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Uncertainty analysis using a fugacity-based multimedia mass-balance model: Application of the updated EQC model to decamethylcyclopentasiloxane (D5)

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ABSTRACT

The EQuilibrium Criterion (EQC) model developed and published in 1996 was recently revised to include improved treatment of input partitioning and reactivity data, temperature dependence and an easier sensitivity and uncertainty analysis. This New EQC model was used to evaluate the multimedia, fugacity-based fate of decamethylcyclopentasiloxane (D5; CAS No. 541-02-6) in the environment over a temperature range of 1–25 °C. In addition, Monte Carlo uncertainty analysis was used to quantitatively determine the influence of temperature and input partitioning and reactivity data on the behavior of D5 under various emission scenarios. Results indicated that emission mode was the most influential factor determining the fate and distribution of D5 in the model environment. When emitted to air and soil, D5 partitioned to and remained in the air compartment where rates of removal from degradation and advection processes were relatively rapid. In contrast, D5 emitted to water resulted in a substantial mass fraction of D5 being accumulated in the sediment compartment, where rates of removal from degradation and advection processes were slow. The mass distributions and fate of D5 in the model environment were strongly influenced by multiple input parameters, including temperature, the mode of emission (especially emission rate to water), K_{OC} and half-life in air. As temperature decreased from 25 °C to 1 °C, K_{OC} and half-life in air became increasingly more influential such that the mass distribution of D5 increased in air and decreased in sediment, resulting in decreased overall persistence.

1. Introduction

Several multimedia mass-balance models have been developed to predict and proved an increased level of understanding of the fate and behavior of chemicals released into the environment (MacLeod et al., 2011; Mackay et al., 2009). These models include, for example, the EQC (EQuilibrium Criterion) model, the RAIDAR (Risk Assessment, Identification and Ranking) model and ChemCAN, to name a few. The overall persistence is calculated based on loss mechanisms and long-range transport is also further predicted by other models such as The OECD Tool (Wegmann et al., 2009), BETR (Berkley-Trent) models (MacLeod et al., 2005), etc.

The EQuilibrium Criterion (EQC) multimedia fugacity model (Mackay et al., 1996; Mackay, 2001) was developed in 1996 and has been widely used to assess and/or predict the likely fate, distribution and transport of chemicals in the environment (MacLeod et al., 2011). In addition to *environmental* properties of the evaluative environment and advection residence times, the EQC model requires *partitioning* properties such as Henry's Law constant (H_C), the organic carbon–water partition coefficient (K_{OC}) and the fish-water partition coefficient (K_{FW}), and *reactive* properties such as degradation half-lives in each environmental compartment (i.e., air, water, soil, and sediment). However, actual measured data for the required chemical properties are often not available or of insufficient or unknown quality. In such instances it is common practice to use values estimated using structure activity relationships (SAR) that may have high levels of associated uncertainty. Partitioning properties such as K_{OC} and K_{FW} are often estimated from K_{OW} (octanol–water partition coefficient): for example, $K_{OC} = 0.41 \times K_{OW}$ (Karickhoff, 1981), $K_{OC} = 0.35 \times K_{OW}$ (Seth et al., 1999) and $K_{FW} = 0.05 \times K_{OW}$ (Mackay, 1982). For this reason, K_{OW} is considered to be a master variable in multimedia models, including the EQC model. However, direct estimation of K_{OC} or K_{FW} from K_{OW} can be subject to considerable error and uncertainty, which contributes to the overall uncertainty associated with the EQC results.

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Recently, a new Microsoft Excel® workbook version of the EQC model (henceforth referred to as the EQC-Spreadsheet model) has been developed collaboratively between the Canadian Centre for Environment Modeling and Chemistry (CEMC) and Dow Corning Corporation. The EQC-Spreadsheet model includes improved treatment of input partitioning and reactivity data, temperature dependence and provides a basis for facilitating sensitivity and uncertainty analysis. The detailed features of the EQC-Spreadsheet or New EQC model are discussed in a companion paper (Hughes et al., 2012), and applied to decamethylcyclopentasiloxane (D5; CAS No. 541-02-6) as an example compound. In addition to improved flexibility with input data entry, the EQC-Spreadsheet version can perform further in-depth assessments using various add-ins and user-defined macros.

As with previous versions of the EQC model, the EQC-Spreadsheet model consists of a series of fugacity-based mass balance calculations that provide a picture of the likely fate of a chemical in a defined evaluative environment. Small variability associated with the input data and parameters may be propagated through the calculations and become a large and unknown source of variability associated with the output results. Typically, the variability associated with input data and parameters may result from natural variability in the environment (e.g., temperature) and from measurement uncertainties (due to experimental errors, lack of knowledge, etc.) associated with the input property values for the chemical being modeled. Thus, the aim of this study was to use the new EQC-Spreadsheet model to systematically evaluate the sensitivity of the model results to variability associated with the chemical property values required as input for the model. Specifically, this study focused on the effect of variability associated with partitioning and reactive property values in the model environment. We also demonstrate how uncertainty analysis may be applied to the EQC-Spreadsheet model and show how the uncertainty of each physical and chemical property input parameter may significantly influence the predicted behaviors of a chemical substance. The uncertainty analysis was performed by the Monte Carlo technique, which is widely accepted for uncertainty analysis of complex systems because continuous distributions of each input variable are simultaneously tested. The Monte Carlo uncertainty analysis also provided systematic results that were used to determine the contribution of each input variable to the total variance associated with the model results for each endpoint. To be consistent with the companion paper (Hughes et al., 2012), decamethylcyclopentasiloxane (D5) was selected as a good example of a substance that requires evaluation using the EQC-Spreadsheet model because of its unusual combination of properties, namely a high vapor pressure and a low water solubility resulting in a very high air–water partition coefficient, a large K_{OW}, but only a moderately high K_{OC} and a wide range of media-specific half lives. In addition, energy of phase transfer for each partition coefficient and activation energy for each degradation reaction were used to run the model at different temperatures.

2. Methods

2.1. The EQC-Spreadsheet model and input parameters

The current study was conducted using the new EQC-Spreadsheet model, which is described in a companion paper (Hughes et al., 2012). The model has been made freely available for download from the CEMC web site (www.trentu.ca/cemc). A Level III assessment (i.e., non-equilibrium steady state conditions) was used for all simulations. Default values for environmental compartment properties (four compartments and ten sub-compartments), advection residence times and the twelve intermedia mass transport velocities were same as used in previous versions of the EQC Model (Mackay et al., 1996; CEMC, 2010). There were no changes to the theory, methodology or equations of previous versions of the EQC model, with the exception that empirical values for chemical properties may be manually entered. Accordingly, the empirical values of K_{OC} and K_{FW} for D5 were used rather than values derived from K_{OW}. This feature was especially important for D5, which does not partition to organic carbon or lipid as expected (SEHSC, 2011).

Chemical-specific data for D5 required for the EQC-Spreadsheet model were preferentially taken from available measured values (Table 1). The EQC-Spreadsheet Level III model calculates various endpoints including fugacities, masses, concentrations, transport rates, reaction rates, advection rates, persistence (or, equivalently, residence time), etc., all of which may be evaluated using the Monte-Carlo uncertainty analysis. However, this study focused mainly on the following three categories of end-points:

(i) Mass distribution:

$$m_i = \frac{M_i}{\sum_i M_i} = \frac{M_i}{M_T} \tag{1}$$

(ii) Persistence (or residence time):

$$P_{advection} = \frac{M_T}{\sum_i A_i} \tag{2}$$

$$P_{reaction} = \frac{M_T}{\sum_i R_i} \tag{3}$$

$$P_{overall} = \frac{M_T}{\sum_i A_i + \sum_i R_i} = \left(\frac{1}{P_{advection}} + \frac{1}{P_{reaction}}\right)^{-1} \tag{4}$$

(iii) Normalized intermedia transport:

$$I_{ij} = \frac{I_{ij}}{E_T} \times 100\% \tag{5}$$

where M_i is mass in an environmental medium i (kg), M_T is mass in the total system (kg), A_i and R_i are the removal rates by advection and reaction, respectively, in a medium i (kg h^{-1}), I_{ij} is the intermedia transport rate (kg h^{-1}) from one medium (i) to another (j), E_T is the total emission rate to the environment (kg h^{-1}), and subscripts i and j denote an environmental medium such as air (A), water (W), soil (S) and sediment (Sed). The normalized terms of m_i and i_{ij} are dimensionless and are expressed as a percentage or in scientific notation when the value was small. Overall there are seven intermedia transport rates: i.e., A → W, A → S, W → A, W → Sed, S → A, S → W, and Sed → W.

Results from a Level-III simulation may be strongly influenced by the mode of emission so various emission scenarios to the model environment were considered. We tested three simple 'evaluative' emission scenarios, where D5 was released to a single compartment of air, water or soil, to evaluate the fate and distribution in the environment. Based on the use pattern of consumer products by the general public, which are considered the major source of release of D5 compared with smaller and more site-specific industrial releases, a realistic emission scenario (see Supporting Information) was also tested in which D5 was simultaneously released to air (94.5%), water (0.8%), and soil (4.7%). In all cases, the total emission rate (E_T) was fixed at 1000 kg h^{-1}. In all cases, the total emission rate (E_T) was fixed at the default value of 1000 kg h^{-1}. Although mass distribution, persistence, and normalized intermedia transport rates are independent of E_T, the value for E_T is critical for calculation of mass and concentrations in the model environment. For this reason, output mass fractions and concentrations generated by the EQC model should be considered significant only in terms of relative magnitude, not absolute magnitude.