EVALUATING AND EXPRESSING THE PROPAGATION OF UNCERTAINTY IN CHEMICAL FATE AND BIOACCUMULATION MODELS

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Abstract—First-order analytical sensitivity and uncertainty analysis for environmental chemical fate models is described and applied to a regional contaminant fate model and a food web bioaccumulation model. By assuming linear relationships between inputs and outputs, independence, and log-normal distributions of input variables, a relationship between uncertainty in input parameters and uncertainty in output parameters can be derived, yielding results that are consistent with a Monte Carlo analysis with similar input assumptions. A graphical technique is devised for interpreting and communicating uncertainty propagation as a function of variance in input parameters and model sensitivity. The suggested approach is less calculationally intensive than Monte Carlo analysis and is appropriate for preliminary assessment of uncertainty when models are applied to generic environments or to large geographic areas or when detailed parameterization of input uncertainties is unwarranted or impossible. This approach is particularly useful as a starting point for identification of sensitive model inputs at the early stages of applying a generic contaminant fate model to a specific environmental scenario, as a tool to support refinements of the model and the uncertainty analysis for site-specific scenarios, or for examining defined end points. The analysis identifies those input parameters that contribute significantly to uncertainty in outputs, enabling attention to be focused on defining median values and more appropriate distributions to describe these variables.

Keywords—Uncertainty Model Mass balance Bioaccumulation ChemCAN

INTRODUCTION

Mass balance models of chemical fate are increasingly recognized as useful tools to facilitate management of chemicals that are released to the environment. Since models are necessarily only an approximation of the actual and more complex fate of chemicals, it is important to communicate clearly the uncertainties associated with model results. Sensitivity and uncertainty analysis can also be useful to the model developer and to users who are interested in applying existing models to new environmental problems. Identifying model inputs that most significantly affect key outputs can focus attention on accurately quantifying the values (and associated uncertainties) of input variables that most strongly influence the model’s predictions and guide efforts to increase model accuracy.

Monte Carlo analysis is currently the technique of choice for quantifying uncertainty in health and environmental risk assessments [1]. It is attractive because it is general and is unconstrained by the type of model that can be analyzed or the selection of input distributions [2]. Recent advances in computer hardware (capable of conducting many individual simulations in a relatively short period of time) and software (which automates generation of stochastic distributions) have made the Monte Carlo approach virtually synonymous with uncertainty analysis in the field of chemical fate assessment.

A characteristic of Monte Carlo analysis is that it tends to be data intensive, requiring parameterization of the degree of uncertainty and the shape of input distributions that are appropriate to each individual input parameter for the specific conditions under examination. This is an advantage in detailed assessments of model uncertainty, but the prospect of manipulating and interpreting a multitude of probabilistic distributions can be daunting to individuals who are unfamiliar with these techniques. Difficulties interpreting results can arise when input distributions with different forms are mixed. If the model is applied to a generic environment or on a broad regional scale, detailed parameterization of the distributions may be impossible. Faced with the difficulties of setting up a Monte Carlo analysis and interpreting the results, model developers and users may choose to leave uncertainty analysis until the end of the modeling process or, regrettably, to forego it entirely.

This article describes an analytical approach for conducting a simple and preliminary analysis of uncertainty in mass balance models of chemical fate that includes sensitivity analysis, analysis of propagation of variance, and comparison of input uncertainties in terms of their contributions to uncertainties in outputs. The approach can be integrated into end-user versions of models without significantly increasing calculation time. It allows uncertainty in model outputs to be expressed by a single factor, and graphical interpretation of the propagation of uncertainty is possible. These advantages are realized by making several simplifying assumptions in the analysis, most notably, that inputs to the model are independent, that uncertainty in all variables can be expressed as a log-normal distribution, and that the models are near linear over the range of uncertainty in inputs. It is recognized that these assumptions introduce a degree of error in the assessment, but experience has shown that the error is acceptable for screening purposes. If the linearity assumption is of concern, a full Monte Carlo analysis can be done, focusing on key input parameters that have been identified by this preliminary analysis.

For simplicity, we do not differentiate between uncertainty in parameters and equations used to describe chemical process

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rates (true uncertainty) and spatial and temporal variability within the environment (variability). Uncertainty and variability can be treated separately when propagating uncertainty through mathematical models [3], but given the present approach is intended as only a preliminary analysis of uncertainty, it seeks only to identify input parameters that contribute significantly to uncertainty in outputs and to provide an estimate of the magnitude of that uncertainty. If a reduction in output uncertainty is desired or a more detailed uncertainty analysis is required, identification of whether uncertainties in important input parameters are predominantly due to uncertainty or variability can help direct further efforts. The present approach assumes the model’s description of contaminant fate is not significantly biased and will give misleading estimates of uncertainty if applied indiscriminately. For example, ChemCAN (Trent University, Peterborough, ON, Canada), as applied below, is formulated to describe chemical fate and partitioning of chemicals that exist in the environment as a single species and would give biased or meaningless results if applied to a speciating metal such as mercury [4].

The present approach is viewed as satisfying the need for an easily interpretable, systematic methodology for assessing uncertainty and sensitivity in chemical fate models that was identified at a Society of Environmental Toxicology and Chemistry Pellston workshop on fate modeling [5]. The analysis is demonstrated on two contaminant fate models, ChemCAN 4.0 for southern Ontario, Canada [4], and a food web bioaccumulation model for Lake Ontario, Canada [6]. The uncertainty estimates from the analytical approach are compared with those from a comparable Monte Carlo analysis to assess the implications of the linearity assumption.

BACKGROUND AND MODEL DESCRIPTION

Among models used to assess environmental fate of chemicals are ChemCAN, the equilibrium criterion (EQC) model [7], CalTOX® [8], and SimpleBox [9], which is a component of the European Uniform System for the Evaluation of Substances (EUSES) [10]. Uncertainty analysis of these models reported in the literature has frequently focused on site-specific and chemical-specific scenarios to which the models have been applied. McKone and coworkers have made extensive use of Monte Carlo uncertainty analysis in conducting chemical fate assessments using CalTOX [3,11–13], often with a focus on contaminant fate in soils and groundwater. Simpler Monte Carlo analyses that assume independence of input variables have been reported by Kuhne et al. [14] to assess error propagation in the case of uncertain physical chemical properties and by Ragas et al. [15], who discuss the implications of model uncertainty on evaluating environmental quality objectives. In Europe, incorporation of uncertainty into chemical risk assessments using EUSES is an area of current research, as discussed by Jager et al. [16] and illustrated by Huibregts et al. [17].

Bioaccumulation models describe the process of contaminant uptake and clearance by individual organisms and transfer of contaminants between organisms at different trophic levels in a defined ecosystem. The large number of inputs required to parameterize food web interactions is a practical obstacle when conducting systematic sensitivity and uncertainty analysis. Sensitivity analyses by changing model input variables by a fixed amount and observing the corresponding changes in the outputs have been reported [18,19]. Burkhard [20] has described a sensitivity and uncertainty analysis of the Thomann et al. [21] and Gobas [22] bioaccumulation models. Evans [23] has reported both sensitivity and uncertainty analyses on a bioaccumulation model of cesium uptake in fish.

MODEL EQUATIONS

The suggested analytical analysis of uncertainty is applied to the ChemCAN 4.0 regional contaminant fate model parameterized for southern Ontario and to the Campens bioaccumulation model parameterized for the Lake Ontario food web. The models can be downloaded free of charge from the Canadian Environmental Modelling Centre website (http://www.trentu.ca/envmodel). The models consist of a system of equations that calculate steady-state concentrations and fluxes of a chemical from input parameters describing the environment, the physicochemical properties of the chemical, and its discharge rate. Both are Level III mass-balance models based on the fugacity concept; however, the uncertainty analysis technique can also be applied to similar models formulated in terms of rate constants and chemical mass or concentration. The ChemCAN environment consists of four homogeneous compartments representing the air, water, soil, and sediment of a defined region. The environment of the food web model includes compartments representing fish and aquatic and benthic organisms at various trophic levels and the water and sediment in which they live. These models are described individually in detail elsewhere [4,6]. The text by Mackay [24] provides a comprehensive description of fugacity models and their applications.

Most mathematical operations in models of this type are multiplicative or additive, and the individual functions between input and output variables are therefore linear. Nonlinear functions include temperature corrections on physicochemical properties using the van’t Hoff equation and addition of resistances to diffusive transport as reciprocals to describe intercompartmental chemical exchange. The first-order analytical approach to uncertainty analysis described here relies on the assumption that outputs are linear functions of each input variable. This condition does apply to some variables in the model, notably emission variables [25]. Experience with the models indicates relationships between inputs and outputs are unlikely to be strongly nonlinear. The reasonableness of the assumption of linearity is evaluated here by comparing the results of the analytical uncertainty analysis to those of a Monte Carlo analysis of similar complexity. If the models are linear or near linear, the results from the two analyses will be comparable. We also suggest that, if the linearity assumption is of concern, it may be appropriate to evaluate it directly, as shown later.

ESTIMATION OF INPUT PARAMETER UNCERTAINTY

The ChemCAN regional model applied to southern Ontario [4] requires 29 variables to describe the environment, five physicochemical property variables, 15 kinetic variables to describe chemical migration between compartments, four environmental degradation half-lives, and five emission variables. Outputs include intermedia fluxes of chemical, concentrations in individual compartments, total contaminant mass in each compartment at steady state, and regional chemical persistences. The Lake Ontario food web model [6] requires four variables to describe the abiotic environment, 64 to define the food preferences of the eight organisms, 56 to characterize the properties of the organisms, and 24 to describe uptake and clearance of chemical by the organisms. Outputs from the
model include chemical concentration in each organism and chemical fluxes between individual organisms and between the organisms and water and sediment of the lake.

As discussed by Slob [2], in cases in which uncertainty in inputs to a model are estimated based on expert judgment, the choice of a log-normal distribution to describe uncertainty is both warranted and advantageous. The log-normal distribution can be parameterized by the mean and standard deviation (σ) or variance (σ^2) of the corresponding normal distribution on a log scale. These parameters are somewhat intangible and are required to be dimensionless because they are deduced by taking logarithms. Variance in log-normal distributions is sometimes expressed by a coefficient of variation [26], which is defined as the ratio of the standard deviation to the mean and is a more intuitive metric than standard deviation itself. An even more readily interpretable measure of variation in a log-normal distribution is confidence factor (Cf) [27]. A confidence factor of, e.g., 3 implies that 95% of all values in the distribution lie between 1/3 and 3 times the median, i.e., it defines the extent to which X might deviate from the median (μ) [2],

\[
\text{probability} \left( \frac{\mu}{Cf} < X < Cf \cdot \mu \right) = 0.95 \tag{1}
\]

The relationships between Cf and σ of a log-normal distribution are

\[
\sigma = \frac{1}{2} \ln Cf \quad Cf = e^{2\sigma} \tag{2}
\]

when natural (base e) logarithms are used. The confidence factors employed here are identical to the dispersion factor [2] and the operational uncertainty factor [15] that have been defined by others to describe log-normal distributions.

Table 1 shows input confidence factors assumed for chemical properties and emission parameters in both models. Table 2 shows input parameters and assumed confidence factors for ChemCAN used in this study. These estimates are recommended as defaults for the model in the absence of site- or situation-specific data. Tables 3 and 4 list input parameters and their associated confidence factors estimated for the food web model. Illustrative estimates of metabolic half-lives for chemicals in each organism were chosen based on the values suggested by Campfens and Mackay [6] for total polychlorinated biphenyls (PCBs).

The confidence factors shown in Tables 1 through 4 were used for all chemicals. In an analysis of a specific, defined scenario, these confidence factors can be adjusted from their suggested default values to reflect uncertainties associated with physicochemical properties and emissions of individual contaminants or the spatial variability of the environmental setting.

**ANALYTICAL SENSITIVITY AND UNCERTAINTY ANALYSIS**

The analysis presented here is an approximate analytical technique based on a Taylor series expansion of the function that relates input variables to outputs. Morgan and Henrion [28] provide a general derivation of these equations. Here we derive the first-order propagation of uncertainty equations in terms of both σ and Cf and apply the technique to mass balance models using log-normal distributions to describe uncertainties.

In a conventional sensitivity analysis, the effect of changing an individual input variable (I) by a fixed amount (∆I) on the output of interest (O) is quantified using

\[
S = \frac{\Delta O}{\Delta I} \tag{3}
\]

The quantity S describes the sensitivity of O to changes in I. The limit as ∆I tends to zero of the above expression becomes

\[
S = \frac{\partial O}{\partial I} = \frac{\partial O}{\partial I} \frac{\partial I}{\partial I} = \frac{\partial O}{\partial \ln I} \tag{4}
\]

In principle, the algebraic equations that relate each input variable to output variables of interest could be deduced for the model, and partial derivatives could be calculated in general terms for each input variable. In practice, because they are complex functions of all input variables, manipulation of the mass balance equations in this manner is prohibitively cumbersome. Sensitivity of output variables to individual input variables is more conveniently assessed by approximating the partial derivatives by individually modifying each input by 0.1% (i.e., ∆II is 0.001) and monitoring the corresponding change in the output parameters.

Extending the sensitivity analysis to predict confidence factors in outputs due to uncertainty in individual inputs is possible by applying the properties of log-normal distributions. In a normal (Gaussian) distribution, σ is defined so that approximately 66% of all possible values fall in the interval between (μ − σ) and (μ + σ). If this normal distribution is used as input to a Monte Carlo analysis, σ could be considered a measure of the output parameter. When using log-normal distributions characterized by σ of the corresponding log-transformed normal distribution, σ is a measure of the magnitude of variation in the input parameter, i.e.,

\[
\sigma_I \propto \Delta II \tag{5}
\]

Likewise, when fit with a log-normal distribution, standard deviation of the output distribution (σ_o) is a measure of magnitude of variation in the output parameter,

\[
\sigma_o \propto \Delta O/O \tag{6}
\]

Assuming partial derivatives are constant over the range in
uncertainty in input parameters (i.e., that the function relating inputs to outputs is linear), it follows that

$$[S] = \frac{\partial O}{\partial O} \frac{\sigma_i}{\sigma_I}$$  \hspace{1cm} (7)

Note that the ratio of standard deviations in the output and uncertainty in input parameters (i.e., that the function relating inputs to outputs is linear), it follows that

$$[S] = \frac{\partial O}{\partial O} \frac{\sigma_i}{\sigma_I}$$  \hspace{1cm} (7)

implying that confidence factors in outputs can be calculated from the partial derivatives (i.e., $S$ for each input) of the mass balance equations.

The analytical analysis can be extended to predict output confidence factors due to uncertainty in all $n$ inputs to the model using the assumption that inputs are independent (i.e., uncorrelated). With these assumptions, variance in the output ($\sigma_o^2$) is the weighted sum of variance contributed by uncertainty in the $n$ individual input parameters ($I_n$),

$$\sigma_o^2 = \frac{\sum I_i \sigma_i^2}{O^2}$$  \hspace{1cm} (10)

Expressed in terms of sensitivity ($S$), the equivalent expression is

$$\sigma_o^2 = \sigma_i^2 S_i^2 + \sigma_i^2 S_{i1}^2 + \cdots + \sigma_i^2 S_{ik}^2$$  \hspace{1cm} (11)

Converting from variance to confidence factors and discarding the negative root yields

$$Cf_{output} = (Cf_{input})^{1/2}$$  \hspace{1cm} (8)

$$\log Cf_{output} = [S] \log Cf_{input}$$  \hspace{1cm} (9)

### Table 2. Assumed input confidence factors ($Cf$) for ChemCAN southern Ontario, Canada, regional parameters

<table>
<thead>
<tr>
<th>Environmental input parameters</th>
<th>Estimated value</th>
<th>Assumed $Cf$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Region surface area</td>
<td>169,000 km²</td>
<td>1</td>
</tr>
<tr>
<td>Percentage of surface covered by water</td>
<td>43.85</td>
<td>1.1</td>
</tr>
<tr>
<td>Average air height</td>
<td>2 km</td>
<td>1.5</td>
</tr>
<tr>
<td>Average water depth</td>
<td>20 m</td>
<td>1.5</td>
</tr>
<tr>
<td>Average soil depth</td>
<td>10 cm</td>
<td>1.5</td>
</tr>
<tr>
<td>Average active sediment depth</td>
<td>1 cm</td>
<td></td>
</tr>
<tr>
<td>Fraction of particles in air</td>
<td>$2 \times 10^{-11}$</td>
<td>3</td>
</tr>
<tr>
<td>Fraction of particles in water</td>
<td>$5 \times 10^{-6}$</td>
<td>3</td>
</tr>
<tr>
<td>Fraction of fish in freshwater</td>
<td>$1 \times 10^{-6}$</td>
<td>3</td>
</tr>
<tr>
<td>Fraction of air in soil</td>
<td>0.2</td>
<td>1.1</td>
</tr>
<tr>
<td>Fraction of water in soil</td>
<td>0.3</td>
<td>1.3</td>
</tr>
<tr>
<td>Fraction of pore water in sediment</td>
<td>0.7</td>
<td>1.1</td>
</tr>
<tr>
<td>Year-round mean temperature</td>
<td>7.4°C</td>
<td>1.1</td>
</tr>
<tr>
<td>Fraction of organic carbon in water particles</td>
<td>0.2</td>
<td>1.5</td>
</tr>
<tr>
<td>Fraction of organic carbon in soil solids</td>
<td>0.02</td>
<td>1.58</td>
</tr>
<tr>
<td>Fraction of organic carbon in sediment solids</td>
<td>0.04</td>
<td>1.5</td>
</tr>
<tr>
<td>Regional air residence time</td>
<td>1.71 d</td>
<td>1.5</td>
</tr>
<tr>
<td>Regional water residence time</td>
<td>617.5 d</td>
<td>1.5</td>
</tr>
<tr>
<td>Density of air particles</td>
<td>2,400 kg/m³</td>
<td>1.5</td>
</tr>
<tr>
<td>Density of water</td>
<td>1,000 kg/m³</td>
<td>1.05</td>
</tr>
<tr>
<td>Density of water particles</td>
<td>2,400 kg/m³</td>
<td>1.5</td>
</tr>
<tr>
<td>Density of freshwater fish</td>
<td>1,000 kg/m³</td>
<td>1.05</td>
</tr>
<tr>
<td>Density of soil solids</td>
<td>2,400 kg/m³</td>
<td>1.5</td>
</tr>
<tr>
<td>Density of sediment solids</td>
<td>2,400 kg/m³</td>
<td>1.5</td>
</tr>
</tbody>
</table>

### Table 3. Abiotic environmental properties of Lake Ontario and associated confidence factors ($Cf$) for the food web model

<table>
<thead>
<tr>
<th>Environmental input parameters</th>
<th>Estimated value</th>
<th>Assumed $Cf$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suspended particulate matter concentration (g/m³)</td>
<td>1.25</td>
<td>3</td>
</tr>
<tr>
<td>Volume fraction sediment solids</td>
<td>0.1</td>
<td>3</td>
</tr>
<tr>
<td>Organic carbon content of suspended matter</td>
<td>0.2</td>
<td>1.5</td>
</tr>
<tr>
<td>Organic carbon content of sediment particles</td>
<td>0.02</td>
<td>1.5</td>
</tr>
</tbody>
</table>

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This equation is a generalization of the equation reported by Slob [2], which is restricted to multiplicative models for which $S$ for all inputs is unity. The contribution of individual input variables ($I_j$) to variance in output can then be calculated as

$$\sigma^2 \approx \sum_{k=1}^{n} \sigma^2 \cdot S^2$$

or, in terms of confidence factors,

$$\sigma^2 \approx \sum_{k=1}^{n} (\ln C_{I_k})^2 \cdot S^2$$

**COMPARISON WITH MONTE CARLO ANALYSIS**

To examine the reasonableness of the assumption of linearity in the analytical approach, ChemCAN was applied to describe the environmental fate of the chemicals in the Appendix, for which emissions estimates had been previously made for southern Ontario [29,30]. Monte Carlo simulations were performed using the commercial software package Crystal Ball® [31] to quantify the degree of uncertainty in calculated chemical fate profile and model sensitivity to individual input variables. Input parameters shown in Tables 1 and 2 were varied log normally according to their prescribed confidence factors using the Monte Carlo engine. The variance in output parameters, including chemical concentrations in air, water, soil, and sediment, and total steady-state mass of chemical in the region was monitored. Output distributions were fit with a log-normal distribution characterized by an output confidence factor. Confidence factors for output distributions were found to be reproducible within ± standard error (SE) 5% using 5,000 discrete Monte Carlo events. Propagation of uncertainty from input to output parameters was determined from rank correlation coefficients between each input parameter and each output parameter. The rank correlation coefficients are squared, summed, and normalized to 100% to calculate contribution to output variance from each individual input parameter. A similar Monte Carlo uncertainty analysis was performed on each input parameter of the food web model, using 10,000 iterations, with input distributions characterized by the confidence factors in Tables 1, 3, and 4. Variations in calculated concentration of chemical in each organism were monitored.

**RESULTS: COMPARISON OF MONTE CARLO AND ANALYTICAL ANALYSES**

Figures 1 and 2 compare output confidence factors calculated from the analytical equations with those obtained from the Monte Carlo analysis of ChemCAN and the food web model. A degree of scatter in the relationships is expected due to randomness introduced by the Monte Carlo analysis. No significant bias is obvious between the analytical and Monte Carlo uncertainty analysis methods for the ChemCAN model (Fig. 1), indicating the assumption of linearity made in deriving the analytical equations to be valid. Agreement between output confidence factors derived from the two analysis methods is not as close for the food web model as for ChemCAN (Fig. 2), but is satisfactory. In general, output confidence factors for the food web model are larger than those for ChemCAN, which

$$C_{f_0} = \exp\{\sum_{k=1}^{n} (\ln C_{I_k})^2 \cdot S^2\}$$

(12)
The degree of uncertainty in input parameters determined by the two methods is consistent, but if quantitative uncertainties are required for high confidence factor outputs, a Monte Carlo analysis may be required.

**DISCUSSION**

Two key assumptions in both the analytical and Monte Carlo analyses described here are that uncertainties in input parameters are uncorrelated and that all distributions can be described as log normal. In reality, some inputs are correlated, notably those that describe certain physicochemical properties (e.g., water solubility and octanol-water partition coefficient) and environmental processes (e.g., rates of sedimentation, sediment resuspension, and sediment burial). Ignoring covariance simplifies the analysis considerably and is consistent with techniques that have been previously adopted for contaminant fate models [14,15]. If this preliminary uncertainty assessment identifies input variables that are uncorrelated as the most significant contributors to output variance, including covariance in the analysis is unlikely to affect the results significantly [32]. Although the log-normal distribution is widely employed and is appropriate for describing uncertainty in many instances, it may not be the ideal distribution to describe uncertainty in every input variable. Bukowski et al. [33] examined the influence of distributional shape on the outcome of uncertainty analysis of additive and multiplicative models and determined that, in the majority of cases, the shape of the input distributions did not significantly affect the degree of uncertainty associated with output variables. However, combinations of uniform and triangular distributions resulted in wider output distributions than combinations of normal and log-normal distributions.

If an analysis that includes covariance and/or distributions that are not log normal is required, Monte Carlo techniques using a commercial software package are likely the most expedient method of performing the analysis, recognizing that analytical techniques are also available [32]. The present approach can provide guidance in that analysis by identifying input parameters that make an important contribution to overall model uncertainty. It is clearly advantageous to use a preliminary uncertainty analysis to identify input variables that contribute significantly to uncertainty, either due to large uncertainties in inputs or because outputs are sensitive, and focus efforts on parameterization of the covariance terms and distributional shapes for these inputs.

If the assumption of linearity is of concern, it can be subjected to a simple test by exploring the effect on $S$ of changes in $\Delta I$ from its value of 0.001 to 0.01 or 0.1. Caution must be used in this exercise to ensure input parameters are not assigned values outside of plausible ranges as values of $\Delta I$ are increased.

It is intuitively as well as mathematically obvious that the degree of uncertainty in output parameters (i.e., $C_{\text{output}}$) is dependent on both the degree of uncertainty in input parameters ($C_{\text{input}}$) and the sensitivity ($S$) to changes in these input parameters. Large uncertainty in output parameters can be caused by large uncertainty in relatively insensitive input parameters (i.e., low $S$ and high $C_{\text{input}}$) or by small uncertainty in highly sensitive input parameters (high $S$ and low $C_{\text{input}}$). The relative contributions of $C_{\text{input}}$ and $S$ are not always clear. The relationship between input and output uncertainties and model sensitivity as developed here is illustrated graphically in Figure 3.

For a given set of input parameters, $S$ is a defined property of the model; therefore, if a reduction in $C_{\text{output}}$ is desired, it is necessary to reduce uncertainty in inputs ($C_{\text{input}}$). Reducing $C_{\text{input}}$ corresponds to traveling down a line of constant $S$ in Figure 3. To achieve a targeted reduction in $C_{\text{output}}$ will require different degrees of reduction in $C_{\text{input}}$ depending on the model sensitivity to that input parameter. The location of a point corresponding to a particular input parameter clearly depicts the relative contributions of $S$ and $C_{\text{input}}$ in determining $C_{\text{output}}$. When presenting the results of uncertainty analyses, it may be desirable to document fully and clearly the values of $C_{\text{input}}$, $S$, and $C_{\text{output}}$ and to depict these results in a diagram similar to Figure 3.

**CASE STUDIES**

To illustrate the utility of the present approach to uncertainty analysis, we examine uncertainty in the ChemCAN model description of the fate of benzo[a]pyrene released to air in...
the southern Ontario region and in the Campfens food web model applied to PCBs in Lake Ontario.

Fate of benzo[a]pyrene released to air in Southern Ontario

For illustrative purposes, it is assumed that benzo[a]pyrene (BaP) is released to air at a rate of 1,000 kg/h in the southern Ontario region and that there is no uncertainty in this emission estimate. Uncertainties in other input parameters are the suggested defaults shown in Tables 1 and 2. Figure 4 shows the ChemCAN 4.0 mass balance diagram for BaP in southern Ontario under this defined emission scenario, with accumulation in soil and sediment dominating the regional fate profile.

A graphical analysis of contribution to uncertainty in total regional inventory of BaP is shown in Figure 5. To reduce output uncertainty, parameters that describe aerosol-air partitioning and dry deposition of BaP to water and soil and degradation half-lives in soil and sediment should be targeted. The most important individual input parameters in terms of contribution to variance in total steady-state mass of BaP resident in the environment are aerosol deposition velocity (31%), fraction of particles in air (29%), and soil degradation half-life (18%). A significant result is that, despite being released to air and the rapid rate of removal by degradation and advection in air, reducing uncertainty in input parameters that describe atmospheric degradation and advection processes for BaP does not translate into a significantly reduced uncertainty in the calculated steady-state inventory of contaminant.

Refinements to the uncertainty analysis of BaP fate should begin with more accurate parameterization of the variance and shape of distributions and introduction of covariance factors between the important input variables that have been identified. In particular, a covariance factor between soil and sediment degradation half-lives should be incorporated in a refined Monte Carlo analysis because these input variables have been identified as making an important contribution to uncertainty in outputs and their median values have been extrapolated from the same limited set of experimental data and general structure–activity relationships.

Bioaccumulation of PCBs in the Lake Ontario food web

Figure 6 shows the dynamics of bioaccumulation of PCBs in the Lake Ontario food web calculated using the Campfens...
food web model, along with the feeding preferences of organisms used as inputs, which were assigned confidence factors of two. The contribution of key input variables to variance in calculated PCB concentrations for two low trophic level species, diporeia and mysids, is shown in Figure 7, and a graphical analysis of contribution to variance in PCB concentrations in the top-level predator, salmonids, is shown in Figure 8. These species represent three distinct trophic levels in the Lake Ontario food web and illustrate the propagation of uncertainty from lower to higher trophic-level species.

Diporeia are invertebrates that feed on organic matter and detritus in bottom sediments and form the base of the food web, along with water-dwelling plankton. Transfer of PCBs from sediments to diporeia is dependent on the assumed lipid fraction of the organisms and on the organic carbon content of sediments. Log $K_{ow}$ is relatively unimportant in determining uncertainty in diporeia PCB concentrations because chemical partitioning to both diporeia and sediments are described in the model by a fugacity capacity based on octanol equivalents. Consumption of diporeia is the major pathway of PCB uptake for mysids, resulting in concentration of PCBs in sediment and parameters that describe chemical uptake from food as important contributors to output uncertainty. Mysids also feed on plankton and respire water, making log $K_{ow}$ a more important relative contributor to output uncertainty than for diporeia.

For salmonids, at the highest trophic level of the Lake Ontario food web, a variety of types of input variables contribute to uncertainty in calculated PCB concentration. Concentration of PCBs in sediment and lipid fraction of diporeia rank among the most important contributors, underscoring the importance of contaminant accumulation at low trophic levels as driving the entire food web. In Figure 8, PCB concentration in sediments stands out clearly as being both sensitive and uncertain, and efforts to reduce uncertainty should therefore focus on accurately describing sediment contamination levels. Refinements to the uncertainty analysis should begin with accurate parameterization of the degree of variability of sediment concentrations in Lake Ontario and on the shape of the distribution that characterizes this variability.

The importance of sediment PCB concentration as a contributor to uncertainty in calculated contaminant concentrations at all trophic levels clearly indicates that the key factor determining the contamination level of organisms in the food web is the overall level of contamination of the environment in which they live. The degree of bioaccumulation is also a function of predator–prey relationships, as illustrated by the influence of parameters that describe salmonids’ feeding rates and chemical uptake by organisms that are consumed, but these influences are of secondary importance.

**CONCLUSIONS**

An analytical approach for providing a preliminary estimate of the degree of uncertainty associated with mass balance chemical fate models has been presented and shown to be consistent with results from Monte Carlo analysis. The approach is intended to be applied to evaluative and screening-level models of contaminant fate, and as such, provides a preliminary estimate of uncertainty in outputs. It is not suggested that the current approach replace Monte Carlo analysis in site- and chemical-specific environmental fate or risk assessment. In these studies, there may be an incentive to parameterize accurately uncertainties in individual environmental and chemical inputs to the model and incorporate covariance in input parameters, and it may be necessary to treat uncertainty and variability separately. However, the current approach is suggested as a useful first step in such an analysis, focusing further efforts on accurate parameterization of input uncertainties that contribute significantly to overall model uncertainty. By documenting and presenting $S$, $C_{input}$, and $C_{output}$, preferably in graphical format, it becomes apparent how model sensitivity and uncertainty in input parameters combine to produce uncertainty in output parameters.

The approach to uncertainty analysis described here is applicable to many existing chemical fate models and does not require detailed parameterization of uncertainties associated with individual inputs. Results of the analysis are easily interpretable by users unfamiliar with statistical mathematics and provide insight into input parameters and contaminant fate process descriptions that contribute to uncertainties in overall environmental fate. The analytical approach is less computationally intensive than Monte Carlo methods and could be incorporated into end-user versions of contaminant fate models without significantly increasing computation time or requirements for computing power. It is hoped that the availability
and demonstrated applicability of this method will encourage more frequent analysis of uncertainty in screening-level model applications and in the preliminary stages of applying models to describe well-defined contaminant fate scenarios. It is highly desirable that the results of this analysis be interpreted in terms of the perceived behavior of the chemical in the system. It is necessary not only to establish that a parameter is contributing to uncertainty but also to understand why this is the case. Information garnered in this preliminary analysis will ensure that refinements in the model, the median value and uncertainty associated with the input variables, and the techniques for uncertainty analysis can be undertaken efficiently.

Acknowledgement—The authors thank the Natural Sciences and Engineering Research Council and the consortium of companies that support research at the Canadian Environmental Modelling Centre.

REFERENCES

31. Decisioneering. Crystal Ball Pro, Ver 4.0. Denver, Colorado, USA.
**APPENDIX**

Chemicals modeled using ChemCAN and the Lake Ontario, Canada, food web model

<table>
<thead>
<tr>
<th>ChemCAN 4.0</th>
<th>Lake Ontario food web model</th>
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<tr>
<td>Benzene</td>
<td>Pentachlorobenzene</td>
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<td>1,2,4-Trichlorobenzene</td>
<td>DDT</td>
</tr>
<tr>
<td>Hexachlorobenzene</td>
<td>Hexachlorobenzene</td>
</tr>
<tr>
<td>Dieldrin</td>
<td>Mirex</td>
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<tr>
<td>Dioxins</td>
<td>Polychlorinated biphenyls</td>
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<tr>
<td>Chlorobenzene</td>
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</tr>
<tr>
<td>1,2,4,5-Tetrachlorobenzene</td>
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</tr>
<tr>
<td>Polychlorinated biphenyls</td>
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