# Modifications of CalTOX to Assess the Potential Health Impacts of Hazardous Wastes Landfills

## Response to Reviewer Comments Received on the Draft Report

**February 1997**

In the report describing these modifications, "Modifications of CalTOX to Assess the Potential Health Impacts of Hazardous Waste Landfills" (McKone et al., 1996), five major modifications were described. These modifications are not only intended for the use of CalTOX at hazardous waste landfills, but for use at other sites and facilities regulated by the Department of Toxic Substances Control. The modifications include 1) a replacement for the existing plant model; 2) allowing continuous input of chemical into the root zone soil; 3) enable modeling of "high" soil concentrations; 4) model dispersion in air to off-site receptors; and 5) model dispersion of ground water to off-site receptors. Following completion of this draft report Comments were solicited and received from individuals and groups with expertise in fields that relate to the proposed modifications to the CalTOX exposure assessment.

Comments were received from five experts representing academic, research, and regulatory agencies:

Professor Donald Mackay
Environmental & Resource Studies Program
Trent University,
Perterborough, Ontario, Canada

Professor Daniel P.Y. Chang
College of Engineering
University of California
Davis California

Victor Palciauskas
Senior Technical Staff
United States Nuclear Waste Technical Review Board
Arlington, Virginia

Andrew Ranzieri
Technical Support Division
Air Resources Board
California Environmental Protection Agency
Sacramento, California

Elizabeth M. Babcock
Land Disposal Section
State Water Resources Control Board
California Environmental Protection Agency
Sacramento, California

Letters containing the experts' comments were receive d and the individual comments are transcribed below. Each comment was assigned a number and specific written responses are provided below each comment.

**Donald Mackay, Trent University**

I. Plant Model Changes.

1. The more I try to model plants the more I become convinced that it is a very challenging problem. The best that can be hoped for is an approximate screening level model which can be used as a basis for justifying a more detailed, separate modeling effort.

> It would be fair to say that the plant model like the rest of the models in CalTOX are rough approximation of the behavior of a chemical. CalTOX does not precisely compute concentrations in any compartment. Our use of CalTOX is predicated on the assumption that when used stochastically, CalTOX captures the range of likely concentrations in the environment. These concentration ranges provide a basis for predicting a range of human exposures and concomitant risks. Therefore, CalTOX is a screening level model because of its simplicity, but the risk range computed is useful for regulatory decision making.

2. The approach is logical and sensible. The key problems will be estimating $K_{ps}$ and $K_{pa}$. Our recent work suggests that the terms of Z in sugar and "other" in equation 38 are probably negligible. There is a danger in including the default value of 10-4 for lipid in phloem. I can't see how it can be justified. 10% sugar is quite high, even for sugar cane. How is Z for sugar to be estimated?

> Based on this recommendation from Dr. Mackay , we have elected to remove Z terms for plant sugars and the assumed existence of lipid in the sugar solution in plants.

3. Equations 39 to 45 seem sensible to me, but there should be a “reality check” to ensure that they give reasonable values.

> Yes, we agree. At this point we are organizing two kinds of “reality check”. First, we are comparing our predictions to those obtained from an independently working model group in Germany. Second, we are conducting experiments with actual air / plant / soil systems to assess how well model predictions correspond to observed behavior.

4. In equation 46 I am confused about the units of "transpire" and likewise Phloem flow in 47. Dimensionally they are correct but the velocity must contain an area correction, i.e. like area per unit soil area. Also phloem flows are usually much less than transpiration flows so the "10 times" velocity concerns me.

> Both "*transpire*" and "$Phlm_{flow}$" represent fluid flows with units of $m^3$ of fluid per m2 of soil. The area correction is included in the parameter values and the text has been revised to make note of this. In addition, the text has been revised to state that it is assumed that the phloem flows are 1/10 of the transpiration flows instead of being 10 times the transpiration flows.

5. The equations seem OK, it's the parameter value selection which concerns me most, especially given the wide variety of plant species.

> The plant fresh mass inventory was based on data from California Gap Analysis Data Dictionary, Calveg Layer, which gave plant types and percent area cover in California. This information was combined with fresh mass densities taken from E.D. Schulze, Encyclopedia of Plant Physiology, Vol. 18. *Plant Life Forms and Their Carbon, Water and Nutrient Relations* (Schulze, 1975). The mean and standard deviations were calculated using area as a weighting factor and the variance also based on variance from type to type.

II. Continuous Input to Soil.

6. Equations 2 to 8 are obviously correct. I did not have time to check equations 9 to 31 in detail. I certainly favor giving the time varying values and the average obtained by integration to ensure that there is no obvious error. Simple numerical checking of a number of results is the best method of ensuring that there are no mathematical or transcription errors.

> We appreciate the advice of this comment. In order to have numerical checking of our of results, we have a Level III (steady-state) fugacity model that we are using to audit the results of the new CalTOX model.

III. Solubility Limit.

7. This section is well done. My only concern is that the use of solubility in water in Eq. 48 is a round-about way of stating that the fugacity can not exceed the vapor pressure. That is the more fundamental criterion. The equations presented as 50-61 seem correct but I always find that it is best to check such equations by running practical examples. I regret that I did not have time to do this. The equations do not treat NAPL flow. The use of the adjectives or subscripts "modeled" and "true"

leaves me uncomfortable. I would have used "effective" and "actual" or the like. The use of true implies that other values are untrue which will reduce credibility.

> We have revised the text to make clear that the equations do not treat NAPL flow. In addition, ask recommended, we have replaced the use of the terms "modeled" and "true" with the terms "effective" and "actual".

IV. Air Dispersion.

I am not familiar with the state of this art, but that approach seems entirely sensible and correct to me. I believe that the equations should be as simple and robust as possible -which they are.

V. Ground Water.

8. Again I an not expert, but the approach seems sensible. There is a risk that the model may be over-sold as predicting accurately the fate in ground water. I find that conditions are highly site-specific so the findings should be heavily qualified. CalTOX is not, and can not be, in competition with numerical GW models.

> We do not intend that CalTOX should compete with numerical ground water models. Appropriate application of ground water models requires extensive site-specific data. Obtaining this data is time consuming and expensive. DTSC requires a model which will account for ground water transport, complete with quantitative uncertainty, so this pathway can be compared with other pathways.

**Summary.**

10. The modifications enhance the applicability of the model and seem correct to me in principle. The model has the very valuable feature of accounting fully for the multimedia mass balance. It can also play a key role by directing subsequent assessment activities towards more detailed medium specific models which treat more highly parameterized conditions. It gives the "big picture" and justification for focusing on selected "little, detailed pictures". I would recommend that the new version be tested thoroughly for bugs and reasonableness, preferably by contract to some eager, critical graduate students.

> We are supporting graduate students at the Center for Nuclear and Hazardous Waste Management at the University of California, Berkeley to provide testing for bugs and for reasonableness.

**Victor Palciauskas at U.S. Nuclear Regulatory Commission**

Comments on Ground Water Model Only

1) The general approach to quantifying dispersion in the CalTOX model is satisfactory and will provide an order of magnitude estimate of these processes. Equation 81 is a reasonable leading order estimate of the effects of transverse dispersion and attenuation (i.e., $\exp\{-R_q x / v_c\}$). I strongly support the view that the mathematical formulation does not need to be complex, because a greater degree of uncertainty enters through geologic heterogeneity, i.e., the values used for the crucial parameters such as dispersivity. This fact should not be underestimated. Below are several specific comments for your consideration.

This comment requires no response.

2) I am somewhat puzzled by equation 83 which, when combined with equation 82, implies that the concentration in the vadose zone $C_{vw}$ is equal to the concentration $C_{gw}$ in the groundwater zone. That is not correct. Equation 82 is a general mass balance equation which states that the contaminant mass flux in the vadose zone (under the site) mixes with the groundwater to a depth Z, when it leaves the site boundary. Equation 82 is correct. But, where did equation 83 come from? Note that the ratio $(\text{area})^{1/2} / v_c$ is simply $t_c$ the <u>time it takes groundwater to flow horizontally under the site</u>. By multiplying $t_c$ with the recharge, one arrives at the distance the water would travel in the vadose zone. This distance is not a correct approximation for Z, the mixing due to dispersion. In fact in our original paper ( Domenico and Palciauskas, 1982), we estimated Z to be

$Z = (D_T t_c)^{1/2} = \{\alpha_T (\text{area})^{1/2}\}^{1/2}$

where $t_c = (\text{area})^{1/2} / v_c$ and $D_T$ is the transverse dispersivity = $\alpha_T v_c$

We have modified the CalTOX model and the report so that equation 83 has been removed and replace with the expression above, that is $Z = (D_T t_c)^{1/2} = \{\alpha_T (\text{area})^{1/2}\}^{1/2}$. Since the expression $(\text{area})^{1/2} / v_c$ is the time it takes ground water to flow horizontally under the site, then recharge x $(\text{area})^{1/2} / v_c$ is, in the absence of dispersion, the distance that contaminated water in the vadose zone would have penetrated into the aquifer in the time it takes the ground water to flow under the site. We have found this distance is useful for establishing fugacity balances between the vadose zone and the aquifer.

3) Z should be independent of recharge (note equation. 82 assumes recharge << $v_c$) and only depends on the dispersion coefficient and time. Because the concentration is not constant in the aquifer, $C_{gw}$ represents the average concentration over the depth Z.

> In the revised model, we represent Z, the distance in the aquifer to which the contaminant mixes as $(D_T t_c)^{1/2}$ so that it is independent of recharge and only dependent on the dispersion coefficient and time.

4) One other process that can sometimes be significant is dilution due to continuous infiltration from the surface (e.g., figure 6). A water infiltrates from the surface through the vadose zone along the flow path, it will mix with the aquifer waters diluting the contaminant concentration. This effect becomes important with increasing infiltration and as the length of the flow path to the measurement point increases. In certain cases it could be at least as important as the transverse dispersion. This process is not important at Yucca mountain due to a very low recharge, but for near surface aquifers in non-arid environments it could be important.

> In the revised report, we make note of the fact that infiltration can cause additional dilution. However, we elected not to explicitly model this effect, because (1) the effective continuous recharge rates in much of California are quite low and thus it is expected that this effect is not likely to reduce concentrations significantly at the sites we are considering, and (2) ignoring this effect will, at worst, result in a slight overestimate of the ground water concentration and will result in small over-estimates of the off-site exposure, which is consistent with the health-protective philosophy of the DTSC with regard to making exposure estimates.

5) Minor typo. In the first line following equation 78 on page 80, you state "for a **pulse** of contaminant...". Actually, the equations are approximate solutions for a **continuous release** of contaminant, i.e. $C(x=0, t) = C_0$ for all t, as you correctly note in the next paragraph.

> We have changed the text on pages 78 and on page 80 we have changedthe text to indicate that the equations are for a continuous release of contaminant.

6) Although not crucial to the overall logic of the dispersion module, I am very skeptical of the suggested method for computing the longitudinal and transverse macro-dispersion coefficients in a porous medium ($D_{lc}$ and $D_{tc}$) from those of pure

water ($D_{lw}$ and $D_{tw}$), e.g., equations 77 and 78. In reality the dispersion coefficient will depend strongly on the spatial distribution of the pore structure of the porous medium, which is not apparent in these two equations. These equations appear to characterize the effects of adsorption on the dispersion coefficient of a porous media. That is, if $K_{dq}$ goes to zero, $D_{lc} = D_{lw}$ and $D_{lc} = D_{lw}$. Thus it seems that $D_{lw}$ and $D_{tw}$ are not dispersion coefficients of pure water, but dispersion coefficients for the porous medium in the absence of adsorption. This is not clearly stated in the manual.

> To address this comment we have revised the report to remove the text that implies that $D_{lw}$ and $D_{tw}$ are dispersion coefficients in pure water. We now state that $D_{lw}$ and $D_{tw}$ are the dispersion coefficients for the saturated porous medium in the absence of absorption.

**State Water Quality Control Board**

1) Thank you for the opportunity to comment on the CalTOX model. Due to the limited time allotted for review, we reviewed only the new ground water module of CalTOX. We understand from your letter that Department of Toxic Substances Control (DTSC) staff intend to use the CalTOX model to establish new Total Threshold Limit Concentrations (TTLCs). More recent correspondence indicates that DTSC staff plan to use CalTOX to establish Soluble Threshold Limit Concentrations (STLCs), as well. These planned uses of CalTOX are significant regulatory decision-making tasks whose results could lead to effects on water quality.

> DTSC does not intend to use CalTOX in the development of Soluble Threshold Limit Concentrations (STLCs). CalTOX will be used to determine risk-based maximum concentration levels which will be considered in selecting the Total Threshold Limit Concentration (TTLC). The CalTOX maximum concentration levels are designed to ensure that humans will not experience an unacceptable health risk from exposure to chemicals in waste by multiple routes of exposure. It is a multimedia, multiple pathway risk assessment. Issues pertaining to water pathways are specifically addressed by the STLC.

2) We found that the revised version of CalTOX is a fugacity- type model which includes an analytical ground water module. The ground water module of CalTOX is designed to simulate a case of a single contaminant release in an extremely simple medium under uniform hydrologic conditions, using a single analytically-derived transport equation. We consider all analytical models, including the ground water module of CalTOX, to have limited applicability to ground water simulations for contaminant fate and transport.

> The use of a simplified analytical module is intentional and consistent with the CalTOX base model. All models, including highly sophisticated numerical ground water models, are a simplification of very complex systems. The problem with these complicated numerical models is that they require a great number of input parameters. Ideally, the inputs to these models are based on measurements made at the site. Our experience is that extensive site-specific data on critical ground water parameters are rarely available at sites regulated by DTSC, due to time and cost constraints. Therefore, many of the inputs to these models must be based on guesses. The outputs of these models are <u>highly</u> dependent on the input values selected by the model user.

DTSC believes accurate treatment of uncertainty of a model output to be more important than alleged precision of a single estimate. Fate and transport of chemicals in the environment is fraught with uncertainty and variability. Good regulatory decisions must be based on technical information which includes this information. Analytical models easily permit propagation of uncertainty and variability through a model. Complex numerical models do not. CalTOX is designed to treat uncertainty and variability explicitly and quantitatively.

Use and Validation of Analytical Models:

3) In order to use an analytical model to simulate ground water systems which are geologically and hydrologically variable in space and time, certain simplifying assumptions regarding the modeled systems must be made. Therefore, the variability of the modeled system cannot be taken into account, and instead a single set of parameters is input into the analytical model. Because the single set of values is not likely to accurately represent the overall contaminant behavior, analytical modeling may result in misrepresentation of contaminant fate and transport processes. Even if stochastic applications are used to reduce their limitations, analytical models still may not fully represent variabilities of ground water systems in space and time. Even when applied stochastically, CalTOX may underestimate contaminant concentrations within ground water, by misrepresenting hydrogeological processes which cause attenuation (e.g. dispersion, sorption and biodegradation). In fact, our results from test cases of the ground water module of CalTOX consistently overestimated attenuation compared to the results from other models (Multimed, MYGRT, Bioplume II, MODFLOW and MT3D). Therefore, we are concerned because overestimation of attenuation leads to underestimation of concentration of chemical constituents which may affect water quality.

This is a demonstration of the problem of running models without quantitatively displaying uncertainty. In order to obtain results from the above ground water models, the user must specify input parameters. For these models, a single value must be selected for parameters (e.g. degradation half-life, hydraulic conductivity, and flow rates). It is likely that the default estimates used in the models are "conservative", so that an off-site water concentrations is not under-estimated. Yet there is enormous variability of in these parameter values, not only from site to site, but with in the same site.

CalTOX is designed to be run stochastically so that a range of off-site water concentrations would be predicted. This range would be based on the range uncertainty and variability in the input parameters. If it was not run stochastically, then it is likely that CalTOX was run using the mean values of

the input parameters and compared with outputs from the models above using "conservative" estimates for input parameters. There would also be significant differences if any of those models do not account for degradation of the chemical in the soil and aquifer.

The appropriate criticism of the proposed CalTOX groundwater model is it range of predicted groundwater concentrations is not valid. Comparison of point estimates of CalTOX run with mean estimates from some other model run with different values is not helpful. DTSC is looking for help in developing a ground water model and default input value ranges which predict the potential range of off-site dilutions that may occur in California.

4) According to recent literature, analytical models should only be used for screening-level investigations, such as are done during the preliminary stages of ground water investigations. Following preliminary investigations and site characterization, if regulatory decision-making is to be based on modeling, then a more advanced model must be selected to further represent the ground water system. The degree of the sophistication of the selected model will depend on the purpose and scope of ground water investigation and complexity of the ground water system. No universal ground water model developed to date, including the ground water module of CalTOX, can accurately simulate contaminant release cases within all types of ground water systems. Even when a highly sophisticated model is used to simulate a release in ground water, the validity of assumptions and simplifications adopted in the model must be evaluated. The CalTOX documents we reviewed did not mention how case-specific validity assessments will be conducted for CalTOX model application. Therefore, we are concerned because CalTOX model applications may be used for regulatory decision-making without any appropriate model validation or evaluation.

The kind of model development described above would theoretically be superior to the simple CalTOX module. However, comprehensive model validation takes a great deal of time and is very expensive. Because we regulate sites of all sizes, the cost of modeling at one can exceed the value of the property or the ability of the responsible party to pay in many cases. We find at these sites it is impossible to get even preliminary data. Yet our department is required to make decisions on the clean up of these sites. Such modeling is not called for at every site regulated by DTSC.

For many chemicals, human exposure via the ground water is not important relative to other pathways. Lipophilic chemicals unlikely to reach ground water. Other labile compounds may degrade before reaching a well. We

need a model which will provide a “screening” level estimate of the extent to which the ground water contributes to the total risk. This estimate needs also to incorporate the range of uncertainty. There are a variety of situations in which extensive ground water model validation cannot take place. It is still important that the ground water pathway be considered in these decisions. The CalTOX module is designed to show the relative importance of multiple pathways complete with th eir uncertainties.

5) Ground Water Flow and Contaminant Transport Processes: We found that the ground water module of CalTOX appears not to respond effectively to major flow and transport processes. CalTOX's modeled results did not change significantly when the following parameters were varied: flow velocity (in both horizontal and vertical directions); size of the leaking landfill; aquifer thickness and porosity; recharge into and out of the aquifer; dispersion coefficients, and flow regime in time. In contrast, each of these factors played a significant role in all other models we have used, and the literature indicates that these factors have major effects on contaminant fate and transport. Furthermore, even when we attempted to use CalTOX in a stochastical manner, CalTOX could not incorporate the effects of anisotropy, heterogeneity, multiple aquifer systems, and transient extraction and injection cases. Therefore, we consider CalTOX not to be fully capable of representing the flow and transport pathways in most ground water systems, especially those which are geologically and hydrologically non-uniform.

It is not clear what the reviewers mean by their comment that CalTOX appears not to respond effectively to major flow and transport processes within the ground water. What they appear to be specifically commenting on is the ground water module which is the Domenico and Palciauskas (1982) model. So their comment seems to imply that the Domenico and Palciauskas model does not respond as they would expect. According to Dr. Palciauskas, who reviewed our application of this model, it has been applied correctly. Thus, to address this comment, we are exploring this issue by conducting more specific sensitivity analyses with this sub-component of CalTOX. With regard to the comment that CalTOX could not incorporate the effects of anisotropy, heterogeneity, multiple aquifer systems, and transient extraction and injection cases, we need to reaffirm that this is not the nature of the model included. Our philosophy as stated in the report is that the mathematical formulation does not need to be complex, because a greater degree of uncertainty enters through geologic heterogeneity, i.e., the values used for the crucial parameters such as dispersivity.

6) Degradation Parameters: Another important aspect of CalTOX regards the parameter values related to a chemical's environmental behavior. CalTOX appears

to consider only degradation-related parameters such as chemical degradation half-life in ground water. When we checked these parameter values, we found that they were strictly based on the chemical itself, without considering hydrogeologic and hydrologic site conditions at all. For example, when trichloroethylene (TCE) is selected as the contaminant, CalTOX automatically inputs a half-life of 810 days as a parameter value, regardless of other site parameters. As a result, CalTOX shows that TCE degrades readily and quickly in ground water, even when site conditions are not suitable for degradation. In contrast, recent literature indicates that the rate of TCE degradation depends on site conditions rather than on time alone.

> As with all the input parameters, the chemical half-life is not used as a single value. The half-life for TCE is assumed to be a lognormally distributed variable. The arithmetic mean is 800 days and the arithmetic standard deviation is 1041 days. Our objective is to capture the range of site degradation value through the distribution. The distributions currently used as default distributions are taken from the Handbook of Environmental Degradation Rates. These are the best values of which we are aware. We would prefer to have California-specific distributions but are unaware of a published basis for such a distribution.

7) Conclusions: We consider CalTOX to be a highly simplified multimedia environmental model that is not fully capable of considering basic hydrogeologic mechanisms, including flow transport and transformation. Furthermore, we consider the ground water module of CalTOX to be neither conservative nor appropriate for determining regulatory levels. Accordingly, we think it is inappropriate to use CalTOX as a universal model for establishing new TTLCs or for any such regulatory decision-making purpose without also incorporating specific site conditions. We also feel that such universal use of CalTOX will mislead the regulated community into misusing CalTOX and similar simplified models without appropriate field investigations, data collection, site characterization, and advanced-level modeling.

> For all the reasons stated above, we believe it essential to develop a simplified model which quantitatively address the uncertainty about movement to and through the saturated zone. The simplified model should accurately portray the uncertainty associated with these processes and not strive only to be "conservative". DTSC must make timely and cost-effective decisions which protect public health and effects on ecological receptors. CalTOX is an attempt to make explicit all of the assumptions in a model with a level of sophistication appropriate for the data available for the majority of sites regulated by DTSC.

The existence of CalTOX and the simplified analytical ground water module does not preclude the use of other more sophisticated ground water model s. Used with default input parameter distributions, CalTOX "screens" for the significant human exposure pathways. If ground water is the pathway driving the risk for a given chemical at a given site, then the responsible party and regulatory agency may want to employ a more sophisticated model which is field validated. However, it is essential that scientists within regulatory agencies be afforded the training and time to thoroughly review these models. Without extensive review, sophisticated ground water models do little to further science in regulatory decisions.

**Daniel Chang, University of California at Davis**

1) Having reviewed the treatment of off-site air dispersion in the draft CalTOX model, it is my opinion that substantial modifications are needed before that segment is applied for risk assessment purposes Perhaps I have not understood the author's intent but based upon the written description supplied, the physical realities of transport off-site do not appear to be taken into account . The problem stems from two sources: 1 ) there is no apparent wind directionality in the model algorithm, i.e., dispersion appears to be equally likely in all directions, most likely leading to a non-conservative and site-to-site variable bias ...it did not appear to me that site specific meteorology could incorporated, even if such data were available; 2) the authors cleverly related the off-site air concentration in to the air concentration within the on-site air compartment. However, the methodology for determining the average mixing depth, $L_r$, is not provided. Since the mixing depth can be as low as just above the ground surface the nighttime radiation inversions, and since this factor appears as a multiplicative term in the denominator of the expression its selection appears to me to be critical and that a linear average would not be appropriate.

> In order to assess the mixing height in the volume of air above the waste disposal site, we use an algorithm published by Hanna et al., (1982). In this scheme, if the land-unit area is greater than or equal to $6 \times 10^8$ $m^2$, then the air-compartment mixing depth, $d_a$, is 700 m; if the area is less than $6 \times 10^8$ $m^2$, then $d_a$ is $0.22\ ((Area)^{1/2})^{0.8}$). For example, for disposal site area of 100 $m^2$, this would result in a mixing height of 10 m.
>
> Since we now use the SCREEN3 model to assess off-site transport, the mixing height use for characterizing off-site concentrations relative to the area source of the site, we use the default mixing height SCREEN3 for the rural, one-hour maximum concentration at a wind speed of 1 m/s for any given downwind distance.

2) In my judgment, the bias produced by the first item may be as large as a factor of 4 to 8 in the extreme, Furthermore, without details about the procedure for determining the average mixing depth to be applied, I cannot estimate whether a conservative or non-conservative bias would result, but it could potentially easily be an order of magnitude or greater. The lack of a clear description of how the air dispersion algorithm model parameters are selected is a shortcoming of the current model documentation and needs to be incorporated.

> Based on this comment and comments received from the California Air Resources Board (ARB), we chose to modify significantly the algorithm used in CalTOX to estimate off-site air concentrations. In order build consensus in this process, we met with staff scientists of the ARB to determine an appropriate strategy for assessing long-term air concentrations at a location off-site for a contaminated area with gas emissions from the soil. The strategy we developed is discussed in the section below responding to ARB comments.

3) My understanding from you is that the model is to be run in a stochastic manner, but again, it is not clear to me how the statistical parameters of the air dispersion model section will be selected. If they are totally random, that would not be an accurate representation of meteorological changes.

> This comment is addressed in the response to the ARB comments in the next section.

4) Health risk assessment methodology and models already exist, with some having greater or lesser data input requirements, e.g., the Health Risk Assessment Model (HRA) that was originally prepared by the California Air Pollution Control Officers Association (CAPCOA) in conjunction with the Air Resources Board (ARB). However, for the most part, unless an very conservative estimate of airborne concentrations is needed, even these models require some site-specific data. Although the more realistic models have fairly complex algorithms, perhaps unwarranted in this case, the simpler ones would seem to me to be capable of incorporation into a "spreadsheet-based" model.

> See response to comment 2) above and the discussion of the algorithm developed with ARB in the next section.

5) Lastly, the latest version of the model User's Guide indicates that the model should e capable of being run with either EXCEL 4.0 or EXCEL 5.0. I was not able to run the latest version with EXCEL 4.0, which is the latest version that I currently have. Therefore, I did not evaluate the model interface itself. I presume that other users will have a similar problem.

> Other users have not had this problem, so we believe there may be a disk error in one of the files you received on your disk.

The general structure of the model seems to be conceptually sound. The interface from compartment to the atmosphere outside the model still needs refinement. Thank you for providing the opportunity to review the model.

> We agree with the statement that the interface from the CalTOX on-site concentration to the areas of the atmosphere outside the model needed refinement an have modified the model significantly as described below.

## California Air Resources Board

As requested by Ned Butler of the Department of Toxic Substances Control (DTSC), we have reviewed the proposed modifications to the CalTOX model. We have focused our review on the air dispersion model described on pages 24 through 27 in the Modifications Document. However, our review did include other parts of the CalTOX model. In addition, our Stationary Source Division has provided one comment.

As we understand the CalTOX model, on-site ambient air concentrations are estimated by the "box" model as described by Gifford and Hanna (1973). off-site ambient air concentrations are estimated by modifying the standard Gaussian plume equation in conjunction with the "box" model in the proposed modifications to CalTOX. We have comments on: 1) the use of the "box" model to estimate ambient on-site concentrations; and 2) the modified Gaussian plume equation used to estimate off-site ambient air concentrations.

### "Box" Model

We do not agree with CalTOX's method of implementing the "box" model proposed by Gifford and Hanna. CalTOX does not implement the "box" model according to it's formulation. In addition, CalTOX compares specialized results of the "box" model to specialized results of the Gaussian plume equations to corroborate the method in which the "box" model is used within CalTOX. The following describes two weaknesses in the use of the "box" model within CalTOX.

A) Inappropriate Implementation of "box" Model:

Gifford and Hanna suggest the following equation for the "box" model over a city.

$$X = (c\,Q) / (Area \times u) \qquad (1)$$

where,

- X = ambient air concentration within the box
- $c$ = dimensionless parameter, a weak function of the area size, approximately a constant
- Q = emission rate within the box (mass / time)
- *Area* = horizontal area of the box
- u = long-term average horizontal wind speed through the box

Gifford and Hanna suggest *c* to be 225 for ground level emissions in areas the size of cities. Data suggest the value of *c* could be from 60 to 600 with a mean around 200 to 250, depending on the data.

CalTOX does not follow Gifford and Hanna's methods for estimating *c*. CalTOX assumes, based on a model for area sources developed by Turner (1970), the constant *c* can be estimated as $(4.3\ (\text{area})^{1/2} / d_a)$, where $(\text{area})^{1/2}$ is the cross-sectional length of an assumed square area containing the source Q and $d_a$ is the mixing height depth.

We are unable to derive the same value for *c* from Turner's equations. Turner's equations are for calculating the off-site concentration from an area source. When modifying the source parameters to account for area sources, Turner's equation does not consider the mixing depth, $d_a$. The parameter *c* in equation (1) is for calculating the on-site concentration within a box with a horizontal area.

Before we can approve the "box" model approach in CalTOX, the documentation needs to include details on how the above assumption for the Gifford and Hanna parameter, $c=(4.3\ (\text{Area})^{1/2} / d_a)$, is appropriate for use in the "box" model. The description should include a step-by-step derivation.

### *Response to: A) Inappropriate Implementation of "Box" Model*

In the original Gifford and Hanna (1973) paper, *c* ranged from 60 to 600 with a mean around 200 for particles and from 5 to 220 with a mean around 50 for gases. We assume this model to be derived from a mass balance for a box element in the atmosphere such that

Gains = Losses

In this system the gains are the total area based emission rate, Q, and the losses are what is carried out of the volume by an air mass moving at a speed u relative to the land surface.

$$Q = X \times (\textit{height} \times \textit{width} \times u) / \varphi$$

where

Q = emission rate within the box (mass / time)
X = uniform ambient air concentration within the box
*height* = height of the air column at the edge of the box = $d_a$

*width* = width of the box perpendicular to the effective wind direction = $(Area)^{1/2}$ in an assumed square region.
u = long-term average horizontal wind speed through the box
$\varphi$ = an adjustment to account for the wind direction variability; this factor is greater than one if the wind does not always blow in the same direction.

rearranging gives

$$X = \varphi Q / (height \times width \times u)$$

multiplying the numerator and denominator by $(Area)^{1/2}$ and substituting $(Area)^{1/2}$ for *width* and $d_a$ for height gives

$$X = \varphi Q (Area)^{1/2} / (d_a \times Area \times u)$$

comparing this to the box-model equation $X = (c Q) / (Area \times u)$ implies that

$$c = \varphi (Area)^{1/2} / d_a$$

In the Gifford and Hanna (1973), paper, the average urban area was on the order of $10^9$ $m^2$ so that, with a mixing height of 1000 m, we obtain $\varphi$ in the range 1.6 to 6 corresponding to *c* in the range 50 to 200. We selected $\varphi = 4.3$ because this value avoids a discontinuity at the edge of the box when we use the box model for on-site air concentrations and the model for area sources developed by Turner (1970) to estimate off-site air concentrations. Since we no longer use the Turner (1970) model, but now use a fit to SCREEN3, this issue is not significant. Nevertheless, this derivation reveals more precisely how we obtained the expression $c = 4.3 (Area)^{1/2} / d_a$.

With regard to the concern that this expression implies an inappropriately strong dependence of *c* on area, we offer the following response. As was noted in our response to Professor Chang's comments, we estimate $d_a$ using an algorithm recommended Hanna et al., (1982). According to this algorithm, for regions less than $6 \times 10^8$ $m^2$, the mixing depth, $d_a$, is $0.22 ((Area)^{1/2})^{0.8}$ and ; if the area is $6 \times 10^8$ $m^2$ or greater, then the mixing height, $d_a$, is 700 m. For sites with an area less that $6 \times 10^8$, which is expected for most disposal sites in California, and with $d_a = 0.22 ((Area)^{1/2})^{0.8}$, we obtain

$$c = \varphi (Area)^{0.1} / 0.22 = 4.5 (Area)^{0.1} \text{ (with c =4.3)}$$

This provides a expression for c which has a weak dependence on area and produces c values in the ranges reported by Gifford and Hanna (1973).

B) Comparison with the Gaussian Plume Equation:

There is no technical basis for the comparison of similarities between the "box" model and the Gaussian plume equation as presented in CalTOX. CalTOX attempts to show these similarities in Appendix B of the CalTOX Part II algorithm descriptions. We recommend that CalTOX remove this comparison. We discuss our basis for this recommendation in the following section.

First, CalTOX re-writes the "box" model equation for the ambient concentration within the box. Substitution of $(4.3\ (\text{area})^{1/2} / da)$ for *c* into equation (1) gives equation (2) following.

$$X = (4.3\ Q) / [(\text{Area})^{1/2}\ d_a\ u] \qquad (2)$$

where,

$d_a$ = mixing depth

The second equation is derived from the Gaussian plume equation. The Gaussian plume equation at a distance x downwind is integrated from $-\infty$ to $+\infty$ in the cross wind direction, y, and in the vertical direction, z, from 0 (ground level) to $+\infty$. The total mass within this integration is then averaged in the horizontal pie wedge sector of 1/16th of the circle and in the vertical over the mixing depth, da. The result is the following equation, (3), to estimate off-site long term concentrations.

$$X = (8 \times Q) / (\pi \times x \times d_a \times u) \qquad (3)$$

where,

x = downwind distance

This is no longer a Gaussian based equation. This is an equation that will estimate downwind concentrations by uniformly distributing the emissions over a pie shaped wedge of 1/16th of a circle in the horizontal direction, the mixing depth, $d_a$, in the vertical direction, and according to the wind speed in the along wind direction. The basis for selecting $1/16^{th}$ of the circle and the equation for the mixing depth, $d_a$, will be discussed later in our comments.

CalTOX then makes a substitution into equation (3) that we do not agree with. The area occupied by a circle with radius x is $\pi x^2$($\pi x^2$=Area). CalTOX then substitutes for x in equation (3) to obtain equation (4). (CalTOX has rounded the constant in equation (4) to 4.4).

$$X = (8 \times q)/(\pi \times x \times d_a \times u) \approx (4.3q)/[(\text{Areas})^{1/2} \times d_a\ u] \qquad (4)$$

CalTOX assumes the similarity between equation (2) and (4) shows that the Gaussian plume model is similar in form to the concentrations predicted by the box model over long time periods and over large areas.

The similarity between equations (2) and (4) are purely coincidental and do not maintain any scientific merit. Equation (4) is for the off-site concentration at a distance, x, downwind. The area in equation (4) is that of a circle with radius x with no physical relationship to the source term. Equation (2) is for the on site concentration of a box. The area in equation (2) is for the source term. Therefore, we recommend that CalTOX remove this comparison between equations (2) and (4).

### *Response to: B) Comparison with the Gaussian Plume Equation*

Based on this comment, we will remove the comparison between equations (2) and (4) in all future documents describing the use of CalTOX for on-site and off-site air concentrations.

**2) Estimation of Off-Site Concentrations**

We do not recommend the proposed method to estimate off-site ambient air concentrations. There are two weaknesses in the CalTOX proposed changes and an additional error in interpretation of an equation. First, the modifications to the Gaussian plume equation are extensive to the point that the basic formulation of the Gaussian equation no longer exist. Secondly, the proposed method to estimate, off-site concentrations on a long term basis does not give any consideration to variable wind directions or different atmospheric stabilities.

A) Modification to the Gaussian plume equation:

CalTOX uses equation (3) for calculating downwind off-site concentrations. Equation (3) is no longer a Gaussian based equation. No basis provided for selection 1/16th of a circle over which to uniformly distribute the emission of the plume. We recommend that CalTOX provide some scientifically justified reasons for uniform distribution of the emissions over 1/16th of a circle.

Additionally, there is no justification for the selection of the mixing zone depth. The equation for mixing zone is only documented in the CalTOX code. It is not presented in the documentation. The equation found in the CalTOX code is:

$$d_a = 0.22(osd + (area)^{1/2})^{0.8} \text{ if } (osd + (area)^{1/2}) < 25{,}000$$

$$d_a = 700 \text{ if } (osd + (area)^{1/2}) \geq 25{,}000$$

where,

osd = off-site distance

For a one kilometer by one kilometer square, the mixing zone depth would be 55 meters. This equation has not been referenced or justified within CalTOX. We recommend that CalTOX provide scientific justification for the equation used to estimate the mixing zone depth for equation (3).

B) Variable Wind Direction

Equation (3) for the estimation of off-site concentrations on an annual basis makes no allowance for variable wind directions. It assumes the wind direction will always be in the direction of the off-site receptor. This may have a tendency to bias annual average off-site concentrations towards overestimation.

We recommend that CalTOX either: 1) acknowledge that there may be a tendency to bias long term off-site concentrations towards-overestimation and document its effects or; 2) propose some changes to equation (3) to account for variable wind directions.

C) Incorrect Description in Text

The proposed modifications to CalTOX describe the concentration as a calculated value at a distance “r” downwind. This is incorrect. The parameter “r” which should be “y”) is the crosswind distance from the plume centerline, not the downwind distance. The dependence on the downwind distance is imbedded in

the $\sigma_y$ and $\sigma_z$ parameters, as $\sigma_y$ and $\sigma_z$ are functions of the downwind distance, x, and the stability class.

This same error is in the original CalTOX descriptions. However, in this case the text describes "y" as the distance downwind, instead of the cross wind distance.

### *Response to 2) Estimation of Off-Site Concentrations; Parts A), B), and C),*

Based on these comments, we chose to modify significantly the algorithm used in CalTOX to estimate off-site air concentrations. In order build consensus in this process, we met with staff scientists of the California Air Resources Board (ARB) to determine an appropriate strategy for assessing long-term air concentrations at a location off-site for a contaminated area with gas emissions from the soil. The procedure we developed has the following framework:

(a) The CalTOX model is used to assess an area source term, that is the source strength Q (mol/s) of contaminant emanating from a landfill or hazardous waste site.

(b) As a basis for estimating off-site air concentrations associated with the gas emissions from a contaminated land unit, use a model that is provided by and approved by the U.S. EPA and widely used by ARB. SCREEN3 (EPA, 1995a) is the model that meets these requirements and can be used to relate area sources to off-site concentrations in terms of contaminated area and distance from the contaminated area to a receptor.

(c) SCREEN3 was used to develop a large set of maximum one-hour concentrations associated with a large set of different areas and different off-site distances.

(d) From these results, a response surface is developed which allows the mapping of this large set of simulations into an algebraic expression within CalTOX to estimate off-site concentrations.

(e) An approach described in the SCREEN3 guidance document is used to convert the maximum 1-hour concentration into an annual average off-site concentration.

The procedures we used to carry out this process are discussed below. The SCREEN3 model (EPA, 1995a) was developed to provide an easy -to-use method of obtaining pollutant concentration estimates based on the screening procedures documents issued by EPA (EPA, 1995b). By taking advantage of the rapid growth

in the availability and use of personal computers (PCs), the SCREEN3 model makes screening calculations accessible to a wide range of users.

We obtained from U.S. EPA a copy of SCREEN3 and ran simulations for the off-site concentrations from an area source. According to the guidance provided by EPA for using SCREEN3, low-level sources (i.e., sources with stack heights less than about 50m) sometimes produce the highest concentrations during stable atmospheric conditions. Under such conditions, the plume's vertical spread is severely restricted and horizontal spreading is also reduced. This results in what is called a fanning plume. The recommended calculation procedure (EPA, 1995b) for low-level sources with no plume rise is to find the maximum 1-hour $\chi u / Q$ using SCREEN3. In the $\chi u / Q$ term, $\chi$ is the ground level concentration, $mol / m^3$, u is the 10-m elevation wind speed, $m / s$, and Q is the source strength, $mol / s$. The recommend procedure is different for rural and urban landscapes. For rural cases, F stability is assumed and for urban cases, E-stability is assumed. The maximum 1-hour concentration is computed for a 10-m wind speed of $1\ m / s$.

In order to develop an algorithm that approximates the behavior of SCREEN3, we ran the area source option to determine the maximum 1-hour concentration associated with rural conditions and a $1\ m / s$ wind speed according to the procedure described above. The urban conditions result in a somewhat lower $\chi / Q$. Thus, we elected to use the rural procedure as more appropriate for assessing off-site health effects. We made hundreds of simulations in which we varied the off-site distance, OSD, from 10 to 2000 m. OSD is the distance measured from the edge of the contaminated site. We varied the area of the site (Area) from 100 to $10^6\ m^2$. Following the recommendations of the SCREEN3 users manual (EPA, 1995a), we excluded situations in which the off-site distance was shorter than the square-root of the area. Figure 1 below summarizes these results and shows how $\chi / Q$ for the area source varies with OSD and Area.

We next developed an algorithm that provides the best fit of the maximum 1-hour $\chi / Q$ with $u = 1\ m / s$. We discovered the best fit of this model with the following algorithm

$$\frac{c}{Q}^{hr} = Area^{(-0.28)} \times 10^{-(1.92+0.00057OSD)} + \frac{117.95}{(1.72 \times OSD + \sqrt{Area}) \times [(OSD + \sqrt{Area})^{0.85}]}$$

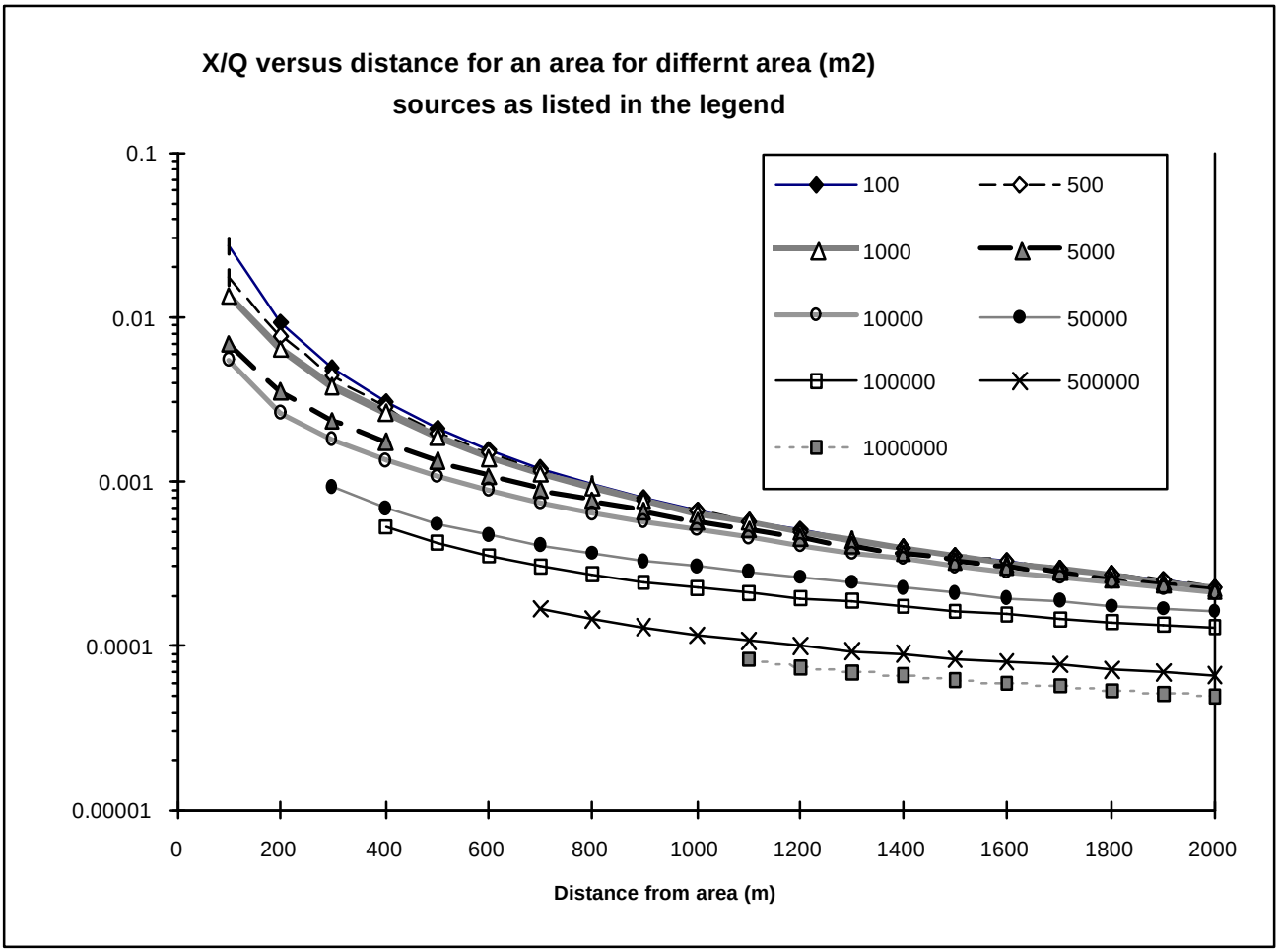


Figure 1. X / Q versus distance and area.

Relative to the set of estimates for $\chi$ / Q obtained from SCREEN3, this estimation equation has an $r^2$ of 0.95, which means that this approximation accounts for 95% of the variance of $\chi$ / Q generated by SCREEN3 over the same ranges of OSD and Area. The mean value of the ratio of approximated $\chi$ / Q to the SCREEN3 $\chi$ / Q is 1, which means the model fits without bias. The standard deviation of this ratio as applied over the ranges of OSD and Area in Figure 1 is 0.3. This means that 66% of the approximated $\chi$ / Q values have a residual error of ±0.3 or less relative to the SCREEN3 estimated values. Comparison of these approximations relative to the SCREEN3 values are shown in Figure 2.

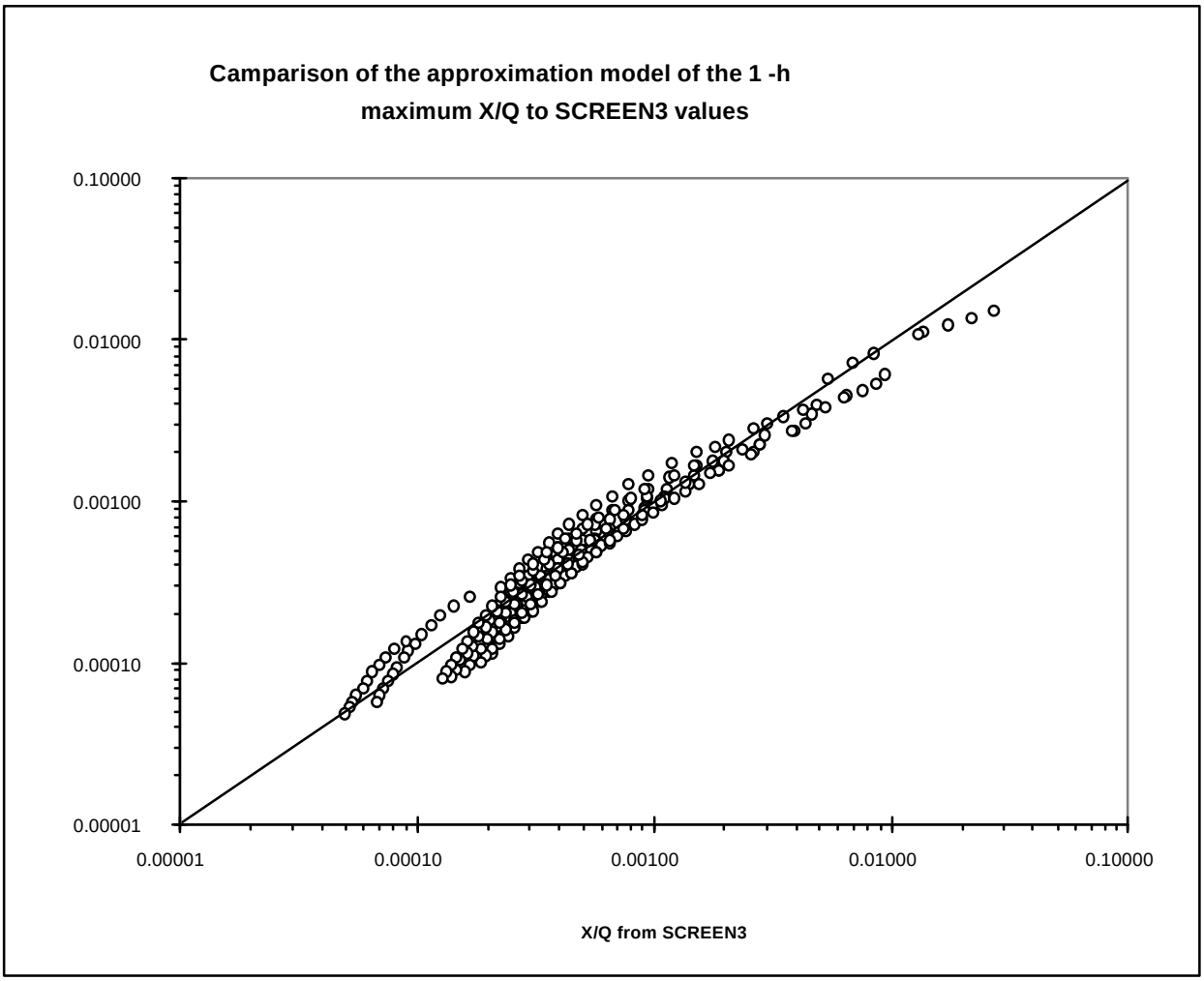


Figure 2. Comparison of CalTOX approximations of X / Q to the SCREEN3 values.

To obtain concentration estimates for the long-term annual averaging time as needed by CalTOX, we use the EPA (1995b) recommended ratio between a annual maximum concentration and a 1 -hour maximum. EPA (1995b) presents ratios for a "general case" of long-term average and the user is given some flexibility to adjust those ratios to represent more closely any particular application where actual meteorological data are used. To obtain the estimated maximum concentration for an annual averaging time, the EPA recommends multiplying the 1 -hour maximum $\chi$ / Q by 0.08 (±0.02). The number in parentheses is the EPA (1995b) recommended limits within which the general ratio may diverge.

Based on these procedures, we determine the annual average off-site air concentrations in CalTOX using the algorithm

$$\frac{c}{Q}^{yr} = 10^{(-1.097 \pm 0.115)} x\{Area^{(-0.28)} \times 10^{-(1.92+0.00057OSD)} + \frac{117.95}{(1.72 \times OSD + \sqrt{Area}) \times [(OSD + \sqrt{Area})^{0.85}]}\}$$

The first term in this expression is the conversion from the 1 hour maximum $\chi / Q$ to the annual average $\chi / Q$ ($10^{-1.097}$ equals 0.08) and includes the residual error that results from using the approximation equation for the SCREEN3 results.

### 3) Deposition Velocity

CalTOX uses a deposition velocity of 500 m / d (assuming m / d is meters per day, we convert the deposition velocity to 0.58 cm / s). There is no basis, reference, or justification for this parameter. We recognize that the deposition velocity is a function of many variables including surface, particle, and meteorological parameters. CAPCOA guidelines recommend 2 cm / s or 5 cm / s depending on the type of release. We recommend CalTOX provide technical justification for it's choice for deposition velocity.

### *Response to: 3) Deposition Velocity*

We have modified the report to include the following text to justify the value of deposition velocity that is used.

The CalTOX model uses deposition to represent fine particles that have a rather long residence time in the atmosphere. We do not model gases using a deposition model, but use a partition / diffusion mass-transfer model. Based on our review of the literature, we find that dry deposition velocities are influenced by numerous factors and there is a wide range of reported values, for example from 0.003 to 6 cm / s (3 to 4900 m / d) reported for deposition rates of long-range radioactive fallout from air to ground surfaces ( Whicker and Kirchner, 1987). Schroeder and Lane (1980) report that dry deposition velocities measured for gases span four orders of magnitude, from 0.002 cm / s (1.7 m / d) to 26 cm / s (22,000 m / d). They report deposition velocities measured for particles in the range from 0.001 cm / s (0.86 m / d) to 180 cm / s (155,000 m / d). For particles less

than 5 μm, McMahon and Denison (1979) report deposition velocities in the range 0.003 to 1 cm / s (2.6 to 860 m / d). Based on these observations above, we represent the range in the deposition factor from air particles to ground surfaces using a lognormal distribution having a geometric mean of 300 m / d (arithmetic mean of 500 m / d) and a geometric standard deviation of 3.0. The values we use differ somewhat lower than CAPCOA guidelines, because we are considering fine particles suspended over a soil and not emissions that are likely to be combustion sources (which have a larger fraction of course particles). In addition, with the way CalTOX is applied, it is health conservative to use longer residence times in the atmosphere (i.e. lower bounds on deposition). This is the opposite of the point-sources and source receptor relationships that CAPCOA typically is used to address.

**Comment from Stationary Source Division**

The preface of the original CalTOX Exposure Assessment Model stated that the dispersion of chemicals in air to locations off-site was not addressed, and that once DTSC reached consensus on the on-site emissions model, dispersion modeling and off-site receptors would be addressed. In our April 5, 1993 comments to DTSC on the draft CalTOX model, we noted that one of the key elements of an off-site exposure assessment for the air pathway is sub-surface off-site gas migration. We understand that the modifications to CalTOX do not include this pathway. Since the modified CalTOX may be used at hazardous waste landfill where sub-surface off-site gas migration may be a pathway of concern, we recommend that this pathway be included.

***Response to: Comment from Stationary Source Division***

This comment suggests that CalTOX may be missing an important pathway: subsurface vapor transport. This would be important only if the off-site vapor transport in the soil was greater than 1% of the off-site vapor transport in the air. For most applications, soil vapor transport will be negligible relative to air vapor transport. The following conditions would be required for this to be important: pressures greater than atmospheric, vapor / gas impermeable barrier between the soil and the atmosphere over the distance between the source and a residence distant from the source.

These conditions may occur at some landfills. Landfills may have a cap under which methane and carbon dioxide is generated leading to increased pressure. If the area between the landfill and the nearest receptor off-site is paved or has some

impermeable barrier, it is possible that the methane generated in the landfill could flow to the residence. This problem has been observed at some older landfills.

For the purposes of developing TTLCs, it will not be possible to develop an algorithm to model this pathway given the time and resource constraints. However, it is possible to eliminate this pathway by defining and limiting the landfills to which wastes containing TTLC chemicals can be taken. A number of factors may mitigate this problem at the modern landfill in which special waste is envisioned to be deposited. First, methane collection should reduce the pressure in landfills. Second, landfills without reduced pressure which are surrounded by pavement or other gas impermeable barriers could be excluded from receiving wastes.

**Summary**

In summary, based upon the documentation provided, the air dispersion modeling portions of the current and proposed CalTOX model require further development. Until the Department of Toxic Substance Control addresses our comments, we cannot endorse the current air dispersion formulation of CalTOX. We should have a discussion on the current model and any proposed modifications to CalTOX in order to obtain a scientifically sound air dispersion module.

***Response to: Summary***

Discussions between DTSC and both groups in the California Air Resource Board commenting on CalTOX have led to the revisions described above.

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