either meterological data set or stack emission test. While it was clear that air concentration and soil concentration results differed when by using both data sets, in fact it was also clear that both data sets seemed to predict some quantities better than the counterpart data set.

With these cautions, it may be fair nonetheless, to make these statements regarding the ability of the ISCST3 to model the impact of dioxin emissions from the CMWSTE:

1) Elevations of dioxins in air and soil were clearly identified in the sampling programs, and they were also clearly modeled by ISCST3. Predicted and measured dioxin elevations in air and soil appear to generally be within a factor of 10 of each other, with both under and over predictions identified above. These elevations appear to be restricted to only within a few kilometers, 2-3 kilometers, and this was also found in the dispersion and deposition modeling. From the soil modeling exercise, it appears as though the model overpredicted soil concentrations to a greater degree the further downwind one went. This suggests that the plume was being depleted by dioxins in a manner that was not duplicated by the ISCST3 modeling.

2) It is clear from the analysis in this paper that the stack emission profile of CDD/Fs is very different from the profiles measured in the soil and in the air. This could be explained by "changes" in the profile at some point between the stack and both air and soil measurement sites, or it could be that there were problems in the measurement of CDD/Fs in either the stack or the environmental media. Assuming no major problems with measurement, it can be said that these trends cannot be duplicated in ISCST3 without the input of congener-specific atmospheric degradation rates, and/or congener-specific soil dissipation rates. Also, one hypothesis offered to explain the change in the dioxin profile from stack emission to air measurement was that some dechlorination might be occurring - the higher chlorinated CDD/Fs may be dechlorinating to form lower chlorinated CDD/Fs. If so, and if attempting to duplicate this trend, the ISCST3 model would need additional algorithms to model these transformations.

While admittedly a limited field test of deposition and soil concentration models, the data used here had these important features, which are not readily (if at all) available for similar model testing of ISCST3 with CDD/Fs: multiple stack tests offering a full suite of dioxin homologue and congener data; a historically high emission rate and over 11 years of emissions such that a signal is left behind in the soil and an imprint in the ambient air while monitoring was occurring, and a reasonable approach to determining the local background of dioxin soil and air concentrations that could be subtracted from the total measured soil and air concentrations to characterize a “signal” of higher dioxin concentrations found near the incinerator.

7.3.8. Air-to-Soil and Soil-to-Air Modeling

The observed air and soil data used in the background demonstration scenarios in Chapter 5 were from the rural background site of the Columbus site described above. These rural data also allow for an opportunity to test the air-to-soil modeling and the soil-to-air modeling algorithms. To summarize those scenarios, actual air concentrations and soil concentrations of the 17 dioxin-like congeners from the rural background site in Ohio were used as source terms. The I-TEQ air and soil concentrations from this site were 0.019 pg/m^3 and 1.37 pg/g, respectively. The individual congener concentrations in air and soil were used to predict concentrations in terrestrial foods (vegetables/fruits, animal food products) and the aquatic environment (water, fish, and sediments). Soil concentrations were not predicted from air concentrations and likewise, air concentrations were not modeled from soil emissions. For this model validation exercise, however, the opportunity presents itself to model air-to-soil impacts and soil-to-air impacts, and then to compare model predictions with observations.

Chapter 4 describes the models for estimating soil concentrations based on dry and wet deposition of particle-bound dioxins. The models were used in the stack emission source category, and in that context, dry and wet deposition amounts are modeled using the ISC3 air dispersion and deposition model. The full amounts of dry and wet deposition (i.e., no subtraction for plant interception) are mixed into a reservoir of soil and dissipated according to a defined dissipation rate. The reservoir of soil for this exercise will be that defined by a 7.5-cm depth, which was the depth of the soil sampling at the rural site in Ohio, and the assumed soil bulk density will be 1.50 g/cm^3. The dissipation rate is 0.0277 yr^{-1}, which corresponds to a half-life of 25 years. Since deposition was not monitored at the rural site, it will be estimated as the particle bound air-borne reservoir times a velocity of deposition. Koester and Hites (1992) measured a dry deposition rate of 0.002 m/sec for dioxins in Indiana. They also measured wet deposition and found it be roughly comparable for two sites. On this basis, dry deposition in this exercise will be modeled using the 0.002 m/sec velocity of deposition and wet deposition will be assumed to be equal to dry deposition.

Chapter 4 also described models for estimating air concentrations given soil concentrations. These algorithms were for the soil source category. The algorithms for volatilization were developed for PCBs and made simplifying assumptions such as no degradation, an infinite source of contaminant, and so on. An “unlimited reservoir” approach was used to estimate the flux of particle bound dioxins from soils due to wind erosion. A near-field dispersion algorithm estimated air borne concentrations given flux estimates of vapor and particle-bound dioxins. Despite using an "unlimited reservoir" approach, it was observed in Chapter 5 that the particle-bound air-borne concentrations were about an order of magnitude less than the vapor-phase concentrations for the demonstration of the soil contamination source category.

The results of this validation exercise are shown in Table 7-1. There is a clear dichotomy in the results. The air-to-soil model appears to model soil impacts reasonably well, with modeled soil concentrations somewhat lower but within the realm of field observations. On the other hand, the soil-to-air modeling did not show a good match. All predicted congener concentrations were 2-3 orders of magnitude lower than observed congener concentrations, and there was a 500-fold difference in observed and predicted TEQ air concentrations.

Regarding the air-to-soil modeling, 11 of the 17 observed soil concentrations were higher than model predictions. All but three congeners were modeled to within a factor of five of observations, and the three other congeners were about a factor of 10 from observations (i.e., either observations were 5 to 10 times higher than predictions, or predictions were 5 to 10 times higher than observations) . The four highest observations are matched with the four highest predictions as follows: 17.7 ppt observed 1,2,3,4,6,7,8-HpCDD versus 9.1 ppt modeled, 161.0 versus 36.2 ppt for OCDD, 4.06 versus 2.74 ppt 1,2,3,4,6,7,8-HpCDF, and 10.7 versus 2.70 ppt OCDF. The observed I-TEQ soil concentration of 1.37 ppt matches well with the predicted TEQ concentration of 0.70 ppt.

While the soil model appears to work reasonably well based only on impact of particle depositions, vapor impacts are not considered, and consideration of such would increase predictions of soil concentrations. As noted above, it does appear that soil concentrations may generally be underpredicted, although for six congeners, the model predictions were higher than observations. Direct vapor deposition could impact soils, but for the soil observations in the rural site in Ohio, all samples were taken in grassy areas, and with a vegetative cover, it is speculated that there would little direct vapor deposition. Therefore, detritus production would be a mechanism for vapor impacts to soils. Barbour, et al. (1980) list a detritus production rate for a setting described as "tallgrass prairie" as 520 g/m^2-yr. Given the concentrations predicted to occur in grass due to vapor transfers, one can estimate the loadings of dioxin corresponding to a detritus production of this magnitude. The predicted TEQ concentration in leafy vegetation due to vapor transfers was 0.27 pg/g dry weight given the rural air concentrations at this site in Ohio. This concentration times the detritus rate leads to a loading of 112 pg TEQ/yr. In contrast, the dry and wet deposition loading estimated by dry and wet deposition of particle-bound dioxins (as described above) is 2130 pg TEQ/yr. Therefore, on a TEQ basis, vapor impacts via detritus production would only be about 5% of loadings by dry and wet deposition of particle bound dioxins. There was also a reasonably narrow range for individual congeners, where detritus loadings were about 5-15% of atmospheric deposition of particle-bound dioxins. Particle-bound dioxins also impact vegetation, and detritus production might be considered as an additional loading due to particle bound dioxins. However, since 100% of atmospheric depositions are loaded into the soil model, detritus production is inherently handled, and considering detritus production would double-count the impact of particle-bound dioxins.

Another factor to consider is the representativeness of the air concentrations. The air concentration profile was generated as the average of 3 samples, one taken in March, 1994, one in April, 1994, and one in June, 1995. It has been observed that air concentrations are higher during winter months (Reed, et al., 1990), and perhaps the inclusion of additional winter samples from the site in Ohio would lead to a higher air concentration profile and higher predicted soil impacts.

Regarding soil-to-air modeling, it is not that clear that emissions and resulting air concentrations above soils at background levels should be lower by up to 2 orders of magnitude than what would occur in background setting. The argument has been made in Volume II, Chapter 2 of this assessment that emissions from tall industrial stacks, followed by long range transport, are principal sources of these compounds in rural environments where the food supply is produced. The question remains as to how much of the contaminant in rural air is due to urban emissions followed by long range transport versus emissions from the soil reservoir source. If the modeling of this assessment is correct, than soils contribute very little to rural air concentrations. However, other evidence developed in this assessment suggests that the soil release and dispersion algorithms of this assessment may be underestimating air concentrations. One piece of that evidence is discussed in the next section below. Plant:soil ratios, defined as the ratio of 2,3,7,8-TCDD concentration in plants divided by that in the soil, were found to be lower in model predictions as compared to literature values. Two possible hypotheses were offered below: 1) the model is underpredicting air concentrations resulting from soil releases, and/or 2) plant:soil ratios derived in experiments are not only the result of soil related impacts, but also from distant sources of air-borne release and long range transport - i.e., the air reservoir is not solely explained by soil releases. This is the same issue that is discussed for the soil-to-air model exercise here. One other possibility for the difference in the inability of the model to duplicate plant:soil ratios would be that the algorithms estimating air to plant transfers are modeling too low a transfer rate. However, the air to plant transfer algorithms were examined in Section 7.2.1 above and in Section 7.3.12 below, which describes a broader air-to-beef food chain validation exercise. In both sections, concentrations of the dioxin congeners in leafy vegetation were compared with model predictions for leafy vegetation, and predicted concentrations were found to be in line with observations. Also, the vapor-phase air-to-leaf transfer coefficient was calibrated with field data, and since it is shown that vapor phase transfers tend to dominate plant concentrations, air-to-plant transfers should, by definition, be modeled adequately.

In summary, this section has shown that the air-to-soil model based on deposition of particle-bound dioxins appears to work well. Vapor impacts would occur primarily by die-back of vegetative materials, but the additional increment to soil concentrations are estimated to be less than 10% by this route. Inclusion of winter-time air concentrations in the average air profile used to predict soil concentrations could lead to higher predictions of soil concentrations and a superior match of predicted and observed soil concentrations in this exercise. The soil-to-air models may be underpredicting air concentrations. The observed air concentrations are 2-3 orders of magnitude higher than predicted to occur by soil emissions alone. This is due, in part, by the fact that some fraction of the observed air concentration is due to long range transport from distant sources. It is not known what fraction this is, but other evidence has suggested that dioxins in rural settings distant from known sources of dioxin release originate, in fact, from those distant sources. Other evidence suggests that the soil-to-air models may still be underestimating the impacts to air from contaminated soils. The only way to truly test the soil-to-air models would be to have air concentrations measured above soils, where it is known that there are no other sources to measured air concentrations. Unfortunately, this data would be hard to develop for the ubiquitous dioxins and none was available for testing.

7.3.9. Transfer of Dioxins From Soils to Below Ground Vegetables

This section describes a validation of the transfer algorithm from soils to below ground vegetables. The equation for calculating the concentration of dioxins in below ground vegetables is:

$$C_{bgv} = \frac{C_s \ RCF \ VG_{bg}}{Kd_s} \tag{7-40}$$

where:

C_{bgv} = fresh weight concentration of below ground vegetables, pg/g

C_s = contaminant concentration in soil, ppt or pg/g
Kd_s = soil-water partition coefficient, L/kg
= $Koc*OC_{sl}$
Koc = contaminant organic partition coefficient, L/kg
OC_{sl} = fraction organic carbon in soil, unitless.
RCF = root concentration factor equaling the ratio of the contaminant concentration in roots (fresh weight basis) and the concentration in soil water, unitless
VG_{bg} = empirical correction factor for below ground vegetation which accounts for the differences in the barley roots for which the RCF was derived and bulky below ground vegetables, unitless

The key contaminant-specific parameter, RCF, was developed from data developed by Briggs, et al. (1982) on the transfer of organic contaminants from solution into barley roots. The soil concentration, C_s, is divided by the soil partition coefficient, Kd_s, so as to convert it to a soil water concentration. The VG_{bg} is an empirical factor introduced to describe the difference between the thin barley roots of the Briggs experiments and the bulky below ground vegetation to which it is applied for the dioxin documents. Evidence shows that dioxins translocate only to a small degree into bulky below ground vegetables (see next section). The assignment of values to VG_{bg} in this assessment also considers other factors pertinent for estimating concentrations for human exposures, including factors which would further reduce whole vegetable concentrations including washing or peeling. Further detail on the algorithm can be found in Chapter 4.

Data from Muller, et al. (1994) was used to validate this model. Specifically, carrots were grown in pots with soil of two concentrations, a control soil and a contaminated soil. Muller, et al. (1994) provided graphs showing the congener group concentrations for soil, and for three parts of the carrot: peel, cortex, and stele. The precise concentrations from these graphs was unavailable. However, the graphs were digitized by Cambridge, Environmental (58 Charles Street, Cambridge, MA; concentration values contained in discussions in a public comment provided to EPA), and their concentrations were used in this exercise. Data in this article also included the soil organic carbon content, 8.1% (OC_{sl} = 0.081).

Part of this data set was used in conjunction with the model displayed above. The VG_{bg} was taken out of the equation and the soil concentration data was input into the model to predict the peel concentrations. The cortex and stele concentrations were not used in the validation exercise. These predicted peel concentrations were compared with the observed peel concentrations. Since the data was available in congener groups and not individual congeners, the values for the parameters RCF and Koc were estimated as the congener-specific value if only one dioxin-like congener was in the congener group (2,3,7,8-TCDD, e.g.), or as the average of the congener-specific values of the multiple dioxin-like congeners in the congener group (the three HxCDDs, e.g.). Finally, the data in Muller, et al (1994) was only given in dry weight terms without discussion of the dry weight fraction, and the model predicts a fresh weight. For this exercise, it was assumed that carrots are 15% dry weight; the fresh weight was divided by 0.15 to estimate the dry weight concentration.

Table 7-16 shows the data that went into this validation exercise and the results. It would appear that the model works reasonably well. The difference in peel concentrations due to soil concentrations is apparent in both the data and the model predictions, and the magnitude of the difference appears to be captured. With one exception, the predictions and observations are within a factor of 4 of each other, with the exception being a factor of 5. Thirteen of 20 predictions/observations are within a factor of 2 of each other. The biggest discrepancies are the HpCDF and OCDF congener groups, with predictions exceeding observations by a factor of about 4 for both the control and contaminated soils. This data is further examined in Chapter 4 to determine the VG_{bg} parameter. Generally, it is concluded from this validation exercise that this data supports the use of the Briggs, et al. (1982) RCF empirical formulation to predict the peel concentration in underground bulky vegetation.

7.3.10. Impacts of Contaminated Soils to Vegetation

There have been several studies in addition to the carrot study described above which have measured plant concentrations of 2,3,7,8-TCDD for plants grown in soils with known concentrations of 2,3,7,8-TCDD or dioxin Toxic Equivalents (TEQs) or dioxin congener groups. One quantity that can be estimated from these studies is a *plant:soil contaminant concentration ratio*. The plant:soil ratio equals the concentration in the plant divided by the concentration in soil in which the plant is growing. Concentration ratios predicted to have occurred in the demonstration scenarios can be compared against those that have been measured in the various studies.

These ratio comparisons cannot strictly be considered model validations. Only the exercise described in the previous section, where experimental data were duplicated with modeling, can be considered a model validation. Still, trends ascertained from the literature will be compared with concentration ratios from the demonstration scenarios. The literature articles measuring soil and resulting plant concentrations of dioxin-like compounds are summarized in

Table 7-17. This table also includes concentration ratios, and separates sections for above and below ground vegetation.

In measuring both the soil and the plant concentration, several of the early literature articles, particularly those from Seveso (Wipf, et al., 1982; and Coccusi, et al., 1979) presumed that the soil in which the plant was growing was the ultimate source for the 2,3,7,8-TCDD contamination of above ground plant parts, if not from direct uptake than from deposition of suspended particles. However, recent research has concluded that the contamination of above ground plant parts is due principally to air-to-plant transfers (Hulster and Marschner, 1993; Muller, et al, 1993; Muller, et al., 1994; Welsch-Pausch, et al, 1995; and others). These cited research efforts have concluded that there is no consistent relationship between soil concentrations of dioxin-like compounds and above ground vegetative concentrations of these compounds, which has led the researchers to conclude that air-to-plant transfers explain plant concentrations (one study did strongly imply a direct soil/plant for dioxin-like compounds for at least one family of above ground vegetables, the cucumber family (Hulster, et al., 1994); this will be discussed below). This fact, coupled with the fact that sources of airborne contamination by dioxins include both distant sources and soil releases, make it difficult to compare literature reports of plant:soil contamination concentrations with those predicted by the soil contamination modeling of this assessment.

Recall that for the soil contamination source category, the presumption is that air concentrations and depositions to which the plant are exposed originate only from the contaminated soil. One would expect that the modeled plant:soil ratio for above ground plant parts would be lower than plant:soil ratios measured in actual field settings, since the field measured ratios are influenced by more than just the soil releases into the air.

What is more pertinent in the demonstration scenarios for comparing plant:soil ratios for above ground vegetation are the results for the “background” scenarios. Here, air concentrations from an actual setting provide the source of dioxins for above ground plants. Simultaneously, soil concentrations which correspond to the actual setting where air concentrations were measured are input into the scenario. Therefore, plant:soil ratios from this demonstration should be analogous, at least, to plant:soil ratios derived from other actual field settings.

Unlike above ground vegetation, the literature is consistent in concluding that soil provides the source for underground soil to root transfers. For this reason, Table 7-17 and the following discussions distinguish between above and below-ground vegetation.

The following plant:soil contaminant concentration ratios for TEQs were estimated for the two scenarios demonstrating background conditions in Chapter 5, Scenarios 1 and 2: below ground vegetables - 0.19 (dry weight basis, assuming vegetables are 15% dry matter, and using tilled soil concentrations which are 50% of untilled soil concentrations), above ground vegetables/fruit - 0.10 (dry weight basis, 15% dry matter, tilled soil concentrations), grass - 0.33 (dry weight, untilled soil concentrations), and feed 0.16 (dry weight, untilled soil concentrations). Some observations from experimental results found in the literature, and comparison with the results of the model, are:

1) The largest body of consistently developed experimental data on soil-plant relationships of dioxin-like compounds comes from a research group in Germany who have published numerous articles for different vegetation and experimental conditions in the 1990s (Hulster and Marschner, 1991; Hulster and Marschner, 1993; Hulster, et al., 1994; Muller, et al., 1993; Muller, et al, 1994). Some of the earlier literature showed much higher impacts to vegetation than measured by these German researchers (Coccusi, et al., 1979; Facchetti, et al., 1986; Young, 1983), which, in the judgement of the authors of this assessment, renders them suspect. One early report, that of Wipf, et al. (1982), does show results consistent with the German research. The observations following will focus mainly on this research from Germany.

2) Experimental results for both above and below ground vegetation suggest that plant:soil ratios decrease as soil concentration increases. For below ground vegetation, this suggests that the movement into plants is not a passive and unimpeded process occurring with transpiration water, for if it were, plant:soil ratios would be constant as concentration increases. For above ground vegetation, the observations given above that air-to-plant transfers and not soil-to-plant transfers better explain plant concentrations, and that air concentrations include soil releases as well as long term transport, leads one to conclude that a consistent relationship between soil concentrations and plant concentrations is not to be expected. An explanation for this trend for below ground vegetative trends could not be found.

The models of this assessment - soil to below ground vegetation, soil to air to above ground vegetation, and air to above ground vegetation - cannot duplicate these observed trends, that is, the models will not show a decrease in plant:soil ratios as soil concentration increases. When soil is the only source of contamination, as in the soil contamination source category, above and below ground vegetation concentrations are a linear function of a biotransfer factor and an appropriate media concentration - air, soil, water. For particle depositions, no transfer parameters are used, but plant concentrations are a linear function of model inputs, including deposition rates, plant interceptions and yield, and a plant washoff factor. Therefore, plant concentrations will be a linear function of soil concentrations for the soil contamination source category.

3) Plant:soil ratios for below ground vegetables for soil concentrations in the low ppt range would appear to be in the 10^{-1} to 10^{-2} range (Muller, et al, 1993; Hulster and Marschner, 1991), which may be a little lower than the 0.19 predicted by the model. Much higher ratios were found in the earlier studies (Coccusi, et al., 1979; Facchetti, et al., 1986; Young, 1983), which earlier had been speculated as being questionable. One earlier study, that of Wipf, et al. (1982), does report ratios similar to these later studies, as noted above. At higher soil concentrations in the sub to low ppb range, plant soil ratios are more in the 10^{-4} to 10^{-3} range (Hulster and Marschner, 1993; Hulster and Marschner, 1991).

4) The results for above ground bulky vegetation, fruits and vegetables, indicate plant:soil ratios that are lower than plant:soil ratios for bulky below ground vegetation, for comparable soil concentrations. The data of Muller, et al. (1994) can be used to demonstrate this point. This data was used over others because the soil concentrations, at 5 and 56 ppt TEQ, are nearer to the background soil concentration of 1.37 ppt TEQ used in the background demonstration scenarios than any of the other studies found. First, their results include total crop dry weight concentrations of TEQs for carrots, lettuce, and peas (including pods) in soils with TEQ concentrations of 5 and 56 ppt. At these two soil concentrations, the carrot:soil ratios were 0.07 (at 5 ppt TEQ soil concentration, dry weight of the carrot) and 0.017 (at 56 ppt). Their lettuce and pea pod:soil ratios for the control and contaminated plots ranged from 0.0016 to 0.016 (total crop, dry weight basis). The modeled plant:soil ratio of 0.10 for vegetables/fruits in the background scenarios is higher than the 0.0016 to 0.016 for lettuce and peas in the Muller, et al. (1994) experiments. This could suggest an overestimation of the modeling of air-to-plant impacts.

5) Several of the articles, both from the German work and the earlier work, noted that most of the concentration was in the outer portions of the below and above-ground vegetation, and not the inner portions. Despite significant increases in soil concentration from the ppt to the ppb range, inner potato tuber concentrations remained constant (Hulster and Marschner, 1991, 1993). This evidence was the principal justification for the use of the empirical adjustment factors termed VG for soil to below ground transfers, VG_{bg}, and vapor-phase air transfers to bulky above ground vegetation, VG_{ag}. The chemical-specific empirical transfers factors for both of these transfers were developed in laboratory experiments with several chemicals using thin vegetation - solution phase transfers to barley roots for below ground vegetation concentrations, and vapor phase transfers to azalea leaves and grass leaves for vapor phase transfers. For the dioxin-like compounds, direct use of these transfer factors would be most appropriate for the outer few millimeters, perhaps, of below and above ground bulky vegetation. The assignment of

a VG of 0.01 for bulky above and below ground vegetation was based on an outer surface volume to whole plant volume ratio for a common vegetation such as a carrot or an apple. A VG of 1.00 was used for grass, since that is a thin vegetation.

Further evidence for the above ground VG came from a study by McCrady (1994), who measured the uptake rate constants of vapor-phase 2,3,7,8-TCDD to several vegetation including grass and azalea leaves, kale, pepper, spruce needles, apple, and tomato. The uptake rate for the apple divided by the uptake rate for the grass leaf was 0.02 (where uptake rates were from air to whole vegetation on a dry weight basis). For the tomato and pepper, the same ratios were 0.03 and 0.08. The VG_{ag} was 0.01 for fruits and vegetables in this assessment. McCrady (1994) then went on to normalize his uptake rates on a surface area basis instead of a mass basis; i.e., air to vegetative surface area uptake rate instead of an air to vegetative mass uptake rate. Then, the uptake rates were substantially more similar, with the ratio of the apple uptake rate to the grass being 1.6 instead of 0.02; i.e., the apple uptake rate was 1.6 times higher than that of grass, instead of 1/50 as much when estimated on an air to dry weight mass basis. The ratios for tomato and pepper were 1.2 and 2.2, respectively. Therefore, since the B_{vpa} in this assessment is an air to plant mass transfer, the McCrady experiments would appear to justify the use of an above-ground VG of a magnitude less than 0.10.

6) An experiment by the Hulster, et al. (1994) on vegetation of the cucumber family contradicted the conventional wisdom that direct soil to root to above ground plant impact would not occur for the dioxin-like compounds. Their results were most striking for zucchini, which showed uniform plant concentrations from inner to outer portions of the zucchini fruit, and the highest whole fruit concentrations and plant:soil ratios they had ever measured, despite careful experimental conditions which physically isolated the fruit from the soil. Pumpkins also showed high plant contamination and plant:soil ratios, with more expected plant concentrations measured for the cucumber. No explanation was offered for these results. It was assumed for this exposure assessment that the fruits and vegetables for human consumption, and the grasses, hay, and other vegetation animals consume, would not follow this pattern.

A principal observation that can be drawn from this examination is that the plant:soil contaminant concentration ratios from the background scenario may be higher than observed in experiments, although this conclusion must be tempered by the fact that the soil concentrations in the experiments were always higher than the 1.29 ppt WHO_{98}-TEQ_{DF} soil concentrations used in the background scenario. One other important observation made above was that, as the soil concentration increased, the plant:soil concentrations decreased. For the experiment where soil concentrations were closest to background, the 5 and 56 ppt TEQ concentrations in the experiments of Muller, et al. (1994), the overprediction by the model was on the order of 10.

The same story is not necessarily told, however, when comparing results from the demonstration of the soil contamination demonstration with these literature ratios. The plant:soil ratios for the background scenarios ranged from 0.10 to 0.33. The following plant:soil contaminant concentration ratios were estimated for the soil contamination scenario. Again, tilled soil concentrations and dry weight vegetative concentrations were used: below ground vegetables - 0.22, above ground vegetables/fruit - 0.00005, grass - 0.003, and feed 0.002. These ratios were calculated using the soil concentrations predicted to occur at the site of exposure, which is valid for the below ground vegetables, but not quite for the above ground vegetation. Ratios calculated by using the near field dispersion models and assuming plants are grown on the impacted soils would result in slightly higher ratios, by about a factor of three. Below ground vegetables still show a clear relationship with soil concentrations, as in the background scenarios. However, now it appears that plant:soil ratios for above ground vegetation are much lower for this demonstration scenario as compared to the background scenarios.

In fact, in a slight variation to this exercise, one could use near background soil concentrations for the soil contamination algorithms and show similarly low plant:soil ratios. In this instance, one can observe that at low background soil concentrations, the soil-to-plant algorithms of the soil contamination source category underestimate above ground plant concentrations.

This observation that plant:soil ratios for above ground vegetation are higher in the literature as compared to modeled ratios for the soil contamination algorithm has to be carefully considered. Two explanations are offered. For experiments conducted outdoors, the source of air reservoirs of dioxin-like compounds are the soil in which the plant is growing as well as from distant sources and long-term transport. Also, it is possible that the model is underpredicting air concentrations and hence underpredicting soil-to-air-to-plant transfers. The same issue arose in Section 7.3.8 earlier, where it was noted that the soil contamination model predicted very low air concentrations given background soil concentrations, much lower than observed background air concentrations. In that section, like in this section, it was unclear whether long range transport explained most of background air concentrations and/or the model was underpredicting air concentrations.

7.3.11. Comparison of Measured and Modeled Vapor/Particle Distributions for Semivolatile Compounds Other Than Dioxin

In Chapter 3, the Junge-Pankow model was described and applied to the dioxin-like compounds in order to partition air-borne dioxins into a vapor and a particle phase. These modelled particle percentages were then compared to measured particle percentages, and a consistent pattern among several field measurements versus model predictions emerged: the model tended to predict that more of the dioxin would be in the particle phase compared to what was measured. Whether the model is “correct” or the measurements are “correct” is a matter of ongoing debate, as described in Chapter 3. This section will compare measured and modelled particle percentages for semivolatile organic compounds (SOCs) other than the dioxins. These include PAHs, PCBs, and organochlorine pesticides.

Table 7-18 presents a summary of the analysis of monitoring data on SOCs from several cities and rural locations. The parameters in this table come from the following empirical correlation, which is described in more detail in Chapter 3:

$$Log\ K_p = m\ Log\ p°_L + b \qquad (7\text{-}41)$$

where:

K_p = particle/gas partition coefficient, $m^3/\mu g$, defined as: Cp $(ng/\mu g)/C_g$ (ng/m^3), where C_p is the concentration associated with aerosols, and C_g is the gas-phase concentration

$p°_L$ = liquid sub-cooled vapor pressure, Pa

m, b = empirically derived slope and intercept from the data sets

The sub-cooled liquid vapor pressures for the SOCs were taken from reports in the literature including values for PAHs (Yamasaki et al., 1984), PCBs (Falconer and Bidleman, 1994), and OC pesticides (Hinckley et al., 1990). The particle-bound fraction, ϕ, is related to K_p, as follows:

$$\phi = \frac{K_p\ [\ TSP\ ]}{1 + K_p\ [\ TSP\ ]} \qquad (7\text{-}42)$$

where:

ϕ = particle bound fraction, unitless (not the same as the particle bound concentration, C_p)

K_p = particle/gas partition coefficient, $m^3/\mu g$

TSP = total suspended particulates, $\mu g/m^3$

If TSP was not reported in the original paper (in most cases), it was assumed that TSP = 98 $\mu g/m^3$ for urban air and 10-42 $\mu g/m^3$ for non-urban air of varying cleanliness.

The two equations above, in combination with the data reported in the literature article, were used to develop the dotted line "observed" particle percentages shown in Figures 7-10 and 7-11. The modeled particle fractions were determined for these sites using the Junge-Pankow model detailed in Chapter 3. According to that model, the particulate fraction is estimated as:

$$\phi = \frac{c\,\Theta}{p^{\circ}_{L} + c\,\Theta} \tag{7-43}$$

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, estimated at 17.2 Pa-cm

In applying this model, values of Θ assumed include 4.2×10^{-7} for "clean continental", 3.5×10^{-6} for "background plus local sources" and 1.1×10^{-5} for "urban" conditions. Further detail on this model can be found in Chapter 3.

The agreement between the measured and predicted aerosol-bound fractions of PAHs is remarkably good, as seen in Figure 7-10. Two model curves are shown for rural air in Figure 7-10b, representing "clean continental background" and "background plus local sources" regimes. Experimental PAH distributions fall reasonably close to the range of particulate values predicted by the model, although the fraction of aerosol-bound PAHs at rural sites (e.g., Lake Superior) is greater than expected for the more volatile compounds. This may be due to a portion of these PAHs being "non-exchangeable" (Pankow, 1988).

Fewer data are available for non-dioxin organochlorine compounds. Figure 7-11 shows the measured particulate percentages of PCB congeners and chlorinated pesticides in comparison to predictions. Again, the two depictions of model predictions for rural conditions, Figure 7-11b, show a range from clean continental to background plus local sources. The monitored data fall below the model values, but the discrepancy is generally not as great as for the PCDD/Fs.

Overall, it can be concluded the Junge-Pankow model appears to predict vapor/particle partitioning very similar to measurements for PAHs, but not as similar for PCBs and chlorinated pesticides, although the match there is still superior to that of PCDD/Fs. This exercise does lend additional credibility, in general, to the Junge-Pankow Model. However, the model and the measurements for PCDD/Fs do diverge, as described at length in Chapter 3, and the debate remains as to which is “correct” for the PCDD/Fs - the model or the measurements.

7.3.12. An Update of the Air-to-Beef Model Validation Exercise

In the previous version of this dioxin exposure document (EPA, 1994) as well as in a journal article (Lorber, et al., 1994), a validation of the air-to-beef food chain model used in this assessment was presented. As a result of public comments received on the review of the dioxin exposure document, that exercise has been refined and updated. This section will review the principal comments made and these updates. Except for a brief overview, this section will not describe the previous air-to-beef model validation exercise.

Figure 7-12 presents an overview of the air-to-beef food chain model. The premise of this modeling exercise to test the beef food chain model for dioxin-like compounds is that air-borne reservoirs of these compounds in rural environments are the "source term" explaining concentrations found in beef. The principal assumption in the validation exercise is that one can define an “average” rural air profile of dioxins, route this profile through the food chain model, and predict an “average” beef concentration. This exercise probably would not qualify as a validation exercise in the traditional sense. Most environmental model validation exercises rely on data obtained from a single site. For a traditional model validation of the air-to-beef model, one would need the following: a representative air concentration profile, including all the dioxin-like congeners, during the lifetime of the cattle, information on the cattle diet during his lifetime, a set of vegetation congener-specific concentrations typical of the cattle diet (and the cattle should be fed from vegetation grown in the area corresponding to the air concentration), and a set of congener-specific concentrations from beef from the slaughtered cattle. As this information was unavailable, the model validation exercise proceeded by attempting to define these “average” air profiles, vegetative profiles, and beef concentration profiles.

The key components of the previous model validation exercise were:

1. The representative air profile was crafted based on a representative profile of urban air concentrations generated as the average of 85 data points of air concentrations from urban settings, coupled with information suggesting that rural air profiles were lower than urban air profiles, by about a factor of 5. The rural air profile was crafted, therefore, by dividing each congener concentration in the urban air profile by 5.
2. Each congener was separated into a vapor fraction and a particle fraction. The vapor/particle partitioning model is described in Chapter 3.
3. The vapor fraction “transfers” into cattle vegetation, including categories described in Chapter 4 as “grass” and “hay/silage”. The particle bound fraction is assumed to deposit onto these vegetation. Dry deposition was modeled as a product of the concentration times a deposition velocity of 0.002 m/sec, based on the findings of Koester and Hites (1992). Also, wet deposition was assumed to equal dry deposition, based on measurements of Koester and Hites (1992) showing these two components to be roughly comparable for settings in Illinois and Indiana.
4. Forty-eight percent of the cattle diet was assumed to be in grass, 48% was assumed to be in hay/silage, and 4% was assumed to be in soil. The concentration in the fat of beef was modeled as a function of the concentrations in these media times a bioconcentration factor.
5. The cattle were assumed to undergo a period of feedlot fattening prior to slaughter. This is a predominant practice in the United States, and it was felt that the observed beef concentrations were from cattle which went through feedlot fattening. Based on previous modeling efforts, the impact of this fattening regime was to reduce concentrations in the body fat by about a factor of 2 compared to body fat concentrations prior to entry into the feedlot. Therefore, concentrations predicted to occur without this feedlot consideration were reduced by 50% to model the impact of feedlot fattening.
6. The “observed” beef concentration profile was crafted as the average of 14 samples from 3 “grab bag” studies measuring the concentration in beef and veal from grocery stores.

Four principal comments received on the air-to-beef model validation exercise following the release of the 1994 dioxin exposure document were:

1. Although the final predicted TEQ beef concentration was reasonably close to the observed beef TEQ concentration, there was not a good match in the concentrations of the individual congeners not a good match of total concentrations (i.e., the sum of the concentrations of all congeners).
2. The air-to-leaf transfer factor was overestimating the impact of vapor-phase dioxins to vegetation.

3. A simple division of the crafted urban profile by 5 to arrive a crafted rural profile would not appropriately consider changes in the profile from urban to rural centers that have been studied and are believed to occur.
4. The results of the USDA/EPA beef study that is described in Volume I of this Exposure Reassessment and in Winters, et al. (1996) is preferable as an observed data set to the grab sample of 14 data points.

The first comment was addressed by revising the air-to-beef model validation exercise based on the next three comments. The discussion of the revised model exercise will now proceed by first reviewing the model changes made, then reviewing the revised air and the new beef concentration profiles used, and how the revised model validation exercise compares with the original validation exercise.

a. Revisions to the air-to-beef model parameters: Table 7-19 compares the four key changes made to the model validation exercise. Following are brief notes on each:
1. B_{vpa}: Chapter 4 describes how this version of the air-to-leaf transfer factor was derived from experiments conducted by Welsch-Pausch, et al. (1995). As seen in Table 7-19, this procedure resulted in a lowering of the transfer factor for all congeners by an order of magnitude and less, except the octa congeners which were lowered by 2-3 orders of magnitude and the hepta furan congeners, which were slightly higher in their current form. It is noted that these B_{vpa} are slightly different than a set of B_{vpa} published as proceedings of the 15th International Symposium on Chlorinated Dioxins and Related Compounds (Lorber, 1995). The procedure to derive the B_{vpa} in this assessment is the same as in that publication. However, this assessment uses a different set of vapor/particle fractions based on a reassignment of dioxin fate parameters. With different v/p fractions, the calibrated B_{vpa} was slightly different.
2. As just noted, the vapor/particle partitioning changed slightly in the current version, due to the reassignment of critical parameters required for the calculation of the vapor/particle percentages. These parameters include the Henry's Constants and the liquid sub-cooled vapor pressures. In their current form, there is generally less concentration predicted to occur in the vapor form, particularly for the penta dioxin, the tetra furan, and the two penta furans. It is noted that the 1994 vapor percentages for the octa congeners were assigned a value of 0.00. In fact, if the percentages were calculated to two decimal places with the 1994 parameters, they would equal 0.02% (or, on a fraction basis, 0.0002) instead of 0.00 as noted. Although a small percentage, it is seen that the air-to-leaf transfer factors for the octa congeners were on the order 10^8 to 10^9. As

discussed in the prior air-to-beef model validation (EPA, 1994; Lorber, et al., 1994), this became critical as assignment of the very small vapor fraction did make a significant difference to octa vegetation predictions, and hence octa beef concentration predictions. For the current exercise, there was no rounding to 0.00; the values calculated and used are 0.2% for both octa congeners with the revised fate parameters.

3. The bioconcentration factors for each congener were uniformly increased by about 30% as compared to the 1994 version. This was due to a recalculation using the same data as was used for the 1994 version. Based on a personal communication with the study author, it was determined that the total dry matter intake by the lactating cow was miscalculated for the 1994 version. Instead of 15 kg/day, the correct total dry matter intake was 21 kg/day. Therefore, intake concentrations decreased by about one-third, and so calculated bioconcentration factors increased by about one-third.

4. The soil concentrations used in the current version were the actual measured soil concentrations corresponding to the site where the air concentrations were taken. As will be described below, the air concentration profile was taken from an actual rural site near Columbus, Ohio. These were the same air profile and soil profile used in the demonstration background scenario in Chapter 5. The soil concentrations used in the 1994 model validation exercise were not model inputs, but were rather predicted by the deposition of particle-bound dioxins. There does not appear to be substantial differences in the two profiles, and as soil is a small part of the cattle diet, these changes were not meaningful to final predictions of beef concentrations.

b. New air profile: While a straight division of an urban profile by a factor of 5 may recognize overall reductions in air concentrations when going from an urban to a rural location, and concurrent reductions in TEQ air concentrations, they may not recognize a key trend observed by researchers concurrently studying urban and rural air profiles. The trend was best stated by Eitzer and Hites (1989), who studied such profiles including a statistical analysis of profiles. As they stated, “The geographic variability suggests the following atmospheric transport scenario. Urban air is contaminated with PCDD/F by proximity to the combustion sources of these compounds. As the air mass moves away from the urban area, it is diluted with cleaner air, lowering the PCDD/F concentrations. As the air is transported, transformations occur changing the profile. One transformation is photodegradation of vapor-phase PCDD/F. The less chlorinated PCDD/F have greater proportions of their total concentration in the vapor phase. Thus, vapor-phase photodegradation during the transport process would have a greater effect on the less chlorinated PCDD/F. Like the washout process, these degradation processes would favor an ultimate PCDD/F profile with enhanced concentrations of the more chlorinated compounds." Simply dividing an urban profile by a factor of 5 did not account for these changes. It should be noted that photodegradation has not been definitely proven to occur and explain the trends noted by Eitzer and Hites (1989). Most importantly, they identified a trend that appears to be true, not only for their profiles, but for air concentration profiles from the Columbus area, as will be described shortly.

Ideally, one would want several rural profiles representing beef production areas in the United States. Lacking that information, what was available was a profile derived from a study of ambient air in the city of Columbus undertaken by the Ohio EPA (OEPA, 1994;1995), and described above in Section 7.3.7 on a model validation exercise of the ISCST3 model. That study included two sampling events of urban air in 1994 and one sampling in 1995. Concurrent with the urban samples were two background rural samples in 1994 and a third in 1995. The rural sampling site was located 28 miles in the upwind direction from Columbus (i.e., it was least likely to be impacted by urban sources in the nearest largest city, Columbus). The sampling program was undertaken to evaluate air quality in the vicinity of a municipal solid waste incinerator. There were six samplers in the city of Columbus, 5 operating for each of the 1994 sampling events (not the same 5), and 6 operating in 1995. Therefore, there were a total of 16 urban air samples. This incinerator was operating in 1994, but was shut down in 1995. Therefore, the 1995 sampling was undertaken to evaluate the air quality in the absence of the incinerator. During the sampling in 1994, OEPA (1994) identified a clear trend in the data: that the measurements were highest in the air samplers which were located in the predominant wind direction, from the incinerator to the air sampler, during the sampling. The 1995 did show a reduction in the measured air concentrations (OEPA, 1995). There was one rural air sampler, so the sampling program included three rural air samples. The three rural air samples did not show any trend related to the incinerator, and as will be seen, were lower in magnitude than the urban samples. Chapter 5 describes how the rural air profile for the background scenario was crafted from these three rural samples.

This revised air-to-beef model validation exercise will use the rural air profile that was crafted for the background scenario. Table 7-20 compares the air concentration profiles discussed above, including the crafted 1994 urban and rural air profiles compared against the Columbus urban air profile and the Columbus rural air profile. The Columbus urban air profile was developed as the average of the 16 data points from the three air sampling, including the assumption that the air concentration was ½ detection limit for all non-detects. The final column shows the ratio of the Columbus urban air concentration with the Columbus rural air concentration.

The Columbus urban air concentration looks substantially like the crafted urban air profile with notable differences only for 1234678-HpCDD, OCDD, and 2378-TCDF. In each of these cases, the Columbus air profile is smaller than the crafted urban profile. The Columbus 2378-TCDF concentration is more than a factor of 5 lower than the crafted urban concentration of 2378-TCDF. OCDD in Columbus is almost a factor of 3 lower than the crafted urban profile, and the absolute difference in the OCDD concentrations of nearly 2.0 pg/m^3 explains most of the difference of about 2.2 pg/m^3 of total dioxin in the profiles (with "total" being defined as the sum of the 17 dioxin-like congeners). The I-TEQ concentrations in the urban profiles are similar - the Columbus urban air I-TEQ concentration of 0.070 pg/m^3 is about 75% of the crafted urban profiles of 0.095 pg/m^3.

The two rural air profiles have the same I-TEQ concentration of 0.019 pg/m^3, but the Columbus rural total concentration is about 50% higher than the crafted rural profile. This is due principally to the higher OCDD and 1234678-HpCDD concentrations in the Columbus profile. Most importantly, it would appear that the Columbus urban and rural profiles conform to the expectations as laid out earlier in the quote from Eitzer and Hites (1989). Specifically, it does appear that the lower chlorinated congeners undergo more of a loss, proportionally speaking, as compared to the higher chlorinated congeners. The ratio of the urban hepta and octa dioxin and furan congeners to their rural counterparts ranges from 1.2 to 3.8; while the range for the tetra through hexa dioxin and furan congeners is 1.0-6.3. The 1.0 ratio is for a congener which has a very low concentration to start with, 0.003 pg/m^3, and whose rural concentration is driven by detection limits. Without this congener, the second lowest ratio is 2.4. In other words, it would appear that a more appropriate range for the tetra through hexa congeners is 2.4-6.3. Of note are the very low changes in the hepta dioxin congener and octa dioxin congener, whose ratios are 1.2. Also of note is the very lower tetra furan congener, which dropped by a factor of 6.3 and is also 6 times lower than the concentration for this congener in the crafted rural profile of the 1994 exercise. These trends for the OCDD and tetra furan congener will later be important in explaining improvements in beef concentration predictions for the current model validation exercise.

c. New beef profile:

The EPA/USDA study on dioxins in beef is described in Chapter 3, Volume II of this assessment and also in Winters, et al. (1996). The congener profile for this study is compared with the congener profile for the 14 grab samples from three studies in the next section on results. It is noted that the EPA/USDA study shows lower congener concentrations for all but one congener, and total and TEQ concentrations that are 2-3 times lower that the 14 grab samples. The precise reason for this difference in profiles is not known, but some possible reasons could be:

1) The three studies from which the 14 samples originated were not statistically designed studies, and may have simply taken samples with higher concentrations.

2) There may, in fact, be a trend of reduced concentrations in the beef because of the time periods in which the data was obtained. Two of the three studies took samples prior to 1990, the other one taking samples in 1992. The EPA/USDA study took samples in 1994. Furst and Wilmers (1995) did note nearly a 25% reduction in cow milk concentrations of I-TEQs taken in 1994 as compared to 1990. This is a much smaller reduction than the 60-70% reduction noted in the two groups of beef samples.

3) There was no detailed examination of the quality assurance programs for the three studies taking grab samples from the grocery stores. There may have been laboratory problems.

4) There has been some data suggesting the leaching of dioxins into milk from milk cartons. The packaging and handling of beef may also introduce dioxins into beef. Since the EPA/USDA beef study obtained samples directly from the slaughterhouse, such introductions by packaging and handling would not occur. However, this explanation was contradicted by three additional grocery store grab samples of ground beef taken in Mississippi in 1995 (Cooper, et al., 1995), which showed concentrations quite comparable to the EPA/USDA beef sampling program. If packaging and handling did effect the 14 grab bag samples, they did not affect the Mississippi sampling.

5) The EPA/USDA samples were from back fat. The back fat samples were from a reservoir in the cow, which at a point nearby, is the fat which is the outer part of meat cuts from the cattle rib area. Back fat itself is not used or consumed. There is very little data on the differences in concentrations of dioxin-like compounds in the different edible and non-edible fat reservoirs of cattle. A recent study showed that there are not significant differences in dioxin and dioxin-like coplanar PCBs among fat reservoirs except a much higher concentration in the lipid of liver (Lorber, et al., 1997). Nonetheless, the grocery store samples were from different reservoirs of fat than the back fat of the EPA/USDA study.

If it is true that the fat concentrations of dioxins are similar across different body reservoirs of fat (with the exception of the lipid in liver), than it is certainly appropriate to conclude that the results of the EPA/USDA statistical monitoring study are a more appropriate representation of edible fat in beef as compared to the compilation of 14 grab samples used in the prior air-to-beef model validation exercise.

d. Results of the revised validation exercise: Table 7-21 shows the 1994 and 1996 model predictions for leafy vegetation, and compares then against five available data sets for leafy vegetation. The data on hay in the US (Reed, et al., 1990) seems to conflict the other available data on the table - it has significantly higher concentrations of the congeners it does have available, particularly the value for 285 ppt concentration of OCDD. This data could have been influenced by a local source, or because of the particular type of hay it was, it may have had much higher particulate dioxin contributions as compared to other grass data sets. One set from a rural setting in the UK (Jones and Duarte-Davidson, 1997), however, also has somewhat high OCDD concentrations at 94 ppt. All other sets had OCDD concentrations less than 25 ppt OCDD. This site in the UK also had relatively high air concentrations at 0.21 pg I-TEQ/m^3 compared to the rural air profile of 0.019 pg I-TEQ/m^3 from the Columbus site used in the exercise here. As described in Section 7.2.1. above, the modeling framework of this assessment used this data set to model a grass concentration of 3.7 pg I-TEQ/g, which is reasonably close to the measured 6.0 pg I-TEQ/g. The other two data sets from the UK are reasonably similar, with the more recent data set (Kjeller, et al., 1996) showing lower concentrations, and in fact, this data was used by the authors (among other data) to suggest that emissions of dioxins are being reduced in the UK. The data set on alfalfa is consistent with this data on grass in the UK.

It is easily seen that the current set of model predictions of dioxins in grass is much more in line with these two UK observations and the US alfalfa observation as compared to the predictions in the 1994 data set. There was a general reduction in the concentrations predicted between 1994 and the current predictions, due primarily to the reductions in the air-to-leaf vapor transfer factor, B_{vpa}. There were noticeable improvements in some of the congeners, particularly the predictions for 2378-TCDF and 12378-PCDF, and to a lesser extent but still noticeable, improvements in 12378-PCDD, 123478-HxCDD, 23478-PCDF, 123478-HxCDF, 123678-HxCDF, 234678-HxCDF, and OCDF. There was also an improvement to OCDD. It was noted above that the vapor fraction assumed for OCDD was 0.00 in the 1994 exercise, but in a detailed examination in Lorber, et al. (1994) and EPA (1994), use of a vapor fraction of 0.0002 for OCDD, which is what the V/P model calculated for the vapor fraction for OCDD, actually resulted in grass concentration approaching the hay concentration found in Reed, et al. (1990). Given the other leafy concentrations, it would appear that an OCDD grass concentration in the 10-30 ppt range is more appropriate than one greater than 100 ppt.

As a final and simple test of the current model predictions for leafy vegetation, the two data sets from the UK were averaged with the one set from alfalfa in the United States and correlated against the two sets of model predictions. The best fit regression line for the 1994 model predictions and this average of three observations had a slope of 0.26, an intercept of 0.84, and importantly a rather poor r^2 of 0.14. In contrast, the best fit regression line for the 1996 model predictions had a slope of 1.13, an intercept of 0.007, and a much improved r^2 of 0.98.

Table 7-22 compares the final predicted and observed beef data sets from the 1994 and the current validation exercise. There are reductions in both the observed and predicted beef concentrations from the 1994 results to the current results. However, given the conclusion stated above regarding the superiority of the EPA/USDA beef data set for this validation exercise, it is most appropriate to compare the predictions made in 1994 and those made in the current exercise with this observed data set. Just by visual inspection, it is seen that notable improvements in model predictions are noted for the following congeners: 12378-PCDD, OCDD, and 2378-TCDF. There are some congener predictions for which the 1994 validation exercise appears to result in a superior match, including 123478-HxCDD, 12378-PCDF, 123789-HxCDF, and 234678-HxCDF. Overall, the TEQ concentration in the current validation is closer to the observed TEQ concentration, although the total concentration appears more favorable for the 1994 validation exercise.

A simple correlation test suggests that the current model validation is superior to the 1994 model predictions. The following shows the results of linear regressions of the 1994 and 1996 model predictions with the EPA/USDA monitoring results assuming ND = ½ detection limit and ND = 0.0:

	Slope	Intercept	r^2
1994 model/ND = ½ detection	0.70	0.58	0.11
1994 model/ND = 0	0.74	0.13	0.16
1996 model/ND = ½ detection	1.02	0.55	0.57
1996 model/ND = 0	0.76	0.25	0.41

As seen, there is a better regression with the current modeling exercise as compared to the 1994 model exercise, with current r^2 of 0.57 and 0.41 compared against r^2 of 0.11 and 0.16.

It is also easy to see why individuals commenting on the air-to-beef model validation exercise of 1994 would note a poor correlation between observed and predicted concentrations. Very poor matches between predicted and observed are seen for 123678-HxCDD, 1234678-

HpCDD, OCDD, 2378-TCDF, 123478-HxCDF, 1234678-HpCDF, 1234789-HpCDF, and OCDF. Overall, the r^2 for the 1994 predictions against the observations from the 14 grocery store samples was 0.16. Also, the slope for this test was the highest of all the tests so far at 2.4, indicating that, for the best fit regression line, observations were higher than predictions by a greater margin than when testing against the EPA/USDA data set. For these tests, the slopes ranged from 0.74 to 1.02.

e. Remaining uncertainties in the validation exercise and in air-to-beef modeling in general: Following is a summary of the key uncertainties of this exercise and of food chain modeling in general:

1. A characteristic rural air environment: A profile of air concentrations of dioxin-like congeners in a rural environment would be better achieved as the average of several profiles in appropriate environments instead of just one.

2. A better understanding of the differences in the EPA/USDA sampling program and the grocery store samples taken earlier: There were 5 possible explanations listed as to why the earlier beef samplings appeared to have uniformly higher concentration profile as compared to the USDA/EPA beef profile. Before fully relying on the EPA/USDA sampling of cattle back fat, it would be appropriate to understand how the concentrations may differ, if any, with fat in beef purchased at grocery stores.

3. Vapor/particle partitioning: A theoretical modeling approach was used to partition the total reservoir of congeners into particle and vapor phases. Monitoring data suggests a different partitioning regime. This dichotomy was discussed in Chapter 3 and further in this Chapter in Section 7.3.11. A carefully designed monitoring experiment could shed some light on vapor/particle partitioning for dioxin-like compounds. This is obviously critical given the major conclusion of the dominance of vapor phase concentrations in explaining beef concentrations.

4. Vapor transfers to vegetation: Like the partitioning issue, the quantification of transfers onto vegetation is critical. There is some suggestion that the Welsch-Pausch experiments for which the air-to-leaf vapor transfer factor was developed may be unrealistic for field situations. Factors which make it unrealistic includes pots raised off the ground, and the grass being a dense monoculture. More typical field situations - at ground level with varied vegetation of lesser density may lead to lower transfers of vapors from the atmosphere to the canopy (M. McLachlan, Bayreuth University, FRG, personal communication). A data set including both field level pasture measurements coupled with a corresponding air profile would

be preferable to the data set of Welsch-Pausch for calibrating a vapor transfer factor, but none could be found for this assessment.

5. Particle depositions onto vegetation: The impact of wet deposition needs to be further investigated. A literature article suggesting that about 30% of particles depositing in rain are retained on the canopy after the rainfall justified the assignment of 0.30 to the parameter, R_w (fraction retained on vegetation from wet deposition). The weathering half-life of 14 days, while often used for dioxins, is also identified as uncertain. This half-life was based on studies on particle depositions on plants. It is possible that the dioxins would preferentially sorb onto the plants. Therefore, while particles themselves may have a 14-day half-life on the plants, the dioxins on the particles may remain behind on the plants and have a much longer half-life. Umlauf and McLachlan (1994) modeled the deposition of particle bound semi-volatile organic compounds (SOCs) to spruce leaves and assumed that the SOCs were fully retained on the leaves. In their publication, they did discuss the transfer of the SOCs from the particles to the leaves. Finally, the deposition velocity of 0.2 cm/sec should be considered further.

6. The bioconcentration factor: Only one study was found from which congener-specific bioconcentration factors for the suite of congeners could be developed, and this was for one cow, for one lactating period, and was for milk and not beef. The differences in bioconcentration between beef and milk need to be further investigated and quantified.

7. Cattle diet and the impact of feedlot fattening: A cattle diet was simplistically assumed to consist of 4% soil and equal parts of grass and non-grass feeds. Perhaps a more representative diet could be crafted, which would lead to a different exposure pattern by the beef cow prior to feedlot fattening. Equally if not more important is the impact of this feedlot fattening. It is clear that commercial beef cattle in the United States undergo a period of feedlot fattening. However, before and after monitoring quantifying the impact of this practice could not be found. Two modeling studies, which assumed that dilution and depuration were occurring during feedlot fattening, estimated that concentrations were halved due to this process. This was the assumption also made in this paper, and it needs to be further evaluated.

7.3.13. *Expansion of the Terrestrial Food Chain Model for Dioxins and Applications to other Foodstuffs in the United Kingdom*

Harrad and Smith (1997) adopted the food chain model developed initially in the first draft of the Dioxin Reassessment (EPA, 1994), expanded it to include soil-to-above ground plant transfers, and applied it to UK data in very much the same manner as in the air-to-plant-to-beef exercise described just above in Section 7.3.12. Soil-to-above ground impacts are assumed not to occur in this assessment, and in Harrad and Smith (1997), they found that soil-to-above ground translocations explained very little of the predicted grass concentrations. They also expanded the initial development of this approach in EPA (1994) to include poultry and eggs, both of which are now modeled in this current assessment.

Although they didn't exactly state where the air data come from in their exercise, it is surmised that they selected a rural air concentration profile of the 17 dioxin-like CDD/Fs they deemed to be typical of UK conditions. Then they routed this concentration through the food chain models to predict the dioxin concentrations in various kinds of animal feeds, and then the concentration in animal meats. They compared predictions of dioxins in grass (one of the animal feeds) to those reported for a bulk herbage representing the years 1979-1988 reported in Kjeller, et al. (1991). They found the ability of the air-to-grass model to predict grass concentration to be "reasonably satisfactory" with predictions falling within an order of magnitude of observations, and I-TEQ predicted and observed concentrations to be close at 1.3 pg/g (predicted) and 0.86 pg/g (observed). They did note more variability in congener-by-congener predictions for the other food products but found that I-TEQ concentrations were reasonably well predicted, including: 1) retail meat products (assumed to be beef, but not identified as such), pg/g fresh weight: predicted - 0.252, observed - 0.254; 2) milk, pg/g fresh weight: predicted - 0.090, observed - 0.057; 3) poultry, pg/g fresh weight: predicted - 0.630, observed - 0.399; 4) eggs, pg/g fresh: predicted - 0.262, observed - 0.194; and 5) potatoes, pg/g fresh: predicted - 0.0072, observed - 0.037.

7.3.14. *Beef and Milk Fat Concentrations when Soil is the Source of Contamination*

Sampling of beef and milk near areas of elevated soil concentrations, or where cattle were raised on soils with known high concentrations of 2,3,7,8-TCDD, were not found in the literature. Therefore, the beef fat concentration of 60 ppt estimated to occur near an area where the soil concentrations of 2,3,7,8-TCDD was 1 ppb cannot easily be evaluated. There are some studies on other animals indicating high tissue concentrations in areas of high soil contamination of 2,3,7,8-TCDD. Lower, et al. (1989) studied animal tissues for wild animals in the abandoned town of Times Beach, Missouri, and compared their results for similar wild animals tissue concentrations found in Eglin Air Force Base in Florida; Seveso, Italy; and Volgermeerpolder, Holland. With 2,3,7,8-TCDD soil levels in these areas in the hundreds to thousands of ppt, tissue levels for earthworm, mouse, prairie vole, rabbit, snake, and liver samples from some of these animals, were in the tens to thousands of ppt.

There is an episode of beef and dairy cows being raised on lots where the soil was heavily contaminated with polybrominated biphenyls (PBB; details can be found in Fries and Jacobs, 1986; and Fries, 1985). Soil concentrations to which dairy and beef cows were exposed were 830 and 350 µg/kg (ppb), respectively. Body fat of the dairy cows had PBB concentrations of 305, 222, and 79 ppt (dairy heifers, primiparous dairy, and multiparous dairy, respectively). Body fat for the beef cows exposed to 350 ppb soil levels were 95 (cows) and 137 ppt (calves). Milk fat concentrations from the primiparous dairy and multiparous dairy cows exposed to 830 ppb soil levels were 48 and 18 ppt.

Fries (1985) estimated a quantity which is useful for purposes of comparison - this quantity is the ratio of concentration in animal fat to concentration in soil to which the animal is exposed. His justification for deriving this ratio is that soil was speculated as the principal source of body burdens of PBB in the data listed above. This is also the case for the soil contamination source category of this assessment. Ratios he derived for body fat of dairy heifers ranged from 0.10 to 0.37, while it was 0.02 and 0.06 for milk fat. For body fat of beef cows, these ratios were 0.27 and 0.39. Fries also measured a ratio of 1.86 for sows and gilts. He attributes much higher sow ratios to their tendencies to ingest more soil.

Analogous ratios can be derived for the demonstration of the soil contamination source category for beef and milk fat. For the demonstration in Chapter 5, the soil concentration predicted to occur at the farm was 0.36 ppb, and the beef fat and milk fat concentrations were predicted to be 0.06 and 0.03 ppb, respectively. These correspond to ratios of 0.17 for beef fat and 0.08 for milk fat. The milk fat ratio compares favorably with PBB ratios derived by Fries (1985), but the beef fat ratio appears generally lower. The beef fat concentrations in the demonstration scenarios were driven by the fraction of soil in the diet of the beef cattle, as were the concentrations in the milk fat. It may be possible that the cattle slaughtered for beef raised in the lots with high PBB concentrations were exposed to more soil than was assumed in the demonstration scenarios. There, soil was 4% of the diet. If this value were increased to 8%, than predicted beef fat concentrations would also double, and the beef fat:soil ratio would be 0.34 instead of 0.17.

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Table 7-1. Observed data for the air-to-plant model comparison exercise.*

Compounds	Rural Background Site			Industrial Site		
	Air	Deposition	Grass	Air	Deposition	Grass
2378-TCDD	0.01	<0.46	0.72	0.017	1.6	2.8
12378-PCDD	0.03	2.3	1.3	0.04	3.8	<0.08
123478-HxCDD	0.04	2.3	0.93	0.04	3.2	0.73
123678-HxCDD	0.08	4.8	2.3	0.09	10.8	6
123789-HxCDD	0.1	3.8	1.8	0.13	8.9	4.2
1234678-HpCDD	0.82	41	22	0.84	51	13
OCDD	2.5	166	94	2.5	153	43
2378-TCDF	0.33	12	14	0.57	18	16
12378-PCDF	0.06	2.5	1.8	0.1	2.2	<0.09
23478-PCDF	0.1	4.1	2.2	0.19	6	1.2
123478-HxCDF	0.3	11	5.6	0.45	12	4.6
123678-HxCDF	0.1	4.5	2.2	0.16	5.7	1.8
123789-HxCDF	0.02	1.8	0.61	0.07	1.9	0.54
234678-HxCDF	0.14	4.8	2.6	0.19	6	2.4
1234678-HpCDF	0.53	19	12	0.71	25	11
1234789-HpCDF	0.11	2.9	1.1	0.14	3.2	0.89
OCDF	0.42	28	13	0.48	35	8
TCDD	0.72	73	66	3.1	509	750
PCDD	0.56	54	33	1.2	477	410
HxCDD	0.65	38	26	0.78	73	38
HpCDD	0.71	41	22	0.73	48	11
TCDF	1.6	24	93	3.3	131	290
PCDF	0.84	27	31	2.3	64	21
HxCDF	0.45	18	13	1.4	26	19
HpCDF	0.22	<1.8	<0.22	0.43	<1.6	<0.31

* Units: air - pg/m^3; deposition - pg/m^2-day; grass - pg/g dry weight of dioxin in the grass. Grass yield for rural = 89 g/m^2 dry weight, for industrial = 42 g/m^2 dry weight.

Table 7-2. Model results comparing the EPA vapor transfer model and the Vapor Deposition Model with the field data for 2,3,7,8-TCDD (concentrations in pg/g dry weight).

Description	2,3,7,8-TCDD grass concentrations, pg/g dry	
	Rural	Industrial
Observed data	0.72	2.8
EPA vapor transfer model	0.25	0.21
Smith et al. (1995) model	0.06	0.05
Trapp & Mattheis (1995) model	0.13	0.1

Table 7-3. Model parameters used in the Hwang and the alternate volatilization models tested in this comparison exercise.

Description	Jury model	Simplified Jury model	Hwang model	Vapor diffusion
I. Soil Parameters				
C_0, initial soil concentration, mg/kg	0.001	0.001	0.001	0.001
θ, volumetric water content, cm^3/cm^3, or unitless	0.23	0.23	NR	NR
a, soil air content, cm^3/cm^3, or unitless	NR	0.2	NR	0.2
ϕ, soil porosity, cm^3/cm^3, or unitless	0.43	0.43	0.43	0.43
BD, soil bulk density, g/cm^3	1.5	1.5	NR	NR
Psoil, soil particle bulk density, g/cm^3	NR	NR	2.65	NR
J_w, water flux, cm/sec	0	NR	NR	NR
foc, fraction organic carbon	0.01	0.01	0.01	0.01
d_z, soil depth of constant concentration, cm	10	NR	NR	10
II. Chemical Properties				
D_g^{air}, chemical gaseous diffusion coefficient in air, cm^2/sec	$4.7*10^{-2}$	$4.7*10^{-2}$	$4.7*10^{-2}$	$4.7*10^{-2}$
D_l^{water}, chemical liquid diffusion coefficient in water, cm^2/sec	$5.6*10^{-6}$	$5.6*10^{-6}$	NR	NR
Koc, organic carbon partition coefficient, cm^3/g	$3.98*10^6$	$3.98*10^6$	$3.98*10^6$	$3.98*10^6$
H, Henry's Constant, atm-m^3/mole	$3.2*10^{-5}$	$3.2*10^{-5}$	$3.2*10^{-5}$	$3.2*10^{-5}$
μ, soil degradation rate, 1/sec	0	NR	NR	NR
III. Model Solution Parameters				
BL, boundary layer thickness, cm	0.5	NR	NR	NR
Time of Volatilization, days	10950	10950	10950	NR

NR = Not required for solution

Table 7-4. Results of model volatilization comparison exercise.

Description	Volatilization, g/cm^2-sec
Hwang model	$1.03 * 10^{-18}$
Full Jury model as coded in EMSOFT	$2.81 * 10^{-19}$
Simplified Jury Model as used in Superfund Soil Screening	$3.89 * 10^{-19}$
Vapor diffusion solution only	$4.03 * 10^{-21}$
Full Jury model, boundary layer = 0.01 cm	$3.02 * 10^{-19}$
Full Jury model, half-life = 25 years	$2.16 * 10^{-19}$

Table 7-5. Comparison of the derivation of the fraction of sorbed dioxin congener based on the octanol air partition coefficient, K_{oa}, or based on the sub-cooled liquid vapor pressure, as done for this document as described in Chapter 3.

Congener	Solving for K_{oa} [1]			ϕ for urban conditions[2]		ϕ for urban conditions as in Chapter 3
	log K_{ow}	H	log K_{oa}	theoretical	empirical	
2378-TCDD	6.81	$3.95*10^{-5}$	9.63	0.09	0.14	0.75
12378-PCDD	6.64	$2.60*10^{-6}$	10.58	0.48	0.40	0.95
123478-HxCDD	7.80	$1.05*10^{-5}$	11.13	0.76	0.60	0.99
123678-HxCDD	7.30	$1.10*10^{-5}$	10.61	0.49	0.41	0.99
123789-HxCDD	7.30	$1.10*10^{-5}$	10.61	0.49	0.41	0.99
1234678-HpCDD	8.00	$1.26*10^{-5}$	11.25	0.81	0.64	0.997
OCDD	8.20	$6.75*10^{-6}$	11.72	0.92	0.78	0.999
2378-TCDF	6.10	$1.44*10^{-5}$	9.29	0.05	0.09	0.73
12378-PCDF	6.79	$5.00*10^{-6}$	10.44	0.40	0.35	0.91
23478-PCDF	6.50	$4.98*10^{-6}$	10.15	0.26	0.26	0.94
123478-HxCDF	7.00	$1.43*10^{-5}$	10.19	0.27	0.27	0.98
123678-HxCDF	7.00	$7.31*10^{-6}$	10.49	0.42	0.36	0.98
123789-HxCDF	7.00	$1.10*10^{-5}$	10.31	0.33	0.31	0.99
234678-HxCDF	7.00	$1.10*10^{-5}$	10.31	0.33	0.31	0.99
1234678-HpCDF	7.40	$1.41*10^{-5}$	10.60	0.49	0.40	0.99
1234789-HpCDF	8.00	$1.40*10^{-5}$	11.20	0.79	0.62	0.997
OCDF	8.80	$1.88*10^{-5}$	11.88	0.95	0.82	0.999

[1] K_{oa}, the octanol air partition coefficient, is solved as, [Kow*R*T]/[H], where K_{ow} is the octanol water partition coefficient, dimensionless; R is the universal gas constant, $8.2*10^{-5}$ atm-m^3/mole-K;T is ambient temperature, 273 °K, H is the Henry's Constant, atm-m^3/mole.

[2] ϕ, the fraction of sorbed particle, is solved as [K_p (TSP)]/[1 + K_p (TSP)]. K_p is solved for either "theoretically", where log K_p = log K_{oa} -12.61, or "empirically" based on field data, as done by Kaupp and McLachlan (1999) as, log K_p = 0.6368 log K_{oa} -8.9111. See Section 7.2.7 for more detail on these algorithms.

Table 7-6. Summary of off-site soil contamination from Tier 1 and 2 sites of the National Dioxin Study.

Site name	On-site # samples/range (ppb)	Off-site # samples/range (ppb)	Comments
Diamond Alkali Newark, NJ	9/60-51,000	537/ND-725	Facility involved in the manufacture of 2,4,5-T; off-site sampling covered a 4000-ft radius including public areas such as a public housing unit, park, streets, and river. Two of 11 samples from a park were positive at 1-3.1 ppb; detection limit was 1 ppb. Other off-site positives were from streets and river sediments.
Brady Metals Newark, NJ	10/1.9-3500	30/1.7-1156	Site directly associated with the Diamond Alkali site summarized above; text did not provide any further detail on off-site soil sampling.
Love Canal Niagara, NY	NA/NA-6.7	20/3-263	Love Canal contamination well documented elsewhere; few details provided in reference for soil sampling programs; it was noted that 3,000 cubic yards of fly ash and BHC cake were taken from Love Canal in 1954 and used as fill at the nearby 93rd Street School, a subsurface sample 3+ ft deep showed a concentration of 6.7 ppb. The off-site summary provided here was from an area identified as Hyde Park.
Vertac Jacksonville, AR	45/<1-1,200	320/<1-33.4	A site manufacturing 2,4,5-T; it is not clear than any of the off-site sampling was for surface soil - summary tables identified it as "various"; text description did not mention off-site soil contamination and indicated that solid and liquid waste were buried on-site in a series of landfills. 2,3,7,8-TCDD was found in fish as far away as 100 miles.
Hooker Chemical Niagara, NY	17/ND-18,600	4/ND-430	A site manufacturing 2,4,5-TCP; subsurface soil sampling ranged from ND to 18.6 parts per million; one off-site surface soil detection noted at 1.1 ppb.
Bliss Tank Property Rosat, MO	NA/ND-430	NA-ND-430	No summary text provided in primary reference; tabular summary identified soil sampling as on/off-site soil; non-detects were noted in 13 off-site dust sampling.
Dow Chemical Midland, MI	#1: 43/0.041-52 #2: 106/ND-1500	11/0.0006-0.45 42/0.003-2.03	Site most extensively studied of those in National Dioxin Study; data identified as #1 was a summary of 1984 data supplied in NDS; #2 was a summary of 1985 data; the 1984 data was further detailed in Nestrick, et al. 1986; see text for further discussions on this site.

Source: EPA (1987)

Table 7-7. Description of soil, sediment, and fish sampling program of dioxin-like compounds undertaken by the Connecticut Department of Environmental Protection.

Site/Sampling Media	Description	Data Available
1. Bridgeport	Year RRF began operation	1987
Soil	Years of collection Number of sampling sites Total number of samples	1987, 1988, 1990 7 21
Sediment	Years of collection Number of sampling sites Water body descriptions Total number of sediment samples Range, samples per water body	1987, 1988, 1990 6 harbor (2), channel (1; off harbor), river, pond (2) 66 4 - 22
Fish	No fish sampling at this site	
2. Bristol	Year RRF began operation	1987
Soil	Years of collection Number of sampling sites Total number of samples	1987, 1988, 1990 4 12
Sediment	Years of collection Number of water bodies sampled Water body descriptions Total number of sediment samples Range, samples per water body	1987, 1988, 1990 2 pond (2) 60 29 and 30
Fish	Years of collection Number of water bodies sampled Water body descriptions Total number of fish samples Range, samples per water body Fish species	1987, 1988, 1989, 1990 2 pond (2) 140 68 and 72 brown bullhead, white sucker, yellow perch

(continued on following page)

Table 7-7. (cont'd).

Site/Sampling Media	Description	Data Available
3. Hartford	Year RRF began operation	1987
Soil	Years of collection Number of sampling sites Total number of samples	1987, 1988, 1990 4 12
Sediment	Years of collection Number of sampling sites Water body descriptions Total number of sediment samples Range, samples per water body	1987, 1988, 1990 3 impoundment (1), cove (2) 90 30 from each water body
Fish	Years of collection Number of water bodies sampled Water body descriptions Total number of fish samples Range, samples per water body Fish species	1987, 1988, 1989, 1990 2 cove (2) 159 81 and 78 carp, channel catfish, white catfish, white sucker
4. Preston	Year RRF began operation	1990
Soil	Years of collection Number of sampling sites Total number of samples	1990 4 4
Sediment	Years of collection Number of water bodies sampled Water body descriptions Total number of sediment samples Range, samples per water body	1990 3 2 ponds, 1 reservoir 30 10 from each water body
Fish	no fish sampling at this site	perch

(continued on following page)

Table 7-7. (cont'd).

Site/Sampling Media	Description	Data Available
5. Sterling	Year RRF began operation	1990
Soil	Years of collection Number of sampling sites Total number of samples	1990 4 4
Sediment	Years of collection Number of sampling sites Water body descriptions Total number of sediment samples Range, samples per water body	1990 2 pond (2) 20 10 from each pond
Fish	Years of collection Number of water bodies sampled Water body descriptions Total number of fish samples Range, samples per water body Fish species	1990 2 pond (2) 40 20 from each pond white sucker, yellow perch
6. Union/Stafford	No associate RRF, used as "control" or "reference" site	
Soil	Years of collection Number of sampling sites Total number of samples	1988 (Union), 1990 (Stafford) 4 (Un), 4 (St) 4 (Un), 4 (St)
Sediment	Years of collection Number of water bodies sampled Water body descriptions Total number of sediment samples Range, samples per water body	1988, 1990 2 pond (Un), reservoir (St) 20 10 from each water body
Fish	Years of collection Number of water bodies sampled Water body descriptions Total number of fish samples Range, samples per water body Fish species	1988, 1990 2 pond and reservoir 47 27 (reservoir), 20 (pond) brown bullhead, white sucker, yellow perch

(continued on following page)

Table 7-7. (cont'd).

Site/Sampling Media	Description	Data Available
7. Windham	Year RRF began operation	1983
Soil	Years of collection Number of sampling sites Total number of samples	1988, 1990 4 8
Sediment	Years of collection Number of sampling sites Water body descriptions Total number of sediment samples Range, samples per water body	1988, 1990 1 reservoir 20 20 from each water body
Fish	Years of collection Number of water bodies sampled Water body descriptions Total number of fish samples Range, samples per water body Fish species	1988, 1989, 1990 1 reservoir 59 59 white sucker, brown bullhead, yellow perch
8. Preston	Year RRF began operation	1988
Soil	Years of collection Number of sampling sites Total number of samples	1988, 1990 4 8
Sediment	Years of collection Number of water bodies sampled Water body descriptions Total number of sediment samples Range, samples per water body	1988, 1990 2 impoundments 40 20 from each water body
Fish	Years of collection Number of water bodies sampled Water body descriptions Total number of fish samples Range, samples per water body Fish species	1988, 1989, 1990 2 impoundments 75 59 brown bullhead, carp, white sucker

Source: CDEP, 1992

Table 7-8. Frequency of non-detects and detection limits for soil, sediment, and fish, for three congeners in the Connecticut Department of Environmental Protection data set.

Congener/Description	Soil	Sediment	Fish
2,3,7,8-TCDD			
Percent of non-detects	50	27	3
Detection limit, ppt	0.13	0.25	0.05
2,3,7,8-TCDF			
Percent of non-detects	3	2	0.2
Detection limit, ppt	NDA (0.09)	0.17	NDA (0.09)
2,3,4,7,8-PCDF			
Percent of non-detects	1	5	7
Detection limit, ppt	NDA (0.09)	0.26	0.04

Source: for percent non-detects: MRI, 1992; for detection limits, draft Monitoring Progress Report for 1988, supplied by CDEP (1992) specific to MRI laboratories; NDA = no data available; number of parenthesis is ½ detection limit for time when non-detect was noted, see text for further information and interpretation

Table 7-9. Results for Connecticut Department of Environmental Protection sampling, including soil, sediment and fish concentrations, and the key concentration ratios of sediment to soil and the Biota Sediment Accumulation Factor (BSAF) ratio.

Site/Description	Soil	Sediment	Fish
A. 2,3,7,8-TCDD RESULTS			
1. Bridgeport			
Number of samples	21	66	no data
Range of concentration, ppt	0.07-4.62	0.20-51.50	
Mean concentration, ppt	0.59	4.53	
C_{sed}:C_{soil} Ratio: 7.7			
2. Bristol			
Number of samples	12	59	140
Range of concentration, ppt	0.01-0.61	0.16-6.50	0.03-0.83
Mean concentration, ppt	0.17	1.67	0.26
fish lipid: 0.038			
sediment organic carbon: 0.190			
C_{sed}:C_{soil} Ratio: 9.8			
BSAF: 0.78			
3. Hartford			
Number of samples	12	90	159
Range of concentration, ppt	0.07-0.32	0.04-23.10	0.03-10.90
Mean concentration, ppt	0.16	1.96	2.41
fish lipid: 0.072			
sediment organic carbon: 0.056			
C_{sed}:C_{soil} Ratio: 12.3			
BSAF: 0.97			
4. Bridgeport			
Number of samples	4	30	no data
Range of concentration, ppt	0.14-0.80	0.08-17.9	
Mean concentration, ppt	0.39	2.75	
C_{sed}:C_{soil} Ratio: 7.1			

Table 7-9. (Cont’d)

Site/Description	Soil	Sediment	Fish
5. Sterling			
Number of samples	4	20	40
Range of concentration, ppt	0.01-7.96	0.07-3.08	0.03-0.37
Mean concentration, ppt	2.12	0.90	0.11
fish lipid: 0.053			
sediment organic carbon: 0.067			
C_{sed}:C_{soil} Ratio: 0.4			
BSAF: 0.15			
6. Union/Stafford			
Number of samples	8	20	48
Range of concentration, ppt	0.02-1.56	0.23-3.69	0.07-0.85
Mean concentration, ppt	0.28	1.58	0.26
fish lipid: 0.041			
sediment organic carbon: 0.178			
C_{sed}:C_{soil} Ratio: 5.6			
BSAF: 0.71			
7. Windham			
Number of samples	8	20	59
Range of concentration, ppt	0.15-0.54	0.18-1.97	0.07-0.60
Mean concentration, ppt	0.25	0.97	0.25
fish lipid: 0.044			
sediment organic carbon: 0.129			
C_{sed}:C_{soil} Ratio: 3.9			
BSAF: 0.76			
8. Wallingford			
Number of samples	8	40	75
Range of concentration, ppt	0.07-6.00	0.03-3.10	0.03-8.92
Mean concentration, ppt	1.61	0.54	1.37
fish lipid: 0.071			
sediment organic carbon: 0.019			
C_{sed}:C_{soil} Ratio: 0.3			
BSAF: 0.68			

Table 7-9. (Cont'd)

Site/Description	Soil	Sediment	Fish
B. TOTALS BY CONGENER (fish lipid = 0.0557, organic carbon fraction = 0.0982 for results below; these are means for the full data set)			
1. 2,3,7,8-TCDD			
Number of samples	770.56	3462.16	5211.06
Mean concentration, ppt			
C_{sed}:C_{soil} Ratio: 3.86			
BSAF: 0.86			
2. 2,3,7,8-TCDF			
Number of samples	776.77	34617.52	5212.53
Mean concentration, ppt			
C_{sed}:C_{soil} Ratio: 2.59			
BSAF: 0.25			
3. 2,3,4,7,8-PCDF			
Number of samples	773.56	3465.62	5211.49
Mean concentration, ppt			
C_{sed}:C_{soil} Ratio: 1.58			
BSAF: 0.47			
4. I-TEQ			
Number of samples	778.42	34622.69	5213.1
Mean concentration, ppt			
C_{sed}:C_{soil} Ratio: 2.69			
BSAF: 0.24			

Source: CDEP, 1992

Table 7-10. Model parameters and results for effluent discharge model validation testing.

Number	Company/City	Plant flow L/hr*10^6	TCDD mg/hr	TSSe mg/L	River flow L/hr*10^8	TSSu mg/L	Lipid %	Fish concentrations pg/g (ppt) whole wt		Multiple Discharges Mill Numbers
								Predicted	Observed	
I. Mills with receiving water bodies of lower magnitude; suitable for model testing according to NCASI (see text for more explanation)										
1	James R. Corp, Old Town	2.52	0.098	127	8.57	2	10.9	1.9	8	49
2	International Paper Co, Jay	6.31	0.56	89	3.21	2	6.2	8.8	41.0	
	Second fish listing						0.6	0.9	3.6	
	Third fish listing						0.9	1.3	2.9	
	Fourth fish listing						6.3	8.9	16.1	
	Fifth fish listing						2.1	3.0	23.1	
3	James R. Corp, Berlin	2.74	0.104	47	5.13	4	3.7	2	7.8	
4	Westvaco Corp, Luke	3.12	0.05	57	0.3	13	4.9	2.8	58.2	
	Second fish listing						4.7	2.7	35.5	
5	Penntech Pap, Johnsonburg	0.87	0.01	44	0.39	17	1.6	0.2	3.6	
	Second fish listing						2.5	0.3	5.8	
6	Chesap. Corp, West Point	2.35	0.038	94	0.41	13	2.1	0.6	0.8	
	Second fish listing						2.1	0.6	1.1	
	Third fish listing						6.2	1.7	2.5	
	Fourth fish listing						4.1	1.1	1.9	
7	Westvaco Corp, Covington	4.18	0.227	46	0.31	13	1.2	2.4	5.9	
	Second fish listing						9.7	19.2	54.1	
8	Union Camp Corp, Franklin	19.7	1.343	60	0.35	0.3	1.9	5.1	1.8	
9	Champion Int, Courtland	9.3	0.716	23	43.3	10	11.1	1.9	3.4	26

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Table 7-10. (cont'd)

Number	Company/City	Plant flow L/hr*10^6	TCDD mg/hr	TSSe mg/L	River flow L/hr*10^8	TSSu mg/L	Lipid %	Fish concentrations pg/g (ppt) whole wt		Multiple Discharges Mill Numbers
								Predicted	Observed	
10	Cont Corp Amer, Brewton	5.63	0.037	13	1.01	6	2.2	0.8	0.6	
11	Boise Casc Corp, Jackson	3.08	0.332	19	8.25	10	5.3	2.1	8.8	5657581213
12	Kimb-Clark Corp, C. Pines	6.91	0.242	19	6.41	18	1.4	0.4	8.8	1357
	Second fish listing						5.8	1.4	30.0	
13	Alab River Pulp, Claiborne	3.53	0.148	87	15.2	12	3.8	0.3	16.8	1257
	Second fish listing						15.5	1.3	28.7	
14	Buckeye Cellulose, Perry	8.71	0.235	39	0.003	2	8.4	14.1	13.2	
15	Geo-Pac Corp, Palatka	5.84	0.093	8	0.04	2	20.3	81.8	1.4	
16	Fed Pap Bd Co, Augusta	4.73	0.076	101	6.56	8	4.1	0.4	4.5	
17	ITT-Rayonier, Inc, Jesup	9.42	0.226	26	7.12	8	2.0	0.6	0.9	
	Second fish listing						5.9	1.8	4.6	
18	Int. Paper Co, Moss Point	2.71	0.434	57	0.25	12	0.7	3.4	7.8	
	Second fish listing						7.7	37.6	34.4	
19	L.R. For Prod, New Aug	2.76	0.552	46	1.62	12	0.9	1.6	3.8	
	Second fish listing						8.8	15.2	98.9	
20	Champion Int, Canton	6.94	0.104	22	0.3	3	3.4	4.3	12.0	
	Second fish listing						6.9	8.8	75.7	
21	Wayerhauser Co, Plymouth	6.15	1.968	15	0.56	8	0.9	20.6	18.2	
	Second fish listing						3.9	89.6	143.3	

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Table 7-10. (cont'd)

Number	Company/City	Plant flow L/hr*10^6	TCDD mg/hr	TSSe mg/L	River flow L/hr*10^8	TSSu mg/L	Lipid %	Fish concentrations pg/g (ppt) whole wt		Multiple Discharges Mill Numbers
								Predicted	Observed	
22	Wayerhauser, New Bern	3.77	0.166	14	1.22	4	0.8	1.3	5.5	
	Second fish listing						8.2	13.2	49.2	
23	Fed Pap Bd, Riegelwood	4.42	0.124	241	2.32	7	0.9	0.2	0.9	
	Second fish listing						8.2	1.7	22.3	
24	Bowater Corp, Catawba	5.3	0.127	13	2.89	5	1.4	0.8	3.2	
	Second fish listing						6.1	3.4	15.3	
25	Union Camp Corp, Eastover	1.4	0.028	2	3.95	15	1.5	0.1	1.2	
	Second fish listing						8.5	0.5	9.1	
26	Mead Corp, Kingsport	1.53	0.01	88	1.53	6	6.4	0.4	1.0	
	Second fish listing						10.7	0.6	6.6	
27	Champion Int, Quinnesec	2.02	0.018	32	1.92	3	1.4	0.2	1.4	
	Second fish listing						1.6	0.2	1.4	
	Third fish listing						16.8	2.2	21.0	
28	Badger P M, Inc, Pestigo	0.24	0	124	0.64	4	24.4	0.5	8.5	
	Second fish listing						1.9	0.04	0.3	
29	James R. Corp, Green Bay	1.57	0.017	177	3.02	14	8	0.3	5.6	
30	Nekoosa Papers, Inc., Nek	4.78	0.191	36	3.18	6	1.7	1.0	7.1	
	Second fish listing						21.5	13.1	67.2	
31	Wayerhauser Co, Rothchild	0.99	0.012	27	2.54	5	1.3	0.1	0.2	
	Second fish listing						16.3	1.0	4.6	

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Table 7-10. (cont'd)

Number	Company/City	Plant flow L/hr*10^6	TCDD mg/hr	TSSe mg/L	River flow L/hr*10^8	TSSu mg/L	Lipid %	Fish concentrations pg/g (ppt) whole wt		Multiple Discharges Mill Numbers
								Predicted	Observed	
32	Int. Paper - Bastrop Second fish listing Third fish listing Fourth fish listing	4.44	1.47	82	10.7	13	1.0 12.3 3.0 6.2	1.1 13.3 16.4 33.9	1.0 3.6 5.5 5.2	
33	Int Paper Co, Pine Bluff Second fish listing	4.34	0.478	71	9.97	7	5.2 10.4	2.8 5.5	8.9 33.9	
34	Nek Pap, Inc, Ashdown Second fish listing	6.07	0.249	21	4.02	42	3.5 1.8	0.8 0.4	4.2 1.7	
35	Boise Casc Corp, Derrider Second fish listing	3.66	0.034	59	0.12	10	8.2 1.4	2.8 0.5	13.7 1.4	
36	Temple-East Inc., Evadale Second fish listing	8.67	0.763	26	1.5	7	1.0 8.0	3.5 28.0	0.7 0.4	
37	Potlatch Corp, Lewiston Second fish listing	5.43	0.407	126	36.4	19	4.4 6.4	0.3 0.5	0.7 0.5	
38	Pope and Talbot, Inc, Halsey Second fish listing	1.83	0.055	14	7.75	7	8.8 9.6	0.8 0.8	4.6 0.8	
SIMPLE MEANS		4.7	0.31	58	5.3	9	5.8	7	15	38 mills / 74 fish
I. Mills with receiving water bodies of higher magnitude; suitable for model testing according to NCASI (see text for more explanation)										
39	Westvaco Corp, Wickliffe Second fish listing	3.53	0.124	34	321.3	129	1.9 7.4	0.001 0.004	1.4 4.8	967

(continued on next page)

Table 7-10. (cont'd)

Number	Company/City	Plant flow L/hr*10^6	TCDD mg/hr	TSSe mg/L	River flow L/hr*10^8	TSSu mg/L	Lipid %	Fish concentrations pg/g (ppt) whole wt Predicted	Fish concentrations pg/g (ppt) whole wt Observed	Multiple Discharges Mill Numbers
40	Int Paper Co, Natchez	5.99	0.228	115	407.2	221	22.6	0.01	3.1	92633394167
41	Potlatch Corp, Mcghee Second fish listing	1.92	0.077	21	375.2	130	3.5 5.8	0.001 0.002	1.4 4.7	92633394067
42	James Riv C, St. Francis Second fish listing Third fish listing	4.46	0.366	36	355.3	107	2.3 2.3 10.8	0.004 0.004 0.017	1.8 0.8 6.0	9.31333439404e+18
43	Georgia Pac, Zachery Second fish listing	4.1	0.718	130	355.3	13	2.0 8.7	0.035 0.15	1.4 1.8	9.26333439404e+18
44	Boise Cac C., St. Helens Second fish listing Third fish listing	5.54	0.122	59	183.5	22	2.0 9.6 3.2	0.008 0.04 0.01	1.3 2.6 1.1	373846
45	Wayerh Co, Longview Second fish listing	8.36	0.071	46	191.6	22	3.0 11.4	0.007 0.026	1.5 5.2	37384446
46	Boise Casc, Wallula Second fish listing Third fish listing Fourth fish listing	3.15	1.1	157	145.8	14	3.9 10.9 25.1 0.7	0.2 0.7 1.6 0.04	5.2 7.9 56.0 0.4	37
47	James River, Clat Second fish listing	6.43	0.097	40	191.6	46	7.0 2.9	0.01 0.005	2.8 1.73	3738444546
SIMPLE MEANS		4.83	0.32	71	280.8	78	7	0.14	5.7	9 mills / 21 fish

(continued on next page)

Table 7-10. (cont'd)

Number	Company/City	Plant flow L/hr*10^6	TCDD mg/hr	TSSe mg/L	River flow L/hr*10^8	TSSu mg/L	Lipid %	Fish concentrations pg/g (ppt) whole wt		Multiple Discharges Mill Numbers
								Predicted	Observed	
III. No fish in NCSRF according to NCASI										
48	Georgia-Pac., Woodland									
49	Lincoln Pulp and Pap, Lincoln									
50	Scott Paper, Westbrook									
51	Scott Paper, Hinckley									
52	Int. Paper Co., Mobile									
53	Scott Paper									
54	Potlatch Corp., Cloquet									
IV. Mill already considered as multiple source										
55	Boise Cas. Corp, Rumford									
56	Gulf St Pap Co, Demopolis									
57	International Paper Co, Selma									
58	James River Corp, Butler									
59	Georgia-Pac Corp, Crosset									
V. Effluent discharge at ND										
60	Finch & P. & Co, Glen F.									
61	Appleton Pap, Roaring Sp.									
62	P.H. Glat. Co, Spring Gr.									
63	Proc & Gam, Mehoopany									
64	Champion Int., Cantonment									
65	Gilman Paper Co, St. Marys									
66	Buckeye Cell, Oglethorpe									
67	Wilamette Ind, Hawesville									
68	Bowater Corp., Calhoun									
69	Mead Corp, Escanaba									
70	Pentair, Inc., Park Falls									
71	Wausau P Mills Co, Brokaw									
72	Longv. Fiber C, Longview									
VI. Mill discharges into estuary, not suitable for model testing										
73	ITT-Ray, Inc., Fernandina B.									
74	Stone Cont Corp, Pan C.									
75	Bruns P. & Paper, Bruns									
76	Int. Paper Co, Georgetown									
77	Alaska Pulp Corp, Sitka									
78	Ketch Pulp & Pap 1, Ketch									
79	ITT-Ray, Inc., Port Angeles									
80	Wayerh Co., Cosmopolis									
81	Wayerh Co., Everett									
82	ITT-Rayonier, Inc., Hoquiam									

Table Headings:				
	Number:	mill number, established for this table only	River flow:	receiving water body flow rate
	Company, city:	abbreviated name and city location	TSSe,u:	effluent, upstream suspended solids
	Plant flow:	effluent flow rate	Fish conc:	concentrations as measured in NCSRF
	TCDD:	2,3,7,8-TCDD discharge rate	Multiple discharges:	other mills assumed to influence fish concentrations
	Lipid:	measured fish lipid, percent		

Table 7-11. ISCST3 and soil model input assumptions and parameters.

Description	Parameter Value and Comments				
I. ISCST3 Model Inputs					
Source Characterization	1992 stack test: 6799 ng/m^3 total; 136 ng/m^3 TEQ emission concentration from tested stack; *extrapolated to:* $3.12*10^{-5}$ g TEQ/sec emission rate considering three stacks, equal to 985 g TEQ/yr				
	1994 stack test: 3685 ng/m^3 total; 64 ng/m^3 TEQ emission concentration from tested stacks; *extrapolated to:* $8.47 *10^{-6}$ g TEQ/sec emission rate, equal to 267 g TEQ/yr				
Dispersion Coefficients	rural				
Terrain	flat				
Regulatory Default Option	yes				
- Stack tip downwash	yes				
- Final Plume Rise	yes				
- Buoyancy induced dispersion	yes				
- Wind profile exponents	regulatory defaults				
- Calm winds processing	calm hours not included in conc. calculations				
- Vertical potential temp. gradient	regulatory defaults				
- Decay coefficient	0 (no decay of contaminant in plume)				
- Building wake effects	Building dimensions were input to the model				
Wind Speed/Stability Category	regulatory defaults				
Wet/dry particle-phase deposition	yes				
Wet/dry vapor-phase deposition	no				
Plume depletion by deposition	yes				
Building height/stack height	36 m, 83 m				
Stack temperature	434 °K				
Exit velocity	5.5 m/sec				
For Deposition Modeling Only	Diam. µm	Mass fraction	Density g/cm^3	Scav. Coef. (liq) 1/(s-mm/hr)	Scav. Coef (ice) 1/(s-mm/hr)
Particle Category 1	1.00	0.88	1.4	0.00043	0.00014
Category 2	6.78	0.09	1.4	0.0046	0.0016
Category 3	20.0	0.03	1.4	0.0066	0.0022
II. Soil Modeling Inputs					
Soil half-live, yrs	All homologue groups assume 25 year half-life				
Particle Fraction (vapor fraction = 1 - particle fraction)	TCDD: 0.49; PCDD: 0.87; HxCDD: 0.97; HpCDD: 0.99; OCDD: 0.998 TCDF: 0.53; PCDF: 0.80; HxCDF: 0.945; HpCDF: 0.985; OCDF: 0.998				

Table 7-12. Comparison of observed and modeled total CDD/F concentration increments at the urban monitoring stations (total = sum of homologue group concentrations; on-site, airport = model results generated using on-site and airport meteorological data; NA = not available).

Station	March 94 Sampling, fg/m^3			April 94 Sampling, fg/m^3	
	Observed	On-site	Airport	Observed	On-site
SN-2	1321	6606	20833	0	0
SE-3	6368	8181	2388	16105	8994
SNW-1	0	8943	1270	557	0
SSW-4	0	0	0	3682	8638
HSCNE	NA	NA	NA	1493	8028

Table 7-13. Comparison of observed and modeled homologue and TEQ concentrations at station SE-3 using on-site meteorological data for model input.

Homologue Group	Stack Emission Rate, ng/dscm	SE - 3, March 94, fg/m^3		SE - 3, April 94, fg/m^3	
		Observed	Modeled	Observed	Modeled
TCDD	32	490	71	851	78
PCDD	97	594	215	1144	236
HxCDD	300	543	666	1402	732
HpCDD	508	424	1126	1378	1237
OCDD	578	384	1281	1575	1408
TCDF	293	904	651	1976	716
PCDF	439	1226	977	2982	1074
HxCDF	648	951	1439	2518	1582
HpCDF	616	718	1366	1846	1502
OCDF	170	134	391	433	429
Total	**3681**	**6368**	**8181**	**16105**	**8994**
TEQ	**64**	**125**	**144**	**309**	**156**

Table 7-14. Results of ISCST3 deposition and soil prediction modeling, comparing measured concentrations for clusters of soil samples with modeled concentrations assuming either the 1992 or the 1994 stack tests.

Cluster–>	On-site			Off-site			Urban			Urban		
Description of Cluster–>	n = 3; on incinerator property			n = 5; just outside property, downwind within 500 m			n = 14; all directions within about 3 km.			n = 12; all directions from 3 to 8 km.		
Homologue	Obs	‘92	‘94	Obs	‘92	‘94	Obs	‘92	‘94	Obs	‘92	‘94
TCDD	1118	265	19	98	93	7	19	38	3	<1	9	<1
PCDD	1820	815	102	64	286	35	13	117	15	2	29	4
HxCDD	1885	1202	351	150	421	123	43	173	51	4	43	13
HpCDD	1666	781	606	654	273	212	154	112	87	20	28	21
OCDD	1431	445	696	2901	156	243	613	64	100	150	16	25
TCDF	2147	1304	187	153	457	66	35	188	27	2	47	7
PCDF	255	2335	425	194	818	149	33	336	61	5	83	15
HxCDF	1195	2769	740	116	970	259	22	399	107	3	99	26
HpCDF	1183	1079	732	193	378	256	37	155	105	5	39	26
OCDF	222	274	212	88	96	74	15	40	31	3	10	8
TOTAL	**1292**	**11269**	**4070**	**4611**	**394**	**142**	**984**	**162**	**587**	**194**	**403**	**146**
TEQ	**466**	**236**	**69**	**45**	**83**	**24**	**9**	**34**	**10**	**<1**	**8**	**2**

notes: soil concentrations in pg/g, obs = observed; ‘92, ‘94 = ISCST3 results using 1992 and 1994 stack test data; “on-site” observed data not expected to represent deposition trends - see text for more details.

Table 7-15. Results of the air-to-soil and soil-to-air model testing

Congener	Observed Soil pg/g	Predicted Soil pg/g	Observed Air pg/m^3	Predicted Air pg/m^3
2378-TCDD	0.39	0.03	$1.4*10^{-3}$	$1.8*10^{-5}$
12378-PCDD	0.14	0.19	$5.2*10^{-3}$	$2.5*10^{-6}$
123478-HxCDD	0.35	0.31	$7.9*10^{-3}$	$4.0*10^{-6}$
123678-HxCDD	0.82	0.36	$9.3*10^{-3}$	$1.4*10^{-5}$
123789-HxCDD	1.23	0.54	$1.4*10^{-2}$	$2.1*10^{-5}$
1234678-HpCDD	17.7	9.1	$2.3*10^{-1}$	$1.9*10^{-4}$
OCDD	161.0	36.2	$9.0*10^{-1}$	$1.3*10^{-3}$
2378-TCDF	0.64	0.06	$2.8*10^{-3}$	$4.2*10^{-5}$
12378-PCDF	0.17	0.20	$6.5*10^{-3}$	$3.5*10^{-6}$
23478-PCDF	0.21	0.26	$7.4*10^{-3}$	$5.1*10^{-6}$
123478-HxCDF	0.16	0.50	$1.3*10^{-3}$	$3.8*10^{-6}$
123678-HxCDF	0.11	0.59	$1.6*10^{-2}$	$2.1*10^{-6}$
123789-HxCDF	0.15	0.11	$2.8*10^{-3}$	$3.4*10^{-6}$
234678-HxCDF	0.67	0.36	$9.2*10^{-3}$	$1.5*10^{-5}$
1234678-HpCDF	4.06	2.74	$6.9*10^{-2}$	$7.0*10^{-5}$
1234789-HpCDF	0.27	0.58	$1.4*10^{-3}$	$3.0*10^{-6}$
OCDF	10.7	2.70	$6.7*10^{-3}$	$8.0*10^{-5}$
TEQ	**1.37**	**0.70**	**$1.9*10^{-2}$**	**$3.6*10^{-5}$**

Table 7-16. Data and results of the soil to below ground vegetable validation exercise.

Congener group	Koc, L/kg	RCF	Control Soil			Contaminated Soil		
			Soil, ppt	Observed Peel, ppt dry	Predicted Peel, ppt dry	Soil, ppt	Observed Peel, ppt dry	Predicted Peel, ppt dry
TCDD	$3.98*10^6$	5200	11.0	1.7	1.2	24.3	2.9	2.6
PCDD	$2.69*10^6$	3900	6.8	1.2	0.8	80.5	5.6	9.6
HxCDD	$2.12*10^7$	18600	23.5	1.6	1.7	176.7	7.3	12.7
HpCDD	$6.17*10^7$	43700	45.6	1.6	2.7	238.6	5.4	13.9
OCDD	$9.77*10^7$	62200	85.4	3.0	4.5	297.4	6.3	15.6
TCDF	$7.76*10^5$	1500	21.8	11.9	3.5	270.7	36.7	43.0
PCDF	$2.88*10^6$	4080	34.8	5.9	4.1	361.9	24.8	42.1
HxCDF	$6.17*10^6$	7410	38.5	3.2	3.8	418.4	22.0	41.0
HpCDF	$3.86*10^7$	29400	49.0	1.2	3.1	667.2	12.2	41.8
OCDF	$3.89*10^8$	180000	46.6	0.4	1.8	687.3	5.0	26.2

Table 7-17. Summary of plant concentration versus soil concentration data for 2,3,7,8-TCDD.

Plant:soil Concentrations	Contaminant Ratio	Reference and Comments
I. Below-Ground Vegetation		
54-167 ppt/ 1-5 ppb	0.01-0.17	Wipf, et al., 1982; results are for 2,3,7,8-TCDD and greenhouse carrots grown in Seveso contaminated soil; the 54 ppt concentration listed was for carrot peels and inner portions; the 167 ppt listed includes the 54 ppt plus additional residues found in wash water and can be described as "unwashed" concentration; 96% of 167 ppt unwashed concentration includes that found in wash water (67%) and peels (29%).
0.8-9.2 ppb/ 2.7-8.3 ppb	0.24-1.73	Coccusi, et al., 1979; results are for 2,3,7,8-TCDD and carrots, potatoes, narcissus, and onions grown on contaminated soil the spring following the Seveso contamination; aerial plant part ratios were 0.25-0.40 - underground part ratios were 0.23-1.73; residues in contaminated plants were found to dissipate when contaminated plants transplanted to unpolluted soils; results show higher ratios than the Wipf, et al. (1982) noted above; results were expressed in fresh plant weight and fresh soil basis; very high ratios and plant impacts render these data suspect.
156-1807 ppt/ 160-752 ppt	1.00-2.40	Facchetti, et al., 1986; results are for 2,3,7,8-TCDD and bean and maize roots grown in indoor greenhouse pots and outdoor pots; unclear whether plant concentrations are fresh or dry weights. Data considered highly suspect due to very high ratios found and also reporting 16 and 37 ppt in roots when "blank" soil had 1.5 ppt (ratios of 10.7 and 24.7).
735 ppt/ 411 ppt	1.8	Young, 1983; results are for 2,3,7,8-TCDD and roots of grass and broadleaf plants at Eglin Air Force Base; unclear whether root concentrations are fresh or dry weight.
0.5-40.2 ppt/ 2-6000	0.001-0.3	Hulster and Marschner, 1991; results at right are for unpeeled potato tubers, in TEQ and dry weight basis. Plant:soil ratio decreased as soil concentrations increased; highest ratios were at the 2.4 ppt low soil concentration. Peeled tuber concentration stayed below 0.5 ppt over all soil concentrations, indicating insignificant within plant translocation. Plant concentrations given in dry weight basis.
0.1-15 ppt/ 6-690 ppt	0.001-0.5	Muller, et al. 1994; results at right describe the range of concentrations and ratios for data on ten congener groups, in two soils (a control and a contaminated soil), and for carrots. For the control soil, which had a TEQ concentration of 5 ppt, typical of background soils, the average plant:soil ratio was 0.10; for the contaminated soil with a TEQ concentration of 56 ppt, the plant:soil ratio was 0.02.

Table 7-17. (cont'd).

Plant:soil Concentrations	Contaminant Ratio	Reference and Comments
I. Below-Ground Vegetation (cont'd)		
0.2-6.0 ppt/ 328-12,800 ppt	0.00001-0.009	Hulster and Marschner, 1993. Results are for potato tubers, peeled and unpeeled, and for potato shoots, results for TEQ and in dry matter terms. Concentrations for peeled potato tubers stayed consistently less than 0.5 ppt, despite soil concentrations, while shoots and unpeeled tubers increased as concentration increased. Plant:soil ratios remained relatively constant for tubers and shoots with soil concentration increases, leading authors to conclude that a soil/plant relationship exists for plants growing in the soil. Less transfer was noted for higher chlorination.
II. Above-Ground Vegetations		
9-42 ppt/ 10 ppb	0.0009-0.0042	Wipf, et al., 1982; analysis of apples, pears, plums, figs, peaches, and apricots grown in Seveso, Italy year following contamination; apples, pears, and peaches showed >95% of whole fruit concentrations listed here was in the peels; analysis of vegetative samples in less contaminated areas showed non-detections at 1 ppt detection limit; reference was unclear as to whether reported concentrations in fruit was based on fresh or dry weight.
8-9 ppt/ 10 ppb	0.0008	Wipf, et al., 1982; concentrations listed were those found in sheaths of corn grown year following Seveso contamination; none found in cobs and kernels at 1 ppt detection limit.
1-63 ppt/ 12-3300 ppt	0.003-0.35	Sacchi, et al., 1986; data was for: "aerial parts" of bean and maize plants, tritiated TCDD amended soil with concentrations ranging as noted, taken at different intervals including 7, 34 and 57 days (one test), 17, 34, and 57 days (another test), 8 and 77 days, and 8 and 49 days, and in tests where soil was and was not amended with peat. Results showed increasing plant concentrations with increasing soil concentrations, but the ratio of plant to soil concentrations was inversely related to increasing soil concentrations (lowest ratios at highest soil concentrations). Soils without peat had higher ratios than soils with peat. Plant concentrations were fresh weight basis; high plant impact and trend for increasing impact over time renders these results suspect.

Table 7-17. (cont'd).

Plant:soil Concentrations	Contaminant Ratio	Reference and Comments
I. Above-Ground Vegetation (cont'd)		
ND (DL=1 ppb)/60 ppt	<0.017	Isensee and Jones, 1971; results are for mature oat and soybean tops, and oat grain and the bean of soybean, in soil treated with [^{14}C]TCDD to achieve a concentration of 60 ppb - no residues of TCDD were found; ratios of 0.14 and 0.28 were found for 2,4,-dichlorophenol (DCP) in oat and soybean tops, and 0.20 for 2,7-dichlorodibenzo-p-dioxin (DCDD) in oat tops; trace amounts of DCP and DCDD were found in the bean of soybean.
10-270 ppt/ 411 ppt	0.02-0.66	Young, 1983; data was for 2,3,7,8-TCDD and above ground plant parts of perennial grasses and broadleaf plants grown on 2,4,5,-T treated soils. Unclear whether plant concentrations are fresh or dry weight basis. Soil concentration was average over 3 depth increments to 15 cm. Crown near soil surface at 270 ppt and 0.66 ratio was highest; plant tops had ratios of 0.02-0.17.
0.3, 0.1 ppt/ 8750,5215 ppt	0.00003, 0.00002	Muller, et al, 1993. Result at right are for whole pear (0.3) and whole apple (0.1) dry weight concentrations (article presented TEQs for two pears from one tree which were averaged, and one apple, and for fresh weight; dry weight was estimated assuming 12% dry matter in pears/apples) and the average concentration over 70 cm (article supplied concentrations for the 0-30 and 30-70 cm depths). Article also provided peel and pulp results and results for congener groups. Article concluded: soil levels were not correlated to fruit concentrations and therefore fruits were impacted by airborne contamination, and that concentrations were higher in peel than in pulp.
0.1-0.6 ppt/ 326-5752 ppt	0.00002-0.0008	Hulster and Marschner, 1993. Results are for inner and outer leaves of lettuce, expressed as dry matter, and in TEQs. Results indicate a drop in ratio as soil concentration increases, and unexpected small differences between inner and outer leaves.
4-38 ppt/ 326-12,800 ppt	0.001-0.01	Hulster and Marschner, 1993. Results are for hay, dry matter, and TEQs. Results indicate a drop in ratio as soil concentrations increase.

Table 7-17. (cont'd).

Plant:soil Concentrations	Contaminant Ratio	Reference and Comments
I. Above-Ground Vegetation (cont'd)		
< 1 ppt/ 326-5752 ppt	0.0001- 0.0003	Hulster and Marschner, 1993. Results are for grass and herbs, dry matter, and TEQs. Results indicate a drop in ratio as soil concentrations increase. For above three entries, results are also given for congener groups. Authors conclude that: little correlation between soil and above ground plant concentrations, and that contamination is by atmospheric deposition.
<0.01, 0.04/ 5, 56 ppt	<0.002	Muller, et al., 1994. Results are for peas at soil concentrations of 5 and 56 ppt; pea concentrations in TEQ and dry weight. Results for pods indicated more impact with ratios at 0.002-0.026. Ratios decreased as soil concentration increased.
0.32, 0.21 ppt/5, 56 ppt	0.004-0.064	Muller, et al., 1994. Results are for lettuce at soil concentrations of 5 and 56 ppt; lettuce concentrations in TEQ and dry weight. Little difference seen between inner and outer leaves, which was unexpected - outer leaves expected to be more impacted. Ratios decreased as soil concentration increased.
0.5-22.6 ppt/ 0.4, 148	0.14-2.5	Hulster, et al., 1994. Results are for zucchini fruit at two soil concentrations of 0.4 and 148 ppt TEQ, fruit results are TEQ and dry weight. Results contradict conventional wisdom that above ground vegetation impact is from air only and mainly an outer surface phenomena; zucchini contamination was uniform throughout plant and plant:soil ratios highest ever found for above ground bulky fruits.
0.6 ppt/ 148 ppt	0.004	Hulster, et al., 1994 Results are for cucumber grown in soil at 147 ppt TEQ; cucumber results in TEQ and dry weight. Results are more in line with most other studies for above ground bulky fruit plant:soil ratios.
7.5 ppt/ 148 ppt	0.05	Hulster, et al., 1994. Results are for pumpkin grown in soil at 148 ppt TEQ; pumpkin results in TEQ and dry weight. Results not as dramatic as for zucchini, but plant concentrations are ratio are still high.
0.4-1.9 ppt/ 2.4-6000 ppt	0.0003-0.3	Hulster and Marschner, 1991. Results are for lettuce, in TEQ and dry weight. Experiments were conducted outdoors with soil covered by a water permeable polypropylene fleece. Plant concentrations showed little variation with large increases in soil concentration, and given the soil covering, this would strongly indicate little root to shoot translocation and that lettuce concentrations were the result of air to plant transfers

Table 7-18. Parameters for the empirical relationship relating the sub-cooled liquid vapor pressure, $p°_L$, to the particle/gas partition coefficient, K_p, of semivolatile organic compounds (SOC).

Setting/SOC	Location	m	b	Reference
I. Urban				
PAHs	Portland, Oregon	-0.882	-5.38	1
PAHs	Portland, Oregon	-0.890	-4.75	2
PAHs	Denver, Colorado	-0.760	-5.10	3
PCBs	Denver, Colorado	-0.946	-5.86	3
PAHs	Chicago, Illinois	-0.694	-4.61	4
PCBs	Chicago, Illinois	-0.726	-5.18	4
PAHs	London, U.K.	-0.631	-4.61	5
PAHs	Osaka, Japan	-1.04	-5.95	6
PAHs	Brazzaville, Congo	-0.810	-5.31	7
OC pesticides	Brazzaville, Congo	-0.740	-5.76	7
II. Rural				
PAHs	Coastal Oregon	-0.724	-4.94	1
PAHs	Lake Superior	-0.586	-3.83	8
PAHs	Lake Superior	-0.614	-4.25	9
PAHs	Green Bay	-1.00	-5.47	4
PCBs, OC pesticides	Bayreuth, Germany	-0.610	-4.74	10

References:
1. Ligocki and Pankow (1989); 2. Hart (1989); 3. Foreman and Bidleman (1990);
4. Cotham and Bidleman (1995); 5. Baek, et al. (1991); 6. Yamasaki, et al. (1982);
7. Ngabe and Bidleman (1992); 8. McVeety and Hites (1988); 9. Baker and Eisenreich (1990);
10. Kaupp and Umlauf (1992)

Table 7-19. Summary of modeling changes from the 1994 air-to-beef model validation exercise to the present update.

Congener	B_{vpa}, unitless		Vapor/Particle Partitioning		BCF, unitless		Cs, pg/g	
	1994	1996	1994	1996	1994	1996	1994	1996
2378-TCDD	$1.0*10^5$	$6.55*10^4$	55/45	51/49	4.32	5.76	0.1	0.4
12378-PCDD	$6.3*10^5$	$2.39*10^5$	26/74	13/87	4.16	5.55	0.6	0.1
123478-HxCDD	$2.3*10^6$	$5.20*10^5$	7/93	3/97	2.02	2.69	0.6	0.4
123678-HxCDD	$6.9*10^5$	$5.20*10^5$	4/96	3/97	1.74	2.32	0.9	0.8
123789-HxCDD	$6.9*10^5$	$5.20*10^5$	2/98	3/97	2.24	2.99	1.2	1.2
1234678-HpCDD	$1.0*10^7$	$9.10*10^5$	2/98	1/99	0.36	0.48	13.9	17.7
OCDD	$2.4*10^9$	$2.36*10^5$	0/100	0.2/99.8	0.52	0.69	69.3	160.9
2378-TCDF	$1.5*10^5$	$4.57*10^4$	71/29	47/53	0.94	1.25	0.8	0.6
12378-PCDF	$3.8*10^5$	$9.75*10^4$	42/58	25/75	0.73	0.97	0.7	0.2
23478-PCDF	$5.3*10^5$	$9.75*10^4$	30/70	16/84	3.10	4.13	0.5	0.2
123478-HxCDF	$5.9*10^5$	$1.62*10^5$	6/94	7/93	2.34	3.12	1.4	0.2
123678-HxCDF	$1.4*10^6$	$1.62*10^5$	6/94	7/93	2.00	2.67	1.3	0.1
123789-HxCDF	$8.3*10^5$	$1.62*10^5$	11/89	4/96	2.00	2.67	0.3	0.2
234678-HxCDF	$8.3*10^5$	$1.62*10^5$	7/93	4/96	1.78	2.37	1.0	0.6
1234678-HpCDF	$6.8*10^5$	$8.30*10^5$	4/96	2/98	0.41	0.55	4.9	4.1
1234789-HpCDF	$6.8*10^5$	$8.30*10^5$	3/97	1/99	0.99	1.32	0.7	0.3
OCDF	$1.7*10^8$	$2.28*10^6$	0/100	0.2/99.8	0.20	0.27	4.1	10.7

B_{vpa}: air-to-leaf vapor transfer factor, unitless
BCF: beef bioconcentration factor, unitless
Vapor/Particle: vapor phase/particle phase percentages
Cs: soil concentration, pg/g

Table 7-20. Comparison of air concentration profiles used in the 1994 air-to-beef model validation compared against the current air profiles.

Congener	1994 urban air profile, pg/m^3	Columbus urban air profile, pg/m^3	1994 rural air profile, pg/m^3	Columbus rural air profile, pg/m^3	Ratio, Col urban/Col rural
2378-TCDD	0.010	0.0065	0.002	0.0014	4.6
12378-PCDD	0.030	0.017	0.006	0.005	3.4
123478-HxCDD	0.025	0.022	0.005	0.008	2.8
123678-HxCDD	0.035	0.035	0.007	0.009	3.9
123789-HxCDD	0.050	0.033	0.010	0.014	2.4
1234678-HpCDD	0.580	0.280	0.116	0.227	1.2
OCDD	2.930	1.053	0.586	0.904	1.2
2378-TCDF	0.115	0.019	0.023	0.003	6.3
12378-PCDF	0.050	0.036	0.010	0.007	5.1
23478-PCDF	0.030	0.030	0.006	0.007	4.3
123478-HxCDF	0.060	0.068	0.012	0.013	5.2
123678-HxCDF	0.060	0.087	0.012	0.016	5.4
123789-HxCDF	0.015	0.003	0.003	0.003	1.0
234678-HxCDF	0.045	0.050	0.009	0.009	5.6
1234678-HpCDF	0.210	0.262	0.042	0.069	3.8
1234789-HpCDF	0-.030	0.044	0.006	0.014	3.1
OCDF	0.173	0.173	0.034	0.067	2.6
TOTAL	**4.448**	**2.220**	**0.890**	**1.380**	---
I-TEQ	**0.095**	**0.070**	**0.019**	**0.019**	---

Table 7-21. Comparison of predicted leafy vegetation samples of the current, revised validation exercise with the previous predictions of leafy vegetations and several observations in the literature (units are pg/g dry weight).

Congener	Predicted 1994	Predicted 1996	US alfalfa[1], 1994	UK grass[2], 1979-1988	UK grass[3], 1996	UK grass[4], 1997	US hay[5], 1989
2378-TCDD	0.1	0.05	0.11	0.03	0.12	0.72	ND
12378-PCDD	0.9	0.18	0.16	0.14	0.07	1.3	ND
123478-HxCDD	0.7	0.18	0.29	0.14	0.10	0.93	ND
123678-HxCDD	0.2	0.22	0.25	3.00	0.17	2.3	1.2
123789-HxCDD	0.2	0.32	0.23	1.40	0.08	1.8	ND
1234678-HpCDD	21.0	4.12	0.85	7.10	2.80	22	30.0
OCDD	6.0	13.20	6.21	24.0	15.60	94	285.0
2378-TCDF	7.2	0.07	0.06	0.46	1.28	14	ND
12378-PCDF	1.4	0.19	0.21	0.18	0.29	1.8	ND
23478-PCDF	0.8	0.16	0.08	0.20	0.28	2.2	ND
123478-HxCDF	0.5	0.26	0.19	0.32	0.21	5.6	ND
123678-HxCDF	0.9	0.31	0.30	0.16	0.09	2.2	ND
123789-HxCDF	0.3	0.04	0.24	0.02	0.02	0.61	ND
234678-HxCDF	0.5	0.14	0.20	0.15	0.09	2.6	ND
1234678-HpCDF	1.4	1.68	0.31	1.90	1.02	12	5.4
1234789-HpCDF	0.1	0.25	0.45	0.14	0.13	1.1	ND
OCDF	0.4	0.96	0.96	2.00	0.98	13	7.5
TOTAL	**42.6**	**22.3**	**11.1**	**41.34**	**32.2**	**178.2**	**---**
I-TEQ	**3.2**	**0.46**	**0.44**	**0.89**	**0.57**	**6.0**	**---**

[1] From an unpublished data set for alfalfa supplied by V. Fiel, United States Department of Agriculture, for a beef feeding study which is currently underway. For these results, all but the hepta dioxin and the two octa congeners were not detected - results above are ½ detection for the two alfalfa samples taken.

[2] Kjeller, et al., (1991); [3] Kjeller (1996); [4]Jones and Duarte-Davidson (1997); [5] Reed, et al. (1990) - detection limits not supplied for non-detects, but described as between 0.31 and 6.5 ppt.

Table 7-22. Results of the 1994 air-to-beef model validation exercise compared against results from the current air-to-beef model validation exercises (all beef concentrations in terms of pg/g lipid; values in parentheses are observations calculated assuming non-detects equal 0.0; values not in parenthesis assume non-detects equal ½ detection limit).

Congener	1994 Validation Results		Current Validation Results	
	Observed beef	Predicted beef	Observed beef	Predicted beef
2378-TCDD	0.13 (0.06)	0.16	0.05 (0.03)	0.13
12378-PCDD	1.17 (0.13)	1.42	0.35 (0.04)	0.37
123478-HxCDD	1.38 (0.74)	0.53	0.64 (0.18)	0.19
123678-HxCDD	4.40 (4.40)	0.16	1.42 (1.21)	0.20
123789-HxCDD	1.08 (0.34	0.21	0.53 (0.26)	0.38
1234678-HpCDD	10.13 (9.99)	1.53	4.48 (4.39)	0.79
OCDD	15.32 (14.84)	1.53	4.78 (3.21)	4.54
2378-TCDF	0.30 (0.25)	2.42	0.03 (0)	0.04
12378-PCDF	0.23 (0.005)	0.37	0.31 (0)	0.07
23478-PCDF	1.11 (0.90)	0.89	0.36 (0.06)	0.25
123478-HxCDF	2.68 (2.44)	0.42	0.55 (0.27)	0.29
123678-HxCDF	0.33 (0.10)	0.68	0.40 (0.12)	0.28
123789-HxCDF	0.30 (0)	0.21	0.31 (0)	0.05
234678-HxCDF	0.38 (0.11)	0.37	0.39 (0.10)	0.14
1234678-HpCDF	2.08 (1.74)	0.21	1.00 (0.75)	0.35
1234789-HpCDF	0.68 (0.07)	0.05	0.31 (0)	0.11
OCDF	1.18 (0.55)	0.05	1.88 (0)	0.13
TOTAL	**42.9 (36.7)**	**11.21**	**17.8 (10.7)**	**8.29**
I-TEQ	**2.51 (1.55)**	**1.85**	**0.93 (0.35)**	**0.61**

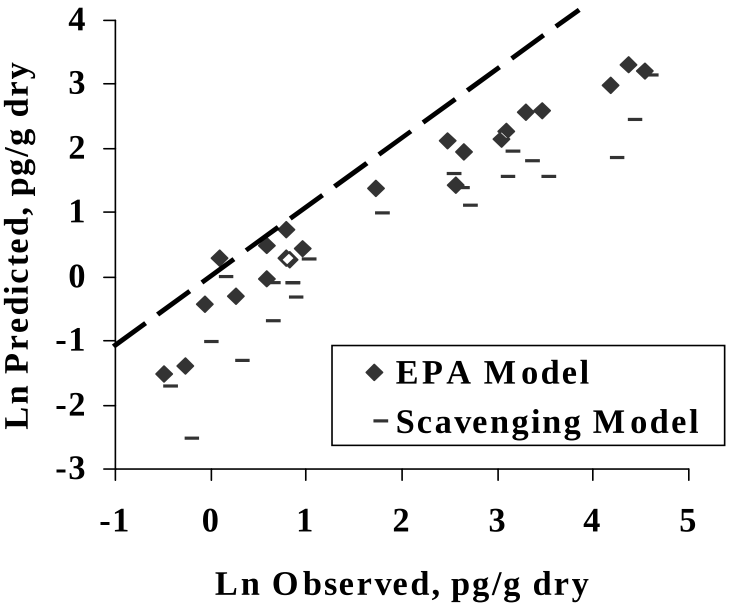


Figure 7-1. Comparison of observed and predicted grass concentrations of dioxin and furan congeners for the EPA and the scavenging models at the rural site. The perfect match of observed and predicted is shown in the dashed observed = predicted line.

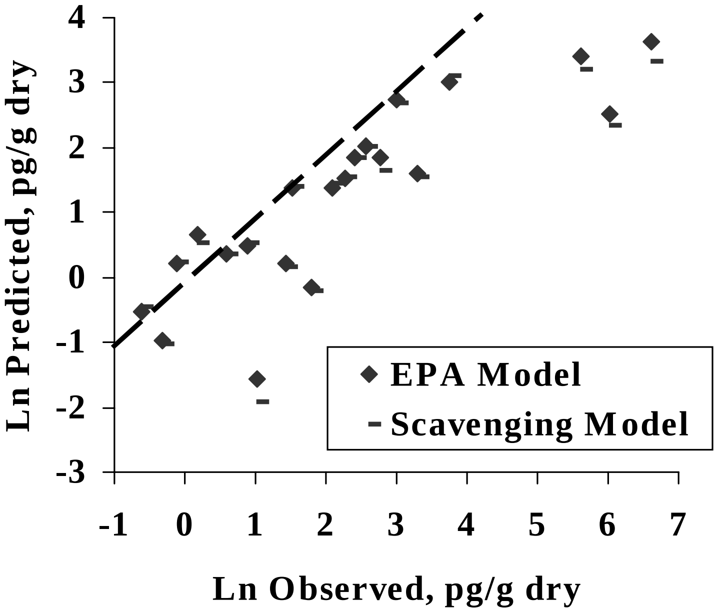


Figure 7-2. Comparison of observed and predicted grass concentrations of dioxin and furan congeners for the EPA and the scavenging models at the industrial site. The perfect match of observed and predicted is shown in the dashed observed = predicted line.

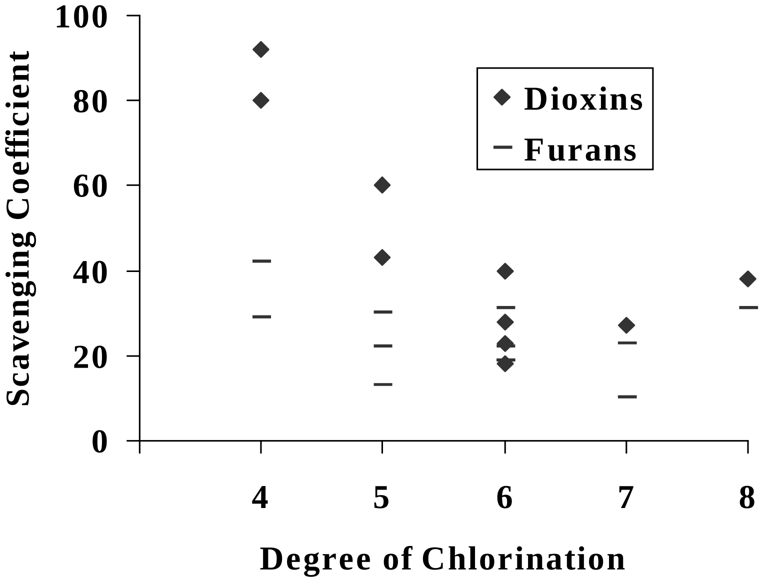


Figure 7-3. The observed scavenging coefficient (grass concentration over air concentration) calculated from the rural site data.

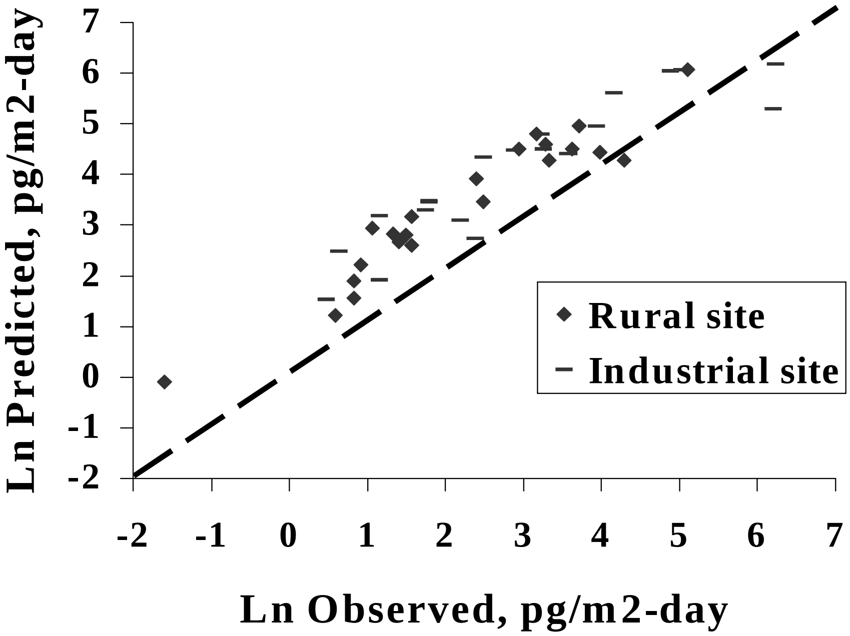


Figure 7-4. Comparison of observed and predicted deposition at the rural and industrial sites. The perfect match of observed and predicted is shown in the dashed observed = predicted line.

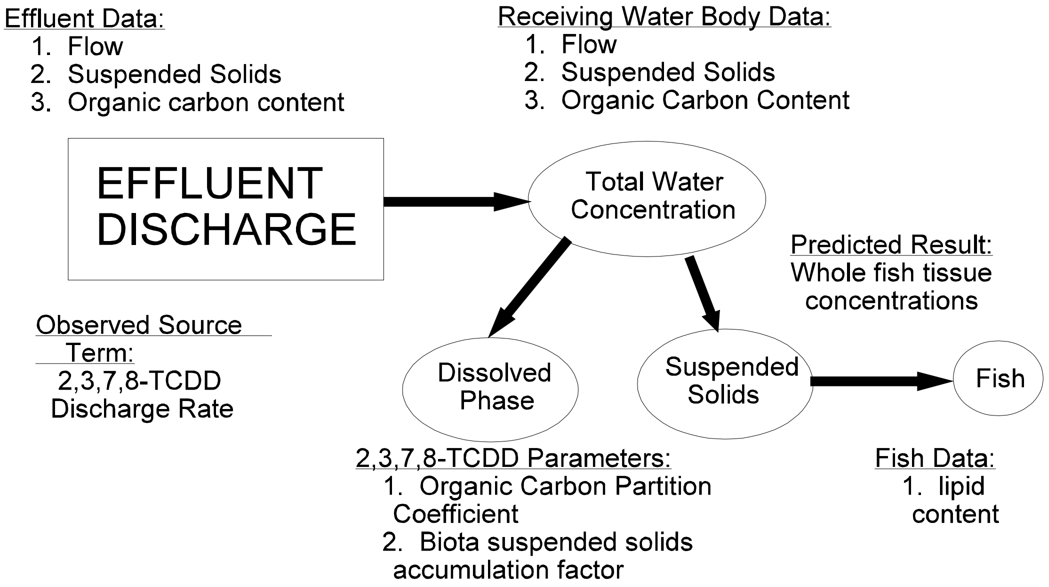


Figure 7-5. Schematic of effluent discharge model showing all parameter inputs and observed fish concentrations.

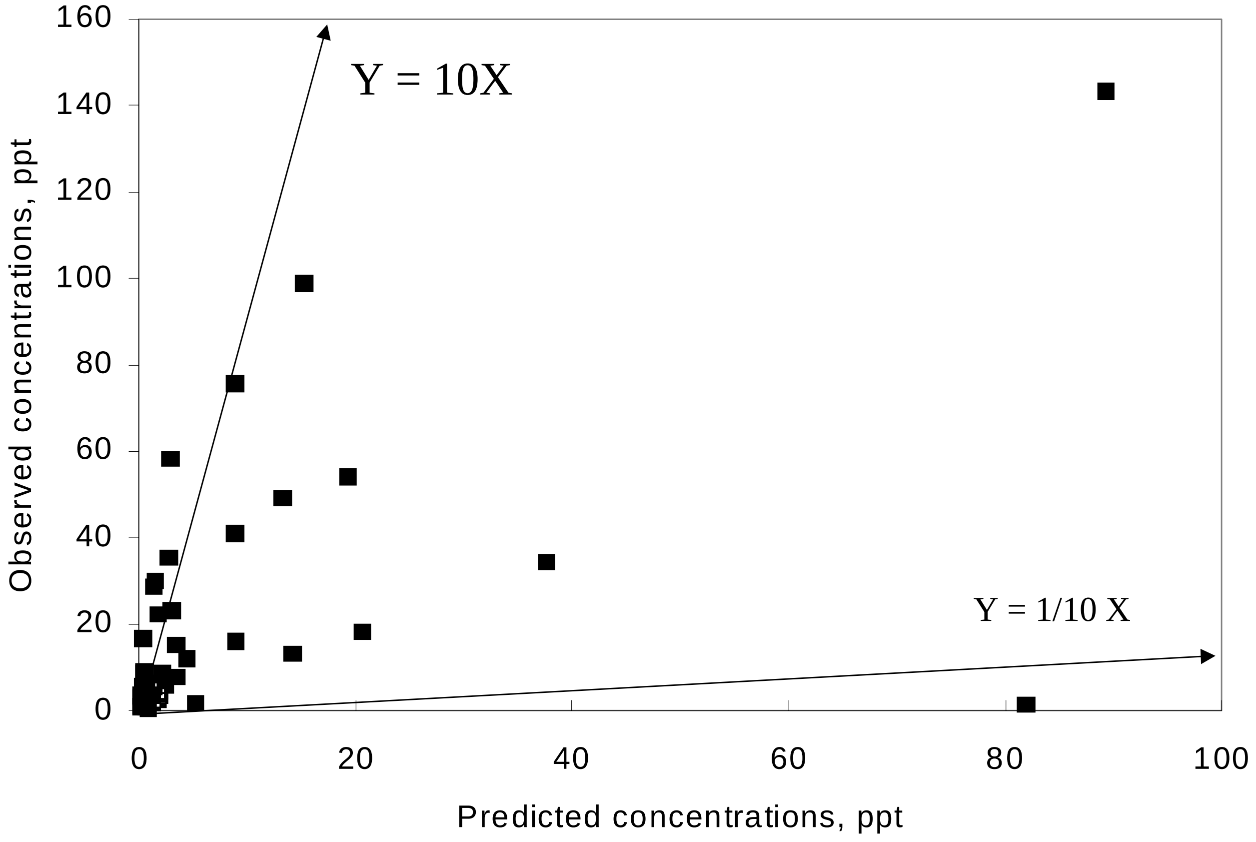


Figure 7-6. Comparison of predicted and observed fish tissue concentrations for validation of the effluent discharge model.

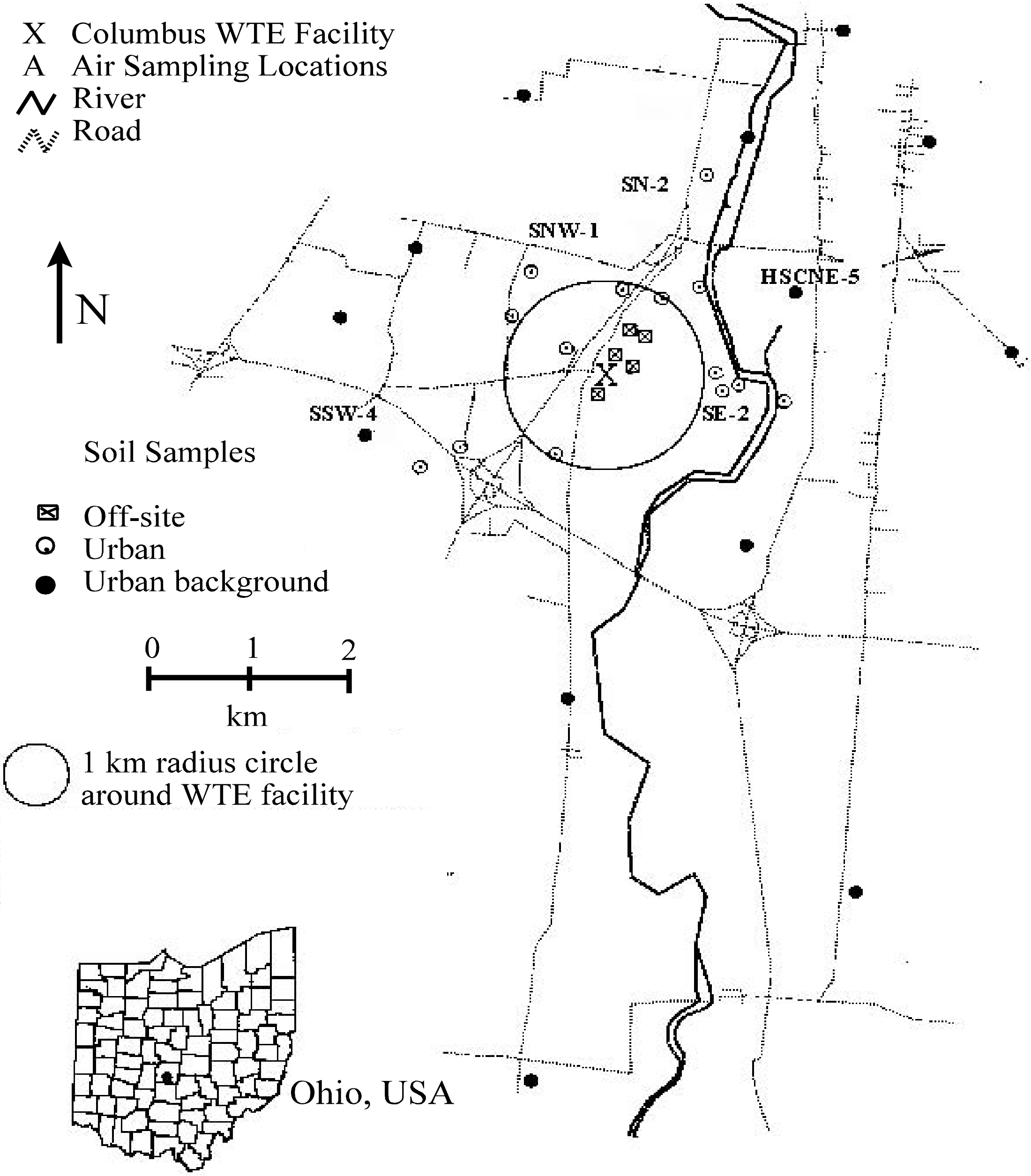
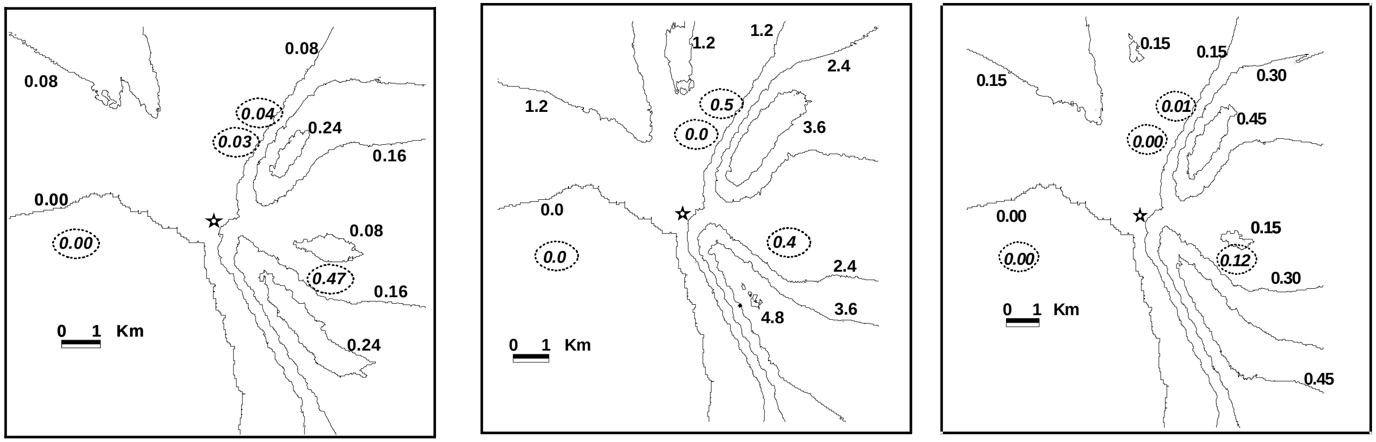
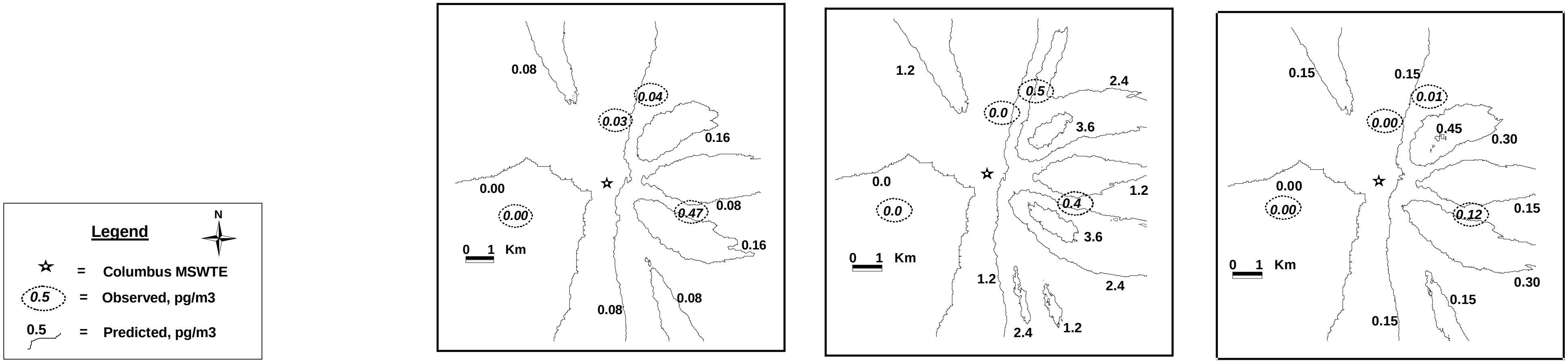


Figure 7-7. Site map showing locations of soil and air samples in the vicinity of the Columbus Municipal Solid Waste-To-Energy (CMWSTE, abbreviated WTE above) Facility.

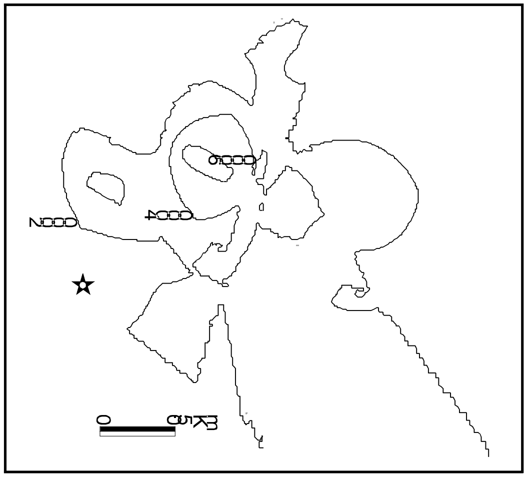


(a) TCDD, March, On-site (b) OCDD, March, On-site (c) TEQ, March, On-site

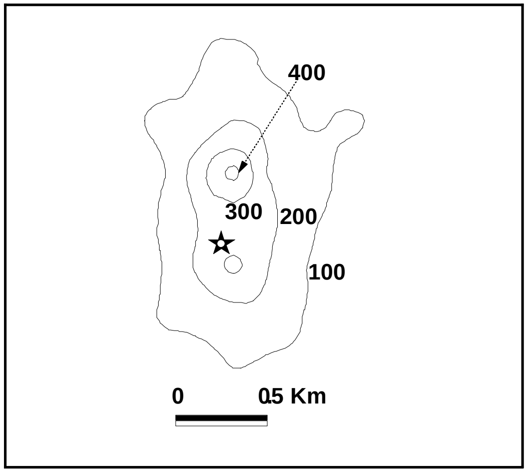


(d) TCDD, March, Airport (e) OCDD, March, Airport (f) TEQ, March, Airport

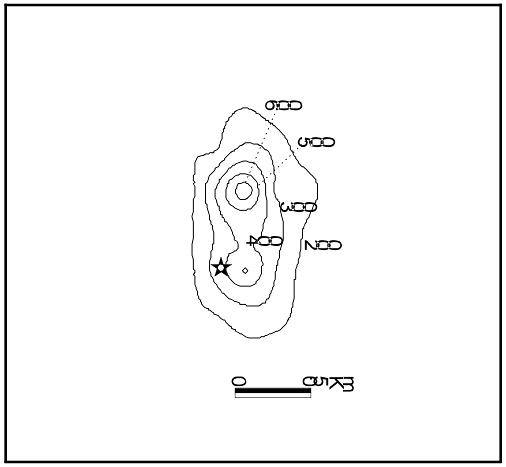
Figure 7-8. Isoline figures of predicted air concentrations overlain by measured air concentrations of TCDD, OCDD, and TEQ (pg/m^3) when using the “on-site” meteorological data set (sub-figures a, b, and c) and when using the “airport” meteorological data set (sub-figures d, e, and f).



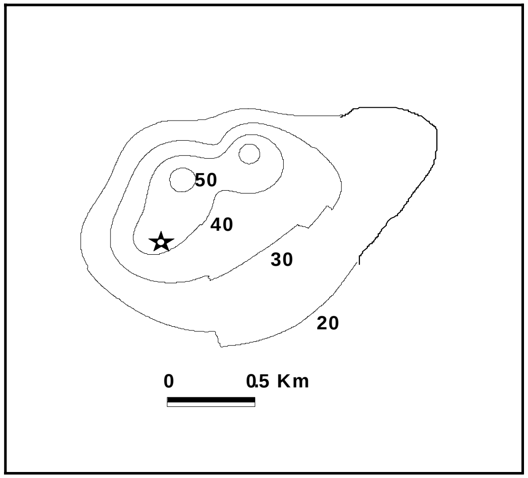
(a) TCDD, Observed



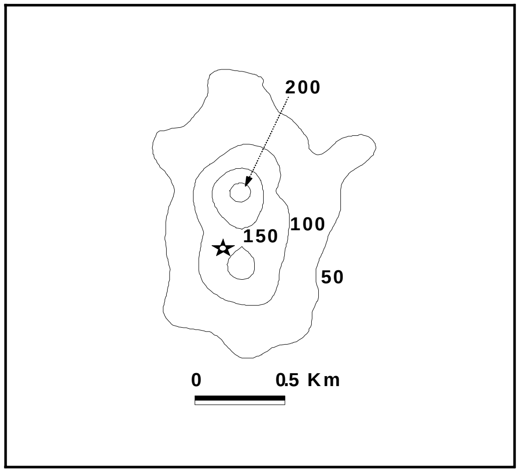
(b) TCDD, ‘92 Stack Test



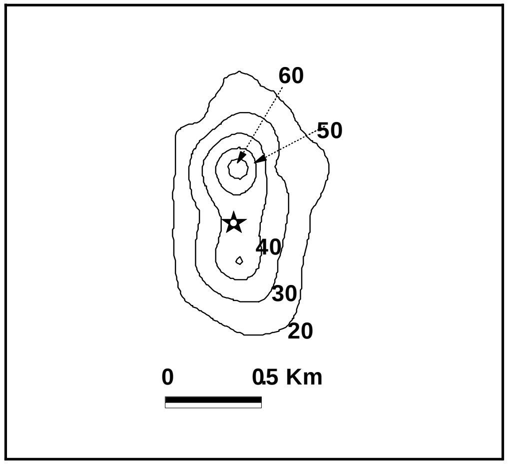
(c) TCDD, ‘94 Stack Test



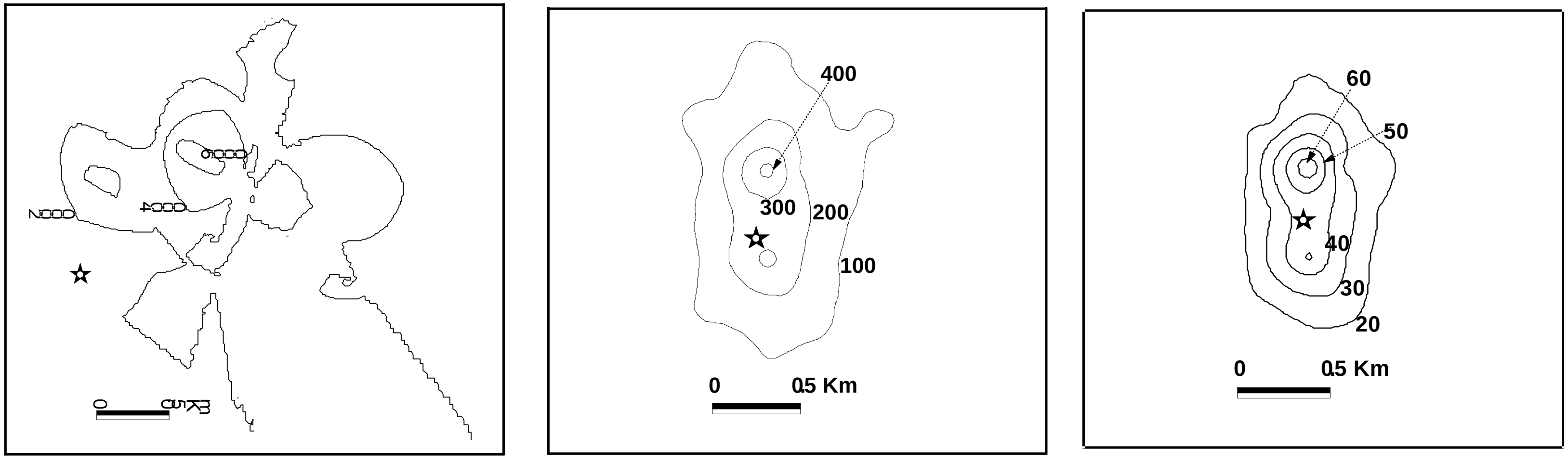
(d) OCDD, Observed



(e) OCDD, ‘92 Stack Test



(f) OCDD, ‘94 Stack Test



. (h) TEQ, Observed

(i) TEQ, ‘92 Stack Test

(j) TEQ, ‘94 Stack Test

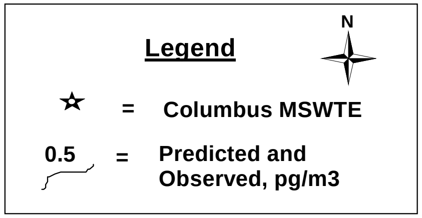
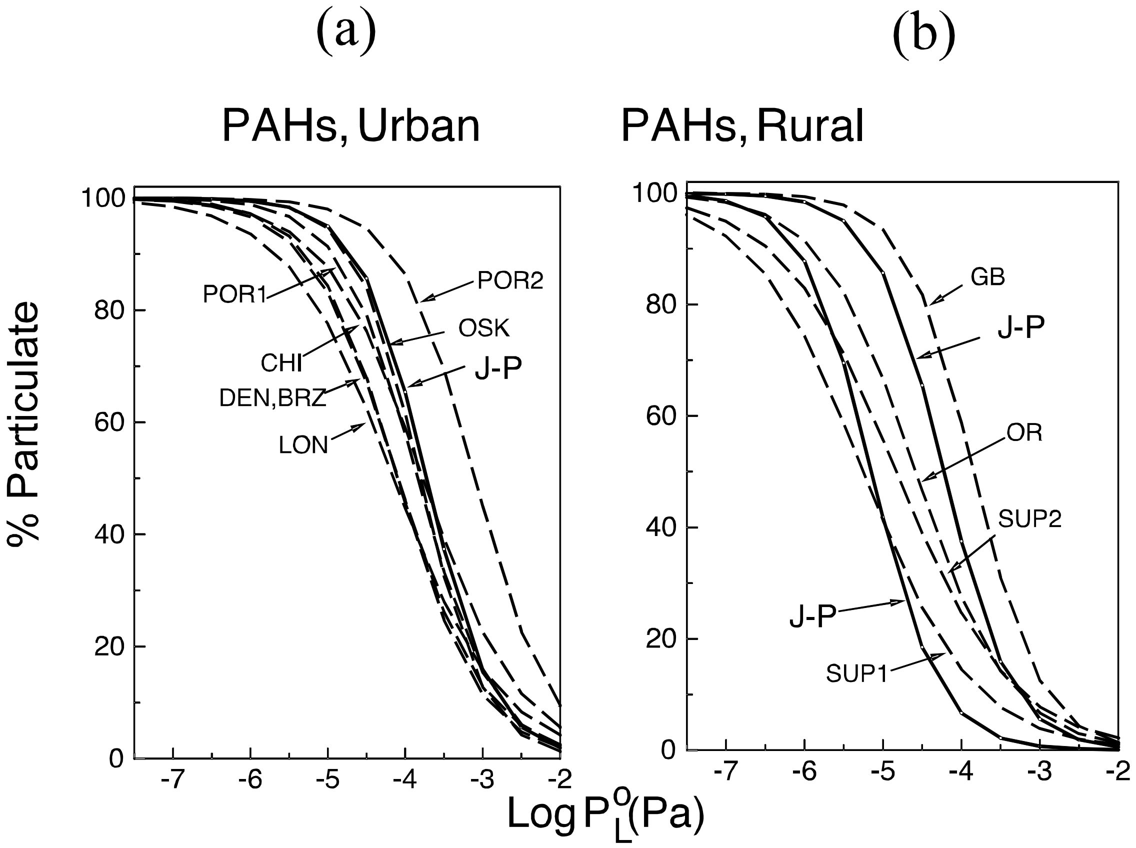
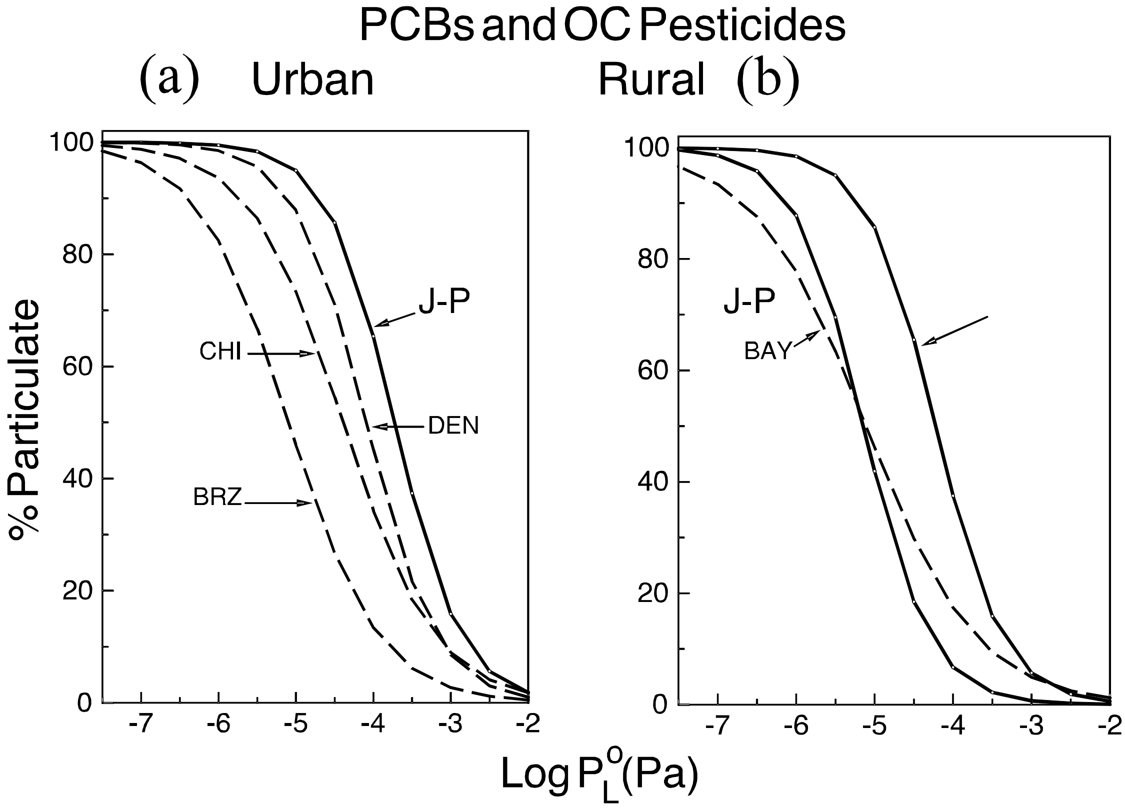


Figure 7-9. Isoline figures of predicted soil concentrations of TCDD, OCDD, and TEQ (sub-figures a, d, g) compared against isoline figures of measured soil concentrations using the 1992 stack emission test (sub-figures b, e, and h) and the 1994 stack emission test (sub-figures c, f, and i).



Key: J-P: Junge - Pankow model; the two solid lines in the rural setting represent clean continental background and background + local sources regimes.
DEN = study in Denver (Foreman and Bidleman, 1990)
POR1 and POR2 = two studies in Portland (Ligocki and Pankow, 1989; Hart, 1989)
CHI = study in Chicago (Cotham and Bidleman, 1995)
SUP1 and SUP2 = two studies in Lake Superior (McVeety & Hites, 1988;Baker & Eisenreich, 1990)
BRZ = study in Brazzaville, Congo (Ngabe and Bidleman, 1992)
LON = study in London (Baek, et al., 1991)
OSK = study in Osaka, Japan (Yamasaki, et al., 1982)
GB = study in Green Bay (Cotham and Bidleman, 1995)

Figure 7-10. Comparison of measured and predicted particulate percentages of PAHs in urban and rural air.



Key: J-P: Junge - Pankow model; the two solid lines in the rural setting represent clean continental background and background + local sources regimes.
DEN = study in Denver (Foreman and Bidleman, 1990)
CHI = study in Chicago (Cotham and Bidleman, 1995)
BRZ = study in Brazzaville, Congo (Ngabe and Bidleman, 1992)
BAY = study in Bayreuth, Germany (Kaupp and Umlauf, 1992)

Figure 7-11. Comparison of measured and predicted particulate percentages of PCBs and organochlorine pesticides in urban and rural air.

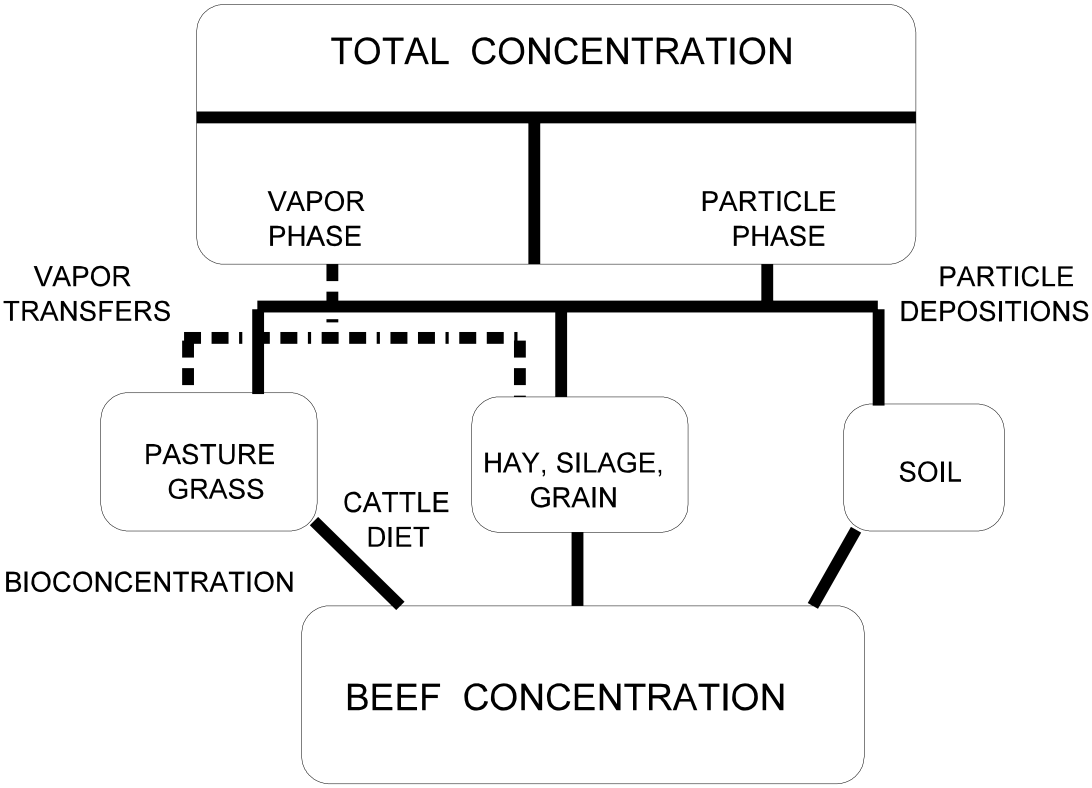


Figure 7-12. Overview of model to predict beef concentrations from air concentrations.