Using Information on Uncertainty to Improve Environmental Fate Modeling: A Case Study on DDT

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Brief:

In global a multi-media model, uncertainty of model results for DDT is quantified by Monte-Carlo Simulation and Bayesian updating is used to improve model results by including field data.

Abstract

Present and future concentrations of DDT in the environment are calculated with the global multi-media model CliMoChem. Monte Carlo simulations are used to assess the importance of uncertainties in substance property data, emission rates, and environmental parameters for model results. Uncertainties in the model results, expressed as 95% confidence intervals of DDT concentrations in various environmental media, in different geographical locations, and at different points in time are typically between one and two orders of magnitude. An analysis of rank correlations between model inputs and predicted DDT concentrations indicates that emission estimates and degradation rate constants, in particular in the atmosphere, are the most influential model inputs. For DDT levels in the Arctic, temperature dependencies of substance properties are also influential parameters. A Bayesian Monte Carlo approach is used to update uncertain model inputs based on measurements of DDT in the field. The updating procedure suggests a lower value for half-life in air and a reduced range of uncertainty for K_{OW} of DDT. As could be expected, the Bayesian updating yields model results that are closer to observations, and model uncertainties have decreased. The combined sensitivity analysis and Bayesian Monte Carlo approach provide new insight into important processes that govern the global fate and persistence of DDT in the environment.

Introduction

Dichlorodiphenyltrichloroethane (DDT) is an insecticide that has been used worldwide since the 1940s for controlling agricultural pests and to combat vectors of insect-borne diseases, such as typhus or malaria. DDT is hydrophobic and resistant to biotic and abiotic degradation, which makes it very persistent in the environment. For this reason, DDT has been banned in several industrialized countries in the 1970ies, and later globally under the Stockholm Convention (*1*). However, its use continues for malaria combat purposes in certain countries, as discussed in (*2*). The global emission inventory of DDT (*3-6*), its partitioning properties (*7,8*), and environmental half-lives (*9-12*) have been investigated extensively. Yet considerable uncertainty remains in properties inferred from these measurements, particularly in the degradation and partitioning properties, owing to DDT's highly hydrophobic behavior. The extent to which these knowledge gaps affect our understanding of the global fate of DDT may be significant. For example, Schenker et al. (*2*) have used past emissions and DDT property data to predict DDT concentrations in various matrices of the environment with a global contaminant fate model. In general, modeled concentrations corresponded well with field data, but several disagreements were identified. For example, the model overestimated atmospheric concentrations of DDT in the Arctic. Schenker et al. (*2*), indicated that the disagreements are likely due to uncertainties in certain model inputs, such as the octanol-water partition coefficient (K_{OW}) of DDT. Pontolillo and Eganhouse (*13*) showed that K_{OW} values of DDT vary by more than three orders of magnitude among different studies.

When model predictions differ from measurements, researchers often attribute these differences to uncertainties in model inputs, as was the case for Schenker et al. (*2*). However, without a detailed and systematic uncertainty analysis, it is not clear that the attribution is correct. Model developers are making progress on this front, with several recent papers reporting on efforts to assess the relative contribution of different model inputs to uncertainty in model results (*14-20*). However, most of these studies are limited to a local scale or rely on analytical uncertainty calculations (*21*) to reduce the calculation time of the uncertainty assessment. MacLeod et al. (*17*) suggest the use of more general Monte Carlo methods (*22*) when chemical-specific fate, exposure, and/or risk assessments are performed. These methods make possible the assessment of uncertainties in non-linear systems and of model inputs with complex and sometimes correlated uncertainty distributions. In addition to the insight into model behavior gained by Monte Carlo techniques, a systematic comparison of model results with field data can improve estimates of uncertain model inputs and provide valuable insight

into the performance of environmental fate models. Our review of the current literature reveals that Monte-Carlo type uncertainty assessments and techniques to update model inputs based on field data are not frequently applied to environmental fate models. Furthermore, model updating methods have, to our knowledge, not been used to reduce model result uncertainties and divergence between model results and field data in a global environmental fate model.

In this paper, we apply Monte Carlo uncertainty assessment methods to the DDT case study presented by Schenker et al. (*2*). We calculate the influence of uncertainties in different types of model inputs (substance properties, emission rates, model parameters of the CliMoChem model (*23,24*)) on time-dependent model results. Rank correlations (RC) between model inputs and outputs are used to identify important processes governing the behavior of DDT in the environment. Using field data, we apply a quantitative method to update model inputs and model results derived from the inputs. Uncertainties in the updated model results decrease strongly, and predicted DDT concentrations are closer to field data. The updated model inputs, in particular substance properties, are presented along with possible explanations for differences between original and updated values. However, the present study can only partially assess the uncertainties that are associated with environmental fate modeling of a chemical such as DDT. We have, for instance, not taken into account model or scenario uncertainties (*25,26*).

Methods

The CliMoChem Model

The CliMoChem model (*23,27*) has been used to calculate the behavior of chemicals in the environment. CliMoChem is a global, zonally averaged, temporally resolved (level IV) environmental fate model with a temporal resolution of three months. For the present calculations, we use the same version of the model as in an earlier study on DDT (*2*), with 30 latitudinally homogenous zones from the North to the South Pole. Monthly averages of air temperature and vegetation types present in the different zones are taken from refs. (*28,29*). The model calculates diffusive and advective exchange processes between environmental compartments (atmosphere, ocean water, vegetation, vegetation-covered soil, and bare soil) such as rain, runoff, or evaporation, and transport in air or ocean water across the latitudinal zones of the model. DDT is emitted into the different zones of the model as a function of time according to the historic emission scenario presented in ref. (*2*), see also Figure S1 in the Supporting Information. For the time after 2005, we assumed that emissions continue at a rate

of approximately 15,000 t per year, according to the base scenario presented earlier (*2*). Model results are predictions of DDT concentrations in different media for each zone of the CliMoChem model between 1945 and 2035.

Monte Carlo Simulations

Monte Carlo Simulation is a technique that is used to construct a distribution of model outcomes for complex, non-linear systems with a large number of uncertain and sometimes correlated inputs (*22,30-32*). First, model input datasets are randomly generated from the domain of possible input values according to the selected uncertainty distributions. Then, in a large set of model runs, model outputs are calculated for each of the model input datasets. From each of these model runs, the output is stored for analysis. Correlations between the model outcome and model input values used in a Monte Carlo Simulation can be used to identify important parameters, assumptions and processes in the model. In the application that follows, we use the CrystalBall software (*33*) to perform 5,000 model runs. To ensure that the number of runs was sufficient, we performed the updating in two different sets of 2,500 runs, and verified that the differences between the results of these two sets of 2,500 runs each and the complete set of 5,000 runs were small. Furthermore, Figure S6 in the Supporting Information displays that about 1,200 runs out of the 5,000 contribute to the updated results with posterior probabilities above 0.02% (which is the prior probability, see below). The cumulative weight of these 1,200 runs is about 90%. In other words, a relatively large part of the Monte Carlo runs have contributed to the updated model results.

We have tracked 90 model outputs in the uncertainty analysis: concentrations in air, ocean-water, and vegetation-covered soil in the Arctic, the temperate, and the tropical regions (nine outputs), every ten years from 1945 to 2035 (10 times).

Prior Uncertainty Distributions

We describe parameter uncertainty using probability distributions for 47 model inputs, including substance properties (degradation rate constants, partition coefficients, and their temperature dependencies), emission rates, and model parameters. The Supporting Information (Table S2) gives detailed information on all model inputs, their probability distributions, and the methods used to estimate them. We have selected log-normal distributions for parameters that were bound between 0 and infinity (such as degradation rate constants, activation energies, and partition coefficients), normal distributions for parameters that were bound between +/- infinity (such as energies of phase change for partition coefficients), and triangular distributions for parameters that are bound between two given values. Uncertainty of DDT emissions was characterized by two scaling factors for past and

future emissions (which have higher uncertainties). Both scaling factors were assigned log-normal distributions around the geometric mean of one. For the release pathways of DDT, we have assumed a triangular distribution for emissions into soil of 80% to 100%, with a most likely value of emissions to soil of 90%, as in ref. (*2*). We did not account for uncertainty of the location and time where DDT emissions occurred, because the model outputs are relatively insensitive to these variables (*34*). Furthermore, we did not attribute uncertainty distributions to some model parameters, in particular the temperature in the model, and the zonal distribution of OH radical concentrations. Establishing reliable uncertainty distributions for these parameters would have been very challenging. Therefore, uncertainties related to these model parameters have to be considered part of the model uncertainty (*25,26*) that we have not considered in the present study.

The CliMoChem model also uses a number of environmental parameters that are uncertain (e. g. particle deposition velocity, organic matter content of a given soil type, eddy diffusion in air, etc.) for which we have estimated uncertainty distributions based on previous assessments (*15,17,18,35*). The Supporting Information (Table S2) provides further details about the magnitude and uncertainty distributions of these parameters. We have assumed that none of the model inputs are correlated, as asserted in previous studies (*14-18,36*).

Using Rank Correlations for Sensitivity Analysis

The rank correlation between a model input and model outcome from a Monte Carlo Simulation can be useful for identifying model sensitivities. CrystalBall calculates the Spearman Rank Correlation Coefficient (*37*) of model inputs and outputs, which was used for the present calculations. A positive rank correlation coefficient for a model input indicates that an increase in the value of that input generally leads to an increase of a model output, whereas negative rank correlations indicate the opposite. The magnitude of the absolute value of a rank correlation for a particular input indicates the importance of that input to the model outcome. In addition to providing insight into importance of specific model inputs, the rank correlations can highlight important processes in the model. For example, emissions have high rank correlation coefficients for concentrations in the Arctic in the 1960s, but much less so after 2000, when rank correlation coefficients for degradation rate constants increase. This can be explained by the fact that emission rates are important for Arctic concentrations as long as DDT is emitted in the temperate zone, close to the Arctic. When emissions shift towards the tropics, the transport mechanism into the Arctic becomes less efficient, and the decrease of Arctic concentrations is driven by the degradation of DDT stocks inside the

Arctic. It is also important to note that model sensitivity to specific inputs can change over time.

Bayesian Monte Carlo Approach

Bayesian updating can be seen as a complex way of calibrating a model. In a simple model calibration, a given single model input is typically adjusted in a way that a given model output matches a field measurement. Bayesian updating techniques do more than this, and adjust several model inputs to many different field measurements simultaneously, and take into account uncertainty of field measurements, to avoid over-fitting.

Different Bayesian updating techniques have been described in the literature (*22,38,39*). Each of these updating techniques has its advantages and disadvantages. Markov chain Monte Carlo (MCMC) or Gibbs sampling both provide sophisticated approaches to updating at the same time the environmental fate model and the statistical error model, e.g. the likelihood function. We have selected Bayes Monte Carlo, BMC (*40,41*) for the present situation, because its implementation into the existing model framework was simple and straightforward.

In the BMC approach, a posterior probability (p'_k) is calculated by assessing the level of agreement between each Monte Carlo run k and the field observations (O). The likelihood function, $p(O|Y_k)$, is the probability of observing O given the model prediction Y_k, and $p(Y_k)$ is the prior probability of model run k, it is equal to $1/U$ with U being the total number of Monte Carlo runs:

$$p'_k = \frac{p(O|Y_k) \cdot p(Y_k)}{\sum_{i=1}^{U} p(O|Y_i) \cdot p(Y_i)} \qquad \text{(eq. 1)}$$

We update on multiple independent observations from various environmental media and geographical regions, so $p(O|Y_k)$ represents the probability of observing all field results considered simultaneously (S = number of independent observations, in the present case $S = 6$, see below, subsection on measurement data used for Bayesian Monte Carlo assessement):

$$p(O|Y_k) = \prod_{s=1}^{S} p_s(O_s|Y_k) \qquad \text{(eq. 2)}$$

We assume a normal distribution for the likelihood function, as used by others (for instance ref. (*41*)) and because we do not have sufficient data to support the choice of a different distribution type (the subscript s of O is dropped in eq. 3):

$$p(O|Y_k) = \frac{1}{\sqrt{2 \cdot \pi} \cdot \sigma_\varepsilon} \exp\left(-\frac{1}{2} \cdot \left[\frac{O - Y_k}{\sigma_\varepsilon} \right]^2 \right) \qquad \text{(eq. 3)}$$

where σ_ε is the standard deviation of the measurement errors in *O*.

The posterior mean of all model inputs and outputs (*V'*) can be calculated from the posterior probability of each model run (p'_k) and the prior value V_k of the corresponding model input or output value of model run *k*:

$$V' = \sum_{k=1}^{U} p'_k \cdot V_k \qquad \text{(eq. 4)}$$

The standard deviation of each of the model inputs and outputs can be found with:

$$\sigma'_V = \sqrt{\sum_{k=1}^{U} p'_k \cdot (V_k - V')^2} \qquad \text{(eq. 5)}$$

To respect the constraint that our probability function (equation 3 above) holds true for normally-distributed measurement errors only, measurements in the environment were converted into log-values and the standard deviations of the log-values were estimated. The concentrations from the model were also converted into log-values and used for the updating. Equally, when calculating updated model inputs, we compiled log-values for the log-normally distributed model inputs.

Measurement Data Used for Bayesian Monte Carlo Assessment

For the BMC assessment, we used the DDT measurements reported in ref. (*2*), (Figure 2 therein). These concentrations of DDT in air, ocean water, and soils of the Arctic, the temperate, and the tropical regions are based on underlying individual measurement studies. We calculated ranges of environmental concentrations and associated measurement errors (σ_ε in equation 3) from the variation in the data between studies. Because measurements in temperate and tropical ocean water and Arctic soils are based on a single measurement each, the ranges of environmental concentrations and associated measurement errors could not be calculated. As a result, these media were excluded from the BMC assessment.

Results and Discussion

Uncertainties of Model Results Prior to Bayesian Updating

Figure 1 shows the predicted temporal evolution of DDT concentrations in Arctic air (left, in pg/m^3) and tropical soil (right, in ng/g) before Bayesian updating. DDT concentrations increase until 1965 and start decreasing afterwards. The slope of the decreasing concentration is greater in Arctic air than in the tropical soils. We attribute this to a longer half-life in soil as compared to air and to the fact that DDT emissions continue in tropical regions.

Vertical bars in Figure 1 show the two-sided 95% confidence intervals. The confidence intervals are larger for Arctic air than for tropical soils. We show later that this is

because of the uncertainties that are associated with temperature-dependent substance properties. In the Arctic, ambient temperatures are much lower than temperatures in the laboratory settings where substance properties are determined. Therefore, substance properties for the Arctic have to be calculated from the measured values, using measured or estimated temperature dependencies. These calculations result in additional uncertainties for the Arctic as compared to tropical regions, because laboratory conditions under which substance properties are measured are typically closer to tropical temperatures. Furthermore, the uncertainty ranges increase after 2005 because uncertainties of future emissions are higher than uncertainties of past emissions. Plots of all concentrations as a function of time with associated uncertainties for all media in all regions are given in the Supporting Information (Figure S2).

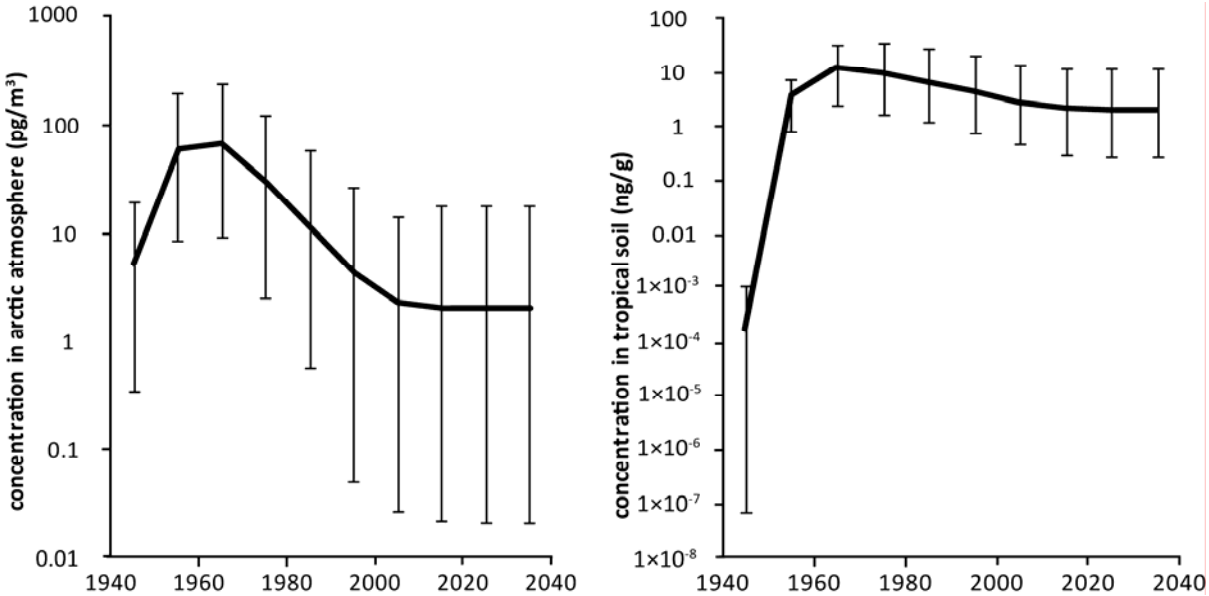

Figure 1: Prior model outputs (Monte Carlo runs without Bayesian updating) depicting the evolution of DDT concentrations in Arctic atmosphere (left) and tropical soils (right). Error bars represent the 95% confidence intervals of the prior model outputs.

Sensitivity Analysis

Figure 2 (left) displays the sum of squares of the rank correlation coefficients in temperate soils for five groups of model inputs: degradation half-lives (4 inputs), partition coefficients (2 inputs), temperature dependencies of half-lives and partition coefficients (6 inputs), emissions (3 inputs), and environmental parameters (32 inputs). For emission-related model inputs, the rank correlation, and thus the model sensitivity, decreases over time as emissions shift away from the temperate zones. In contrast, sensitivity of the model to the degradation rate constants and temperature dependencies increase when transport of newly emitted DDT

into the temperate zone and degradation of stocks from previous emissions become dominant processes. In the Supporting Information, rank correlations of the five groups of model inputs with concentrations in all media and in all geographical regions over time are given. Figures S2 and S3 show that temperature dependence is much more important for concentrations in the Arctic than in temperate regions, and is almost negligible in the tropics.

Figure 2 (right) presents the temporal evolution of the highest rank correlations (RC) between model inputs and concentrations in the tropical atmosphere. Until 2005, the atmospheric degradation rate constant (k'_{air}) is the most influential model input (RC = −0.94); it influences long-range transport from temperate regions into the tropics, and also the residence time of DDT in tropical air. The model is also sensitive to $\log K_{OW}$ (RC = −0.18), which is used to estimate partitioning into soil and particles in air and ocean water. Also the scaling factor for past emissions (S_{past}) has a high importance (RC = 0.17, until 2005). After 2005, the importance of S_{past} decreases, and the importance of the scaling factor for future emissions (S_{future}) increases correspondingly (RC = 0.54). Because the future emissions occur in the tropics, the rank correlation of S_{future} to concentrations in tropical air is considerably higher than that of S_{past}, because no transport intervenes between the emissions and the modeled concentrations in the tropics. As a consequence, the importance of the atmospheric degradation rate constant (k'_{air}) also decreases slightly after 2005 (RC = −0.78).

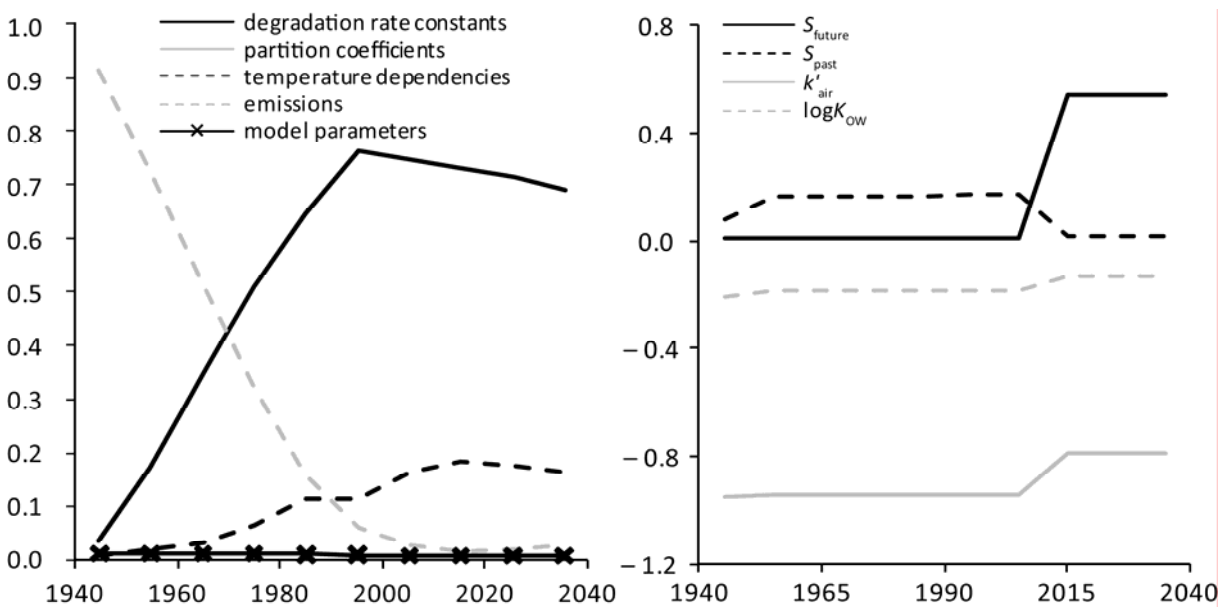

Figure 2: Sum of squares of rank correlation coefficients for five groups of model inputs to concentration in temperate soil (left); rank correlations of the model inputs with the highest rank correlations to concentrations in the tropical atmosphere (right) over time .

Plots of the model inputs with the highest rank correlations to concentrations in all media and geographical regions are given in the Supporting Information (Figure S4). In all of these plots the future emissions become one of the most important contributors to model outcome uncertainty after 2005, even for the Arctic. The rank correlation of the scaling factor for future emissions (S_{future}) for concentrations in air (in all climatic zones) increases sharply in 2005 and remains constant from 2015 to 2035. This shows that DDT concentrations in air are strongly influenced by future emissions immediately after their occurrence. A similar behavior can be observed for oceans, although the increase in the rank correlation between the scaling factor for future emissions and concentrations in oceans is not as sharp as for concentrations in air. Finally, the rank correlation between the scaling factor of future emissions and concentrations in soils continues to increase until the end of the simulation period. This indicates that past emissions influence concentrations in soil for much longer than concentrations in air and ocean water. In accordance, the rank correlation between past emission (S_{past}) and concentrations in soils continues to decrease for several years after past emissions have ceased.

Bayesian Updating of the Most Important Model Inputs

Table 1 shows prior and posterior statistics for some of the most influential model inputs. Half-lives in soils (k_{soil}) and ocean water (k_{water}) remain fairly unchanged, indicating that literature data on degradation half-lives is well suited to reproduce measured DDT concentrations in the environment. The scaling factor for past emissions (S_{past}), the ratio of emissions into soil (R_{soil}), and the $\log K_{AW}$ also do not change appreciably from prior to posterior values, even though the sensitivity analysis indicated they are important to the model. This again implies that the distribution of values taken from the literature is appropriate for this type of environmental fate calculation.

The posterior DDT degradation rate constant in the atmosphere (k'_{air}) is approximately three times faster than previously assumed (*2*). Quantitative Structure Property Relationship (QSPR) data from the AOPWin software (*42*) indicates that DDT reacts quickly with OH radicals in the gas phase (even faster than the posterior estimate), but to establish the prior value of the atmospheric degradation rate constant, data from AOPWin was combined with measurements derived from smog chambers studies (*9,10*), which suggest longer half-lives for DDT in the gas phase. Because in the model the concentration of DDE in air relative to that of DDT was lower than in the field data, we considered in ref. (*2*) that the atmospheric degradation rate constant for DDE might have to be reduced relative to that of DDT. However, the Bayesian updating suggests that the degradation rate constant of DDT might

have to be increased, and the value initially given for DDE (also from AOPWin) might be appropriate.

The median of the posterior logK_{OW} of DDT is 0.2 log units higher than the prior median, which was estimated from a large number of direct but highly variable measurements. Pontolillo and Eganhouse (*13*) collected values of logK_{OW} between 3 and 7. However, based on additional knowledge from DDT field data, we find posterior uncertainty to be significantly tighter with the 95% interquantile range only about +/– 0.85 log units. Accordingly, logK_{OW} values below 5.16 do not seem to be well suited to describe DDT field data with the CliMoChem model. This might indicate that the lower part of the range of logK_{OW} values found by Pontolillo and Eganhouse is attributed to experimental difficulties measuring logK_{OW} for highly lipophilic chemicals.

Finally, temperature dependencies of all properties (Ea_{soil} for degradation rate constants in soil, ΔU_{AW} and ΔU_{OW} for logK_{AW} and logK_{OW}, respectively) have been increased by the Bayesian updating. Temperature dependencies are fairly uncertain so that it is possible that they were all underestimated. However, this could also indicate that the latitudinal temperature profile in the CliMoChem model, as used in ref. (*2*), should be steeper. In other words, real temperatures in the Arctic could be below the current values assumed in the model. The increase in the temperature dependencies of substance properties corresponds to decreasing the temperature in the Arctic by 2–3 °C. Another point might be that some processes in the environment take place at temperatures that are below the monthly averages that we use in our model (e. g. degradation in air might take place in the high atmosphere with temperatures significantly below the ones at the earth's surface).

Table 1: Most important model inputs before (columns "prior") and after adjustment with the BMC approach (columns "posterior").

	Prior			posterior		
	2.5%	50%	97.5%	2.5%	50%	97.5%
S_{past} (–)	0.77	1	1.29	0.76	0.99	1.26
R_{soil} (–)	0.82	0.9	0.98	0.82	0.9	0.97
k_{soil} (d^{-1})	2.32×10^{-4}	6.77×10^{-4}	1.97×10^{-3}	2.63×10^{-4}	5.83×10^{-4}	1.13×10^{-3}
k_{water} (d^{-1})	4.66×10^{-4}	1.35×10^{-3}	3.95×10^{-3}	5.00×10^{-4}	1.69×10^{-3}	4.29×10^{-3}
k'_{air} (cm^3/d/molecule)	5.17×10^{-9}	8.98×10^{-8}	1.55×10^{-6}	2.67×10^{-8}	2.64×10^{-7}	6.30×10^{-7}
logK_{AW} (–)	–3.55	–3.35	–3.15	–3.56	–3.36	–3.14
logK_{OW} (–)	5.16	6.01	6.86	5.34	6.21	7.03
Ea_{soil} (kJ/mol)	13.6	30.0	66.2	15.5	35.8	74.4
ΔU_{AW} (kJ/mol)	33.4	72.6	112	35.4	74.4	112
ΔU_{OW} (kJ/mol)	–54.2	–15.3	23.9	–58.3	–20.0	19.4

Comparison of Model Results with Field Data

In the comparison of model results with DDT field data in ref. (*2*), several disagreements were highlighted, and possible reasons for the disagreement discussed. Under the new evidence gained from the sensitivity analysis and the Bayesian Monte Carlo assessment, it is useful to reconsider these points. The model results presented in ref. (*2*) showed atmospheric concentrations in the Arctic that were about one order of magnitude above measurements. The increased degradation rate constant in air reduces DDT concentrations in the atmosphere, yet this applies to all regions. The increased temperature dependence of the air-water partition coefficient that is suggested by the BMC approach leads to a more efficient scavenging of DDT by rain from the atmosphere and, thus, reduces DDT concentrations (and travel distances) in the atmosphere, in particular in the Arctic. Model results from ref. (*2*) further showed that DDT concentrations in ocean-water were constant along latitudinal zones, or even increasing towards the poles, whereas field data showed a decreasing trend towards the poles (although this trend is based on very few measurements). The zonal distribution of DDT in ocean water is not expected to be significantly modified by the BMC approach, because the measurement data in oceans is subject to high uncertainties and does therefore not contribute to the updating notably. The effects of the BMC approach on model results are discussed in more detail in the following.

Figure 3 shows the cumulative distribution functions of measurements, prior model results, and posterior model results (after the BMC approach) in 1995. As examples, we show concentrations in Arctic air and temperate soils. As could be expected, the posterior values for model inputs from the BMC approach result in model predictions that are closer to the measurements than are the initial Monte Carlo simulation results in both cases. Notably, in Arctic air, the DDT concentration predicted by the model (the median of the results from the BMC approach) is within a factor of three of the median of the measurement data, as compared to about one order of magnitude difference prior to the Bayesian updating. Similarly, in temperate soils, the median of the BMC model results lies between the median of the original model results and the measurement data. However, improved model fit was not consistently observed across all regions and phases. In the temperate atmosphere, the posterior model output shifted away from the measurements (see Figure S5 in the Supporting Information). This is likely because the reduction in the deviations between measurements and model results in other compartments were quantitatively more important in the overall updating process.

The graphs with the temporal evolution of DDT (Figure 1) can be redrawn with the results from the BMC approach (Supporting Information, Figure S2). Uncertainty ranges in the model results decrease due to the additional information that has been gained from the measurement data. Furthermore, concentrations in soils (in particular in the temperate region and the Arctic) seem to decrease more slowly than originally predicted. The reason for this can be found in the increased temperature dependencies of partition properties and half-life in soil. This suggests that DDT might be more persistent in the Arctic and temperate soils than initially predicted.

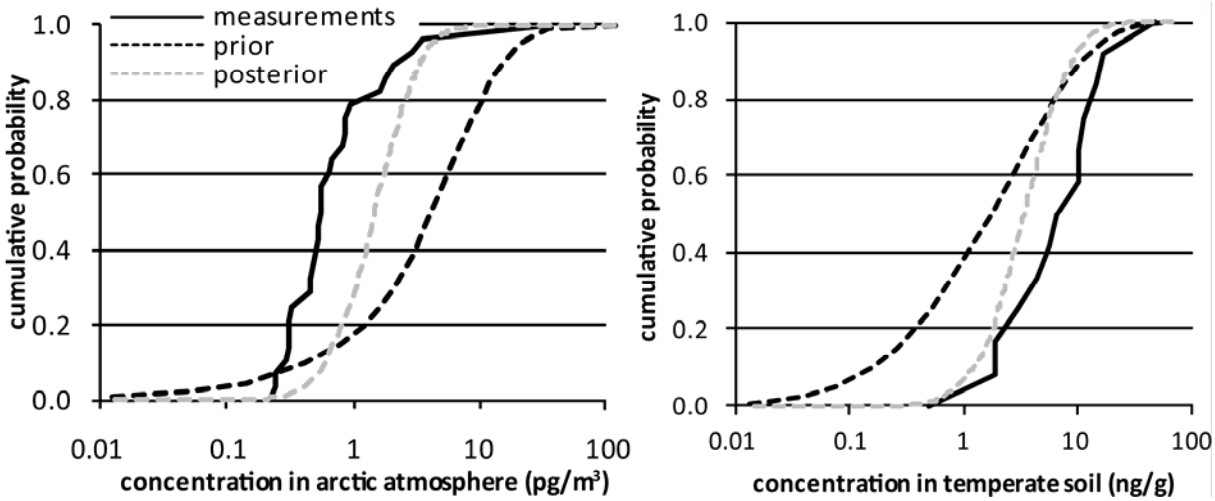

Figure 3: Cumulative Distribution Functions (CDFs) for measurements, prior-, and posterior-model results in Arctic atmosphere (left) and temperate soil (right) in 1995. The *y*-axis shows the probability that the corresponding results (measurements or model data) are below or equal to a given value on the *x*-axis.

The Bayesian Monte-Carlo simulations and the sensitivity analysis have increased the understanding of the processes that govern the global fate and persistence of DDT. Substance properties of DDT and emission data have been identified as the most important sources of uncertainty. The Bayesian updating provides insight on how to select and restrict model inputs. For example, the scaling factor for past emissions has not been markedly modified by the updating, indicating that the information we used probably represents the amount of DDT emitted relatively well. This is important because there is only little information available on DDT emissions (only two different studies were used to construct the emission scenario presented in ref. (*2*)). Furthermore, the Bayesian updating suggests that uncertainties in the K_{OW} of DDT might be lower than previous estimates. In the case of the atmospheric degradation rate constant, additional information has been gained that might help to select the optimal degradation rate constant among different suggestions from measurement or QSPR data. When the environmental fate of other substances is modeled in the future, we suggest that Bayesian updating techniques be used in order to take advantage of all available

observations to reduce uncertainties. Updating methods, such as the Bayesian Monte-Carlo method that was employed here, reduce differences between model results and field data. We hope that the present manuscript contributes to an increased awareness of uncertainty, and illustrates that better predictions and subsequent policy-decisions may be taken when uncertainties are explicitly considered in future modeling studies.

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References

(1) UNEP, Stockholm Convention on Persistent Organic Pollutants. http://www.pops.int/documents/convtext/convtext_en.pdf. Accessed on 31.3.2001.
(2) Schenker, U.; Scheringer, M.; Hungerbühler, K., Investigating the global fate of DDT: model evaluation and estimation of future trends. *Environ. Sci. Technol.* **2008**, *42*, 1178-1184.
(3) Li, Y. F.; Bidleman, T. F.: Usage and emissions of organochlorine pesticides, Canadian Arctic contaminants assessment report II, Physical environment, part II, chapter A.2, Minister of Indian Affairs and Northern Development, 2003.
(4) Li, Y. F.; Macdonald, R. W., Sources and pathways of selected organochlorine pesticides to the Arctic and the effect of pathway divergence on HCH trends in biota: a review. *Sci. Total Environ.* **2005**, *342*, 87-106.
(5) Li, Y. F.; Venkatesh, S.; Li, D., Modeling global emissions and residues of pesticides. *Environ. Model. Assess.* **2004**, *9*, 237.
(6) Li, Y. F.; Zhulidov, A. V.; Robarts, R. D.; Korotova, L. G.; Zhulidov, D. A.; Yurtovaya, T. Y.; Ge, L. P., Dichlorodiphenyltrichloroethane usage in the former Soviet Union. *Sci. Total Environ.* **2006**, *357*, 138-145.
(7) Schenker, U.; MacLeod, M.; Scheringer, M.; Hungerbühler, K., Improving accuracy and quality of data for environmental fate models: A least-squares adjustment procedure for harmonizing physicochemical properties of organic compounds. *Environ. Sci. Technol.* **2005**, *39*, 8434-8441.
(8) Shen, L.; Wania, F., Compilation, evaluation, and selection of physical-chemical property data for organochlorine pesticides. *J. Chem. Eng. Data* **2005**, *50*, 742-768.
(9) Krüger, H. U.; Gavrilov, R.; Liu, Q.; Zetzsch, C.: Entwicklung eines Persistenz-Messverfahrens für den troposphärischen Abbau von mittelflüchtigen Pflanzenschutzmitteln durch OH-Radikale, Deutsches Umweltbundesamt, 2005.
(10) Liu, Q.; Krueger, H. U.; Zetzsch, C., Degradation study of the aerosol-borne insecticides dicofol and DDT in an aerosol smog chamber facility by OH radicals in relation to the POPs convention. *Proceedings to European Geosciences Union,* Vienna, **2005**.
(11) Mackay, D.; Shiu, W. Y.; Ma, K. C. *Illustrated handbook of physical-chemical properties and environmental fate for organic chemicals*; Lewis: Boca-Raton, 1997; Vol. 5.

(12) Aislabie, J. M.; Richards, N. K.; Boul, H. L., Microbial degradation of DDT and its residues - A review. *New. Zeal. J. Agr. Res.* **1997**, *40*, 269-282.
(13) Pontolillo, J.; Eganhouse, R. P.: The search for reliable aqueous solubility (Sw) and octanol-water partition coefficient (Kow) data for hydrophobic organic compounds: DDT and DDE as a case study, U. S. Geological Survey, 2001.
(14) Fenner, K.; Scheringer, M.; Hungerbühler, K., Joint persistence of transformation products in chemicals assessment: case studies and uncertainty analysis. *Risk Anal.* **2003**, *23*, 35-53.
(15) Hertwich, E. G.; McKone, T. E.; Pease, W. S., Parameter uncertainty and variability in evaluative fate and exposure models. *Risk Anal.* **1999**, *19*, 1193-1204.
(16) Luo, Y. Z.; Yang, X. S., A multimedia environmental model of chemical distribution: Fate, transport, and uncertainty analysis. *Chemosphere* **2007**, *66*, 1396-1407.
(17) MacLeod, M.; Fraser, A. J.; Mackay, D., Evaluating and expressing the propagation of uncertainty in chemical fate and bioaccumulation models. *Environ. Toxicol. Chem.* **2002**, *21*, 700.
(18) Maddalena, R. L.; McKone, T. E.; Hsieh, D. P. H.; Geng, S., Influential input classification in probabilistic multimedia models. *Stoch. Env. Res. Risk A.* **2001**, *15*, 1-17.
(19) McKone, T. E., Uncertainty and variability in human exposures to soil contaminants through home-grown food - a Monte Carlo assessment. *Risk Anal.* **1994**, *14*, 449-463.
(20) Meyer, T.; Wania, F., What environmental fate processes have the strongest influence on a completely persistent organic chemical's accumulation in the Arctic? *Atmos. Environ.* **2007**, *41*, 2757-2767.
(21) Slob, W., Uncertainty Analysis in Multiplicative Models. *Risk Anal.* **1994**, *14*, 571-576.
(22) Morgan, M. G.; Henrion, M.; Small, M. *Uncertainty a guide to dealing with uncertainty in quantitative risk and policy analysis*; Cambridge University Press: Cambridge etc., 1990.
(23) Scheringer, M.; Wegmann, F.; Fenner, K.; Hungerbühler, K., Investigation of the cold condensation of persistent organic pollutants with a global multimedia fate model. *Environ. Sci. Technol.* **2000**, *34*, 1842-1850.
(24) Wegmann, F.; Scheringer, M.; Moller, M.; Hungerbühler, K., Influence of vegetation on the environmental partitioning of DDT in two global multimedia models. *Environ. Sci. Technol.* **2004**, *38*, 1505-1512.
(25) Dubus, I. G.; Brown, C. D.; Beulke, S., Sources of uncertainty in pesticide fate modelling. *Sci. Total Environ.* **2003**, *317*, 53-72.
(26) Hertwich, E. G.; McKone, T. E.; Pease, W. S., A systematic uncertainty analysis of an evaluative fate and exposure model. *Risk Anal.* **2000**, *20*, 439-454.
(27) Wegmann, F., The global dynamic multicompartment model CliMoChem for persistent organic pollutants: Investigations of the vegetation influence, the cold condensation and the global fractionation. PhD Thesis. ETH Zurich, **2004**.
(28) Defries, R. S.; Townshend, J. R. G., Ndvi-Derived Land-Cover Classifications at a Global-Scale. *Int. J. Remote Sens.* **1994**, *15*, 3567-3586.
(29) Legates, D. R.; Willmott, C. J., Mean Seasonal and Spatial Variability in Gauge-Corrected, Global Precipitation. *International Journal of Climatology* **1990**, *10*, 111-127.
(30) Helton, J. C.; Johnson, J. D.; Sallaberry, C. J.; Storlie, C. B., Survey of sampling-based methods for uncertainty and sensitivity analysis. *Reliability Engineering & System Safety* **2006**, *91*, 1175-1209.
(31) Helton, J. C.; Davis, F. J., Latin hypercube sampling and the propagation of uncertainty in analyses of complex systems. *Reliability Engineering & System Safety* **2003**, *81*, 23-69.

(32) Helton, J. C.; Davis, F. J., Illustration of sampling-based methods for uncertainty and sensitivity analysis. *Risk Anal.* **2002**, *22*, 591-622.
(33) CrystalBall, Crystal Ball Homepage. http://www.crystalball.com/crystal_ball/index.html. Accessed on 15.12.2007.
(34) Schenker, U.; Wegmann, F.; Scheringer, M.; Hungerbühler, K., Emission scenario comparison. ETH Zurich. *Unpublished, available upon request.* **2006**.
(35) McKone, T. E.; Bodnar, A. B.; Hertwich, E. G.: Development and evaluation of state-specific landscape data sets for multimedia source-to-dose models, Ernest Orlando Lawrence Berkeley National Laboratory, 2001.
(36) Smith, A. E.; Ryan, P. B.; Evans, J. S., The Effect of Neglecting Correlations When Propagating Uncertainty and Estimating the Population-Distribution of Risk. *Risk Anal.* **1992**, *12*, 467-474.
(37) CrystalBall, How does Crystal Ball calculate sensitivity? http://www.decisioneering.com/support/simulation/cbl_gen_004A.html. Accessed on 12.1.2008.
(38) Beven, K.; Binley, A., The Future of Distributed Models - Model Calibration and Uncertainty Prediction. *Hydrological Processes* **1992**, *6*, 279-298.
(39) Patwardhan, A.; Small, M. J., Bayesian Methods for Model Uncertainty Analysis with Application to Future Sea-Level Rise. *Risk Anal.* **1992**, *12*, 513-523.
(40) Brand, K. P.; Small, M. J., Updating uncertainty in an integrated risk assessment: Conceptual framework and methods. *Risk Anal.* **1995**, *15*, 719-731.
(41) Sohn, M. D.; Small, M. J.; Pantazidou, M., Reducing uncertainty in site characterization using Bayes Monte Carlo methods. *J. Environ. Eng.-ASCE* **2000**, *126*, 893-902.
(42) US-EPA, EPIWin Suite. http://www.epa.gov/opptintr/exposure/pubs/episuitedl.htm. Accessed on 12.2.2008.