CalTOX, A Multimedia Total-Exposure Model for Hazardous-Waste Sites

Part IV: Comments and Responses

The Office of Scientific Affairs

Department of Toxic Substances Control

California Environmental Protection Agency

Sacramento, California

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DESCRIPTION

The first three CalTOX reports have undergone three review and revision cycles focusing exclusively on the technical and scientific issues. Part IV contains the summarized comments and responses to those comments for each of the three cycles. Chapter one contains the responses to the first review. Eight well-known scientists representing various fields including chemical transport, toxicology, risk assessment, uncertainty analysis and soil science were sent the first draft in the summer of 1992. The comments from the second review cycle are shown in chapter two. The second draft of CalTOX document was made available to scientists within the six departments and boards of the California Environmental Protection Agency in the winter of 1993. Chapter three contains the comments for the public. The third draft was made available to anyone in the summer of 1993.

Including Part IV would have added significantly to the size of this document. However, this part may be obtained through the computer bulletin board established by the Office of Scientific Affairs. The spreadsheet user's guide has information on how to access the computer bulletin board.

FOREWORD

The first three CalTOX reports have undergone three review and revision cycles focusing exclusively on the technical and scientific issues. This part contains the summarized comments and responses to those comments for each of the three cycles. Chapter one contains the responses to the first review. Eight well-known scientists representing various fields including chemical transport, toxicology, risk assessment, uncertainty analysis and soil science were sent the first draft in the summer of 1992. The comments from the second review cycle are shown in chapter two. The second draft of CalTOX document was made available to scientists within the six departments and boards of the California Environmental Protection Agency in the winter of 1993. Chapter three contains the comments for the public. The third draft was made available to anyone in the summer of 1993.

It may be difficult to interpret some of the comments from previous review and revision cycles. The current draft is not the draft the commentors reviewed and the structure of the document has changed in response to these comments.   Photocopies of the original letters containing these comments have not been included in this document. They would have added significantly to the size of this document. Photocopies of the original letters are available from the Department of Toxic Substance Control. Please send a check for $15.00 made out to the Department of Toxic Substances Control. The address is:

Document Requests
Office of Scientific Affairs
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Please indicate that you would like to receive the original comment letter for the CalTOX review cycles.

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Chapter I. Comments of Reviewers of Draft Dated August 1992

We acknowledge the following reviewers of the draft version, dated August 1992, of the CalTOX model.

Donald Mackay, University of Toronto, Toronto, Ontario Canada
Curtis Travis, Oak Ridge National Laboratory, Oak Ridge, TN
Bonnie P. Baylock, Oak Ridge National Laboratory, Oak Ridge, TN
Louis Thibodeaux, Louisana State University, Batton Rouge, LA
Richard E. Green, University of Hawaii at Manoa, Honolulu, HI
Mitchell J. Small, Carnegie Mellon University, Pittsburg, PA
Kevin Brand, Carnegie Mellon University, Pittsburg, PA
William F. Kastenberg, University of California at Los Angeles
Dale Hattis, Clark University, Worcester, MA
John Schaum, Office of Research and Development, USEPA
Matt Lorber, Office of Research and Development, USEPA
Jon Chen, General Science Corporation, Laurel, MD
Brian Davis, California Department of Toxic Substances Control, Sacramento, CA

Comments that Require No Response

Comments by D. Mackay

In general it is well done. The treatment of soil as a three layer system is particularly good and represents a considerable advance on existing models which treat the soil as either a single layer, as a lager number of layers, or using a more complex continuous function.

The expressions used are sensible, state-of-the-art and should give reasonable results. Ultimately, of course, the test is to apply the model to a number of chemicals and attempt to validate it.

Comments by M. Small and K. Brand

The CalTOX model represents a significant scientific advance for integrated environmental fate and exposure models of this type. The comprehensive coverage of potential exposure routes is particularly noteworthy. LLNL has drawn from a wide range of disciplines to bring together appropriate sub models into an integrated whole. Innovative, state-of-the art representations are used for the various fate and transport processes and their associated constitutive relationships. This is a model that can rightfully be viewed as a repository for much of the current knowledge of environmental pollution and exposure processes. Furthermore, the approach for characterizing uncertainty is appropriate and effective.

LLNL is to be commended for tackling the formidable problems of developing such a comprehensive and integrated framework for assessing the health risks imposed by contaminated sites.

Both Parts II and III discuss the uncertainty of the input parameters, including suggested coefficients of variation along with default mean values. This encourages the user to think about uncertainty and provides a foundation upon which further uncertainty analysis can be performed or considered.

Comments by L. Thibodeaux

All-in-all I cannot find any technical flaws in the model given the assumptions of its development and intended use. I think it is a balance of good science and practical algorithms to yield an engineering tool for estimating average chemical concentrations important to exposure assessments at hazardous waste sites.

To me the fugacity approach requires a little extra effort in gaining an understanding of the model because I work and think using the more traditional approach. For the first time I forced myself into a true understanding of the fugacity approach. It is technically correct.

The compartments are well defined and the assumptions are clearly stated.

The fugacity approach will be tough for the non-expert trying to gain a basic grasp of the model.

Equations, prose, figures, etc. throughout the document are amazingly typo-free.

Comments by D. Hattis

Overall, I think the work represents an important tool for rapid first-cut analysis of potential exposures resulting from the presence or release of toxic material in or in the immediate vicinity of residential areas.

Clearly, the current version of CalTOX is intended and helpful primarily for quantifying lifetime exposures to community residents living on former hazardous waste sites, not the shorter term fluctuations that would be of interest for acute toxicity assessments.

As indicated at the end of the document, the author hopes to continue work on this tool in the future in the form or better distributional characterization of both interindividual variability and uncertainty, in preparation for a full Monte Carlo treatment of the variability and uncertainties in calculated exposures. This should be enthusiastically encouraged. In the meantime, the tool as it stands is likely to be quite useful for first-cut screening of hazards at waste sites where possible future residential use is contemplated.

Comments by C. Travis and B. Blaylock

On the whole, the documentation was comprehensive and well-documented.

For use as a screening level tool to be used in conjunction with detailed follow-up risk assessments CalTOX is an excellent model.

One particular attribute of the model is the consideration of contamination of mother's milk in the exposure assessment. This pathway is not frequently considered in risk assessments although it is a good indicator of the exposure of sensitive sub populations to contaminants.

Comments by R. Green

It is an impressive contribution, and should be very useful if used appropriately (i.e. with caution). Hopefully, the model use will be monitored by some technically competent personnel in DTSC who will be able to identify gross errors so that adjustments could be made in subsequent applications.

This report is well written and documented. The approach is rational and is well-supported by published literature. ... The examples provided by the author (BaP and PCE) apparently provide reasonable estimates of environmental partitioning at the regional level, but it would be stretching the point to call this a validation for a site-specific situation. I would expect it to be satisfactory as a "screening tool", that is a means of comparing the behavior of different chemicals at a given site, or perhaps to compare different sites contaminated with a given chemical. The model is not likely to give accurate site-specific results, even if site-specific parameters are provided, during a period soon after contamination has occurred. The limitations of the model for highly dynamic situations seem apparent. Transport between compartments is highly dependent on empirical parameters which define the effect of the boundary layer on transport rates. Even the Jury approach, to which the compartment model is compared for the flux to air from the soil surface, is not likely to be accurate for highly volatile chemicals soon after "application" because of non-equilibrium conditions. The use of equilibrium coefficients during periods when non-equilibrium conditions exist will surely result in an under-prediction of fluxes into the atmosphere. On the other hand, the compartment model should provide reasonable predictions of system behavior when longer term (weeks to months to years) periods are considered.

Comments by J. Chen

The CalTOX model appears to be a significant step forward in the development of fugacity-based partitioning models. The modeling approach appears to be soundly based in the available literature. An important concern regarding the model is that it is a partitioning model and therefore only crudely approximates site specific conditions. As with all partitioning models its use should be limited to establishing priorities for sites to be studied in more detail.

Comments by J. Schaum and M. Lorber

This work is impressive in terms of scope of effort and technical innovation. The model promises to be an important tool.

The model is comprehensive in its treatment of the transport, transfer, and transformation of soil contaminants; the mass balance equations were carefully and correctly developed; unit conversions were also carefully and correctly made which is not a trivial issue—lack of care can lead and has led to erroneous model outputs; and the default values of parameters seem to be generally in line with accepted literature values.

The use of the Jury model to develop simple regression models suitable for spreadsheets is clever and innovative.

Comments to Which We Have Responded

Comments by D. Mackay

Comment: Emissions to surface soil are not discussed along with emissions to air, subsurface soil and surface water in the Abstract; and emissions to surface water are not discussed along with emissions to soil and air in the Introduction.

Response: This has been fixed.

Comment: Diffusion in the water phase of soil is not included in the discussion on page 10.

Response: This has been fixed.

Comment: Nomenclature is more complicated than necessary and sometimes gets mixed up. In particular the introduction of fugacity capacities for compartment phases and total compartments on page 25 is confusing.

Response: This paragraph has been revised to make clear the distinction between total compartment fugacity capacity and the fugacity capacity of the component phases that make up that compartment.

Comment: The development of equations using rate constants for transport is more convoluted than necessary; this includes equations starting on pages 51 and beyond.

Response: The material referred to has been revised to make more clear and concise the development of the transport rate constants. In addition summary tables have been provided for the diffusion terms to make it easier for the reader to trace and reconstruct these expressions.

Comment: A brief user's manual for the model would be advisable and would make it more user friendly. It should include hardware and software requirements and a short description of the steps necessary to run the program.

Response: We are currently working on a user's manual that will be a supplement to this report. It will include hardware and software requirements and a short description of the steps necessary to run the program.

Comment: Page 13, 2nd para., line 7: should be diffusion not dispersion

Response: This has been fixed.

Comment: Page 19, 2nd para., line 7: change to Reuber et al (1987)

Response: This has been fixed.

Comment: Page 21, Eq. 10 and following paragraph: K_{Di} should have units of L/kg and 1/1000 converts L to m^3. Equation 11 should state units of L/kg (this problem also occurs in Eqs. 29 and 31.

Response: This has been fixed.

Comment: On page 21 it should be noted that vapor pressure and solubility should both be for the same state—either solid or liquid.

Response: It is now so noted.

Comment: Page 24, Eq. 21: "a" is not defined.

Response: Text has been added to define this parameter.

Comment: Page 26, the sentence in the first two lines could not be understood by this reviewer.
Response: The sentence has been revised to make its meaning more clear.

Comment: Page 42: Equations are given for advective flux and non-diffusive air-soil flux. Equations for other non-diffusive processes are not defined. Should they not be summarized in a Table.
Response: We have added a table to summarize these non-diffusive processes.

Comment: Page 43: Is the last sentence of the paragraph on photolysis correct?
Response: Yes it is. Contaminants on the actual surface of the soil, such that they are readily exposed to sunlight can have residence times on the soil surface comparable to those in the atmosphere, that is hours to days for compounds having chemical bonds that are easily broken by photon absorption.

Comment: Page 45: Should include a table of physical and chemical properties used in the calculations.

Response: The suggested table has been added.

Comment: Page 54: T_{ba} = 0.5 and T_{bs} = 0.01, Where did these come from? Also, T_{ab} and T_{sb} are not defined.

Response: T_{ab} N_a and T_{sb} N_s are the gains to plant biomass from air and root-soil compartments in mol/d. T_{ba} and T_{bs} are the rate constants for losses due to exchanges with air and root-zone soil, in day^{-1}. Expressions relating to exchanges between vegetation and air and between vegetation and soil are obtained by requiring that the fugacity of plants is the average of the fugacities in air and soil. Based on the literature cited in this report, it becomes clear that the fugacity of the total plant mass (that is, both roots and above-ground biomass) is somewhere between that of the root-zone soil and the air. This is the basis for assuming that the fugacity of the plants is the average of the root-zone soil and air fugacities. This leads to the definitions of T_{ab} and T_{sb}, which are now provided on pages 56 and 57 of the revised report (where p is used in place of b as the designation for the plants compartment), and results in the requirement that T_{ba}=0.5 and T_{bs}=0.01.

Comment: Page 52: The term Y_{ag} is a diffusive mass transfer constant. Why introduce this now?

Response: In the revised report all of the diffusive-mass-transfer coefficients are introduced in the section describing diffusive-mass transfer at compartment boundaries.

Comment: Page 64: What are the estimates of K_d values for uranium based on?

Response: Estimates of the K_d values for uranium in root-zone soil, vadose-zone soil, and sediments are based on environmental abundance data in the report of the United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR report 1988). This is clearly noted in the revised report.

Comment: Page 64: Check values of chemical properties for BaP. This reviewer suggests MW=252, VP=7.3×10^{-7} P, Sg=0.0038 and H=0.048 Pa-m^3/mol.

Response: We checked the values of chemical properties for BaP and in the revised report, we are using MW=252, VP=7.3×10^{-7} P, Sg=0.0038 and H=0.048 Pa-m^3/mol.

Comments by M. Small and K. Brand

Comment: The key issue of concern in my view is the appropriateness of the idealized "unit-world" approach with its spatially homogenous compartments. Such an approach, while definitely providing insight on broad-scale trends and differences in partitioning between different chemicals is less useful for predicting actual concentrations at actual exposure points. Significant concentration gradients are usually present in the principal medial to which pollutants are released, such as the air, surface water, or ground water, and more customized (media-specific) models are required to capture these variations vis-a-vis the spatial distribution of potentially exposed individuals.

Response: As is noted in the CalTOX reports and as further noted by this reviewer, the CalTOX model is **not** intended to used to perform detailed, full-scale risk assessments of large "critical" sites, but rather as a consistent screening mechanism for smaller sites where full-scale risk assessment might only serve to delay the process of evaluation and remediation. As noted by this reviewer, "In this context, the unit-world option, particularly with such a rigorous and comprehensive implementation as provided by the CalTOX model, appears much more attractive."

Comment: I believe the CalTOX model could and should provide a tool for the intended purpose of the Department of Toxic Substances: as a broad screening mechanism for relative risk and site prioritization. I use the words "could and should" rather than "does," because there is a critical remaining need for verification of the model at actual waste sites. The validations presented in the report, focusing on large-scale regional or national concentration averages, are insightful, but do not directly address the utility of the model for waste-site evaluation.

Response: CalTOX is a regional-scale multi-pathway total exposure and dose model that links environmental concentrations in outdoor air, surface water, ground water, and soil layers to exposure media concentrations in personal air, tap water, household soil and dust, food products, recreational waters, and breast milk. Much of the uncertainty associated with CalTOX is in the intermedia transfer factors, particularly the air / soil, air / water, air / plant, and soil-layer transfers. These intermedia processes are a limiting factor in any transport model, whether simple or complex. (For example, one of the big problems in modeling the carbon cycle is the intermedia transfer of CO_2 at the ocean-atmosphere interface). In order to validate the quantitative estimates of exposure produced by CalTOX, we are working now to compare these values to measured concentrations and predictions by other models. The comparison to measured values is being carried out for three chemical species: (1) a widely used industrial organic solvent with high vapor pressure and low solubility, (2) a widely used non industrial organic chemical, such as a pesticide, with low vapor pressure and very low solubility, and (3) a metal such as arsenic or lead. Data as well data collected at specific sites is being used to evaluate CalTOX predictions. The model will also be validated against other multimedia models, such as the CHEM-FATE model from Health and Welfare Canada and the DOE MEPAS model, and against EPA transport models (SESOIL, EXAMS, ISCLT [with continuous area sources]). However, the results of these effort will not be published in the current CalTOX documents but in a follow-up report to be issued in the middle part of 1993.

Comment: In spite of the very good first-order treatment of uncertainty, more needs to be done to guide the user in their consideration of uncertainty. Guidance will be needed to assist in the choice of uncertainty distributions for each of the input parameters. Further guidance will be necessary to help assessors recognize the possible correlations among variables.

Response: We certainly agree that more needs to be done to provide guidance to user of CalTOX with regard to the assessment of uncertainty and the characterization of probability distributions to be used in an uncertainty analysis. However, it is beyond the scope of the current report to include this information. We are preparing a separate report on the treatment of sensitivity and uncertainty in the CalTOX model. In this report, we are examining four key issues with regard to characterizing uncertainty: (1) uncertainty in predicting the relation between sources of contaminants and concentrations in the accessible environment; (2) uncertainty in quantifying potential dose factors (PDFs) that relate environmental concentrations to levels of exposure; (3) the amount of uncertainty in exposure estimates contributed by the uncertainty in intermedia transfer factors relative to interindividual variability; and (4) the relationship between integrated individual risk and population risk. This strategy will provide scientifically defensible results for describing uncertainty in the development of a risk-based soil cleanup standard. This task will meet the needs of the DTSC to have an analysis of the uncertainty associated with various combinations of assumptions related to the soil-cleanup-calculation process. A sensitivity analysis will be used to screen the parameters that are dominant contributors to overall uncertainty.

Comment: A procedure for setting the dimensions of the compartments needs to be defined before the fugacity approach is applied.

Response: It is correct that a procedure for setting dimensions of compartments is needed before the fugacity approach is applied. However, this information is provided in the report. The thickness or depth of each compartment is discussed in the sections describing these compartments. The area of contaminated landscape is site-specific and is provided as part of the landscape input table. Once this information is provided the dimensions of the compartments are defined.

Comment: Another point that needs further clarification is where these “unit worlds” are to be located: are they to be placed immediately above the contaminant source or are they to be placed over the receptor point of the exposed population?

Response: In the revised report, we make it clear that, indeed, the so-called “unit worlds” are to be placed at the point of contamination, that is over an area of some 500 to 10^7 m^2. However, it is the policy of the DTSC that when an acceptable soil concentration at a site is declared, that the basis for this declaration is that the receptor location (or receptor point) is coincident with the originally contaminated site. This is done to account not only for current land use patterns but also for future land use patterns. Four types of future land use patterns are currently under consideration for the application of CalTOX. These are residential, industrial, commercial, and agricultural land use. Landscape data for the residential, commercial, and industrial landscapes have been developed and are included in the revised report. For the residential landscape, the soil surface is assumed to be mostly free of structures and covered with vegetation. In the commercial landscape, the soil surface is assumed to be mostly covered by buildings or parking and road surfaces; there is almost no vegetation coverage and very little water infiltration to soil. Also, volatilization from soil is reduced substantially. In the industrial landscape, roughly half of the land area is assumed to be capped by structures or road surfaces. Landscape data for the agricultural landscape is still under development.

Comment: Page 3, the text mentions that “transport processes that lead to the dispersion of substances within a single medium” will be considered. As I understand it intra-compartment variation of concentration only occurs between the different phases not within them.

Response: In the CalTOX model, there is no explicit modeling of concentration gradients within environmental media. However, some of the intermedia transfer terms (such as those between soil and air, between ground soil and root soil, and between air and water) depend to some extent on what is assumed about the distribution of contaminants within the compartments involved in the mass exchange. For this reason, we provide a section that describes the assumptions that we make regarding the gradients of concentration within compartments so that the user understands how the contaminant inventory of a compartment is treated in the process of calculating mass exchange rates between compartments.

Comment: Page 36, at the bottom of the page, the sum of v_{wind} and $current_w$ is discussed. However, it is not clear whether this is a vector or absolute sum.

Response: The text has been revised to make clear that this is an absolute sum.

Comment: Page 39, the second paragraph states that the root-zone depth must be "at least 0.4 times the boundary layer depth." This sounds like an error for, if this is the case, then the boundary layer depth could exceed the thickness of the soil layer.

Response: The boundary layer depth is not a real physical depth. It is the depth used to transform the diffusion coefficient into a mass-transfer coefficient at the compartment interface. Its value is selected to provide the correct flux at the interface. A large value for this parameter does not suggest that the actual boundary layer is greater than the compartment depth, but that the gradient used to determine mass transfer is quite small.

Comment: Why is there no diffusion transport between the root and vadose-zone soil compartments?

Response: In the report it is stated that the root-zone soil layer must be thick enough to act as an effective non-escape barrier for contaminants in the vadose zone. For the majority of compounds for which CalTOX will be applied (including such volatile compounds as PCE and TCE), this condition requires only that the root depth be 1 to 2 m or less (and in some cases much less). However, there are some highly volatile compounds for which the depth of the root zone must be as much as 10 to 20 m. For these compounds, the user is given a warning if the root zone is not given the appropriate depth. We felt that the benefits of including this restriction to the program structure were more than balanced by the magnitude of mathematical difficulties eliminated by allowing this restriction.

Comment: In equations 74, 91, and 96, the fraction $1/\rho_{sd}$ is used in the advection terms to determine mass transfer rates. I take this to be ρ_w/ρ_{sd} with the density of water implicitly defined with a magnitude of one. This would units work out provided the densities are in kg/L.

Response: Actually the terms as written are correct. In each of these equations the solid-phase advection terms (*erosion, deposit, resuspend*) have units of kg/m^2-d. When divided by the solid-phase densities, in kg/m^3, and multiplied by the solid-phase fugacity capacity, mol/m^3-Pa, these terms have units of mol/(m^2-Pa-d), which are the correct units for calculating transfer coefficients.

Comments by L. Thibodeaux

Comment: Is L_i^n correctly defined in Eq. 6? I had trouble going from Eq. (6) to Eqs (80) and (81), for example.

Response: The parameter L_i^n should actually be R_i^n. This has been fixed in the revised document.

Comment: What was the reason for not including a gain / loss term for chemical movement from the vadose zone and ground water compartments to surface water compartments. It seems that subterranean seepage from buried wastes into rivers, lakes, estuaries, etc. is a fairly common occurrence.

Response: There are several reasons why we did not include transport from vadose-zone and ground water zone to surface water. Primarily, this would add greatly to the mathematical complexity of the model. In addition, at this point we do not actually model concentration and transport in ground water, only the flux to the ground-water zone, so it would difficult to model transport from ground water to surface water. However, this is certainly an important issue that must be revisited as we apply, validate, and update the CalTOX model.

Comment: The soil compartment creation is very interesting and clever; I think. I am not sure I follow it completely. The write up is too brief in my opinion. It is a radical departure from the norm for handling the soils compartment. Consider a more detailed explanation for an appendix.

Response: This point is well taken, the approach used for the soils compartment involves more effort than would be appropriate to summarize in this document. In order to comply with the need to describe and defend this model in more detail, we are preparing a separate manuscript, which deals only with modeling of the soil compartment. We are planning to submit it to the journal *Environmental Science and Technology* so that it gets wide circulation.

Comment: Continuing comments on the soil compartment model: If mathematical simplicity with good flux simulation is desired, consider the model of Thibodeaux and Hwang (*Environmental Progress*, **1**: 42-46, 1982). Dieldrin emission data from two sources are simulated.

Response: The Thibodeaux and Hwang model was considered for use in CalTOX and is discussed in the manuscript in preparation that is discussed above. The Thibodeaux and Hwang model describes vapor diffusion as being soil-phase controlled and essentially assumes that contaminant concentrations in a soil layer remain constant until all the contaminant in a layer is lost to air. There is an initial depth of incorporation that is considered chemically “wet”. Chemical evaporates from interstitial soil surfaces and vapor diffuses upward through the pores to toward the air-soil interface. As evaporation proceeds, a hypothetical “dry” zone develops near the surface, and liquid vaporization occurs from the plane formed between this zone and the remaining wet zone. Thus, contaminant release occurs by the “peeling away” of successive unimolecular layers of contaminant from the “wet” zone. Over time this process results in a “dry” zone of increasing depth from the soil surface and a “wet” zone of decreasing depth below the dry zone. It is assumed that soil properties are uniform, that no vertical movement of soil solution occurs, that there is no adsorption on soil particles and no chemical reaction in the soil. The model has been validated against measured emissions of Dieldrin during a period of 24 days after application. We elected not to use this model because it was designed for predicting flux over short time periods, not inventories over long time periods, because it had only been validated for one chemical, and because the assumptions of no adsorption on soil particles and no chemical reaction in soil were too restrictive for our purposes.

Comment: Starting on page 50 (of the draft document) the definitions of terms in Equations 59 through 62 and the development of the steady-state models and the transient models in not transparent to me. The fact that you did correct steady-state and transient component mass balances of these compartments is lost by the effort spent in defining terms to render the final equation forms so that easy closed-formed solutions to the linear differential equations result. This is a case where the mathematical end, which is important, got in the way of the engineering / science of the process description. The general reader will have difficulties with the theory section because of this, in my opinion.

Response: The material referred to has been revised to make more clear and concise the development of the transport rate constants. In addition summary tables have been provided for the diffusion terms to make it easier for the reader to trace and reconstruct these expressions.

Comments by D. Hattis

Comment: The treatment of environmental compartments as single boxes, without provision for geographic dispersion, of course means that the system cannot provide more than a plausible upper limit of long term exposures for cases in which sensitive receptors are located at a variety of distances away from a site of emission. With some additional work, or instructions for coupling the current model to conventional air and ground-water dispersion models and population density data, this limitation could be substantially reduced. Additional adaptations would be required in the model to adapt it to circumstances in which the site of contamination were located at a commercial or industrial area.

Response: We agree with the implication of this comment that appropriate linkages of CalTOX with atmospheric and ground-water models would allow users to more realistically estimate the distribution of exposures in the vicinity of a toxic-substances release site. And, indeed, we have initiated an effort to provide such linked models as part of the CalTOX package. However, we do not fully agree with the implication of this comment that without explicit treatment of geographic dispersion, CalTOX can only provide plausible upper limits on exposure. It may be true that for a regional population (within some 10 km of the site boundary) the CalTOX approach serves as an upper bound estimate on exposure and risk. But CalTOX was not designed to characterize exposure within this large region. It was designed to characterize exposure within or at the boundaries of a toxic substances release site. In characterizing this potential exposure, the CalTOX model was designed to give the expected potential exposure and the uncertainty in this estimate.

Comments by C. Travis and B. Blaylock

Comment: The author mentions that GEOTOX has been used to determine the inventory of chemical elements and organic compounds in soil following exposure events. The text is unclear about whether the GEOTOX model is used as the soil compartment or whether GEOTOX is mentioned as background information about soil models in general. In this same section, the authors mention radioactive fallout deposition on agricultural lands (Whicker and Kirchner, 1987). Is the model developed by Whicker and Kirchner incorporated into CalTOX? If not, does CalTOX have a similar component to account for radioactive fallout?

Response: The GEOTOX model is mentioned as background information about soil models in general. The text has been revised to make this clear.
Many aspects of the Whicker and Kirchner model have been incorporated into CalTOX, in particular the treatment of surface soil as a compartment distinct from root-zone soil and the treatment of above-ground plant parts as distinct from the roots with regard to intercepting air and soil contaminants.

The CalTOX model is capable of accounting for radioactive fallout, but would need an added component capable of representing external dose before it could be used for risk assessments of radioactive fallout.

Comment: In CalTOX, vegetation is modeled as a single biota compartment consisting of air, water, and plant lipids. Instead of making assumptions, adding uncertainty to the model results, why not directly incorporate the seven compartment Paterson and Mackay (1989) model? This would not introduce an inordinate amount of complexity to the model.

Response: Because the analytic solution of the CalTOX model is a closed-form algebraic solution, adding five more compartments to the model would add a great amount of unnecessary complexity to the model. Thus, we elected to keep the model as simple as the current science justifies. The seven-compartment Paterson and Mackay model reveals that chemicals typically partition from air to leaves or from soil to roots, and that, for the purposes of CalTOX, a two-compartment plant model could capture this partitioning with as much precision as a seven-compartment model.

Comment: A major drawback of the model is that it does not explicitly model the flow and dilution of contaminants in ground water. By considering contaminant concentrations in the water leaching from the vadose zone soil as an upper bound on ground-water concentration, the model eliminates an extremely important aspect of environmental transport. In addition, by using this vadose-zone soil concentration, the model is likely to greatly overestimate human exposure to contaminants via the ground-water pathway. Since CalTOX cannot predict ground-water concentration where receptors are located (farther away from the site), the model is deficient as an environmental transport model in this environmental medium. While omitting the ground-water transport component may simplify the CalTOX model considerably, it also adversely affects the exposure results.

Response: As is discussed in the report, CalTOX is designed for estimating concentrations in environmental media at a hazardous waste site. In this sense it is a screening level model that allows the user to screen impacts associated with contaminant concentrations in the soil, air, and water media that are contaminated within the prisim or vertical cross section of the a waste site. In their efforts to apply CalTOX as a screening model, the DTSC has explicitly required that the model screen potential risk by first addressing the concentration in the soil layers, surface water, air, and ground water solution at the contaminated site and **not** concentrations in these media available to the first receptor off site. The CalTOX model is fully capable of making adjustments to the these media concentrations in order to determine dilution that results from off-site transfers. But, for its use as a model that realistically address the range of potential exposures on-site, we elected not to include off-site dilution effects.

Comments by R. Green

Comment: The limitations of the model for highly dynamic situations seem apparent. Transport between compartments is highly dependent on empirical parameters which define the effect of the boundary layer on transport rates. Even the Jury approach, to which the compartment model is compared for the flux to air from the soil surface, is not likely to be accurate for highly volatile chemicals soon after "application" because of non-equilibrium conditions. The use of equilibrium coefficients during periods when non-equilibrium conditions exist will surely result in an under-prediction of fluxes into the atmosphere. On the other hand, the compartment model should provide reasonable predictions of system behavior when longer term (weeks to months to years) periods are considered.

Response: This comment is well taken. The CalTOX model was not design for assessing environmental transport during periods of a few weeks to a few days when transport processes (such as flux to the atmosphere from soil) are dynamic and highly variable. Thus, the model would not be appropriate for assessing the impacts of pesticide applications in the first days and weeks after application. Instead CalTOX is intended for addressing processes that determine the fate of contaminants for periods of months to years. We have added language to the document to emphasize the time scales for which CalTOX is intended.

Comment: The qualitative characterization of parameter precision (by way of approximate CV classes) is useful as a start toward characterizing the uncertainty of the model results for a given situation. Perhaps the author could go a step further by somehow indicating the likely direction and magnitude of error that might be anticipated for the various transport and transformation / degradation computations and the impact that such errors would have on the decisions that will be made by regulators.

and

Comment: Concerning our expectations for the accuracy of predictions from such a model for site-specific situations, it is good to keep in mind that even the most sophisticated "leaching models" are not adequate at the present time to accurately predict the C(z,t) relationship for pesticides or other solutes as they move through the soil and vadose zone to ground water. They are, however, useful for screening of chemicals or for providing guidance for designing monitoring programs. Uncertainty in model results arises from the failure of the model to describe mathematically the nature of the actual processes as well as the uncertainty in site characterization and model parameters. The author has addressed these issues at various places in the report, but more could be done to represent the impact of likely errors on the final results in such a way that the users of the model will be guided in deciding how much confidence to put in the modeling results.

also by **Chen**

Comment: It would be useful to know how the individual coefficients of variation combine to form an overall coefficient of variation for the modeling results.

Response: We recognize the need for carrying out the types of sensitivity and uncertainty analyses that the reviewers suggest. Uncertainty analyses of the type suggested are on the list of tasks that are part of next year's effort for CalTOX and work in this area has already begun. At the Asilomar Meeting in October, both input sensitivity analyses and uncertainty analyses were carried out for CalTOX models of fate and exposure for Tetrachloroethylene and Benzo-a-pyrene.

Comment: The author has addressed the need for uncertainty analysis in the Summary and Discussion section of Part III, but such an analysis for Part II would be useful also.

Response: This is a good suggestion and we have added a discussion of the need for uncertainty analyses to the summary and discussion section of Part II.

Comment: p.13, par. 1: Why are pesticide applications represented as a continuous input?

Response: As is state in the report, CalTOX is not intended for short time periods, but for simulation of contaminant behavior over a period of decades. Over this sort of time scale, we expect the application of pesticides to appear as an approximately continuous input.

Comment: p. 6l, par. 2: In line 7 the source is defined as "released to air and deposited to the soil surface"; in the last two lines the chemical is said to be "incorporated ...in the root-and vadose-soil compartments".

Response: For continuous inputs the source term is modeled as being continuously and uniformly added to the air, ground-surface soil, or surface water. For compartments with a specified initial inventory, such as root-zone soil and vadose-zone soil, the source term is considered to be the initial compartment inventory. The report has been revised to make clear this distinction.

Comment: p.8 (Figure 1) and p.63 (Figure 7): The "surface soil" compartment in Figure 1 is called the "ground-soil" compartment in Figure 7 and several other places in the report; seems it would be best to settle on one term throughout the report.

Response: We have revised the report so that the term ground-surface soil is used throughout to describe this compartment.

Comment: p.22, par. 1: The K_{oc}-K_{ow} relationship is sufficiently variable for different classes of chemicals that a single value for the relationship should not be used.

also by **Lorber**

Comment: A minor issue of model flexibility, but on page 15, it is stated that a particular relationship between K_{oc} and K_{ow} is hardwired into the model. Another approach would be to have the user input a K_{oc} value.

Response: The default correlation for K_{oc} is only used when the user does not specify a value of K_{oc} as an input. The option for a user-specified override of the default correlation was not described in the report. In the revised report, this option is described.

Comments by J. Chen

Comment: As stated in the documentation, the model should not be applied to soil spills less that a year old. The selection of one year appears to be arbitrary and based on limited data. The information provided suggests that the time period may be longer or shorter than one year based on soil properties. Is it possible to provide guidance on the appropriate time period based on site-specific soil conditions?

Response: Actually, the selection of one year is not arbitrary, and is selected for three reasons, (1) this model is intended for applications to populations for which the exposure duration is on the order of 10 to 30 years, (2) the calibration of the simplified soil flux model is based on optimizing the box model results to the more precise model over the period from 1 year to 30 years after initial incorporation in soil, and (3) the hydrologic and climate properties used in the model are annual averages and thus the model is not intended for resolution in periods less than one year. We have attempted to make these limitations more explicit in the revised report. Also, as noted by the reviewer, the accuracy with which the model can predict soil concentrations for periods of less than one year after application does vary with the both the chemical properties and the soil properties. However, in this document, we believe that it could only add confusion to suggest that the limit on model’s time resolution for periods less than one year should be considered as chemical and site specific. Since the model is being used for long-term applications, we decided at this point to use the one-year limit on model resolution as a limit for all chemicals and sites. In our current work on model validation, we hope to learn enough to provide more explicit guidance on the limits of time resolution inherent in CalTOX.

Comment: In order to avoid misuse of this model, the documentation should be more specific concerning the kinds of studies to which it is appropriately applied.

Response: In the revised report, it is noted that the model is intended for estimating on-site contaminant concentrations in a time period of from one to thirty years following initial incorporation of soil contamination.

Comment: It would be useful to know how the individual coefficients of variation combine to form an overall coefficient of variation for the modeling results.

Response: See response above under **Green**.

Comment: The assignment of a high coefficient of variation for K_{ow} and a lower coefficient of variation for K_{oc} is questionable. Structure activity models exist which provide very good estimates of K_{ow} for a broad range of organic chemicals. K_{oc} estimates on the other hand are usually based upon regression equations of K_{oc} versus K_{ow} or water solubility for limited ranges of chemicals.

Response: In the revised report, K_{ow} is assigned to the *b* or *c* coefficient of variation (CV) category and K_{oc} is assigned to the *c* CV category. These assignments imply that K_{ow} estimates are expected a have a CV which is as much as an order of magnitude smaller than the CV associated with K_{oc} estimates.

Comments by W. Kastenberg

Comment: Given that only two of the seven compartments are fully dynamic, the beginning of the report (which describes the model as dynamic) is somewhat misleading. Moreover, the author has not discussed the limitations inherent in steady-state compartments. The examples included in the report deal with steady-state inputs. Hence, I would only recommend using CalTOX (at present) for steady-state, i.e. long-term calculations. The report should address the limitations of assuming steady-state for some of the compartments.

Response: Only two of the seven compartments (the root-zone and vadose-zone soil compartments) are fully dynamic because the contaminant residence times in these compartments are orders of magnitude larger than the remaining five compartments. These large residence times are due to the relatively large volumes, masses, and contaminant storage capacities of these soil compartments relative to the other compartments.

Comment: Listed below are landscape properties for California sites used in CalTOX and a forerunner program, GEOTOX. We have been using the California landscape data in GEOTOX and have discovered these differences between inputs for CalTOX and GEOTOX. We are puzzled as to why the differences are so big.

Property	units	CalTOX	GEOTOX
land surface runoff	m / y	0.1	0.23
deposition velocity of air particles	m / d	500	334
biota dry-mass inventory	kg / m^2	0.7	31
biota dry-mass fraction	none	0.2	0.33
evapotranspiration from soil	m / d	0.000515	0.00115
evaporation from surface water	m / d	0.0000043	0.000032
average wind speed	m / d	150,000	346,000

Response: These differences reflect our efforts to improve the data used in the model and make it consistent with information provided in references, which were not available at the time GEOTOX was developed. For example the deposition velocity of 334 m / d used in GEOTOX is a geometric mean value whereas the value of 500 m / d is a arithmetic mean value. The biota inventory of 31 kg / m^2 used in GEOTOX is more typical of a mix forested areas and grasses whereas the value of 0.7 kg / m^2 used in CalTOX is representative of grasses and small gardens. Also, given the variance expected in these parameters, as reflected by the CV scores, with the exception of the biota inventory, we do not agree that the differences noted are "so big."

Comment: Page 45 discusses the use of coefficients of variation (CVs) with respect to input data. The author makes the assumption that all of the uncertainties, both model and data uncertainties, can be represented by a lognormal distribution. This is simply not the case. Defining 5 CV values may be appropriate, given our state of knowledge, but the placement of data in a category is subjective. I would recommend that the user develop their own subjective ranking, or perhaps a group of users along with the Department staff develop an agreed-upon set of CVs. It is not clear to us why log mean CVs are mentioned and what they are used for.

Response: We are a little confused by this comment, because we **do not** assume that all the variance in a given input can be represented by a lognormal distribution. In fact, we elected to use the CV to represent the variance because it does not require any *a priori* assumptions about the shape of a the underlying distribution that gives rise to the variance.

Comments by J. Schaum and M. Lorber

Comment: The claim is made that the model is "dynamic and "time varying". However, I am not sure I would agree with these descriptors. Dissipation and degradation rates are considered, volatilization rates vary as a function of time and soil concentration, and soil concentrations at a source vary as a function of time and do vary over time. However, once releases are estimated from the soil compartments, the remaining compartments are assumed to attain instantaneous equilibrium conditions in broad regional compartments. I have seen these descriptors used more often when referring to models, which loop over time intervals, typically daily time intervals; which do incorporate daily weather impacts; which are much more spatially resolved (river reaches, watershed drainage units, ground-water finite elements, site-specific descriptions of land features for air dispersion modeling, and so on; which are very (very) difficult to use, but which more accurately have time varying contaminant compartments. But it is true that these more complex models also tend to assume instantaneous equilibrium when a contaminant goes from one compartment to another. Still, it seems that the claim of being "dynamic" is more supported in the case of the more complex model.

Response: Although it seems reasonable that increasing the complexity of a model should result in better model predictions, it should be recognized that increasing the complexity of a model can be motivated by the need to make a model more credible. Making a model more credible does not guarantee that it is also more precise. As revealed in the example below one can increase the complexity of a model and thus improve its credibility, but without concurrently improving the precision of the model inputs one does not necessarily increase the precision of the outputs. Figure 1 below illustrates two models for predicting the deposition of a contaminant from the atmosphere to the surface of vegetation and the subsequent transfer to the fruit portion. For a risk assessment, in which we want to characterize the relation between the contaminant concentration in air and the concentration in edible portion of vegetation, a two-compartment model that includes both deposition to leaf surfaces and translocation from leaves to fruits is more credible than a one-compartment model that combines all of the plant components into single "black box." However, if our goal is to maximize precision, the two-compartment model may not be the optimum choice.

Consider the plant system show in Figure 1 below as a one-compartment system bounded by the dotted line. The rate of transfer of contaminant from air to leaf surfaces is *I* mg/d; the plant has a mass of *M* kg; and the rate constant for weathering of contaminant from the leaf surfaces is λ (day $^{-1}$). For this system the steady-state concentration, $C_{T,}$ of contaminant in the overall plant system is given by

$$C_T = I\ /(M\ \lambda)$$

Because we do not recognize the translocation process in this simple model, we must assume that this is also the concentration in the fruit portion of the plant.

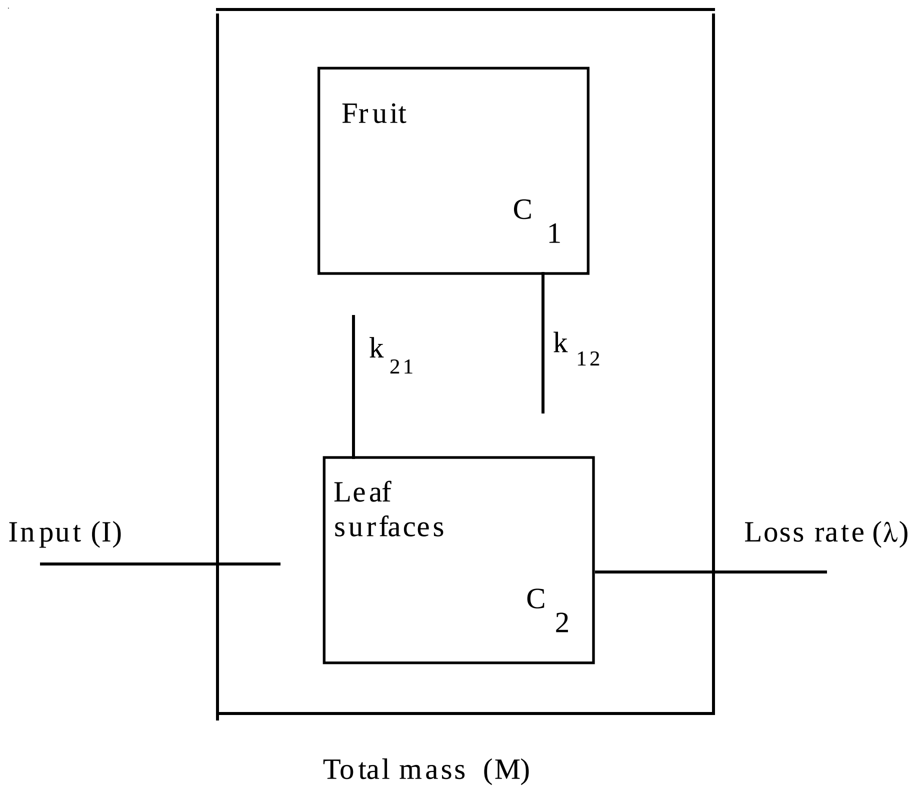

Figure 1

In a two-compartment model that includes mass M_1 of the fruit compartment and rate constants k_{12} and k_{21}, which describe the rate at which a contaminant is translocated between leaf surfaces and fruit, the steady state contaminant concentration in the fruit is

$$C_1 = k_{21} I/(k_{12} M_1 \lambda).$$

In order illustrate how lack of precision in estimating the two rate constants can effect model precision, we assign the parameters M, I, λ, and k_{12} the value 1, M_1 the value 0.5, and k_{21} the value 0.25. In addition, we assume that the parameters M and M_1 have been measured with a geometric standard deviation (GSD) of 1.2, λ with a GSD of 1.5, k_{21} and I with a GSD of 2.0 and k_{12} with a GSD of 3.0. Figure 2 illustrates the spread of concentrations in fruit estimated with the simple (one-compartment) and complex (two-compartment) models. In these figures the expected value or mean of the estimated concentrations is shown by an open diamond and the geometric mean (or median) value by an asterisk. The 90 % confidence bounds are marked by an x and the 95 % confidence bounds are marked by an open circle. We see that, although the median value of fruit concentration estimated using the "complex" model has a lower value than that estimated using the "simple" model, the mean values of fruit concentration for the two models are comparable and the complex model actually has a slightly higher value. This is

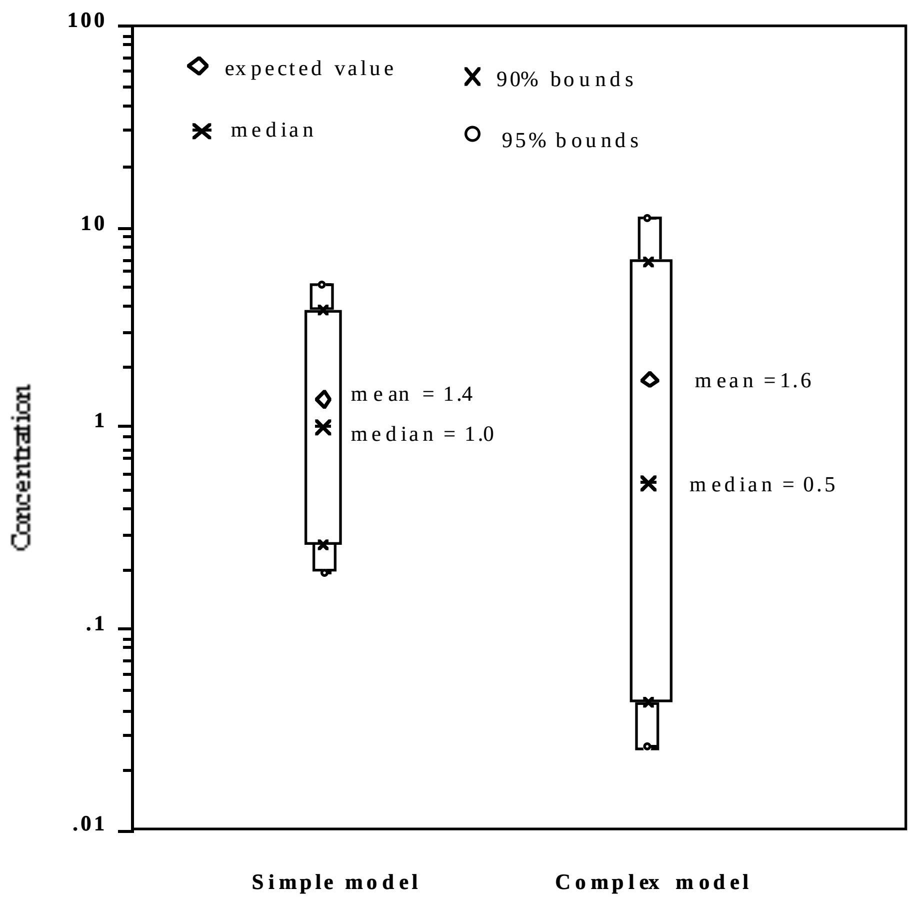

Figure 2

attributable to the large variance in the model parameters. The complex (or more credible) model only gives a lower expected value of concentration when we increase the precision of its parameters. Moreover, the more complex and (supposedly) more credible model gives us less precision in estimating concentration.

This simple example illustrates the logic we used in avoiding the types of complex models that can lead to highly imprecise predictions because they require as inputs many parameters that simply cannot be measured or understood. These models are also almost impossible to validate. Nonetheless, even though CalTOX is not highly complex, we do consider it a dynamic model in the sense that it tracks changes in contaminant concentration over the times scales for which it was designed to track these concentrations, years to decades.

Comment: On the issue of broad regional compartments, I have read and reread this document and have not yet found any crisp discussion on the spatial resolution of this model. Many statements in the report lead me to conclude that the model is appropriate for broad regional extrapolations, and not specific in terms of meters and or kilometers of distance from a source. Thus, can CalTOX be used to evaluate the impact of a Superfund-like site, which can impact neighboring areas such that contaminant levels vary widely, in comparison to a broadly impacted region that has uniform contaminant levels.

Response: CalTOX is model designed to primarily address vertical transport. Thus when horizontal transport processes become significant relative to vertical transport processes, the accuracy of the model will decrease primarily because, by ignoring horizontal losses, CalTOX will overestimate persistence. When we designed the model it appeared that this effect might become important at a scale of 1 km^2. Thus in the revised report, we state in the section titled “Overview of the CalTOX Model” that: “It is designed to model a landscape on the order of 1 to 10 km^2 associated with a toxic-substances release site. Smaller landscape areas can be treated with the model, but in such cases the model is likely to overestimate the persistence of contamination.” However, it should be recognized that, based on our ongoing efforts to validate the model using field studies, this limitation appears to be over-stated and that the model might actually work well for sites of less than 1 km^2 area. This issue will be discussed more in future versions of the CalTOX manual and in the report that we are preparing on validation studies.

Comment: An ongoing problem with the development of models for use by regulators, scientists, or other users; who are perhaps not as attuned to the specific algorithms used, model sensitivities, and so on; is the reliance on the model developers “initial,” “default,” “recommended,” etc. model parameters. There is very little guidance on assignment of parameter values (although chemical parameter values are offered in a separate spreadsheet file). There is also no sense of the sensitivity of the model parameters to model output. There is no easy answer for this problem—whatever a model developer does in the way of guidance on parameter selection is never enough for a reviewer. Still depending on a model developer’s set of parameters, and there are a lot for this model, is a fatal flaw. Would a casual user be able to tailor model runs with parameter changes based on site-specific information, personal preferences on technical assumptions that can be influenced by parameter selection?

Response: Yes, the way the program is currently structured, the user could tailor model runs with parameter changes based on site-specific information, personal preferences, or other sources of information.

Comment: In the report, the assertion is mad the “In CalTOX, the modeling of contaminant transport in surface water is based on the assumption that nearly all the contaminant mass is in either liquid or suspended solid phases.” This may be an appropriate assumption for soluble contaminants, but is clearly an inappropriate assumption for PCBs, dioxin-like compounds, and other strongly hydrophobic and persistent compounds known to accumulate in bottom sediments of water bodies.

Response: It is appears the reviewer has misread the description of the model compartments. We model water bodies using two compartments each with two phases (water and sediment particles). What we refer to as the *surface water compartment* is used to represent the water column portion of a water body and what we refer to as the *sediment compartment* is the sediment zone of the water body. When we state that “the modeling of contaminant transport in surface water is based on the assumption that nearly all the contaminant mass is in either liquid or suspended solid phases," this refers to the fact that we are ignoring accumulations of contaminants in water biota in determining the contaminant inventory of the water column. This does not mean that we ignore the large potential accumulation of contaminants in the sediment column below the water column.

Comment: A minor issue of model flexibility, but on page 15, it is stated that a particular relationship between K_{oc} and K_{ow} is hardwired into the model. Another approach would be to have the user input a K_{oc} value.

Response: See response to comments by **Green** above.

Comment: The assertion is made on page 48 that, "we have developed landscape data sets that are representative of California," but later in the same paragraph, it is stated "Table I summarizes data that we use to represent of the California landscape" (of underlined because it appears to be a typo). Are Table II values to be used in all circumstances, or are there other data sets?

Response: The typo has been fixed. With regard to the second part of this comment, the values originally listed in Table II are not used in all circumstances and there are other data sets. We have developed landscape data sets that are representative of three types of California sites—residential, commercial, and industrial. We are also working to develop data for a fourth landscape type—agricultural. In the revised report, the values of landscape properties are not listed in Table II but are listed in an appendix that has been added to the report.

For the residential landscape, the soil surface is assumed to be mostly free of structures and covered with vegetation. In the Commercial landscape, the soil surface is assumed to be mostly covered by buildings or parking and road surfaces; there is almost no vegetation coverage and very little water infiltration to soil. Also, volatilization from soil is reduced substantially. In the Industrial landscape, roughly half of the land area is assumed to be capped by structures or road surfaces. In Tables B-1 through B-3 in Appendix B of the revised report, we summarize the landscape data that is used to represent these three California landscapes in the CalTOX analyses.

Comment: The CV classes in Table II should be described in a footnote to the Table.

Response: This has been done in the revised report.

Comment: Some comments on the surface water parameters listed in Table II:

1. Suspended sediment of 8.9 kg/m^3. My conversion places this at 8900 mg/L, which is much too high—suspended sediment concentrations are more typically 8.9 mg/L. This could be a typo.
2. Surface water current is 0 m/d, which is probably okay for a lake, although in reality there is never a zero current since there are inflows and outflows to all water bodies.

3. More problematic and related to the above comment is the setting of sediment deposition and resuspension equal. This is clearly not the case for a quiescent water body.
4. What is the justification behind assuming 0.00815 fraction of land area in surface water? For a typical California watershed is less than 1% of the land area from a birds-eye view, comprise of surface-water bodies.

Responses:

1. As noted by the reviewer the suspended sediment load of 8.9 kg/m^3 is too high. But, as far as we can determine, it is only high by a factor of 10. We now use 0.8 kg/m^3. This arises in part because much of the surface water in California is derived in large part from river systems, which have higher sediment loads than lakes. A sediment load of 8.9 mg/L is more typical of lakes and ponds in the eastern parts of the U.S. The erosion rate in California water sheds is in the range of 10 to 500 $tonnes/km^2/y$ and the typical river runoff is 1 to 20 inches/y (13 to 51 cm/y).
2. This current is used only to define the resistance to mass transfer at the surface of a water body. It is not used to establish a hydrologic balance of a water body. The model results are not sensitive to this parameter unless it is a very fast-flowing river, in which case mass transfer at the surface of could be much higher than above a stagnant lake or pond.
3. Because much of the surface water in California is derived in large part from river systems, which are more likely to have a balance between deposition and sedimentation, we elected to make these parameters equal. However, it should be noted that all of the inputs to CalTOX are under continuous review.
4. If we exclude San Francisco and San Pablo Bays, then indeed less than 1% of the California land area is in surface water. If we include San Francisco and San Pablo Bays, than roughly 1.5% of the California land area is in surface water (van der Leeden, F., F.L. Troise, and D.K. Todd (1991) *The Water Encyclopedia* (Lewis Publishers, Chelsea, MI)).

Comment: Similar to the comment above on suspension and deposition of sediments in water bodies being equal, the assumption that suspension equals deposition of soil particulates to and from the air might be questioned—neither assumption is justified as appropriate for default conditions

Response: The assumption that suspension equals deposition of soil particulates to and from the air is made to avoid the situation in which, on a long term basis, the air either accumulates or is depleted of soil particles. In addition, it should be noted that all of the inputs to CalTOX are under continuous review.

Comments To Which We Can Not Respond at this Time

Comment by L. Thibodeaux

Comment: The Sample Applications section is not a convincing test of the CalTOX model. At first glance, it seems as if the model concentrations are within the reported of measured range. However, the reader is not given enough information about how the number sources and ranges of data were selected. For example, with TCE in U.S. cities; how many cities and how were these selected? Another example, for 2μg / kg in biota; is this for all U.S. wheat samples ever analyzed? The source of the data for both PCE and TCE is given. One question that might be asked is were these concentrations selected so as to be within the range of model output values? The report needs to provide more information in the Sample Applications section so the reader has to assume less.

Comments by D. Hattis

Comment: The author focuses attention primarily on producing estimates of chronic (essentially lifetime) exposure. This is the type of exposure characterization that is most frequently required in the assessment of hazardous waste sites. However, there are other potential applications (such as applications to teratogens) in which it would be desirable to have estimates of exposure fluctuations that occur over shorter periods.

Comment: The coefficient of variation values provided in these reports represent either uncertainty (imperfection in knowledge) or interindividual variability (real differences in parameters applicable to different individuals). I am sure that the author is aware of this distinction, but he evidently has not had time enough to fully incorporate it into his work. The coefficient of variation associated with most of the breathing rate and other uptake factors seem to be interindividual variability (although even here, it is not clear that the data have been analyzed in such a way as to uniformly produce estimates of the true long-term variability in intake processes, etc.—for example, my vague recollection is that the water intake variability estimates are based on three-day diaries of individuals' water consumption.) By contrast, the coefficients of variation given for chemical properties, and resulting intercompartmental transfer rates clearly represent uncertainty.

Comment by J. Schaum and M. Lorber

Comment: The parameters in Table II are described as "Landscape properties," which implies that they are physical parameters—which essentially they are. However, they do vary in terms of site specificity. For example, the 1 cm surface layer is a theoretical and not measurable depth. On the other hand, the depth of surface water is more site specific. This is the one category of data where it could be argued that if potential users of this tool may have the ability to easily change these parameters based on specific applications, they may wish to know the importance of these physical parameters and assumptions on model outcome, and the least amount of background on these parameters is provided in this document.

Chapter II. Comments of Reviewers of the Draft Dated January 1993

We acknowledge the following reviewers of the draft version, dated January 1993, of the CalTOX model.

Department of Toxic Substances Control

Site Mitigation Technical Guidance Workgroup
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Barbara Coler, Region 2
Janet Naito, Region 2
Harlan R. Jeche, Region 3
Manny Alonzo,, Region 4
Louis Levy, Region 3

Department of Pesticide Regulation

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John Sanders, Environmental Monitoring and Pest Management Branch
Micheal Dong, Worker Health and Safety Branch

State Water Resources Control Board

Jon Marshak, Central Valley Region
Walt Pettit, Executive Director

Office of Environmental Health Hazard Assessment

Robert A Howd, Pesticide and Environmental Toxicology Section
Julio Salinas, Hazardous Waste Toxicology Section
Robert Brodberg, Fish and Sediment Evaluation Unit
Melanie Marty, Air Toxics Unit
Stanely V. Dawson, Air Toxics Unit
Lynne Haroun, Reproduction and Cancer Hazard Assessment Section

Scientific and Technical Comments

General Comments

1. TGWG / Jeche / Naito: Many of the major assumptions of CalTOX are conservative (plant uptake model, homogenous compartments, leachate as equivalent to ground water concentrations) which result in overestimation in media concentrations and, hence, overestimation of risk / hazard and subsequent calculation of overly conservative soil clean-up numbers. With more pathways, there are more layers of conservatism, leading to more conservative clean-up numbers.

> A mass transfer model is not necessarily conservative. The flux model is designed to match the best estimates of other models. All pathways are considered in the model, but the conservatism exists only if all pathways are assumed to exist at the site under consideration.

2. Reed / Pettit: How does the assumption of homogenous compartments affect the model outcome? The assumption of homogeneous compartments may lead to widespread misapplication if it is adopted as the standard CalEPA model.

> Validation is necessary to determine how the assumption of homogenous compartments might affect model predictions. However, it should be understood that all models attempt to reduce the complexicity of the universe; exclusion and aggregation is done in all models. Because CalTOX considers a long time horizon, highly resolved spatial considerations (such as homogeneity of compartments) are not at all as important as process considerations (degradation and partitioning of the chemical in the environment) for the determination of the cumulative inventory. And determination of the long-term cumulative inventory is more important than the estimation of concentration. Practically speaking, for a large site with heterogenous compartments, CalTOX can be run in parallel for all sub compartments.

3. TGWG / Reed / Haroun / Marty / Jeche / Salinas / Johnson / Pettit / Baker: What assumptions underly the limitation of CalTOX to sites between 1 to 10 km2? The minimum and maximum areas to which CalTOX can be applied should be defined. If the model has a specific lower limit, this should be stated; if the model has no upper limit, this should be stated. Since most hazardous waste sites are roughly four orders of magnitude smaller than 1 km2, how accurate and robust would CalTOX be for such sites? ATES needs a model for small sites (dry cleaners, etc.). Why would the model overestimate in smaller landscapes? In Part II on page 72, CalTOX is referred to as a regional-scale model, whereas, in Part III, it is stated that CalTOX is suitable for use at small sites. Clarify.

CalTOX is a box model which assumes a slow flow through using annual wind speeds for outdoor air. CalTOX models vertical, not horizontal, movement. Because CalTOX ignores horizontal losses, the boundaries of the box are less important for larger sites, because the loss from the box is minimal. However, for specific chemicals at smaller sites, the loss at the boundaries can be significant and then the model breaks down. The site size at which the breakdown would occur is not known but will be tested in the validation studies using field data. It should be noted that soil, not air, is the primary compartment of concern at sites.

4. Salinas / Haroun / Pettit: There should be a discussion on how CalTOX is intended to be used and how results should be interpreted. There should be a clear presentation of the assumptions, conditions and limitations of the model.

The assumptions, conditions, and limitations of the CalTOX model will be clearly described in the executive summary. Among other limitations, the CalTOX model is not intended for use in performing detailed, full-scale risk assessments of large sites, but rather as a consistent screening mechanism for smaller sites where full-scale risk assessments may only delay the process of evaluation and remediation. CalTOX is a box model with the site boundaries representing the box boundaries. Therefore, the model does not look at off-site receptors.

5. Marty: How readily adaptable is CalTOX to evaluating health hazards from facilities which emit chemicals into the air? ATES needs a model that can be adapted for a wide variety of sources and that can work with dispersion models such as ISCST.

CalTOX is a core product made up of several smaller models and can be considered essentially modular in nature. Therefore, it can be modified in a number of ways to fit program needs. For example, the fate and transport model may be used separately from the exposure model, and various dispersion models for air and ground water may be adapted for use with CalTOX.

6. TGWG: What is the accuracy of CalTOX? An order of magnitude accuracy is not adequate for the determination of soil clean-up levels. The accuracy of the primary migration pathways (vadose zone, air, ground surface) and exposure pathways (soil ingestion, soil contact, inhalation) should be demonstrated first.

Results using CalTOX will be potentially more defensible on a scientific basis than other methods currently in use for predicting risk because of its consideration of fate and transport, its use of scientifically-based algorithms, and its ability to utilize site-specific parameters. The use of the word "accuracy" may be applicable for the ability of the model to predict chemical concentrations in environmental and exposure media, since is is possible to compare the prediction of the model to environmental sampling and personal monitoring data. However, the use of "accuracy" for the risk assessment section of the model is misleading, since risk assessment is based on a series of unprovable assumptions, and there is no way to gauge the "accuracy" of any risk assessment methodology.

An order of magnitude "accuracy" is the best that any risk assessment method would be able to predict.

7. TGWG / Anderson / Coler / Salinas / Johnson / Haroun / Marty / Marshack and Pettit / Howd: Verification program for CalTOX should greatly improve the reliability of the environmental fate modeling portion. CalTOX should be verified at sites representing a wide range of hydrogeologic situations. Validation of CalTOX must be performed by comparing to approved risk assessments using a variety of pathways and chemicals. Validation is required since CalTOX may be considered an extension of a safety study. Validation of CalTOX should be carried out by running the model independently of a validation data set (not calibrated against a data set). Validation / verification could cover specific pathways (like dermal), specific compartments (like plant uptake), and should consider the comments of Small and Brand (Carnegie Mellon). The results of any validation or verification should be included in this document. A comprehensive case study (a worked out example of application) should be included either in this document or in a users manual. Evaluation of the model with actual site data, comparing results with traditional risk assessment methods, should be carried out.

The Office of Scientific Affairs (OSA) is committed to a validation process. CalTOX model equations will be validated against other multimedia models, such as the CHEM-FATE mode from Health and Welfare Canada and the DOE MEPAS model, and against EPA transport models, such as SESOIL, EXAMS, and ISCLT (with continuous area sources). Comparison to measured values is being carried out for three chemical species: 1) a widely used industrial organic solvent with high vapor pressusre and low solubility, 2) a widely used non-industrial organic chemical, such as a pesticide, with low vapor pressure and very low solubility, and 3) a metal such as arsenic or lead. OSA toxicologists will run CalTOX on a variety of sites that have acceptable site characterization data and risk assessment reports.

8. TGWG: Suggested evaluation procedure: 1) compare CalTOX with site risk assessment; 2) perform a sensitivity analysis to identify input parameters that can be obtained cost effectively on a site-specific basis and the methods for obtaining them; 3) perform the uncertainty analysis as proposed in Part IV. Include TGWG in the verification process.

The Office of Scientific Affairs (OSA) would appreciate input from the Technical Guidance Workgroup on sites with acceptable site characterization data and risk assessment reports that could be used for comparison with results generated by the CalTOX model. Sensitivity analysis could be performed to determine the most important input parameters at these sites. Then solicitation of information on methods for obtaining site-specific values for these parameters could be carried out through discussions between the technical staff of the Department.

9. Howd: Evaluating the success of CalTOX should include: the relative amount of training required to use the model, how long it takes to evaluate a site with CalTOX, and how believable the results are.

> The Office of Scientific Affairs agrees that these evaluative parameters should be considered in the testing of the model.

10. Salinas: It would be more appropriate to refer to the model as a transport or distribution of contaminants model rather than as an emissions model.

> The Office of Scientific Affairs believes that the term, "emissions", is the best descriptor of the model's capability at present.

11. Salinas: The model does not consider the transformation of chemical in the environment to more toxic chemicals. Chemical transformation is considered to result in detoxication and disappearance from the environment.

> CalTOX considers one chemical at a time and is not capable of dealing with two chemicals at once. For those circumstances in which a chemical may "disappear" because of transformation to a more toxic chemical, CalTOX should be run again for the more toxic chemical. In this second run, the reactions occurring in the environment would provide an input (or gain) of the chemical to the compartment where the reaction takes place. See Part II, Figure 2. Without doing this, an underestimate of risk is possible for certain chemicals, such as, TCE to vinyl chloride or chromium III to chromium VI.

12. TGWG: Define "low concentration". What is the accuracy of CalTOX for "high concentrations"?

> A low concentration for CalTOX is a concentration below the solubility limit for the chemical under consideration. In regard to high concentrations, the model does not handle concentrations of chemicals which exceed the binding capacity of the chemical in any phase (i.e., solubility in water, pressure limits in the gas phase).

13. Salinas: The consideration of only vertical migration is unrealistic and results in overestimating chemical concentrations in air and ground water, since these compartments are acting as environmental sinks in CalTOX.

> The air compartment is vented by cross-wind flow and, thus, is not acting as an environmental sink. At present, the assumption in CalTOX is that there is no dilution of the vadose zone leachate. This is intentional.

Part II

14. Marshack: CalTOX cannot manage complex hydrogeologic conditions, and consideration should be given to fate of chemicals in complex geology.

> CalTOX does not deal with variability in soils. No model addresses this issue. The more complex models work no better and require more input data. Part of developing CalTOX involved doing a sensitivity analysis of the parameters required for more complex models and using the results of this analysis to collapse parameters and/or assumptions into a simplified model.

15. Marshack: Consideration should be given to the fate of chemicals that are highly mobile in permeable soils (benzene, chromium VI).

> CalTOX is capable of modeling mobile chemicals in permeable soils.

16. Marshack: Leachable soil concentration data rather than total concentration data should be considered as a more accurate measure of a chemical's ability to migrate to ground water.

> At present, CalTOX assumes the chemical concentration in leachate from the vadose zone to be the upper bound concentraton in ground water.

17. Pettit: It is doubtful that the leaching portion of the CalTOX model is capable of predicting sufficiently accurate results for specific sites.

> The validation process will be addressing this question.

18. Jeche: Prove that fugacity works.

> Fugacity is the basis of a number of environmental fate and transport models. The verification and validation of the CalTOX model will provide proof for using fugacity-based modeling of transport and transformation.

19. TGWG: CalTOX should be compared to more complicated submodels within key compartments (like the vadose zone compartment) to see which approach more accurately calculates risk/hazard.

> This will be accomplished as the model is verified and validated.

20. TGWG/Jeche: How does CalTOX handle ionic organic chemicals, radionuclides and inorganic chemicals, since fugacity models are not applicable to these classes? How accurate is CalTOX in its treatment of these classes compared to its treatment of nonionic organic chemicals? Are there models better than Jury's for inorganic chemicals?

> For an ionic organic chemical, the Kow value entered into CalTOX must be the value measured at the pH of the soil at the site. Then transport modeling is

carried out using site-specific partition factors to estimate the inventories for all compartments. However, it should be noted that there is no good way of predicting KD from Kow values for ionic organic chemicals. Therefore, KD values must usually be measured. If the chemical under consideration is nonionized at the site, the fate and transport of the chemical in its nonionized state is determined using fugacity-based modeling. For inorganic chemicals, the assumption is made that transport can only occur by the chemical dissolving in and flowing with water or by resuspension on particles. The gas phase is ignored, and partitioning between only the two phases of liquids and solids (water and soil) are considered. Therefore, KD values must be measured or otherwise determined for water-phase/solid-phase surface soil, water-phase/solid-phase root-zone soil, water-phase/solid-phase vadose zone soil, and water-phase/solid-phase sediments. These KD values are then used to estimate the inventories for all compartments. For radioactive chemicals, these chemicals should partition between phases of a compartment and between compartments in the same way as their non-radioactive counterparts. The accuracy of the model for predicting environmental fate and transport will be dependent on the reliability of the measured partition coefficients. The validation of the CalTOX model will include the modeling and measurement of ionic and inorganic chemicals.

21. TGWG: How can CalTOX accurately represent the variety of surface waters (rivers, lakes, estuaries)? Its accuracy needs to be demonstrated.

At present, CalTOX looks at surface waters in a generic manner and does not have any specific surface water models embedded within it. However, differences among ponds, lakes, and rivers can be specified in the CalTOX model by the specification of water depth, water velocity, sediment depth, and depth/area ratio.

22. TGWG/Salinas: How does CalTOX deal with chemicals which interact with each other in the environment? What is the effect of chemical mixtures on the fugacity concept? If CalTOX cannot consider interactions between chemicals, this should be stated as a caveat.

It is unlikely that there will be significant interactions between chemicals at environmental concentrations. CalTOX deals with a single chemical per run. The assessor must add risks and hazards of multiple chemicals manually.

23. Brodberg: Will CalTOX accept a direct input into the sediment compartment, for example, when dredged material might be sampled?

CalTOX accepts direct input for soil concentrations in root-zone and vadose zone only.

24. Salinas: Use terms such as transport or migration rather than dispersion or advection in this section. Since dispersion refers to migration of solid or gases in the atmosphere, it is not appropriate to refer to dispersion of an inorganic chemical in soil. Since advection refers to horizontal air transfer, it is not appropriate to use this term in a model which does not deal with horizontal migration of chemicals.

> The terms dispersion and advection are used in this section as they are used in standard textbooks on transport and fate.

25. Salinas: Pg 3-7. Clarify the definition of compartment. Are the phases within a compartment considered to be subcompartments? How do phases interact within each compartment? How do phases interact between compartments independently from the other phases?

> Phases are not subcompartments; they are constituents of the compartments (gas, solid, and liquid phases) which are assumed to be in chemical thermodynamic equilibrium (see pg 5, first paragraph, December 1992 draft version).

26. Howd: Pg 8, Figure 1. This figure indicates that vadose zone soil does not output to or receive input from anything (a single arrow passes through).

> The figure has been corrected to show that the vadose zone receives input from the root zone soil and outputs to ground water.

27. Howd: Pg 8, Figure 1; Pg 12, Figure 3; Pg 11, Table I; Pg 17. These figures and table indicate that there is no upward motion of contaminants from the vadose zone to the root zone; whereas, it is stated on pg 17 that chemicals can move upward (as is expected). Correct the inconsistency.

> The text on pg 17 has been corrected by removing the reference that contaminants in the vadose zone soil can move upward to the root zone. At the present time, the model only addresses downward movement through the vadose zone soil.

28. Johnson: Pg 9. Define "quasi-steady state".

> In the context of this statement, quasi-steady state refers to the assumption that gains or losses within the soil compartments are slow enough that other compartments behave as though they are in steady state relative to soil.

29. Salinas: Pg 11, Table I. Transformation and decay are not included as gains in this table but is pictured as a gain in Figure 2. Losses from vadose soil to surface soil and from surface water to air are not included in Table I.

Transformation and decay are not explicitly considered by CalTOX at present. There is no loss from vadose soil to surface soil in CalTOX. Diffusion to air from surface water has been added to Table I.

30. Salinas: Pg 12, Figure 3. The Biota compartment should be renamed Plants. The flow between compartments is unnecessarily complicated or unrealistic, for example, surface water has no pathway to biota. Justify combining minerals and lipids in a single phase.

The Biota compartment has been renamed Plants.

31. Jeche: Pg 13. How does CalTOX handle a one-time release?

CalTOX assumes that a one-time release or contamination of soil has occurred at least one year prior to the time that the chemical concentrations in soil were measured.

32. Haroun / Dong / Howd: Pg 13. Although the text indicates seven compartments, eight are described.

The text will be revised to clearly state that CalTOX considers seven environmental compartments and that concentrations in ground water are presently represented by vadose zone leachate concentrations.

33. Coler / Salinas / Marty: Pg 14. Explain the box model vs gaussian plume model. Since the box model assumes uniform concentrations, overestimations may occur. The box model is substantially different from the gaussian plume model used by ARB. The box model for the atmosphere is overly simplistic, and results would be unpredictable.

This section has been expanded to include a discussion of the gaussian plume model.

34. Baker: Pg 14. The box model should provide conservative estimates of air concentrations for area sources such as sites undergoing remediation. However, for off-site air concentrations, a gaussian dispersion model is recommended rather than diluting concentrations from on-site to off-site receptor points.

The CalTOX model addresses only on-site receptors. It is hoped that an appropriate scientifically-based air dispersion model can be added in the future to estimate off-site air concentrations. Any such model would be subjected to the same peer review as this version of CalTOX.

35. Jeche: Pg 15. Root and leaf uptake should remain separate so that final concentration in each part can be considered, for example, in regard to the concentration eaten and by what species.

Other, more complex fugacity models for predicting plant uptake were analyzed and then collapsed into a simplified model. The plant uptake model discussed here is not intended to result in concentrations of the chemical in roots and leafs for eventual exposure via the ingestion route. Rather the plants compartment represents one of the seven compartments which are involved in the fate of chemicals in the environment.

36. Johnson / Salinas: Pg 17. Provide a better definition for root-zone soil, like a zone below which no direct volatilization occurs. The assumption that the root zone is considered the non-escape depth should be emphasized.

The root-zone soil layer must be thick enough to act as an effective non-escape barrier for contaminants in the vadose zone. This condition requires that the root depth be 1 to 2 m or less for the majority of contaminants at hazardous waste sites. For those highly volatile chemicals for which the depth of the root zone must be 10 to 20 m, CalTOX warns that that the root zone is not given the appropriate depth. The text discussing the root-zone soil will be revised.

37. Baker: Pg 22-24. The approaches described for estimating the fraction of a contaminant that may be bound to aerosol particles in air need to be validated or compared to emission equations in U.S. EPA "Air / Superfund National Technical Guidance Study Series".

The air model is based on an extensive review of the aerosol / atmospheric physics literature. The papers used are the most widely cited papers in this literature. We believe that such papers should provide the primary inputs for CalTOX.

38. Howd: Pg 23. Using the weight and surface area values given in this discussion results in an average diameter of 0.04 micron. This seems too small and may affect air / particle partition ratios.

The number, 0.04, is the ratio of volume to area for a particle, equal to 2 / 3 of the radius. Therefore, the diameter is about three-fold larger or around 0.1 micron. This is a small but reasonable particle size.

39. Jeche: Pg 25. Discuss in greater detail the literature supporting the assumptions made in the Plants (Biota) section.

We believe that this section provides sufficient detail.

40. Jeche: Pg 38. The soil transport section of CalTOX is based on a model verified for agricultural soils. Can CalTOX be used for urban compacted soil, clay stone, rocky, or clay and sandy soils?

Soil types are defined by the properties of bulk density, moisture content, total porosity, and fraction of organic carbon. Values for these properties and their distributions may be entered as site-specific parameters into CalTOX. Alternatively, default parameters may be used which represent specific soil types found in California.

41. Johnson: Pg 39. Is soil roughness considered in regard to soil boundary layers in CalTOX? Do the calculations at the bottom of this page assume a normal distribution for a geometric standard deviation? Is this appropriate?

Boundary layer thickness is an input to model. Therefore, soil roughness is neither included or excluded and is dependent on how the input data are developed. The default value used in CalTOX is based on experiments using pesticide applications. The value is derived from water evaporation relative to soil moisture content and implicitly includes a roughness factor. The calculations assume a log normal distribution.

42. Salinas: Pg 39. Space equivalent to the discussion on precision of estimates should be given to accuracy of the estimates.

The precision and accuracy of estimates is discussed in Part IV.

43. Jeche: Pg 40. TCE data do not provide a broad enough range to compare with other organic chemicals.

The graphical representation of predicted TCE concentrations and surface flux is intended as an example, not as a validation for the overall modeling capabilities of CalTOX for all organic chemicals.

44. Johnson: Pg 41, Figure 6. The Jury model, upon which CalTOX is based, was developed using data over a time period of less than or equal to one year, whereas, CalTOX is intended to model transport over 30 years. Is the time scale appropriate? The x axis in the third figure represents flux and should be in mass/area.time.

It may not be appropriate to extend the Jury model out to a 30 year time frame. More data are needed to validate its use over this period. Therefore, the figures in Figure 6 has been truncated to a 10-year period. Also the x axis in the third figure has been corrected to read mmoles/m3/day.

45. Jeche: Pg 42. It is illogical to assume that radon has the same properties as organic compounds.

The measured fluxes of radon were used to estimate the water side boundary layer thickness above sediments in order to solve equation 56, which provides the fugacity mass transfer coefficient on the water side of the surface-water and sediment interface.

46. Howd: Pg 42-46. Low-volatility, high-Kow chemicals, ionic chemicals, and inorganic ions can be irreversibly trapped in soil pores or into the insoluble soil matrix with time. Lack of parameters for this process may result in excessive loss rates at long time points. This should be considered in the model.

> Those chemicals so trapped do not move and essentially remain in place, because there is no removal mechanism. At present, there is no basis for defining a trapping coefficient and perhaps no need for such a coefficient, since CalTOX does well with these chemicals in validation studies.

47. Reed: Pg 43. The derivation of the flux from the air compartment out of the system is not explained in the text. Is equation 72 the appropriate equation? Clarify.

> Yes. See page 55, equation 72, for derivation of this flux equation.

48. Salinas: Pg 44. Photolytic decomposition of organic chemicals to CO_2 and H_2O is unlikely within the time frame of CalTOX.

> For certain chemicals, such as surfactants and some pesticides, decomposition can proceed quite rapidly.

49. Coler: Pg 45. It is unclear how CalTOX addresses these hydrolytic reactions on a chemical-specific, condition-specific basis.

> First order rate constants must be entered into CalTOX by the user. These rate constants represent the sum of all reactions that occur in the environment.

50. Salinas: Pg 45. Arsenic is not a good example of a detoxification process, since all forms of arsenic are considered carcinogenic.

> Arsenic is discussed here as an example of a chemical which can undergo oxidation and reduction reactions in the environment, not as an example of detoxification via such reactions.

51. Salinas: Pg 47. Reliability and precision are inappropriately used in the discussion of molecular weight. Molecular weight is obtained by adding atomic weights.

> The sentence will be rewritten to state that molecular weight is obtained by adding atomic weights and subtracting the binding energy effect. In molecular weight the whole is not the sum of the parts.

52. Jeche: Pg 47. Kow is important in this model and is used to estimate many other partition coefficients, yet the document states that Kow estimation can be off by as much as 30 times.

The fact that it may be difficult to obtain an accurate measure of Kow does not detract from the underlying scientific theory for its use.

53. Johnson: Pg 48. One must use caution in applying physiochemical parameters at sites. Many such parameters have been derived under laboratory, not field, conditions, and it is not always easy to choose the parameters which appropriately reflect site conditions.

This is correct. Part of the guidance which would accompany the use of the CalTOX model should be a description of appropriate methods and/or criteria for choosing physiochemical parameters.

54. Salinas: Pg 49. If a chemical is sorbed onto sediments, it is no longer part of the solution; therefore, it is conceptually wrong to state that "concentrations in .. waters can exceed .. solubility limit".

This is correct. The text has been corrected and clarified to state that "the observed ratio of inventory to volume in surface water can exceed the solubility limit when there is sorption of the contaminant onto suspended sediments...."

55. Haroun: Pg 49. It would be helpful to cross reference equations 32 to 35 in the discussion on diffusion coefficients.

This is done.

56. Salinas: Pg 54. In regard to the discussion on the air compartment, it is wrong to assume net transfer in a steady state. The adjacent compartments are surface soil and air, not deep soil.

The text will be corrected for clarification. There can be net transfer from one compartment to another in a steady state. In a steady state, gains equal losses within compartments.

57. Salinas: Pg 56. Ocean, not plants, is the major mass fraction of the biosphere.

The sentence has been changed to "terrestrial biosphere".

58. Howd: Pg 57. "Ground-soil" should be changed to "Surface-soil" compartment.

The term will be changed to "ground surface soil".

59. Coler: Pg 63. Discuss more fully the origin and quality of the data used here for these sample applications.

This is beyond the scope of this document.

60. Haroun: Pg 63. Were the reactivities of TCE and PCE included in the sample applications? If so, it should be stated.

> No, the reactivities of TCE and PCE were not included in the sample applications.

61. Salinas: Pg 63-65. Justify the use of the source term concentrations of 0.02 mol/km2.d TCE and 0.01 mol/km2.d for PCE. There are numerical discrepancies between the data on coefficients reported by Howard (1990) and the numbers given in this document for TCE and PCE; for example, Howard reports a Kow equal to 2511 while the document lists a value of 400 for PCE.

> The source term concentrations were obtained by dividing annual use by land area. The correct reference is Verschueren (1983), not Howard (1990). The text has been corrected.

62. Jeche/Salinas/Reed/Howd: Pg 64, Table V. Why use tritium and uranium as examples for a model for organic chemicals?. Omit the tritium example unless it can be expanded for use in validating the model. The text does not provide enough information to understand this table. The production and introduction of tritium and uranium does not correspond with the stated use and purpose of CalTOX. Uranium does not fit the presumptions of CalTOX for interphase transport processes. Since uranium concentrations are not due to continuous atmospheric depositions, the claimed agreement of CalTOX with environmental abundance is confusing.

> Tritium is a good candidate for use in validating CalTOX because it behaves like water and ends up in all compartments, many data exist, and its properties are well characterized. Because tritium is present at the Lawrence Livermore National Laboratory Superfund site, this site and this chemical could be used in the validation process.

63. Salinas/Reed: Pg 66. Figure 7. It is unlikely that PCE would deposit to soil once released into the air as shown in this figure. Why is there movement of PCE from biota to the soil compartment? This is not consistent with Figures 1 and 3.

> Diffusion is a two-way process. When examining the relative likelihood of the loss of PCE from air to surface soil compared to the gain of PCE from surface soil to air, there is almost a thousand times more PCE moving from surface soil to air than there is PCE moving from air to surface soil. Figures 1 and 3 will be corrected to show that transfer can occur from the plants compartment to the root-zone compartment. However, in the case of PCE, it can be seen that the plants compartment is acting as a pump from soil to air, since there is 50 times more PCE moving from soil to plants (and then to air) as there is PCE moving from plants to the root-zone soil.

64. Salinas: Pg 69-72. Summary should be rewritten, omitting historical considerations (pg 69), the discussions on exposure and health risks, and uncertainty (pg 71). The discussion should center around the accuracy, precision, verification, reliability, validity, validation, scientific and legal defensibility of CalTOX.

The summary will be revised to accurately reflect the contents of the section. The validation and verification of CalTOX will be the subject of a separate report.

65. Howd: Pg 81. The Kow definition is inverted.

No, it is not. {mg/L(octanol)}/{mg/L(water)} = L(water)/L(octanol)

Part III

66. Salinas: Intake should be defined as amount of substance. Some terminology used in the document is not consistent with US EPA Guidelines for Exposure Assessment, 57FR, May 1992. Omit potentially from potentially exposed individual. Intake should be referred to as average daily intake. Use the correct citation for the Federal Register reference.

We have attempted to keep the terminology consistent with Risk Assessment Guidance for Superfund, Part A. "Potentially" has been removed from the definition of intake. In Appendix A: Terminology, we have indicated where and why our definitions differ from U.S. EPA documents. We use the term "intake" rather than "average daily intake", because "intake" is the term used in the equations described in Risk Assessment Guidance for Superfund, Part A. All citations will be checked.

67. Haroun: Make terms consistent between the intake equations and the CR/BW parameters listed in Table II, Part IV. Either modify the equation or give the equations for obtaining the listed CR/BW values.

The tables in Part IV has been corrected to make the terms consistent with the equations in Part III in regard to CR/BW values.

68. Coler: When certain exposure pathways are considered in CalTOX, do they always drive the results? For example, when plant uptake models have been used, plant uptake became the significant pathway even though this pathway was not the pathway of concern at the site.

The question is: is the model wrong in its prediction of the relative importance of certain pathways, or are regulators wrong for not considering those pathways? CalTOX will highlight those pathways important to consider. For example, plant uptake and subsequent ingestion of contaminated foods may be important an important pathway for lipid soluble chemicals, such as dioxins.

69. Naito: Plant uptake models have a high degree of uncertainty, and quantification of this uncertainty would be useful. Validation using fruit, vegetable, and nut plants would be useful.

McKone has two papers in the literature addressing this uncertainty, and these are listed in the references. Validation of fruits, vegetables and nuts is a good idea and will be considered in the validation exercise.

70. Naito: Three soil compartments are described in CalTOX. Which soil concentration is used in CalTOX to calculate soil remediation goals?

CalTOX accepts input values for root zone and vadose zone soil concentrations.

71. Jeche: Model assumes a rural setting. Discuss how to apply to other settings.

CalTOX provides algorithms for pathways which include food intake of produce, meat, dairy products and eggs grown or raised on site. Those pathways which are not applicable to the site under study may be excluded by entering a zero value for specific exposure parameters as listed in Part IV, Table VI.

72. Salinas/Haroun: There are many errors in the equations in Part III (unbalanced units, numerical errors in formulas).

These errors have been corrected.

73. Jeche: Pg 9. We do not have sites with surface water. Our concern is with water run-off.

Certain human exposure input parameters may be set to zero to exclude exposure pathways (such as water needs provided by surface water) that are not applicable to the site under study.

74. Salinas. Pg 10. Inter-media transfer factor is not clearly explained. The advantages of using this approach are unclear; the approach appears to be inconsistent with US EPA guidelines and to add unnecessary complexity to the model.

The discussion has been revised to more clearly describe the inter-media transfer factor approach and its consistency with US EPA guidelines.

75. Salinas: Pg 11. If the spill has occurred in the past why not just sample the site?

At most hazardous waste sites, investigation begins with limited sampling. If the sampling data are judged to be adequate, the chemical concentrations for root-zone and vadose soil layers may be entered into the CalTOX model. CalTOX will then predict the levels of the chemical in other environmental media, the potential exposure to on-site human receptors, and the risk/hazard posed by that exposure. Alternatively, with limited site characterization data, CalTOX may be used to calculate a preliminary remediation goal for the site.

76. Salinas / Haroun: Pg 11. Define chronic. What is "lifetime exposures to the chemical .. "? 30 or 70 years?

Lifetime exposures to the chemical, in terms of exposure duration and averaging times, are input parameters to the model and, therefore, may be whatever time interval considered appropriate. As mentioned elsewhere, it is expected that the Office of Environmental Health Hazard Assessment will review the human exposure parameters. At present the default values for exposure duration and averaging times are 14 years and 25600 days, respectively. The model is intended for exposure durations from 10 to 30 years.

77. Reed: Pg 11. Provide the basis for the assumption that soil contamination has occurred more than one year before soil concentrations are measured.

CalTOX is not designed to model fate and transport during the period of days and weeks immediately after contamination occurs when environmental transport processes are rapidly changing. Rather, the model is intended for the modeling of environmental fate and transport months and years after the contamination has occurred. The simplified soil flux model within CalTOX has been calibrated using optimized box model results over the period from one to 30 years after contamination has occurred. The text has been revised to clarify the basis for this assumption.

78. Jeche: Pg 11. We do not allow residential use, the growing of food, the grazing of cattle, or the raising of chickens on site. If the model does not consider dispersion, there are no sites in the 1 to 10 Km2 size range, and the DTSC cannot consider risks to adjacent schools, residents, etc. The model does not consider the on-site industrial worker. For these reasons, the third and fourth conditions of the CalTOX model are invalid.

A residential scenario is often considered at hazardous waste sites. Rural sites or sites where food is grown for home consumption are occasionally encountered. As mentioned elsewhere, tests will be performed to determine the site size limits for CalTOX. Model parameters can be adjusted to consider the on-site industrial worker.

79. Salinas / Haroun / Jeche: Pg 12. Does Cap refer to total or respirable particulates? Define air particles.

No distinction is made between respirable and total particles. According to the U.S. EPA guidelines, all airborne particles that have moved past the mouth would be considered in estimating intake. The definition of Cap has been revised.

80. Haroun: Pg 13. The assumption of an exposure frequency of 365 days per year is reasonable only for a residential scenario. Consider rewriting Part III to make the text receptor neutral, rather than assuming that the receptor is a resident.

> This is a good suggestion and the document has been so revised.

81. Jeche: Pg 15. Household soil should also include air-borne dust blown into the house.

> At present, the chemical concentration in household soil is considered equal to the chemical concentration in surface soil. It is implicit in this assumption that all household soil comes from dust blown into the house.

82. Reed / Howd: Pg 16-17. The distinction between exposed and protected produce is not clear. Protected produce are not protected from water contamination. Is protection from rain splash a criterion for classification? If so, it should be stated. Please explain the distinction of protected crops and how it relates to the indicated fruit and vegetable classes. Define edible plant parts.

> The text has been corrected to indicate that protected produce refers to protection of edible parts from exposure to air contaminants. Edible plant parts are those parts which can be eaten.

83. Jeche: Pg. 17. Is it contradictory to state that root crops are protected from air and water by soil, yet soil may be contaminated by rain washing contaminants from air and that soil can subsequently contaminate protected crops?

> The transfer of contaminants from air to soil is considered in the fate and transport portion of the CalTOX model (see Figures 1 and 3, Part II). In the exposure portion of CalTOX the soil concentrations used are those estimated by the fate and transport model from all environmental processes.

84. Marty: Pg 17. Citrus fruits should not be classified as a protected crop, since chemicals can penetrate the peel, and peel may be used as a spice or flavoring agent.

> Strictly speaking, this is true; however, reasonable consideration should be given to the total mass that could be ingested.

85. Jeche: Pg 21. The rainsplash partition coefficient does not consider the height of edible parts of plants.

> It is not necessary for contaminated surface soil to splash onto the edible parts of the plants in order for the plant to become contaminated. The CalTOX model assumes partitioning of the chemical from soil to all plant parts.

86. Brodberg: Pg 26. Is there a factor for actual assimilation of chemical from fish to humans?

> The actual assimilation of the chemical in fish by humans via absorption by the gastrointestinal tract is not considered, since the ingestion intake equations provide estimates of administered, rather than absorbed doses.

87. Salinas: Pg 50. Where is the equation relating surface soil to air particulates for input into equation 50?

> The concentration of chemical bound to air particles, Cap, is estimated by the transport and transformation model described in Part II from concentrations measured in root-zone and vadose zone soil.

88. Salinas: Pg 53. The dust concentration in a home is a default value and not the result of transport and deposition. Multiplying dustin times Cg overestimates the chemical concentration in dust.

> Multiplying dustin by Cg would not necessarily overestimate the chemical concentration in dust. It should be noted that this is not a critical area of the model. The Murphy and Yocom 1986 study may not be the most appropriate citation to use as the source of the concentration of indoor particles attributable to surface soil, but a better reference has not been located.

89. Salinas: Pg 54. Even using an alpha of 0.0001, an overestimate of concentration may occur because the house floor is, at best, in contact with surface soil, not root-zone soil.

> In the CalTOX model, surface soil is a very thin layer no more than one cm in thickness. Therefore, the foundation of the house would most likely rest on root-zone soil.

90. Salinas: In equations 57, 68, 70, 76, 78, 79, 80, and 81 the units do not balance. Equation 71 states that dermal uptake is a direct function of the thickness of skin, that skin facilitates penetration. Explain. In equation 74, fdc should be 1.0, and units do not balance. For equation 78, is FC the fraction contacted of body surface, time, or environmental medium? What is the 1.7 factor in equation 79? Equation 80 is arithmetically and conceptually wrong. The units do not balance, and the equation states that dermal uptake is a function of soil layer thickness on skin and inverse function of soil concentration (the higher the concentration the lower the uptake). Also uptake cannot be a function of soil layer thickness because only the contact zone is subject to penetration.

> Those equations in which the units do not balance have been corrected. For equation 57, the bathroom ventilation rate has been changed from m3/hour to m3/minute to balance the units. Equations 68 and 70 are correlation equations,

not mathematical predictions; therefore, the units will not balance. Equation 71 is not a dermal uptake equation. It is an expression of the absorption ratio. For equation 74, the fdc has been changed to 1.0. For this equation as well as equation 76, the exposure frequency has been changed from days/year to episodes/year to balance the equation. In equation 78, FC is the fraction of soil on the skin which is contaminated soil (Cg). Also, for this equation, EF has been changed to events/year to balance the units. The 1.7 in equation 79 is the conversion factor that adjusts for the difference in skin thickness when fully hydrated (in contact with water) and when less hydrated (in contact with soil) in units of cm3 water/cm3 soil. The equation will now balance. Equation 80 has no concentration term and, thus, is not the inverse function of soil concentration. The relationship between the thickness of the soil layer on the skin and penetration is discussed in McKone and Howd, 1992. This reference will be included in the text.

91. Jeche: Pg 56. How accurate is an average bathroom ventilation? How much does this really affect exposure?

The ventilation rates in the shower, bathroom, and house and the equation utilizing the ventilation rate of the bathroom were based on assumptions and data provided in a peer-reviewed journal article, McKone 1987.

92. Reed: Pg 56. How are the sizes/volumes of the bathroom and house considered in equations 57 and 58?

The default ventilation rates provided in Table III (Part IV) are based on the assumption that the volumes of the shower, bathroom, and house are 2, 10, and 600 m3 and the number of air changes per hour range from 2 to 10 in the shower, 1 to 10 in the bathroom, and 0.5 to 2 in the house (see McKone 1987, McKone and Bogen 1992).

93. Howd: Pg 57. What are the units of phi?

Phi is unitless. The text has been corrected.

94. Reed: Pg 58-60. According to equations 63 and 64, FI for equations 65 and 66 should have the units of hour/day rather than unitless as stated.

FI is unitless. The denominators of equations 63 and 64 have been corrected to provide the units of h/d to the numbers 16 and 8. The numerator of equation 64 has been corrected to provide the units of h/d to the number 8 in "8BRr.

95. Howd: Pg 58-60. Is the time spent in the shower/bathroom subtracted from total time spent breathing at home for calculating total breathing at home? Clarify and correct if necessary.

No.

96. Jeche: Pg 61. If there is insufficient knowledge, why consider the transfer of chemicals through the skin and into blood?

CalTOX is a model based on the Risk Assessment Guidance for Superfund / Human Health Evaluation Manual(RAGS / HHEM). RAGS / HHEM does consider dermal uptake, therefore, it is appropriate for CalTOX to address this as a scientific issue.

97. Reed: Pg 62. In equation 67, is SA in cm2 or m2? Is CF 10L / cm / m2 or 10L / (cm times m2)?

SA is in m2. CF is 10L / cm times m2. The text has been corrected.

98. Salinas / Reed: Pg 64-66. Cite references for the approach described in ii. Cite references for equations 68-70.

The reference is: T.E. McKone and R.A. Howd, Estimating dermal uptake of nonionic organic chemicals from water and soil: I. Unified fugacity-based models for risk assessments. Risk Analysis, 12:543-557, 1992. This has been stated in the text.

99. Jeche: Pg 70. The model does not take into account that most adults work and are not home 24 hours a day.

The model does consider this for specific appropriate parameters.

100. Howd: Pg 72. The definition of ARsoil is uninterpretable; there are extra words.

The typographical error in the text has been corrected.

101. Jeche: Pg 75. Ground and Surface Water: 3) Is soil contaminated by irrigation water and irrigation water itself two different pathways? 5) How much seafood would be contaminated? Is it assumed that all sites are on the coast?

The CalTOX model assumes that the soil is the primary source of contamination. Runoff from contaminated surface soil may enter surface water and leachate from the vadose zone acts as the surrogate for ground water (see Table I, Part II). Therefore, soil may be the source of contamination of irrigation water but is not assumed to be contaminated by irrigation water. However, the contaminated irrigation water may provide an exposure pathway as listed. The amount of contamination of seafood would depend primarily upon the partitioning of of the chemical under consideration between the surface water and fish tissue (see the discussion accompanying equation 20, Part III). In CalTOX the risk assessor chooses reasonable exposure pathways to be considered depending on site-specific characteristics. If the site encompasses a possible fishing area, then this pathway should be addressed.

102. Haroun: Pg 77-79, Section D. The terms hazard, hazard index, and hazard quotient are not consistently used. Be specific.

In this section, hazard refers to noncarcinogenic systemic effects; hazard quotient refers to the ratio of a single chemical intake to its reference dose, both over similar exposure periods; and hazard index is the sum of more than one hazard quotient for multiple chemicals and/or multiple exposure pathways. The text has been corrected where appropriate.

103. Salinas: Pg 77. Use lifetime average daily intake or lifetime average daily dose rather than chronic daily intake. It should be clearly stated that the slope factor is to be considered a constant for policy reasons, since the model is intended to be used stochastically.

Chronic daily intake is the term used by the U.S. EPA in the Risk Assessment Guidance for Superfund, Volume I, Human Health Evaluation Manual (Part A), 1989. The slope factor is an input which is chosen by the user and will be dependent upon the policy and regulatory circumstances of the risk assessment being performed.

104. Haroun: Pg 78. Discuss the limitations in a risk assessment when criteria values do not exist for the chemicals of concern.

This issue lies outside the scope of the technical basis of the CalTOX model.

105. Salinas/Howd: Pg 78. Justify the basis for selecting seven years as minimum for chronic exposure. The wording "more than seven years" is unnecessarily restrictive, since the concept relates to long-term exposures. Use "approximately seven years".

The text has been corrected.

106. Dong/Reed: Pg 77-78. The calculated intakes represent the potential, not absorbed, doses. Intakes would have to be converted to absorbed doses to compare with slope factors given in units of absorbed doses. Describe the method to be used for route-to-route extrapolation of a reference dose and accounting for route-specific absorption factors.

These procedures must be performed outside of CalTOX. The intakes calculated by the CalTOX model represent administered or applied doses. Most reference doses and cancer slope factors appearing in the U.S. EPA Integrated Risk Information System (IRIS) are based on administered doses. Any method involving correction of intake and/or criteria values for absorption, such as route-to-route extrapolation, must be done manually. A paragraph discussing this issue has been added to the text.

107. Jeche: Pg 79. It is hard to believe that all exposure pathways are considered in CalTOX.

CalTOX considers all reasonable exposure pathways as described in Chapter 6 of the US EPA Risk Assessment Guidance for Superfund.

108. Haroun/Reed: Pg 79. Add that only RfDs can be used in equation 83. Provide an equation for converting RfCs to RfD in mg/kg/day.

An explanation has been added to the text.

109. Haroun/Reed: Pg 79. Add a discussion on segregating the hazard index by mechanism of action and/or toxic endpoint. Summation of hazard quotients without differentiating end points may not be appropriate.

Since CalTOX considers one chemical at a time, the hazard quotients for all relevant exposure pathways would be summed by the model. The model does not have the capability to segregate hazard quotients for a chemical that may have differing toxic endpoints, depending on route of exposure. This has been stated in the text.

110. Salinas: Pg 82. It is fact, not assumption, that all environmental compartments are connected.

The text has been corrected.

111. Salinas: Pg 82. How far from the contaminated site can CalTOX predict risk associated with exposure to that site?

The fate and transport section of CalTOX is an emissions model and does not presently contain a dispersion component. Therefore, CalTOX predicts only the on-site risk or hazard.

112. Salinas: Pg 83. "Present" soil concentration should be "estimated" soil concentration, since CalTOX is modeling the concentrations at the contaminated site.

The CalTOX model accepts root-zone and vadose-zone soil concentrations as input values which may be measured or estimated. The term, "present", is a clear descriptor. However, the definition has been modified.

113. Howd: Pg 86. It is better to define absorbed dose for inhalation exposure as that which is retained in the body after inhalation exposure. In this way insoluble particles may be considered.

The definition has been so revised.

114. Salinas: Pg 86-90, Appendix A. Definition of exposure given here is not consistent with that given by US EPA. Exposed produce definition is too limited because it excludes all root plants. Clarify that exposure point refers to the geographical location of contact between the chemical and the receptor. The definition of protected produce is misleading, because these crops are potentially the most subject to environmental contamination. Population at risk definition should be revised by omitting "in the vicinity of", since CalTOX does not model lateral migration or dispersion.

Exposed produce refers to exposure to ambient air contaminants. Therefore, root crops are considered protected produce. The definition has been modified to clarify that exposed produce are also exposed to soil and water. The exposure point definition has been modified. Protected produce refers to protection from air contaminants. The definition has been modified to clarify that protected produce are exposed to soil and water. The population at risk definition is a general definition not intended to be specific to the CalTOX model.

Part IV

115. Marty: ATES must adopt guidance on conducting uncertainty analysis for the Hot Spots program. We would like consensus with other CalEPA departments on how such analysis should be conducted. Keep us informed on progress of this section.

> The DTSC feels that it is inevitable that risk assessment will eventually include quantitative estimates of the variability and uncertainty which everyone knows exists. We have decided that it is better to take the lead and define the methods and distributions to be used. We have provided the document and the default distributions for your review and we are responding to your comments, because we feel consensus is important. Since this is a new method, it will undoubtedly undergo an evolutionary process. We expect to continue the open review process as we implement CalTOX as long as it remains apolitical and constructive.

116. Nazemi: Any guidelines developed for the use of uncertainty analysis could have signficant implications for other programs. We would like to participate in any proceedings regarding the risk management use of the model.

> See answer to comment 115.

117. Haroun: Expand the introduction to describe this section and its relationship to Parts II and III. Include a discussion on the assumptions of the model's ability to represent dynamic processes.

> See the revised document.

118. Haroun: It is unclear in this section whether the model is intended only for residential scenario assessment or for commercial and industrial scenarios as well. Exposure parameters appear to be for residential scenarios, but landscape properties are provided for industrial and commercial landscapes as well. Clarify.

> See the revised document.

119. Brodberg: Will the approach of the model eventually be expanded to a full probabalistic one?

> For exposure assessment, we are proposing that the distributions described be used in conjunction with a Monte Carlo simulation. Monte Carlo simulation is a probabilistic method.

120. Dawson: How is uncertainty analysis to be performed? Outline the methods to be used. Discuss the issues.

See the revised document.

121. Johnson / Dong: Do a sensitivity analysis to identify the important parameters. Expand the discussion in this section to include the concept of sensitivity analysis. This discussion should include recommending performing a sensitivity analysis to identify the subset of parameters upon which to perform uncertainty analysis. This would also identify those parameters whose CV may have less importance.

A section on sensitivity analysis has been added. Since the elimination of pathways and differing chemical parameters will effect the sensitivity of the model, a single sensitivity analysis will not be meaningful for all applications. Therefore, we recommend a sensitivity analysis be done for each application.

122. Salinas / Marty / Dawson / Nazemi: The appropriate probability density function for each parameter should be described. Almost all of the variables are assumed to be normally distributed which may not be an accurate assumption. There is no mention or evidence for the use of lognormal distributions.

Using coefficients of variation (cv) to represent the variance does not require any a priori assumptions about the shape of the underlying distribution that gives rise to the variance. The cv's were computed by dividing the mean by the standard deviations. The means and standard deviations were computed from data. When running CalTOX stochastically, a distribution will have to be specified. Most often this will be a longnormal distribution.

123. Salinas / Marty / Dawson: How were coefficients of variation classes generated? Which CV assignments were based on data and which from judgement? Distinquish between uncertainty due to lack of information and variability in data. References are needed for support and sources of values in Tables B-1 through B-3.

These coefficients of variation were broken into classes ranging from 1 to 15. The value of 15 was selected as a reasonable upper bound. The decision to create five classes was subjective. All cv's were based on some data, however, the values are not precise. This is presently being worked on and will continue to change.

124. Salinas: Pg 1. The validity of the intakes or estimated soil concentrations is not only related to the accuracy of the input parameters but is also related to whether the assumptions and algorithms are correct, and whether the limits of the model are recognized.

See the revised document.

125. Howd: Pg 2. Use of the term "true value" is confusing, because all values within the range are potentially "correct". It is more accurate to state that 10% of the values are

estimated to equal the mean rather than that there is a 10% chance that the mean is the true value.

The document has been revised.

126. Marty: Pg 8-14, Tables B-1 through B-3. Annual average precipitation should not be a default value, because there are data. Many of these parameters would covary; this should be considered when the uncertainty analysis is developed for CalTOX.

The issue of covariance will be investigated.

127. Nazemi: It is unclear whether the interdependence of certain variables is take into account in the uncertainty analysis, and incorporation of such interdependencies should be considered.

See response to comment 126.

128. Salinas: Pg 7. High reliability is not related to variability.

This section will be substantially revised.

129. Reed: Pg 8. Is it assumed that the area covered by house/road is negligible in the residental landscape?

At the present time, yes.

130. Dong: Check all default values.

We are attempting to do this and put it out for review to increase the checking.

131. Howd: Pg 10, Table B-1; Pg 12, Table B-2; Pg 14, Table B-3. Environmental temperature should be an "a" variable in degrees K. The estimate of the uncertainty in long-term mean temperature might be a "c" variable in degrees C but should have a numerically smaller CV in K.

This has been changed.

132. Salinas: Pg 17. Justify the basis for selecting 30 years as the exposure duration.

This is the arithmetic mean. The geometric mean is 9.37 which is consistent with the U.S. EPA default values.

133. Marty: Pg 17-19, Human anatomical properties. The age grouping 0 to 15 yr old should be further broken out. What is the advantage to this consolidation? Why do the body weight values listed here differ from present DTSC and US EPA values (EPA Exposure Factors Handbook)?

There is little difference among children relative to between children and adults. It would complicate the use to the spreadsheet if we broke out children into more than one group. It does not affect the intake estimates except for soil ingestion which will break out the children. See the revised document.

134. Salinas: Pg 17. Were only bottle-fed babies included in the body weight 0 to 15 yr old age category, since breast-fed babies were excluded? How does this affect the body weight?

The breast-fed infant intake is dealt with separately in the model. A risk/hazard for the breast-fed infant is computed for comparison to the child-adult exposure.

135. Salinas: Pg 18. The CR/BW parameters should be defined as "normalized parameters" to indicate their non-traditional presentation. CR/BW parameters should not be used because there are no distribution frequencies available for normalized data.

The ratio is a better way of handling these correlated variables. The drinking water study by Ershow and Cantor (1989) report the water consumption per body weight.

136. Salinas: Pg 19. The work by Layton (1992) has nothing to do with breathing rates. Omit the statement and replace with relevant information from the US EPA Exposure Factors Handbook.

Layton's paper is an examination of breathing rate, oxygen utilization and caloric intake. It has been published in an peer-reviewed journal. We believe it to be highly relevant to the issue of breathing rates.

137. Marty: Pg 20-22, Food Intake. How were values for food intake by children generated from the reference cited (Yang and Nelson, 1986)? Would the effects of contaminated foods be diluted in young children as a result of lumping children into 0 to 15 yr age grouping?

These references had age specific intakes which were used to compute age-group weighted averages. These groups were combined by pooling means and variances using appropriate statistical techniques. The grouping may dilute the mean. However, the pooling of groups will inflate the variance, if there are large differences.

138. Jeche: Pg 20. Food intake data are averaged, and the model is based on non-metropolitan sites.

The model can accommodate pathways found in non-metropolitan areas. It is not intended that every pathway will be used in every application. If the particular application shows the model to be sensitive to parameters in one of the food pathways, this can be investigated in more detail.

139. Brodberg / Marty: Pg 21. OEHHA has recommended 23 g fish / d as the California sportsfisher consumption value. CAPCOA uses a higher fish ingestion rate.

This value would be less than one standard deviation above the mean assuming the listed mean value of 0.00035 kg fish per kg body weight per day and a listed cv of 0.4.

140. Salinas: Pg 21. A triangular distribution does not have a variance or CV.

The concept of variance is independent of the assumed distribution. Therefore, a triangular distribution can have a variance, a standard deviation and a coefficient of variation.

141. Marty: Pg 22. Lumping soil intake values for the 0 to 15 yr old age group would result in underestimating the dose to young children. The parameters listed in CalTOX are below the US EPA recommended values for young children.

The listed mean ingestion rate is equivalent to 64 mg / day, and the upper 95% confidence level on the mean is more than 1000 mg. Based on the existing literature, these estimates are the best estimates. The use of the Monte Carlo will capture the upper bounds.

142. Jeche: Pg 23. It is questionable to assume that shower patterns are the same in Australia and California.

We would welcome alternative suggestions which provide estimates based on a study of California showering patterns. However, this was the best information we were able to obtain.

143. Jeche: Pg 25. Grit is not dirt, soil is ingested incidentally, and, therefore, the soil intake by chickens is an over estimation.

This is probably true depending on soil type which would be a site specific parameter. However, that is why the mean estimate is assigned a relatively high coefficient of variation.

144. Howd: Pg 25. Calculation of water turnover in mammals using the relationship described gave very large inappropriate values. Check the described method.

This was a units problem where the results are really liters per day, not liters per hour.

145. Marty: Pg 26. ATES uses much larger values for ingestion of water by cattle and by hens. Other parameters differ significantly from CAPCOA guidelines.

> The listed values are mean parameter estimates. It is likely that the ATES and CAPCOA values are upper bound estimates. If this does not explain the difference, we need to compare the scientific basis for the two parameter estimates.

146. Jeche: Pg 14 and 31, On pg 14, T is 283 K; on pg 31, T is 293 K.

> The value on pg 14 is the average ambient temperature of the California environment which is 10 C. The value on pg 31 is used to compute a partition coefficient which requires a temperature of 20 C which is the temperature laboratories use for these measurements. This discrepancy is being addressed.

147. Howd: Pg 30. KD values for ionizable chemicals are difficult to calculate because the ionic forms may have specific binding mechanisms different from that of nonionized forms. A simple correction for dissociation is probably inappropriate for highly dissociated molecules in high-clay soils, which have a very large surface area susceptible to ionic interactions. This potential problem should be mentioned.

> This issue is addressed in the revised Part II document (see, for example, Part II, page 9, 10, 57)

148. Jeche: Pg 33 and 34. These equations are not backed up by hard data.

> These distribution coefficients and concentrations factors are essential for providing an estimate of plant uptake. Without these parameters, the food intake pathways would have to be ignored. Ignoring pathways is not health-protective. The equations shown are believed to be the state of the art. However, we welcome any alternative methods.

149. Jeche: Pg 36. The fraction of total intake represented by soil in the chicken diet is based on an erroneous assumption, and, therefore, the fat-diet partition factor estimation for chickens may be off.

> The fat-diet partition coefficient is assumed to be independent of the amount of chemical consumed. The fat content of the animal is more important.

150. Jeche: Pg 37. The bioconcentration factor for fish is based on too many estimates.

> The bioconcentration factor for fish is critical to estimate the concentration in fish. Without an estimate of the concentration of chemical in fish, the fish ingestion pathway is not quantifiable. To the best of our knowledge, the

equation presented represents a reasonable approach. Again we welcome alternative suggestions.

151. Brodberg: Pg 37. Using bioconcentration factors will underestimate fish tissue levels. Modeling bioaccumulation will be a better estimate for ingestible fish tissue especially for sediment as a sink.

The bioaccumulation is difficult and uncertain. CalTOX is a screening level model, and until the science and policy is settled on this issue, bioconcentration will be used.

152. Jeche: Pg 39. The model first states that air is related to household soil, then states that bathroom air and house air are ratios of tap water.

The household air is related to the outside air, household dust, vapor migrating in through the soil under the house and vapors from the tap water.

153. Jeche: Provide the input parameters for the 20 chemicals of concern.

If it is decided that soil clean-up values for the 20 chemicals of concern are required, these values would eventually be estimated using a version of CalTOX that has been revised and has obtained the consensus of the regulatory community. It is expected that the input parameters used to make the estimates would be provided with the list of soil clean-up values.

154. Salinas: Include a list of references for Part IV.

A list of references has been provided.

Part V

155. Jeche: MacKay questions the validity of estimates of human exposure based on work of Travis and Arms. Second and third generation extrapolations of data may cause the original intent to be lost. Brand states that the fugacity approach has not been demonstrated to represent reality in site applications. Chen says that a partitioning model only crudely approximates site specific conditions.

Non-technical Comments

Policy

1. TGWG/Levy: It is not necessary to develop a ground water dispersion model, since the Water Resources Control Board would rather not allow for dispersion. Why include water exposure pathways in risk quantitation; just clean up to MCL, background, or non-detectable levels per WRCB policy.

A ground water dispersion model would provide a potentially more realistic estimation of risk or hazard due to exposure to ground water contaminated by a site. Such a model add-on would give greater flexibility to CalTOX, since CalTOX could be run with or without dispersion, depending on the requirements of the regulatory agencies involved.

2. Woodling: A ground water component can be added to CalTOX.

3. Pettit / Marshack: The State and Regional Water Boards must protect against impairment of any beneficial use of the waters of the State not just against threats to human health. Therefore, human health-based risk assessments are not suitable for determining risk to water quality and water as a resource.

The exposure and risk characterization portions of the CalTOX model do focus on human exposure and health risks. However, the fate and transport portion of the model which predicts chemical concentrations in potentially affected environmental media may be used separately from these other portions for a variety of objectives, including fulfilling the mandate of the State and Regional Water Quality Control Boards in regard to water quality. As mentioned elsewhere, CalTOX is essentially modular and can be modified in a number of ways to fit program needs.

4. Marshack: CalTOX does not consider resource impacts, anti-degradation mandates, aquatic life and wildlife impacts.

The CalTOX model predicts the fate and transport of a chemical in multiple environmental compartments then utilizes those results to estimate human exposure and risk. Alternatively, the fate and transport portion of the model may be used separately to address resource impacts, degradation, and other ecological issues.

5. Marshack: Ground water should be considered a receptor instead of a pathway.

6. Marshack: Soil levels should be determined based on non-exceedance of water quality limits in ground water.

7. Baker: Most remediation sites do not have on-site receptors; therefore, there is a need to address assessment of off-site exposure. Key elements of an off-site exposure assessment for the air pathway are wind blown particulates, dispersion of gaseous emissions, and sub-surface off-site gas migration.

8. Haroun: The document should state that the cancer slope factors developed by OEHHA should be used in preference to those from US EPA or other sources.

This will be so stated in the policy guidance for the use of the CalTOX model.

9. Reed: Pg 78. Omit the reference to OEHHA and refer to the potency list as the CalEPA list.

This has been done.

10. Haroun: OEHHA should review the default exposure parameters.

The Department of Toxic Substances Control agrees that OEHHA should review the default exposure parameters for accuracy and consistency within the CalEPA.

11. TGWG: Input parameters must be validated.

We agree.

12. Reed: Pg 20. DPR food intake analysis may differ from that of DTSC. Is the cursory analysis of DTSC sufficient for addressing food intake for screening purposes?

13. Naito: One of the largest sources of uncertainty is the derivation of cancer potency values. It may be more appropriate to use chemical-specific biologically-based models.

The Office of Scientific Affairs (OSA) agrees. However, the Office of Environmental Health Hazard Assessment (OEHHA) has primary responsibility for establishing cancer potency values for California.

14. Alonzo: The document should specify the level of quality and quantity necessary for analytical data to be input to the model as well as the appropriate sampling strategy. The minimum number of samples per compartment as well as the minimum number of compartments to be characterized should be specified.

The determination of adequacy of site characterization data is a policy question. The required input parameters are listed in the document. The Technical Guidance Work Group may be able to provide guidance as to the minimal amount of site-specific data required to run CalTOX for a site. CalTOX does not require direct sampling of any environmental compartment except soil, because CalTOX uses the soil concentration to estimate concentrations in other media. However, in order to make these estimates, various partition coefficients are required. Therefore, environmental sampling for obtaining data to calculate site-specific partitioning will be required. The specification of methods to be used and number of samples required should be the subject of future discussions of the Technical Guidance Work Group as more information becomes available identifying the input parameters of importance.

15. Salinas / Marty / Haroun / Howd: The software should be made available for review with the document. The assumption is made that a users manual will be prepared.

See the answer below.

16. Pettit: Because the spreadsheet format for CalTOX allows users to modify parameters at will, regulatory agencies will have to either independently model the site with CalTOX using data submitted to the agency by the user or will have to verify the user's model. In either case, it is unrealistic to expect the staff of regulatory agencies to acquire the necessary skills to perform these tasks.

The Office of Scientific Affairs agrees that regulatory agencies will have to check the results obtained by outside users. For example, we may require the user to submit a spreadsheet workbook for the site in question, run a dummy data set in order to identify and check the changes made, and ask the user to scientifically justify those changes. After consensus is obtained on the scientific underpinnings of CalTOX, the Office will prepare a user's manual, a user-friendly "front end" to the spreadsheet, and will present a series of training classes for CalTOX.

17. Howd: Issues that must yet be addressed include: how to collect and input appropriate chemical concentration data, rules for using the default environmental and exposure variables, how to work through the program modules, and rules for collecting site-specific information.

18. Nazemi: The document does not discuss how the model and its uncertainty analysis would be used to make risk management decisions.

Editorial

1. Salinas: There should be a table of contents, summary, and references for the entire document. The table of contents should show the page number for the various contents. Verify that the correct name of the Office of Scientific Affairs is used throughout the document.

This has been partially done.

2. Reed: Make format, terms, and reference citations consistent throughout the document.

We have attempted to make all terms consistent.

3. Salinas: The present format of Part II resembles a paper for publication rather than a section of a document.

4. TGWG: It should be explained in Part II that CalTOX is an all inclusive model and that methods are given for excluding pathways on a site-specific basis (located in Part

IV). It should be explained that inclusion of all pathways will overestimate risk/hazard.

This has been done.

5. Dong: Provide a graphic overview of the model in the executive summary and for each part (Parts II and III). A modification of Figure 1 or 3 in Part II could serve as an overview but needs to be modified to clearly show soil as the primary contaminated environmental medium contaminated at a hazardous waste site, to show that soil air, water, and food constitute the expsoure media, and to show that these four exposure media are subsets of the seven source compartments.

This has been done.

6. Dong: Correct typographical errors.

We have tried to find and correct the typographical errors.

7. Dong: Consider Kevin Brand's comments.

Part II

8. Salinas: Part II. Revise to clearly show the derivaation of the algorithms, how equations relate to each other, and then present the final equations used in the spreadsheet in a tabular form. This section is complex and difficult to understand.

Revisions have been made to clarify the text.

9. Dong: Part II. Move equations 1 through 5 to pg 21 and equation 6 to pg 53. Equations 98 to 118 should be moved to an appendix with further discussion on derivation, explicit specification of the source medium for which each is intended, and with references. This would clarify the Part II for most readers not mathematically inclined and would provide needed information to other readers on the key equations of the distribution process. The paragraph at the bottom of pg 67 may be moved to precede the individual sample applications (pg 63) in order to facilitate the appreciation of the sample applications.

We have decided to leave the organization of the text essentially unchanged.

10. Howd: Part II. There are two pages numbered 43.

This has been corrected.

11. Dong: Part II. Move pg 46-52 to Part IV for better coherence.

See response to comment 9.

12. Salinas: Part II, pg 3. Omit the term "policy issues". No policy issues are discussed in this section.

We disagree.

Part III

13. Haroun: Part III, Pg 6. Add a description of Part IV in the introduction.

This has been done.

14. Haroun: Part III, Pg 7. Add that terms, abbreviations, and definitions are found in Appendix A.

This has been done.

15. Salinas: Include the tables referenced in Part III but only appearing in Part IV. Repeat them in Part IV emphasizing the uncertainty aspects.

All tables referenced in Part III now include the additional descriptor that the tables may be found in the supplemental report.

16. Salinas: Part III. Use mg/kg.day.

The term mg/kg/day is used because it is commonly used in risk assessment guidance documents.

17. Dong: Part III. Consider moving the exposure pathways from pg 74 to 76 to the first part of Part III as an overview.

This has been done.

18. Haroun: Part III. Call out the location of the tables cited as being in Part IV.

This has been done with a call out to the supplemental report.

19. Haroun: Part III, pg 49-53. Suggested changes in wording provided (see Haroun memo pg 3-4).

This has been done.

20. Haroun/Reed: Part III, pg 51. Call out to equation 48 should be to equation 50.

This has been corrected.

21. Reed: Part III, pg 73. Place the ingestion intake list before the inhalation intake list for consistency in what has been previously discussed.

This has been done.

22. Salinas: Move Table VI from Part IV, Appendix B to Part III, pg 76.

23. Reed: Part III, pg 77. The terms oncogenic and non-oncogenic describe more accurately the risk assessment endpoints rather than cancer and non-cancer.

Cancer is a more commonly used, easier-to-understand term.

24. Haroun: Pg 78. Give full citations for IRIS, HEAST, and the OEHHA list.

These will be provided in the references.

25. Marty: Pg 78. Amend definition of reference dose to read "a level of exposure at or below ...".

This has been done.

26. Haroun/Salinas: Pg 79. Revise wording in the last paragraph for clarity (See Haroun memo, pg 5, Salinas memo, pg 11).
This has been done.

27. Haroun: Pg 88. Under Cexposure, environmental compartment should be changed to exposure medium.

This has been done.

Part IV

28. Salinas: Part IV, Pg 4. The footnote should read "IBM-compatible microprocessors" and "Macintosh microprocessors".

29. Jeche/Haroun: Include a table of abbreviations and acronyms. Describe Appendix A in the introduction to Part III.

Chapter III. Comments of Reviewers of Draft Dated June 1993

We acknowledge the following reviewers of the draft version, dated June 1993, of the CalTOX model.

R. Merryman, California Conference of Directors of Environmental Health (CCDEH)
N. R. Reed, Department of Pesticide Regulation (DPR)
M. Finch, Department of Toxic Substances Control (DTSC)
J. Crisologo, Department of Toxic Substances Control (DTSC)
R. A. Streeter, Environmental Resources Management, Inc. (ERM), representing the Southern Pacific Transportation Company
G. W. Fuhs, DTSC Hazardous Materials Laboratory (HML)
A. C. Nye, Industrial Compliance (IC), representing the Southern Pacific Transportation Company
B. L. Roberts, International Technology Corporation (IT)
V. M. Guvanasen, Leighton and Associates, Inc (LAI)
S. J. Daugherty, Orange County
D. M. Snyder, Russell Resources, Inc. (RRI)
J. R. Odermatt, San Diego County
M. Schneider
A. B. Sheldon
H. M. Schueller, State Water Resources Control Board (SWRCB)
W. H. Crooks, B. Yeadon and V. Izzo, California Regional Water Quality Control Board, Central Valley Region (CRWQCB/CVR)
Y. Cohen, University of California, Los Angeles
M. Lobascio and H. Tuchfeld, Woodward-Clyde Consultants (WCC)
R. Scofield, ENVIRON, representing the Western States Petroleum Association (WSPA)

The following reviewer's comments on the draft version dated, December 1993 are also included in these responses

W. Pettit, State Water Resources Control Board (SWRCB)

Technical and Scientific Comments

General Comments

1. Schueller (SWRCB): The National Research Council admonishes against many aspects of the proposed uses for which the CalTOX model has been developed (see memo from SWRCB to Kahoe, Cal/EPA, March 10, 1993). Because of this, it may be impossible to defend CalTOX model results in regulatory disputes.

> Please see the section "Water Board and Related Comments".

2. Schueller (SWRCB): The CalTOX document should include a detailed and comprehensive illustration of the model output and how that output would be used to enforce numerical standards.

> We have divided the implementation of CalTOX as a DTSC policy into parts. First, we have sought to establish the scientific and technical basis of the policy. Once this has been completed we intend to address the policy issues of application. These comments represent the third and final round of review of the model. We intend to address the policy issues raised above in the near future.

3. Yeadon and Izzo (CRWQCB/CVR): The CalTOX model should only be used at small sites with a single contaminant.

> Application of CalTOX will be based primarily on the limitations discussed in the executive summary.

4. Lobascio and Tuchfeld (WCC): The model addresses only one chemical at a time, and exposures from the chemicals are not additive. These limitations reduce its usefulness, and the model should be modified.

> Current USEPA guidelines dictate the risk from chemicals at a site be treated one at a time. The risks are then summed to obtain a site risk. In order to minimize needless differences, DTSC plan to follow USEPA risk characterization guidance.

5. Streeter (ERM): The CalTOX model should permit incorporation of site-specific data documenting the specific chemical species found at sites where evaluation suggests that this is a pertinent issue (contaminants which speciate in the environment and have widely different toxicities).

> It is envisioned that any of the parameters in the CalTOX model can be a DTSC-specified default value or a measured site-specific value. It is essential that the

physical and chemical parameters input for a chemical are appropriate for the species of chemical found at a site.

6. Streeter (ERM): It should be possible to override the default methodology with a different technique more appropriate to a given site.

Initially, probably only the parameter values will be permitted to be altered. If an alternative model is more appropriate than CalTOX for a particular application, this model may be used provided the responsible party demonstrates the alternative models superiority for the application.

7. Daugherty (Orange Co): Is the model applicable to underground storage tank sites? If so, it should be clearly stated. If not, a reason should be given.

Theoretically, this model could be applied to the individual chemical constituents of the stored liquid which have been measured in the soil. At present the model could not be used in the forward direction to determine risk from chemicals in non-aqueous phase liquids (NAPL). However, in most cases it could be used to back calculate health-based target soil clean levels for an individual chemical constituent of NAPL given acceptable risk level or hazard index. These are strictly technical issues and do not address regulatory jurisdiction and policy.

8. Lobascio and Tuchfeld (WCC): The concept of fugacity is not intuitive and straightforward, especially when it is applied to migration of metals. The concept and approach will be difficult to explain to parties involved in site cleanup. Consideration should be given to converting the fugacity approach into more traditional methodology and offer fugacity as an alternative for comparisons.

This is a partition model. We have chosen to use fugacity because it simplifies the mathematical model. Fugacity is a well established principle in chemical thermodynamics and environmental chemistry.

It has been shown that the fugacity approach can be extended to metal species. The application of CalTOX to sites containing metals may be delayed until the model establishes a track record on sites with non-ionizable organic compounds, but DTSC intends to expand the model to address metals.

9. Lobascio and Tuchfeld (WCC): Compartmentalized models obey mass conservation laws, but other physical laws, particularly diffusion in porous media, must be considered for realistic fate and transport modeling results.

CalTOX does treat diffusion in porous media. See the soil portion of Part II of the document.

10. Streeter (ERM): There must be provision in the model for the detailed evaluation of exposure pathways of concern using site-specific data collected from the media of concern.

See response to comment 5.

11. Yeadon and Izzo (CRWQCB/CVR): Sufficient site specific data should be collected to adequately characterize the site rather than relying on a simplistic model to determine cleanup levels. If CalTOX is used at a site, the modeling effort should be focused on a sensitivity analysis.

> At some point every decision requires a model, site-specific data in and of itself is not adequate for a decision. Our intention is to allow responsible parties (RPs) to determine the level of site-specific data they wish to obtain to replace default parameter values. A sensitivity analysis will be used to determine which parameters are most important. The less site-specific information collected on a site, the greater the uncertainty and the broader the range of health-risk based soil clean up levels. Since the target soil clean up level will be based on a lower bound estimate, it will be in the interest of the RP to obtain site specific data to reduce that uncertainty.

12. Scofield (WSPA)/Finch (DTSC/R2/SMB): Part I, pg 26; Part II, pg 8-10; Part III, pg 10. The constraints to the CalTOX model are extremely limiting; virtually no site would meet all of the required conditions. Many sites have high metallic contamination, a history of recent spills and/or flooding, and are smaller than 1 to 10 km2.

The limitations will be addressed individually.

As noted in response to comment 8, metals can be accommodated by the model. However, there is great uncertainty associated the soil-water partition coefficient (Kd) for some metals. These uncertainties may be so great that it will be necessary for RPs to measure Kds at the site. Without site-specific data, the target clean-up level may be so low that level cannot be achieved.

> CalTOX is intended to model exposures relevant to the needs of Superfund-type risk assessments. It is not intended to predict risks resulting from exposures due to recent spills. Immediately after a spill of a chemical on the ground, transport processes operate which are not relevant in assessing long term transport and, therefore, they are not modeled by CalTOX. The length of time required before CalTOX can be applied varies with site conditions and the chemical of interest. We have selected one year as a length of time which will ensure that CalTOX is never used inappropriately.
>
> The model requires the site to be larger than 1,000 m2 as stated on pg 26 of Part I and pg 8 of Part II. This would be equivalent to a range between 30 x 300 ft. lot.

We do not believe this minimum size limit will exclude many sites which fall under DTSC jurisdiction.

13. Scofield (WSPA): Limitation of the CalTOX model to sites where soil contamination is the primary source excludes sites where ground water is the primary contamination source. This could result in complications associated with using different risk assessment systems for ground water sites and soil sites.

There is an option in the CalTOX model to determine exposure when measured ground water concentrations are specified. Risks could include those associated with ground water concentrations.

14. Scofield (WSPA): Limitation of the CalTOX model to an exposure duration of 10 to 30 years excludes consideration of mean exposure durations of 9 years in single family residences and 2 to 3 years in an apartment.

There is nothing that would limit the application of CalTOX to shorter term exposures. However, CalTOX is not intended for use to compute exposures resulting from chemical spills of less than one year. This statement was meant to direct people toward the chronic effects and away from accidental analysis.

15. Scofield (WSPA)/Lobascio and Tuchfeld (WCC)/Streeter (ERM): Risks can only be calculated for on-site receptors. At many sites, the primary concern is off-site receptors. Risk to off-site receptors needs to be more explicitly addressed. Why off-site dispersion of air-borne contaminants is omitted is not apparent.

The initial objective of CalTOX was to provide an integrated multi-media emissions model. We feel it is important to first implement the model with narrow, achievable objectives. Once it has been successfully implemented for these situations, CalTOX will be expanded to address additional situations. We are planning to address the off-site dispersion modelling in the future. We hope to obtain input from other boards and departments in the CalEPA to be sure our models are consistent.

16. Streeter (ERM): It would be simple to include an ambient air concentration normalized to a unit emission rate for a given receptor area as an input parameter. This concentration would come from a dispersion model and would be used in conjunction with a site-specific emission rate to predict ambient air concentrations and estimate risks at specific off-site locations.

See response to comment 15.

17. Scofield (WSPA)/Schueller (SWRCB): Why is the model to be used only for screening-level evaluations as stated in the Executive Summary? It appears that the model is intended for more refined evaluations. Modify the documentation to state why the model is to be considered only a screening tool at this stage and what is to be

done when more refined risk evaluations are required. Is CalTOX to be used as a screening tool as described in the "Responses to Comments" no. 4 or as "the DTSC standard default model for assessing risk" as stated in the DTSC memo of June 30, 1993?

> The exact application of CalTOX has yet to be determined. However, it is envisioned that it will be used at an early stage to evaluate risk at a large percentage of the sites regulated by the DTSC. To this extent it will be a screening model. With little site specific data, the uncertainties associated with risk and health-based soil levels will be large. Obtaining more site specific data will reduce the uncertainty and likely reduce the cost of cleanup. For some sites, it may be cost effective to use more refined models to reduce the uncertainty further. However, responsible parties will have to prove to DTSC that an alternative model is superior to CalTOX for a specific application. So CalTOX is a screening model and the DTSC standard risk assessment model to which other models must be compared.

18. Schueller (SWRCB): If CalTOX is to be used as a "consistent screening mechanism for small sites where a full-scale assessment might delay the process of evaluation and remediation", is it possible that full-scale risk assessments would never be appropriate for small sites?

> See the response to comment 17.

19. Scofield (WSPA): The model needs to be validated by comparison with actual data at sites. Comparison of reasonable maximum and most likely exposure risk estimates (RME and MLE) with 90th and 50th percentiles of probabilistic risk estimates from a previously evaluated site would be useful.

> These comparisons will be done by DTSC and no doubt, many others once the spreadsheet becomes available. DTSC is currently preparing a series of reports on comparisons so far.

20. Scofield (WSPA): The model needs to be validated against existing vadose zone models (EPA SeSoil; USGS VS2DT). The validation processes need to be explained.

> Preliminary efforts have been made to compare the results predicted by CalTOX with those of SESOIL. We are in the process of generating a brief report on this work which should be available by March 1994. The results are similar. Since most other models including SESOIL have not been fully validated themselves, it is unclear when time will be made to complete an exhaustive comparison.

21. Schueller (SWRCB): Circulate the validation / verification results for comment when the testing is completed.

> All validation / verification results will be made available.

22. Schneider: Models, such as the CalTOX model, based upon theoretical considerations lack substantiating field-derived environmental fate data and, thus, contain many uncertainties. Such models should not be used for regulatory purposes. The linearized multistage model is based on radiobiological effects; but,it is unlikely that all environmental pollutants act on biological systems like radiation.

> CalTOX attempts to address the uncertainty quantitatively. Uncertainty is unavoidable, but not a reason to avoid decisions. The DTSC has no control on the models used to obtain cancer potencies. CalTOX uses cancer potencies determined by the CalEPA Office of Environmental Health Hazard Assessment and the USEPA.

23. Cohen (UCLA): In CalTOX the concentration in soil is dependent upon the deposition rate of the chemical from the atmosphere. The concentration in the plant tissue is not based on the deposition rate but is based on the concentration in the soil and on a transfer factor multiplied by the concentration in the air phase (to account for accumulation due to deposition). The mass balance is violated because the chemical deposited onto the soil increases the soil concentration and is later assumed to also be deposited onto plant tissue without accounting for the surface coverage of the plants.

> In CalTOX, the deposition from air is partitioned between soil and plants in a way that conserves mass. This is done with an interception function that determines the fraction deposited directly to plants, the remainder falls on soil. The chemical that attaches to plant surfaces can be removed by weathering, or by uptake into plant tissues. There is also uptake of chemical to plant tissues from root-zone soil. However, the use of rate constants for each of these processes prevents the violation of mass balance. In addition, the rate constants are calibrated so that the mass potential (or fugacity) of the plant does not exceed that of the soil or air.

24. Lobascio and Tuchfeld (WCC): The CalTOX model should be more explicitly focused on evaluating remedial alternatives. There are no explicit references to remediation scenarios, such as, asphalt pavement, concrete foundation of a new building, or layer of clean soil.

> Efforts will be made to provide inputs which would simulate asphalt pavement and other non soil barriers. However, initial efforts will be made to apply the model to on-site residential exposures with no barriers. Once this has been successfully accomplished the model may be expanded.

25. Scofield (WSPA): The CalTOX model should not be used to estimate soil cleanup levels because of the uncertainties associated with the use of partitioning models.

> The computation of health-based soil levels is the most important aspect of CalTOX. We believe that it is lack of data and uncertainties about fundamental physical processes that limit our ability to predict intake and health-based soil

levels. Therefore, the compartment models used in CalTOX are not what limits our precision. We intend to use the model stochastically to address issues of uncertainty quantitatively.

26. Lobascio and Tuchfeld (WCC): A list of cleanup levels generated by the CalTOX model with the default input parameter values would be useful for comparison with the US EPA Preliminary Remediation Goals (PRGs).

> This list is something that may be produced in the future, however, the goal of CalTOX is to make the model sufficiently easy to use that people will use it to generate a default value. This will ensure that the most current input values are used and a list will not be locked into regulation. Government generated lists can become dangerous because it is difficult to change them as new information becomes available.

27. Daugherty (Orange Co): The CalTOX model should be coordinated with the model used by EPA Region IX for PRGs. Could the PRG model be used in preliminary hazard assessment prior to the use of the CalTOX model?

> We are in contact with the group at Region IX which generated the PRG list. We believe it is in the Department's best interest to be consistent with Region IX. It would be possible to generate a list of "PRGs" using only default parameters and the CalTOX model on a routine basis. The entries in the list will probably not be identical to the list generated by Region IX due to the requirement that DTSC use California Potency Values. However, it is our intention is, to the extent possible, to work with USEPA and other regulatory agencies to maximize consistency.

28. Scofield (WSPA) / Snyder (RRI) / Lobascio and Tuchfeld (WCC): It is impossible to test the model without testing the software. Will the spreadsheet be issued in draft for comment and "beta tested"? WCC will be pleased to participate in the review of the software.

> We are planning to provide the software to a select group of users for a beta test in the first half of 1994.

29. Snyder (RRI): Has consideration been given to the format for input data sets with regard to compatibility with other data management tools? Will sample data sets be provided?

> CalTOX is being developed on a EXCEL spreadsheet. Macros will be written to facilitate some data entry. No interfaces have been designed for other data management tools in the first version.

30. Snyder (RRI): Will agencies get data sets from users to run on an agency spreadsheet to verify results and make sure results were not biased by spreadsheet modifications? What documentation will be provided for users who want to check

calculations and consider modifications? How will the DTSC handle proposals to modify the spreadsheet for special circumstances? Will some cells be protected to prevent modification?

> DTSC will require regulated parties to submit disks with all relevant CalTOX runs and a report describing the specific application. The data used in these runs will be compared with the default data to identify non-default parameters. All non-default parameters will need to be described and justified. The submitted parameters will be run on a DTSC maintained spreadsheet to ensure that the computed results are correct. If users wish to use models other than CalTOX they will need to be justified to DTSC staff. The alternative model must be demonstrated to be scientifically superior to CalTOX for the application and that the needed data will be collected for that model. Site-specific modification of the CalTOX model will not initially be permitted.

31. Snyder (RRI): Will the spreadsheet run under Lotus, QuatroPro, etc. as well as EXCEL? Will the spreadsheet be able to export data to files or only print? Does the output include tabulations of data inputs, parameter default and non-default values, date and time of run, as well as results?

> The spreadsheet will run on Lotus and probably on other spreadsheet programs. However, it is a large complex nexus of equations. It is currently written in EXCEL with different colors and fonts to make interpretation easier. Other spreadsheets may not contain these aids which will make understanding the spreadsheet more difficult. As with any spreadsheet you can export data and print.

32. Snyder (RRI): Will help be embedded in the spreadsheet? Does the spreadsheet include checking routines to make sure data inputs and parameter values are not out of allowable ranges?

> The printed output will include whatever the users chooses to print which can include default and non-default inputs, date and time of run and results. Macros will be included to aid users.

33. Snyder (RRI): How long does the spreadsheet take to recalculate when run on a 25 MHz 386SX? How much faster for the same machine with a math coprocessor? How long on a 25 MHz 486?

> Run deterministically on a 386/25, the spreadsheet requires less than one minute and it is faster on a 486. The math coprocessor does not appear affect deterministic runs.

34. Scofield (WSPA)/Crooks (CRWQCB/CVR): Some comments made previously did not receive a response.

Please see the end of these comments.

Part I Comments

35. Daugherty (Orange Co): The relationship of risk assessment and risk management should be thoroughly discussed in the executive summary. Statements about irreducible and reducible uncertainties and the state of validation studies should be included in the executive summary. This would place the use of the model in the context of a public policy decision and would allow justification for professional judgement when use of the model is not appropriate.

The objective of this document is to describe the scientific basis of the CalTOX model. It is not intended to address the public policy context.

36. Fuhs (HML): The explanatory text accompanying the (E)(ED)/(AT) term in equations 2 (pg 7) and 6 (pg 18) and in paragraph 4 (pg 21) should include statements on the requirement of compatibility of the units of time in (ED) and (AT) and that other conversion factors are needed if the exposure is in h/d over a lifetime.

These equations are consistent with the USEPA Risk Assessment Guidance for Superfund documents. This consistency is a conscious effort on the part of the authors of CalTOX.

37. Reed (DPR): Pg 13. Figure 1 should be Figure 2.

Thanks, we fixed it.

38. Daugherty (Orange Co): Pg 17, Table I. The transfer of vapors from water to air is not included as an exposure pathway. Does this mean that this transfer is not considered by the DTSC to be significant?

The present objective is to implement CalTOX for an on-site residential exposure scenario. Under this scenario, the house would be located in the soil that is the source for ground water contamination. Therefore, volatilization from ground water would be trivial compared volatiles coming from the soil. The entry of soil vapors into the house from root zone soil is modeled. Once the on-site residential scenario is implemented the model is extended to other scenarios, this pathway will be investigated.

39. Streeter (ERM): Pg 27. If CalTOX cannot be used for time periods less than one year, the model cannot be applied to short-term residential, occupational, construction, and trespasser scenarios.

> CalTOX requires that the chemical has been in the soil on a site for more than one year, so that it has established steady-state in the environment. Given this assumption, the model can be applied to all of the above scenarios.

Part II Comments

40. Daugherty (Orange Co): It is important to understand how contaminant concentrations in environmental media at a site are converted into intakes. Basic fate and transport equations showing how measured soil concentrations measured at one time are converted to exposure concentrations at another time would be helpful. Provide an example by taking a soil sample value through the vadose zone to ground water and through the root zone to air. The soil concentrations could be taken through the equations for fugacity capacity, transfer and loss rate constants, and changes in contaminant inventory in order to calculate the equilibrium concentration in ground water and air. Use a volatile carcinogen with a very low MCL to demonstrate the applicability of leachate values to ground water contamination.

> The text is designed to describe the model. It will be available as a spreadsheet, we expect that the user's manual will provide some example calculations.

41. Scofield (WSPA): The CalTOX model does not allow for variations in soil properties within a site when modeling the transfer of vapors from the soil to the air. These variations are important for sites that are differentially contaminated.

> The compartment model assumes that the soil is homogeneously contaminated within each one of the three soil compartments. This simplification is necessary to develop the model. The variability of soil concentrations is handled through stochastic inputs to the model.

42. Yeadon and Izzo (CRWQCB / CVR): The model is too simplistic. The vadose zone in CalTOX is modeled as one compartment and does not consider the variations in site geology or lithology. The model considers aqueous advection as the sole means of transfer of VOCs from the vadose zone to ground water. The uncertainty of the transformation rate constants leads to further uncertainty in the estimates of transport of VOCs to ground water.

> Variations in lithology and site geology are required for more refined models. CalTOX is designed to deal with sites for which this detailed information has not been collected. If this information is collected, then a more refined model may be justified. The uncertainty will be addressed quantitatively.

43. Cohen (UCLA): There is a problem in averaging when dealing with uniform and non-uniform compartments. Assuming equilibrium for conditions where equilibrium does not exist will lead to errors in predictions.

> We are not assuming chemical equilibrium (i.e. equal fuagacity) in all compartments. We are assuming the compartments and their constituent phases are at quasi-steady state with regard to mass exchange. In CalTOX, nonuniformity in contaminant mass potential is addressed by allowing each compartment to be at a different fugacity or mass potential. This allows us to represent concentration gradients in the soil column.

44. Scofield (WSPA): Ground water is considered a sink and not a source and cannot be used to assess risks from vapors coming from contaminated ground water.

> See response to comment 38.

45. Scofield (WSPA): The CalTOX model does not accommodate mixtures of substances.

> CalTOX is designed to be consistent with the USEPA RAGS policy. RAGS assesses risk on a chemical by chemical basis and sums risks.

46. Scofield (WSPA): The surface soil layer is quite thin and assumes no regular soil turnover beyond the first centimeter. This may not be a valid assumption in agricultural scenarios.

> CalTOX will initially be implemented for an on-site residential exposure scenario. Once this has been successfully accomplished the model will be extended to other exposure scenarios.

47. Scofield (WSPA): The generalization of the Henry's Law constant used by the authors of the CalTOX model is more accurate at higher contaminant concentrations than at lower concentrations. Therefore, CalTOX may be more appropriate for use at medium rather than low concentrations.

> We are not aware of any evidence of this. Please provide literature citations to support this contention.

48. Scofield (WSPA): The box model does not provide spatial resolution in air concentrations and cannot estimate off-site air impacts or distinguish on-site "hot spots."

> The use of a box model does not preclude off-site exposure estimation, although, the model is presently configured for an on-site exposure. In a well mixed medium like air, hot spots are not thought to significantly affect estimation of intake.

49. Scofield (WSPA): The document is unclear regarding definition of time steps during model calculations.

This model is not a numerical model requiring a defined step time. CalTOX is a closed form analytical solution relating risk and soil clean up levels.

50. Scofield (WSPA): The document must clearly state how the total mass is accounted for among the model compartments.

Please see the section in Part II titled “Transfer-Rate, Loss-Rate and Gain-Loss Equations”.

51. Scofield (WSPA): It was very difficult to follow the complete derivation of the governing equations in the soil compartment discussions.

Handwritten derivations will be made available to interested parties.

52. Scofield (WSPA): Pg 1, Pg 77. Substitute the term "distribution" for "dispersion" when describing contaminant movement between compartments in order to avoid confusion with "dispersion" as used in vadose zone contaminant transport.

The document has been revised.

53. Cohen (UCLA)/Daugherty (Orange Co): Pg 10. It is alarming that CalTox cannot be used when the contaminant concentration exceeds the solubility limit in any phase. Many hazardous waste sites contain pure phases or water immiscible phases (such as, nonaqueous phase liquids, NAPL). This restriction represents a severe constraint on its use.

This is a limitation of compartment models. CalTOX does not have a pure phase compartment which occurs when the limit of solubility is exceeded. While this may seem to be a severe limitation, it is not. It will limit the forward calculation of risk. However, the utility of CalTOX is in the reverse computation of health-based soil target levels. Health-based soil target concentrations are usually below the saturating concentrations of chemicals.

There are a number of ways to address this problem. Many of the excellent suggestions that follow will be investigated. At the present time, we intend to use CalTOX to compute target soil clean up concentration levels which do not exceed the limits of solubility. While this may limit the use of the model, a major objective with CalTOX is to establish scientific credibility. Therefore, we have developed a model which we are confident will succeed for a defined set of conditions. It is important that we apply it successfully, and once show the utility of CalTOX, then expand the model. In CalTOX, we are not attempting to develop a model that can be used everywhere immediately.

54. Yeadon and Izzo (CRWQCB/CVR): The CalTOX model ignores the process of NAPL advection, gaseous advection, aqueous diffusion, and gaseous diffusion. NAPL advection and gaseous diffusion can dominate the VOC transport processes in the vadose zone.

> CalTOX as currently configured is not designed to address NAPL. Gaseous and aqueous diffusion are explicitly modeled in all three soil compartments. See Part II of the document.

55. Scofield (WSPA): Pg 10. The CalTOX model does not accommodate sites contaminated with high levels of substances but could be expanded to do so. Fugacity concepts can be used up to saturation and can be used to accommodate free product behavior.

> See responses to comments 53.

56. Daugherty (Orange Co): NAPL could be crudely accommodated by calculating a flux based on the ideal gas law for vapors, and on the maximum solubility for aqueous phase, both proportioned by mole fraction (Raoult's Law).

> See responses to comments 53.

57. Odermatt (San Diego Co): A screening level analysis to evaluate the possibility of an existing NAPL at sites should be included in the CalTOX model. The analysis recommended is that published by Feenstra, Mackay and Cherry (1991, Ground Water Monitoring and Review, v. XI, No. 2, pp. 128-136)).

> See responses to comments 53.

58. Sheldon: Since no practical and reliable method exists to rule out the actual absence of NAPL, and CalTOX cannot be used at sites where NAPL is present, it should be stated in the document that CalTOX should not be used for baseline health risk assessments at sites where historical subsurface releases of such substances have occurred.

> See responses to comments 53. Also, the presence of NAPL does not preclude the use of CalTOX to compute target soil levels which would be lower than saturating concentrations.

59. Yeadon and Izzo (CRWQCB/CVR): Traditional soil sampling methods should not be used with the CalTOX model since these methods cannot identify the presence of NAPL. The presence of NAPL in the vadose zone becomes the driving force by orders of magnitude in determining the potential impact to ground water.

> See responses to comments 58.

60. Fuhs (HML): Pg 11. In the second paragraph "mass" means contaminant mass only, not the mass of the matrix.

The document has been revised.

61. Daugherty (Orange Co): Pg 14, Table I. The transfer of vapors from water to air is not included as a process by which contaminants are exchanged or lost.

Diffusion to air includes volatilization.

62. Fuhs (HML): Pg 19. In the second paragraph, it appears that "fugacity" refers to the contaminant, not the plant or soil mass. Therefore, substitute "in" for "of" in those phrases "... fugacity of the ... plant mass ..." Perhaps you mean "fugacity capacity of ..."?

The document has been revised.

63. Daugherty (Orange Co): Pg 21, first par. The document states that the diffusion depth below which a contaminant is unlikely to escape by diffusion is on the order of a meter or less for all but the most volatile contaminants and cites Jury et al. (1990). However, Jury et al. (1990) qualify their results in several ways. The CalTOX document should clarify its statement or better define "most volatile contaminants". Does the DTSC consider volatilization insignificant for contaminants of some unspecified vapor pressure at a depth greater than one meter?

The CalTOX model is designed to require the user to select a root-zone depth that meets the condition that this compartment is deep enough to make transfer from the vadose zone to the surface less than 5% likely. Unfortunately, there is not a simple prescription for the vapor pressure that converts to this condition since the condition of “volatile” in soil relates to both chemical properties and soil characteristics. We are working on a report that describes this process that will be issued as a stand-alone document.

64. Fuhs (HML): Pg 23. Add a statement on anoxic sediments. The escape of gas from the methanogenic layer in bodies of water with significant loading of biodegradable organic matter can cause a turbulent exchange with overlying water. This can affect the fate of contaminants and the oxygen in the water column.

As is noted in the executive summary the CalTOX model is intended to be used as a model to shed light on whether and/or which compartments require more detailed process modeling. We believe that the type of process modeling suggested by this comment should be used in a more detailed surface-water model but should be left out of a comprehensive model such as CalTOX.

65. Cohen (UCLA)/Lobascio and Tuchfeld (WCC): Pg 23. Assuming that the concentration of contaminant in ground water is the same as the concentration in vadose-zone leachate ignores the possibilities of reactions and dispersion in the soil

zone and dispersion in ground water. The exclusion of analytical ground water transport and saturated mixing modeling is a serious limitation of the model because of the inadequacy of compartmentalized models to realistically evaluate impact to ground water.

> As is noted, we do not currently model ground-water dilution but only represent the contaminant concentration entering the ground water zone. We are exploring the use of ground-water models that can be integrated with CalTOX to represent the dilution of contaminants in the ground-water zone. It should be noted, however, that the soil-layer models in CalTOX do include reactions that reduce the quantity of contaminant that moves from vadose zone to saturated zone. In addition, to be consistent with the policies of the Water Board to address potential degradation of aquifers, it is essential that CalTOX explicitly address the quantity of contaminant entering an aquifer, even if we later allow the model to address ground-water dilution.

66. Lobascio and Tuchfeld (WCC): Pg 23. a 1-D advection, dispersion, retardation and decay analytical solution of the transport equation, with a decaying pulse source as the boundary condition is recommended for modeling the impact on ground water. The pulse source would represent concentrations before and after remediation, the source decay could be evaluated by mass balance where source depletion depends on volatile emissions and leaching. If no ground water transport model is included, pathways involving ground water should be eliminated from CalTOX in order to reduce confusion, misuse of CalTOX, and waste of future resources.

> See response to 65. Based on our review of the literature, we could not find a model of the type suggested that has sufficient reliability to make a significant increase in the precision of CalTOX. It should be noted that in many cases the leachate can be an indicator of contaminant concentration in ground water. Also, the CalTOX model allows the user to explicitly specify ground-water concentrations if these are available.

67. Cohen (UCLA): Pg 41. The use of mass transfer coefficients for water/air exchange recommended for flowing streams is inappropriate for non-flowing streams or waste water impoundments. The correlation of Southworth (1979) defies the theoretical principles that govern water/air mass transfer processes. Comparing the prediction of the Southworth model to predictions made by other models shows significant differences when tested over a wide range of conditions.

> As noted in the Part-II report, we use a different model for mass-transfer from flowing and non-flowing water bodies. The type of estimation error noted here is accommodated in CalTOX by applying uncertainty factors to all mass-transfer coefficients. Also our sensitivity analyses indicate that the uncertainty associated with these mass-transfer coefficients does not have a significant impact on the predictions of risk.

68. Daugherty (Orange Co): Pg 42, last sentence. A citation should be given for this statement on boundary layer thickness.

A citation has been added.

69. Lobascio and Tuchfeld (WCC): Pg 43-48. It is uncertain whether the Jury model will be accurate over a 70-year time frame, whether the fugacity approach has been applied to the convection-dispersion equation, and whether the model has been field validated in non-agricultural settings. Dr. Jury should review the document.

The issue raised by this comment is discussed in both the executive summary and in the discussion of the Part-II report. Dr. Jury was asked to review the report.

70. Scofield (WSPA): Pg 43-48. The CalTOX model was calibrated to the Jury model (1983) and is calibrated to perform only when there is a continuous column of contaminated soil and, thus, may not be useful for other spatial distributions of contamination.

CalTOX was calibrated to a spatial distribution in which there are different concentrations in root- and vadose-zone layers. As is noted elsewhere, CalTOX is not designed to address more complex spatial variations of contaminant.

71. Lobascio and Tuchfeld (WCC): Pg 43-48. The CalTOX model treats the vadose zone as a single compartment with a constant chemical concentration. Such a model does not adequately simulate most sites where the vadose zone and contaminated area vary greatly in thickness. What should be simulated is a pulse of contaminant moving vertically through the vadose zone, smearing as it moves due to dispersion, until it encounters the water table. CalTOX cannot estimate the peak or the average concentration of such a pulse.

Please see response to comment 70. Also, it should be noted that the collection of samples and most sites does not provide sufficient information to construct detailed spatial distributions of zone boundaries and contaminant concentrations.

72. Cohen (UCLA): Pg 43-48. The more accurate analytical solutions for modeling the transport of chemicals in the soil (by evaluating mathematical error functions) can and should be incorporated into the spreadsheet model. How is the transfer of mass from one soil compartment to the next calculated? How are the "transport coefficients" for transport across the exchange boundaries between the soil compartments determined?

Both the method used to construct transport coefficients and our reasons for not using more complex analytical solutions are discussed in detail in the Part-II report.

73. Scofield (WSPA): Pg 43-45. The depths of each soil layer are fixed and contaminants in each layer are assumed to be well-mixed. Thus, it appears impossible to input initial conditions where site contamination varies with depth or horizontally. The assumption of instantaneous and complete mixing does not reflect the physical system and could result in an overestimation of the vertical transport of chemicals in certain environments.

> Depths of soil columns are not fixed but are specified by the user. Because the initial concentrations are input by the user, these inputs can not be under predicted unless they are under-predicted by the user. It is noted in our report that the CalTOX model approximation to the Jury et al. model does initially under predict flux. However, we go on to demonstrate that over a period of time exceeding one year this has little impact on the overall reliability of CalTOX relative to the Jury et al. model.

74. Cohen (UCLA): Pg 48. The fact that CalTOX under predicts the initial concentrations while it over predicts the flux suggests that there may be a critical problem in the approach used in the model. The soil compartment model in CalTOX falls short of reality.

> Because the initial concentrations are input by the user, these inputs can not be under predicted unless they are under-predicted by the user. It is noted in our report that the CalTOX model approximation to the Jury et al. model does initially under predict flux. However, we go on to demonstrate that over a period of time exceeding one year this has little impact on the overall reliability of CalTOX relative to the Jury et al. model.

75. Cohen (UCLA): Pg 49. How is the effect of soil moisture taken into account? The process of infiltration of soil by rain is complicated and the convection velocity will vary with depth and time.

> The effect of soil moisture on contaminant transport is discussed in the Part-II report. We are aware that the infiltration is complicated and that convection velocities and infiltration can vary with depth and this is why we consider an uncertainty analysis an integral part of the CalTOX model since there is currently no method for reliably addressing such random and chaotic processes in transport models.

76. Fuhs (HML): Pg 53, . Oxidations resulting from oxyradical formation are important but eludes modeling.

> This is true. See response to comment 77.

77. Fuhs (HML): Pg 53, last paragraph. Irrespective of the work of Boethling, the consensus is that site-specific estimates of microbial transformation of compounds are necessary.

We agree. Without site specific measurements, such processes will be assigned a large coefficient of uncertainty in the CalTOX model.

78. Fuhs (HML): Pg 57, bottom. The correlation between Koc and total organic carbon (TOC) in a soil is lost for soils with less than 0.1% TOC. Studies on the adsorption of hydrophobic organic contaminants to various soils could be done to reduce the uncertainty of these important estimates.

We agree. Please see response to comment 75.

79. Cohen (UCLA): Pg 62-63. A serious flaw of the CalTOX model is that the model does not consider the dynamics of rain scavenging (see Tsai et al. Environ Sci Technol 1991) and disregards the fact that the rain scavenging of particle-bound chemicals will be governed by the particle size distribution.

CalTOX includes simple rain-scavaging models for both particles and gases. We found no advantage with regard to model reliability in making these models any more complicated than they are since the model reliability is limited by the partition factors used in these models rather than the sophistication in the models.

80. Scofield (WSPA): Pg 66. The principal advective transport mechanism of infiltration occurs during storm events and is not representative of the long time intervals of months to decades prescribed by CalTOX. Also, there is no consideration of the initial wetness of the soil profile which could lead to overestimation of the vertical distribution of chemicals in the vadose zone in arid soils.

Long-term infiltration from soil is included as an advection process in CalTOX. The initial water content of the soil is used in the model since soil water content is used to determine the fugacity capacity of soil.

81. Scofield (WSPA): Pg 69. The loss process to ground water with no gain process from ground water could introduce significant errors to the transport model. There is no correction for dilution of vadose zone leachate by clean ground water, no accounting for the multiple phase transport of a contaminant such as gasoline, no consideration of smearing of chemicals within the vadose zone because of water table fluctuation in the soil column, and no allowable transfers between surface and ground waters. Therefore, CalTOX has limited application at sites where these conditions exist.

Please see response to comment 65.

82. Scofield (WSPA): Pg 71. CalTOX is used for regional modeling in the sample application described here. If CalTOX is a regional-scale model as stated in page 8 of responses to academic comments, than it should not be used to evaluate specific sites.

CalTOX has evolved from a calibrated regional fugacity model to a local (1000 m2 or greater) model. This evolution has been guided by peer review, model verification, and model validation.

83. Guvanasen (LAI): Pg 73. Recent research indicates that density-driven advective vapor flow is the dominant transport mechanism for dense chlorinated volatile organic compounds (tetrachloroethylene (PCE), trichloroethylene (TCE)) in the unsaturated zone (Sleep and Sykes, Water Resources Research 25:81-92, 1989; Falta et al., Water Resources Research 25:2159-2169, 1989; Mendoza and Frind, Water Resources Research 26:379-387, 1990). Since advective vapor flow is not in CalTOX, the results could be in error for these chemicals.

This type of mass transport only applies at very high contaminant concentrations and not at the types of dilute concentrations for which CalTOX was designed. When contaminant concentrations are this high, one does not need a model to decide that there is a level of risk that must be addressed.

Part III Comments

84. Scofield (WSPA): The exposure pathways discussion focuses strictly on residential scenarios. Exposure to vapors in trenches is not considered in the CalTOX model.

> At the present time, our objective is to define a manageable application scope and implement CalTOX for that purpose. Currently, we are focusing on an on-site residential exposure. Once this has been successfully implemented we intend to expand the scope of the model. It may be expanded in a number of areas such as non-residential exposures, NAPL, and off-site exposures.

85. Streeter (ERM): The model is directed towards rural sites and thus requires the user to select applicable scenarios with great care. This focus may prevent the application of the model for industrial / urban sites.

> Yes, great care should be used. The model is developed around the ten intake equations found in the USEPA's Risk Assessment Guidance for Superfund, Human Health Evaluation Manual Volume I: Part A (1989). This method has been applied to industrial / urban sites over the past four years.

86. Scofield (WSPA): The CalTOX model does not allow for the separation of secondary exposure pathways from primary source pathways which would be useful when there is a large degree of uncertainty or when only a fraction of the population is exposed to the secondary pathways.

> Any exposure pathway can be turned off if it is deemed inappropriate for a particular application. The model can be run with and without secondary pathways.

87. Guvanasen (LAI): The plant, surface-water and bottom sediment compartments should be available as optional exposure pathways only, because they are rarely found at industrial sites, unnecessarily complicate the model, and would require entering zero parameter values an inordinate number of times.

> Please see the responses to comments 85 and 86 above.

88. Lobascio and Tuchfeld (WCC) / Daugherty (Orange Co): Pg 10. The model assumes the site to be from 1000 m2 to 10 km2 in area. May the model be applied to smaller sites? McKone has stated that the model is applicable to a 30 x 100 foot area (city lot size). The model description should be revised.

> The model may be applied to 1,000 m2 areas which would be 10 m (30 ft) by 100 m (300 ft). The size limitation are site and chemical specific. For many situations, the minimum size could be less. The model description has been revised. CalTOX has evolved from a calibrated regional fugacity model to a local

(1000 m2 or greater) model. This evolution has been guided by peer review, model verification, and model validation.

89. Schueller (SWRCB): Pg 10. What are the criteria for classifying a site as large or small? A detailed example would help.

The model will be limited to sites greater than 1,000 m3. References to small and large sites have been eliminated.

90. Scofield (WSPA)/Streeter (ERM): Pg 15-24. Exposure via secondary food pathways may be overestimated in the CalTOX model because of the high uncertainty of plant uptake factors. Therefore, the plant uptake component of the CalTOX model should be used in the calculation of soil cleanup levels only where suitable data are available. The substantial uncertainties regarding plant, animal and fish uptake equations should be emphasized in the document for all the biological compartments. The predicted bioconcentration factors are developed from regression equations based on chemical-specific octanol-water partition coefficients which do not hold for all compounds.

A major thrust of the CalTOX model is to treat uncertainty quantitatively and explicitly through the use of stochastic modeling. Ignoring these pathways, uncertain as they may be, is inappropriate. In some cases, these pathways may be significant contributors to total daily dose.

91. Nye (IC): Pg 25-26. Cooking reduces the amounts of highly chlorinated lipophilic chemicals (DDT, PCBs, dieldrin) in cooked fish by 25% to 74% (Zabik et al, 1979; Puffer and Gossett, 1983). Equation 20 could be modified to include a factor to account for these losses.

We will look into these papers. Thank you for this input. This is exactly the dialog we wish to maintain with the public.

92. Nye (IC)/Streeter (ERM): Pg 29-39; Pg 47-48. For chemicals that are metabolized in animals, the use of transfer factors described in the CalTOX model would overestimate the chemical concentrations in animal-derived food products. Depuration should be taken into account, or a statement should be added that the CalTOX approach should not be used for chemicals metabolized in animals. Similarly, for chemicals that are rapidly metabolized and excreted in the mother (such as PAHs), the use of the Bbmk transfer factor may overestimate the biotransfer of chemicals into breast milk. A cautionary statement should be added to the document.

This is important limitation of the model in CalTOX. It is an area we are actively seeking to improve.

93. Nye (IC): Pg 49. Change the phrase "indoor exposure to dusts ... tracked in from soil" to "indoor exposure to dusts ... that have infiltrated from outdoor soil" in order to include all mechanisms (open windows, etc.).

> Dust coming in from open windows is account for by the relationship between the air particles and indoor air. This pathway is for soil that is tracked indoors.

94. Scofield (WSPA): Pg. 50. The CalTOX model does not distinguish between respirable particulate matter and total suspended particulate matter. The DTSC response that EPA guidelines require the consideration of all particles that move past the mouth does not acknowledge the actual practice in risk assessments. From a dose-response viewpoint, respirable particulate matter should be separated from non-respirable suspended particulate matter.

> The intake equations are intentionally designed to harmonize with USEPA policy. Our current approach complies with USEPA policy.

95. Daugherty (Orange Co): Pg 54. A vadose zone to indoor vapor exposure model has been developed by Orange County and the Shell Development Company and should be included in CalTOX. Also a similar simplified model for transport from the vadose zone to ground water should be included in CalTOX.

> Has the Orange County / Shell model been published in a peer reviewed scientific journal? If so, please provide DTSC with the citation. The model currently uses the model published by Johnson and Ettinger. (1991) Environ. Sci. Technol. 25:1445. One of the author is from Shell.

96. Lobascio and Tuchfeld (WCC): Pg 55-61. There is no water temperature, viscosity, or droplet size input parameters for the inhalation of vapors during a shower / bath (see Foster and Chrostowski's shower model).

> Please provide the literature citation for this model. The published work on this subject we cite shows these factors to be much less significant than those required by the current CalTOX shower model for normal showering conditions.

97. Nye (IC): Pg 63. A statement should be added referring to the list of permeability coefficient values in the Dermal Exposure Assessment: Principles and Applications (EPA / 600 / 8-91 / 011B).

> This document is designed to describe the model. The separate evolving document “Parameter Values and Ranges for CalTOX” will contain recommended values and appropriate citations.

98. Nye (IC): Pg 70. McKone (1991) predicted that the mean amount of TCDD in soil absorbed through the skin is 30%. The upper bound value derived by the EPA Workgroup from experimental studies is 3% (EPA Dermal Exposure Assessment:

Principles and Applications. EPA/600/8-91/011B). Using the McKone model, Burmaster and Maxwell (Risk Anal 11:491-7, 1991) calculated that benzo[a]pyrene (BaP) is nearly 100% absorbed from the soil to skin after 12 hours, whereas it is 51% dermally absorbed in an acetone vehicle over 24 hours in the rhesus monkey (Wester et al., Fund Appl Toxicol 15:510-6, 1990). These data indicate that the McKone model may considerably overestimate dermal absorption of highly lipophilic chemicals in soil.

In CalTOX, we use the McKone-Howd (Risk Analysis, 1992) model for estimating transfer from water/soil to skin and not the McKone (1991) model. The McKone-Howd model is quite similar to the EPA dermal guidance model in its predicted values.

99. Scofield (WSPA): Pg 80. The CalTOX model does not allow segregation of hazard quotients for different toxicological endpoints.

The model is run assuming one chemical with one RfD. It can be run multiple times with different RfD's.

100. Reed (DPR): Pg 81. The document should point out the inappropriateness in summing indiscriminately all hazard quotients regardless of endpoints/target organs which may be route-specific.

The manual is intended to describe the model. Risk characterization is a policy issue. It is likely that it will be consistent with USEPA policy.

101. Scofield (WSPA): The CalTOX model cannot calculate risk-based remediation levels for acute or subchronic exposures.

Please see response to comment 84.

102. Scofield (WSPA): The CalTOX model should include indoor air quality modeling beyond inhalation exposure during showering. Activity pattern databases should be used to assess indoor exposure and risk.

These will be considered, to the extent possible, in deriving the input data. This is not an indoor air quality model. That level of detail this suggestion would require would not be commensurate with the detail in other portions of the model. The model as currently configured is large and complex. It would greatly increase the size and complexity to add this level of detail in all areas. It is unlikely that this will be undertaken.

103. Scofield (WSPA): (Pg 58?). The CalTOX model does not subtract the time spent in the shower from the time spent at the site. Therefore, the individual spends 24.27 h/d at the contaminated site.

The document has been revised.

Parameter Values

104. Daugherty (Orange Co): Since the theoretical basis of the CalTOX model has been well based and well reviewed, inputs into the CalTOX model will be all important. Thus, the "Response to Comments" no. 52 stating that the high inaccuracy in partition coefficients does not detract from the underlying scientific theory misses the point. The point is that CalTOX will be used to make decisions about the public health and requires both sound theory and accurate inputs.

Distributions for the physical and chemical parameters will be specified. Therefore, the model will capture uncertainty in these parameters.

105. Daugherty (Orange Co): The CalTOX model should be examined for the possibility of unrealistic combination of inputs. Caveats should be included in the document on unrealistic inputs or combination of inputs. Statements should be added on how to consider transitory conditions, such as a vadose zone wetting front or perched waters.

This is a good point and when identified these problems will be identified in the users manual. Correlations will be specified and limits on ranges identified.

106. Lobascio and Tuchfeld (WCC): Rate coefficients can only be evaluated simultaneously with other input parameters. The inability to isolate the measurement of a single parameter obscures the relationships which it may have to characterize the local environment and prevents the user from making rational assignment of values for the parameter in a different location.

This comment is unclear. We fully intend to conduct sensitivity analysis on the applications of CalTOX. This will identify the sensitive parameters and focus the remedial investigation.

107. Scofield (WSPA)/Lobascio and Tuchfeld (WCC): It is difficult to evaluate the sensitivity of the model to various input parameters, since the document provides only limited discussion of these sensitivities. Extensive guidance should be provided on performing sensitivity and uncertainty analysis.

Explicit guidance will be provided.

108. Streeter (ERM): Appropriate guidance on the use and significance of stochastic presentation of risk estimates is essential.

Explicit guidance will be provided.

109. Lobascio and Tuchfeld (WCC): A model with over 100 input parameters is a very complex model with large uncertainty when used due to the inability to provide site-specific data for the input parameters.

> Yes, and collection of site-specific data will reduce the uncertainty. A sensitivity analysis on a particular application will show the limited number of parameters influencing the risk. This will provide direction in site characterization.

110. Scofield (WSPA): The parameter values recommended for CalTOX should undergo peer review and public comment. What procedure will the DTSC use to obtain public review: comments on a proposed list of values or active participation from the public in establishing the values? What will be the schedule for updating of values?

> DTSC wants the default parameter distributions to be of the best most current science. Therefore, an advisory panel of CalEPA scientists will meet on a bi-annual basis to review proposals to update default distributions. DTSC will welcome proposals from the public based on studies published in the open peer-reviewed literature.

111. Scofield (WSPA): Adjustment should be made for periods spent away from the site using activity pattern databases.

> Please provide specific proposals.

112. Cohen (UCLA)/Scofield (WSPA): Additional documentation should be provided for the derivation of the CV values.   There is lack of justification for numerous selected parameter values.

> As stated in the preface, this document, “Parameter Values and Ranges for CalTOX”, is a work in progress and is intended to show the general direction of the DTSC. It is a work in progress. Justification will be provided for all values.

113. Crisologo (DTSC/R4/SMB): The process for arriving at default parameters should be given.

> Please see response to comment 112.

114. Crisologo (DTSC/R4/SMB): . How long a time frame is needed for sampling to obtain site-specific data to replace default parameters?

> We are working with Hazardous Materials Laboratory to establish the criteria for site-specific measurements.

115. Scofield (WSPA): Mean and CV values are presented as arithmetic mean values while the distributions are assumed to be lognormal. The document does not explain

how the parameters are transformed into "lognormal" space within the CalTOX program.

> The stochastic spreadsheet add-in programs allow the user to define lognormal distribution in linear or log space. We define them in linear space. The equations to transform the parameter value may be added in a future addition if it does not lead to confusion.

116. Scofield (WSPA): Some of the generic correlations upon which CalTOX relies for physico-chemical parameters are based on very limited data sets. The high degree of uncertainty of the generic correlations results in high CV values, which results in overestimation of predicted exposures.

> The objective of CalTOX is to move away from concern about over-prediction or under-prediction. The focus is to quantitatively express uncertainty. Therefore, the objective will be to reduce the uncertainty associated with a given exposure scenario.

117. Lobascio and Tuchfeld (WCC): Pg 5. Consistent information on the uncertainty and variability of the input parameters should be provided with the model accompanied with extensive documentation and clear guidance on how to use the information for uncertainty and sensitivity analysis.

> This will be addressed in the future .

118. Lobascio and Tuchfeld (WCC): Table II. The 0.0042 kg/kg-d fruit and vegetable intake is equivalent to 294 g/day which is high compared to the US EPA average consumption value of 78 g/day. The default beef intake value of 0.0026 kg/kg-d is equivalent to 182 g/day for a 70 kg adult, while the EPA average value is 44 d/day (EPA Exposure Factors Handbook, 1989).

> The CalTOX food ingestion rates specify average daily intake of meat, vegetables/fruit, milk, eggs and fish consumed by people unrelated to source. This is then adjusted by the fraction local to indicate the fraction of total that may be contaminated by chemicals emanating from the site under consideration. The USEPA reference is for ingestion of local meat and vegetables. Therefore, the fraction local is included in the USEPA estimates.

119. Nye (IC): Table III. For body surface fraction with soil contact, the US EPA lists 0.25 as a reasonable worst case (EPA Dermal Exposure Assessment. Principles and Applications. EPA/600/8-91/011B) while the CalTOX model lists 0.3 as the estimated mean value. In addition, Thompson et al. (Risk Analysis 12:53-62, 1992) have used a point estimate of 0.2 as describing the 85th percentile for the exposed body surface distribution. McKone and Layton (1986) indicate that the 0.26 to 0.3 fraction of skin surface represents the hands, arms, legs, neck, head, and feet. It is difficult to imagine any reasonable situation that would result in a greater fraction of skin surface area that

may be exposed to soil. Therefore, the 0.3 estimated mean value should be replaced with a lower value.

> This comment is useful and the issue of a more realistic range of values for the fraction of skin surface actually having soil on it needs further consideration. We are looking into this issue.

120. Nye (IC): Pg 14, Table III. For soil adherence to skin, the 0.2 mg/cm2 recommended by the EPA (EPA Dermal Exposure Assessment. Principles and Applications. EPA/600/8-91/011B) is a better approximation of the estimated mean value of whole body soil loading on the skin than the 0.5 mg/cm2 value listed in Table III. The 0.5 mg/cm2 value is derived from the deliberate intimate contact of hands with soil. Such contact may not be representative of normal behavior.

> Yes, this point is well taken. In order to make the inputs to CalTOX reflect expected values and the standard deviation associated with these values, we will look into a revision of this number.

121. Lobascio and Tuchfeld (WCC): Pg 14, Table III. The default soil ingestion rate of 2.2x10-6 kg/kg-d for children is equivalent to 0.0638 g/day for a 29 kg child which is low compared to the US EPA values of 0.2 to 0.8 g/day (EPA Exposure Factors Handbook, 1989).

> These inputs are based on the published work of Calabrese and others.

122. Scofield (WSPA): Pg 9 and Table III. Some mean parameter values are questionable. For example, is the mean exposure duration 9 years (the geometric mean) or 30 years (the arithmetic mean)? The "fraction of meat, local" should be changed to "fraction of meat, farm families". The value for this parameter (listed as 0.44) would be far less for non-farm families. A review of all parameter values and ranges should be conducted.

> The actual default inputs are specified in the separate evolving document “Parameter Values and Ranges for CalTOX”. We will retain the term local because it is more generic.

123. Reed (DPR): Pg 12. DPR food intake analysis may differ from that of DTSC. Is the cursory analysis of DTSC sufficient for addressing food intake for screening purposes?

> This is a work in progress and we anticipate it continually being improved. Please provide specific suggestions and supporting data.

124. Scofield (WSPA): Pg 28 and Table V. For hydrophobic, lipophilic substances, biota to sediment accumulation factors (BSAF) provide more accurate estimates of chemical concentration in fish than the bioconcentration factors (BCFs) used in the

model. Also the lipid content of the fish must be considered, since an overestimation of lipid content in fish can lead to an overestimation of chemical concentration in fish.

> At present, BSAF data are limited and this would prevent application of the model. As more data become available, DTSC will consider updating CalTOX to incorporate the new information.

125. Nye (IC): Pg 31. Equations 23 and 24 are incorrect, based on McKone and Daniels (1991). Wshower and Whouse appear to be switched.

> The document has been revised.

126. Daugherty (Orange Co): Pg 32-38, Tables VI, VII, VIII. Caveats regarding the proper input of organic carbon for sorption and possibly other input parameters should be included in the document, for example, using the TPH concentration from diesel fuel contamination as the fraction of organic carbon to calculate a retardation factor for napthelene leaching from the diesel fuel.

> Such a caveat may appear as the document evolves.

127. Scofield (WSPA)/Lobascio and Tuchfeld (WCC): Pg 32-38, Tables VI, VII, VIII. A selection of landscape property data sets representative of California is not possible.

> We believe that the range of parameter values for sites found in California be and has been defined. We welcome specific challenges supported by citations from the peer-reviewed literature. This range will represent a default situation. Site specific data can be substituted for default values where appropriate.

128. Lobascio and Tuchfeld (WCC)/Daugherty (Orange Co): Pg 32-38, Tables VI, VII, VIII. The default value for soil particle density is 2.4 g/cm3, while the average value ranges from 2.65 g/cm3 for clay to 2.75 g/cm3 for sand (The Nature and Property of Soils, 9th Ed., Brady, 1984). A particle density value of 2.4 g/cm3 may be realistic for the surface and the root zone because of the effect of organic matter in lowering the value from the 2.65 to 2.75 typical of mineral particles. However, the particle density for the vadose zone should be 2.7 g/cm3, since organic carbon content is negligible in subsurface solids.

> The soil particle density value will be changed to a value that reflects the correct range for the types of soils found in California.

129. Lobascio and Tuchfeld (WCC): Pg 32-38, Tables VI, VII, VIII. Why is soil bulk density excluded as an input parameter, when this parameter affects volatilization emission rates and leaching rates, is related to soil porosity and can be used to calculate soil air content?

Four parameters can be used to define the volume, density, and composition of soil. These are (1) bulk density, (2)water content, (3)pure particle density, and (4)air content. Selecting any three of these fixes the fourth. We elected to select water content, particle density, and air content as the parameters to use for model inputs.

130. Daugherty (Orange Co): Pg 32-38, Tables VI, VII, VIII. The value of 0.01 for fraction of organic carbon in the vadose zone seems high, while the value of 0.012 for the fraction of organic carbon in the root zone seems low. Provide the citations. The sum of air-filled and water-filled porosity (or total porosity) of the vadose zone is greater than that of surface and root zone soils (0.4 vs 0.3). It does not seem reasonable to model deeper soil as more porous than shallow soil, when the effects of compaction should reduce porosity at depth.

As was stated in the preface to this report, all model inputs are currently under review. We welcome this comment regarding our preliminary input values and will give it consideration as we revise our input data values.

Non-technical Comments

Editorial Comments

1. Guvanasen (LAI): The accepted rules for representing mathematical expressions should be followed (ANSI/IEEE Standard Letter Symbols for Units of Measurement, 1978):

a. Symbols for physical quantities are single letters modified by one or more subscripts or superscripts. The same letter symbol should appear throughout the work for the same physical quantity. Area, runoff, Intakedwi, IRdrink should be A, r, Idwi, IR,dri.

b. The product of two quantities a,b, is indicated by writing ab. In many equations in Parts II and III, multiplication signs are used and are superfluous.

c. If more than one slash (/) is used in any algebraic term, parentheses must be inserted to remove ambiguity. Thus a/b/c should be (a/b)/c or a/(b/c).

d. Please note that "(kg[DM]/m2-d)" should be "(kg/(m2•d)) dry mass".

A rewriting of the symbols used will not take place at this time. If specific equations are ambiguous and impedes understanding of the basic processes, please identify them.

2. Fuhs (HML): Part I, pg 9, line 2. "benifits" should be "benefits".

The document has been revised.

3. Fuhs (HML): Part I, pg 16, par 3, line 1. The sentence should be "... used in CalTOX ..."

The document has been revised.

4. Fuhs (HML): Part I, pg 27, par 3, last line. "compliment" should be "complement".

The document has been revised.

5. Fuhs (HML): Part II, pg 17, line 2. The sentence should be "... using single letter ..."

The document has been revised.

6. Fuhs (HML): Part II, pg 36, par 2, last sentence. The sentence should be changed to read "... the modeling of ... mass transfer must include both turbulent and molecular processes at these transition zones that cannot be lumped or neglected".

The document has been revised.

General Policy Questions

1. Streeter (ERM): It is important to emphasize that the results of risk assessment modeling need to be considered in the context of multiple issues (realistic future site use, implementibility, permanence, short-term health risks, etc.). The CalTOX model is a tool and not a doctrine.

An excellent point.

2. Merryman (CCDEH): It is not clear whether local agencies will be required to use the CalTOX model. Using CalTOX may not be appropriate at the smaller sites that local agencies typically oversee, unless a streamlined version of the model is developed for such use.

We are not addressing issues like this during the technical comment period. It is unlikely that DTSC will require local agencies to use CalTOX. We believe that the advantages will become apparent when compared to current methods of risk assessment. Local agencies may find useful applications or wish to use portions of the model.

Water Board and Related Comments

These comments and responses were sent to the Clean Waters Division of State Water Quality Control Board for their review. They asked that some wording be added. That wording appears in italics.

1a. Sheldon: Because the CalTOX model will always predict some finite contaminant mass loading to ground water, every modeled site could result in some contaminant level increase over background. Theoretically, every site modeled using CalTOX will have to be remediated because of the nondegradation policy of the Porter-Cologne Water Quality Act. The Cal/EPA must rectify the conflicting policy objectives of the State Water Board and DTSC in order for CalTOX to function as a legally defensible decision-making tool.

Please see response below. *The policy is antidegradation, not nondegradation which is an important distinction. Cleanup remediation under the anti-degradation policy would only be required for aquifers with beneficial use. The extent of cleanup would be required only to the extent it is technologically and economically feasible. (SWQCB)*

1b. Merryman (CCDEH)/Daugherty (Orange Co): The CalTOX model should clearly define its regulatory applicability in light of the different approaches to site evaluation taken by the DTSC (receptor approach) and the State Water Resources Control Board (SWRCB) (protection of ground water resources). Cal/EPA must reconcile the resource protection perspective of the SWRCB with the source to receptor risk assessment perspective of the DTSC.

Please see response below. *The perspective of the two agencies is not mutually exclusive. Selection of a remedial approach which satisfies both perspectives should occur on a site-by-site basis. (SWQCB)*

1c. Crooks (CRWQCB / CVR): The CalTOX document should be amended to clearly state that the model assesses health risks from contaminated sites, that other considerations (beneficial uses and risks to water resources) are involved in determining remedial action goals, and that State and Regional Water Boards also have site assessment and remedial action jurisdiction.

Please see response below.

1d. Pettit (SWRCB): The model, as presently conceived, would be inadequate to accommodate the State Water Resources Control Board's (State Water Board) and the Regional Water Quality Control Boards' (Regional Water Board) needs because it is designed to predict threats only to human health. Under the Porter-Cologne Act, the State and Regional Water Boards are charged with protecting all beneficial uses of the waters of the State. Consequently, we must be concerned with any of the many conditions that can impair any beneficial use but which would not necessarily constitute a threat to human health. Take for example, taste or odor levels that would make drinking water unpotable or low levels of boron that would make the water unsuitable for agricultural uses.

Please see response below.

1e. Pettit (SWRCB): Under the California Water Code and applicable regulations and policies enforced by the State and Regional Water Boards, the primary objectives of water quality regulation are (1) to restore water quality to levels that will at least protect beneficial uses, (2) to maintain existing water quality where water is unaffected by contamination, and (3) to regulate discharges to protect beneficial uses and comply with water quality control plans and policies. Only under limited circumstances would waste be allowed to remain in the waters of the State if it affects beneficial uses and only under limited circumstances is degradation of the waters of the State allowed.

The CalTOX model, on the other hand, is governed by the fundamental principle that the waters of the State may be polluted so long as the accepted risk to human health is not exceeded. This approach conflicts with State Water Board policy in that it considers only one beneficial use and implicitly establishes a right to degrade the waters of the State. Consequently, the risk assessment approach employed in the CalTOX model would have only limited application, if any at all, in our routine regulatory activities.

In evaluating these comments, the differences between the two approaches should not be disregarded as merely different means to the same end; the differences are fundamental. These differences arise from the fact that, although there is some overlap in responsibility among some of the agencies within Cal/EPA, the statutory charge to the State and Regional Water Boards is separate and distinct from the charge to the Department of Toxic Substances Control. The approach used by the State and Regional Water Boards is fundamental to the accomplishment of our mission while employment of the risk assessment approach would prevent the accomplishment of that mission.

Please see response below.

1f. Schueller (SWRCB): An explanation should be provided at the beginning of the document for how the requirements of both the SWRCB and the DTSC will be fulfilled, given the differences in the approaches employed by these departments.

> All the comments grouped in comment 1 above pertain to a significant difference in the policies of the State Water Board and the DTSC. The State Water Board interprets their authorizing legislation and related regulations to require them to restore water quality and maintain water quality as the primary objective in deciding on a remedy for a hazardous waste site. This approach to environmental regulation leans toward restoring environmental conditions to their pre-contaminated state. DTSC interprets its authorizing legislation and related regulations to require the Department to consider nine criteria in the selection of remedy. Risk to human health and the environment, cost, and implementablity are some of these criteria. Environmental restoration is not an explicitly stated goal and the concept of risk and cost/benefit pervades the legislation and regulation. These differences, in addition to the fact that the Water Boards have a statutory charge to protect beneficial uses that extend beyond the scope of DTSC's area of responsibility, may lead the DTSC and the Water Boards to select remedies which differ from one another. However, remedies can be selected that satisfy the regulatory mandates of both agencies. (SWQCB)
>
> This fundamental difference transcends the debate about CalTOX. CalTOX is a tool designed to provide DTSC decision makers with a more realistic estimate of the risk to human health. Human health is part of one of the criteria which must be considered in remedy selection. Once it has been successfully implemented for this purpose, it will be extended in the future to address other risks including ecological risks. CalTOX is not a substitute for risk management, it is intended to inform the risk manager. CalTOX is not central to the policy debate between DTSC and the Water Board. The success or failure of CalTOX as a risk assessment policy will have little or no effect on this larger debate.

2. Pettit (SWRCB): In order to help prevent the model from being misused, there should be an explicit statement of the uses for which it is designed (e.g., screening; qualitative comparison of proposed actions; quantitative predictions for regulatory requirements) and the conditions and limitations for its use.

We intend to do this.

3a. Pettit (SWRCB): To date, the CalTOX model has not been successfully field verified. Until the predictions produced by the model have been shown to accurately reflect reality, the model must be viewed as experimental and not yet suitable for regulatory use. To underscore why we believe that field verification is essential, the State Water Board engaged the University of California at Davis in 1990 to determine the state-of-the-art with regard to predicting the fate and transport of constituents in the vadose zone (See Attachment). Their report concluded that the state-of-the-art has not yet progressed to the point that vadose zone fate and transport models are capable of producing the quality of results needed for regulatory purposes. Consequently, we believe that until the model has been verified under all conditions for which it was designed, it must be considered experimental. Furthermore, the fact that the CalTOX model is a stochastic (statistical) model suggests that it will not be able to provide the accuracy or the certainty required to carry out our regulatory mandates.

Please see response below.

3b. Pettit (SWRCB): Many aspects of the proposed model are at odds with some of the findings reported in Ground Water Models - Scientific and Regulatory Applications, a study on the use of ground water models published by the National Research Council in 1990 (See Overview, Conclusions and Recommendations, pp 1-21):

"...At the present time, conceptual issues and / or problems in obtaining data on parameter values limit the reliability and therefore the applicability of flow models involving unsaturated media, fractured media, or two or more liquids."

"Although models for important reactions like oxidation / reduction, precipitation, and biodegradation exist, they are complicated to formulate and solve, difficult to characterize in terms of kinetic parameters, and largely invalidated in practical applications. Thus the transport of multiple reacting constituents such as trace metals and organic compounds cannot be modeled with confidence."

"Generic models are useful as a tool for initial screening but can never be used as a replacement for site-specific models."

"Several agencies have guidelines that encourage the use of contaminant transport models. There are many different types of models, model applications, modeling objectives, and legal frameworks. Agencies cannot specify a list of government-approved models. A model that is appropriate for one problem may not be, and probably is not, applicable to another problem."

"Ground water models do and should vary in complexity. The complexity of the model used to analyze a specific site should be determined by the type of problem being analyzed. While more complex models increase the range of situations that can be described, increasing complexity requires more input data, requires a higher level and range of skill of the modelers, and may introduce greater uncertainty in the output if input data are not available or of sufficient quality to specify the parameters of the model."

"One of the key requirements in successfully applying flow or contaminant transport models is good-quality, site-specific data...In cases where particular model parameters are not or cannot be characterized, model prediction becomes much less certain because predicted variable like hydraulic potential or concentration could take on a much broader range of possible values."

Comment 3 questions the use of models in general, and CalTOX in specific, for predicting the transport of chemicals in the vadose zone. A number of uncertainties associated with transport models are cited from the 1990 National Research Council report. We agree with many of the uncertainties cited. This is why CalTOX treats uncertainty quantitatively. CalTOX does not provide a single estimate of concentration in vadose zone leachate or a single risk estimate. The model displays a range of values in the form of a distribution. The less site-specific information, the broader the range.

Many of the criticisms of models, including CalTOX, are related to a skepticism of the relationship between models and reality. Unfortunately, every decision based on potential future harm involves a model. One cannot know exactly what future harm will occur, therefore, we must establish a relationship between present conditions and potential future harm. Often times these relationships or “models” are implicit. The decision may be to require the responsible party to remediate a site until a chemical can no longer be detected. In this case, the implicit model is that the limit of detection by the analytical method used is relevant to that future harm. Usually, the implicit models used by regulatory agencies are not continuously evaluated in the light of new scientific developments. The models become outdated, but the objectives set by those models continue to be enforced.

With CalTOX, we intend to make the DTSC model explicit and subject to scrutiny. We expect that there will be changes in the model. The default input parameters will change as new information becomes available in the peer reviewed scientific literature. The model structure may change as more accurate relationships are published and are deemed appropriate. The objective of CalTOX is to provide risk managers with as accurate an estimate of risk as possible, including the uncertainty around that estimate of risk.

The DTSC regulates a wide array of sites within California. The DTSC has overseen the remediation of sites which range from house lots to military bases of 90 sq. miles. On small sites, site characterization can exceed the cost of clean up. On many sites, obtaining data to justify the use of a complex model would increase the cost and delay the remediation, and have little effect on the remediation decision. The DTSC needs a model which can accommodate varying amounts of site-specific data. CalTOX fulfills this requirement.

CalTOX is a generic compartment model which reduces a site to seven compartments. Chemicals are moved from compartment to compartment, degraded or removed from the site based on landscape parameters and chemical properties. It is a model with a large number of simplifying assumptions. All of these factors reduce the ability of CalTOX to precisely determine the exact fate of chemical in the environment, but more precise models require parameter estimates which are very expensive to obtain. Based on site-specific data needs, CalTOX can be applied at most of the sites within the DTSC regulatory jurisdiction. In fact, default parameter input distributions are specified which are intended to characterize the range of input parameters found at sites in California under the DTSC regulatory jurisdiction. Using only these default distributions and site-measured soil concentrations, extremely broad risk estimate distributions may be computed. Such generic estimates may be all that is required for some sites. For other sites, more site-specific measurements may be cost-effective. Then at some sites, sophisticated models may be justified because the needed input parameters have been measured.

In summary, estimates of risk are required by regulation and models are an inevitable part of DTSC risk estimates. Explicit models are superior to implicit models. Models must be selected based on available data and hypothetical accuracy. Uncertainty should be treated quantitatively and addressed in the risk management process. CalTOX has been developed for these purposes and has data requirements consistent with the range of sites falling under DTSC jurisdiction.

4. Pettit (SWRCB): We agree with the comment of Professor Richard E. Green, University of Hawaii at Manoa, that it is doubtful that the leaching portion of the CalTOX model is capable of producing results sufficiently accurate to be used for site-specific situations. Consequently, the model would have little applicability for State and Regional Water Board use.

Please see response to comment 3. Also, please note that, on the whole, Dr. Green’s review was generally supportive.

5. Pettit (SWRCB): CalTOX is designed to model sites that are on the order of 1-10 square kilometers while many of the sites with which the Regional Water Boards are involved fall outside this size limitation. Because of this and the assumption of homogeneous compartments, we feel that there is great potential for widespread misapplication of the model if it is adopted as the standard model for Cal/EPA.

The minimum size limit is on the order of 1,000 m2 which should accommodate most sites. We believe that a compartment model is appropriate given the decisions DTSC is required to make.

6. Pettit (SWRCB): The spreadsheet format used by CalTOX allows users to modify default parameters at will. Because of this, regulatory agencies will have to provide resources to either independently model the site with CalTOX using the dischargers data or verify the model used by discharger with a validation test. We believe that, under the foreseeable budgetary conditions, it is unrealistic to expect regulatory agencies to acquire the necessary highly skilled personnel to perform these tasks.

We anticipate that requiring regulated parties to submit their data electronically will greatly reduce the amount of time required to verify the computations and enhance the review. One of the objectives in the development of the model was to reduce the time and cost associated with DTSC oversight. CalTOX should significantly reduce the amount of time required to prepare and review a risk assessment.