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Macleod, M.

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BETR Global – A geographically-explicit global-scale multimedia contaminant fate model

Matthew MacLeod[1†], Harald von Waldow[1], Pascal Tay[1], James M. Armitage[2,3], Henry Wöhrnschimmel[1], William J. Riley[4], Thomas E. McKone[4,5] & Konrad Hungerbühler[1]

1 –Swiss Federal Institute of Technology (ETH Zurich), Zurich, Switzerland.
2 – University of Toronto at Scarborough, Toronto, Ontario, Canada.
3 – Aarhus University Hospital, Department of Occupational Medicine, Aarhus, Denmark
4 – Lawrence Berkeley National Laboratory, Berkeley, California, USA.
5 – University of California, Berkeley, California, USA.

† – Corresponding author. Current address: Department of Applied Environmental Science, Stockholm University, SE-106 91 Stockholm, Sweden.
matthew.macleod@itm.su.se

Abstract

We present two new software implementations of the BETR Global multimedia contaminant fate model. The model uses steady-state or non-steady-state mass-balance calculations to describe the fate and transport of persistent organic pollutants using a desktop computer. The global environment is described using a database of long-term average monthly conditions on a $15^o \times 15^o$ grid. We demonstrate BETR Global by modeling the global sources, transport, and removal of decamethylcyclopentasiloxane (D5).

Capsule

Two new software implementations of the Berkeley-Trent Global Contaminant Fate Model are available. The new model software is illustrated using a case study of the global fate of decamethylcyclopentasiloxane (D5).

1. Introduction

Multimedia mass-balance models are well-established as scientific and decision-support tools for understanding the behavior of chemical pollutants in the environment (MacLeod et al., 2010), especially persistent organic pollutants (Wania & Mackay, 1999). Global-scale multimedia mass balance models have been particularly important in establishing the link between chemical emissions in industrialized regions and their presence in the Arctic. Global models often applied to study transport of persistent chemicals to the Arctic in the past describe the environment as a set of latitudinal zones, and are spatially discretized only along a north-south axis (Scheringer & Wania, 2003). In 2005, the BETR Global multimedia contaminant fate model was introduced (MacLeod et al., 2005a). It described the global environment as a set of linked multimedia regions on a $15^o \times 15^o$ grid.

The 2005 version of BETR Global was used to model the global fate and transport of polychlorinated biphenyls (PCBs) (MacLeod et al., 2005a), and the transport and deposition of a set of persistent organic substances to the North American Great Lakes (MacLeod et al., 2005b). A modified version of the model capable of simultaneously modeling the fate and transport of a weak acid and its conjugate base was developed to study the global mass balance and transport of perfluorinated acids (Armitage et al., 2009a; Armitage et al., 2009b). The model was recently used to analyze the global mass budget of PCBs and the effects of a climate change scenario on their steady-state global distribution (Lamon et al., 2009). Most recently, as part of the work of the Task Force on Hemispheric Transport of Air Pollutants (TF HTAP), BETR Global has been applied to quantify inter-continental source-receptor relationships for persistent organic pollutants in support of the Convention on Long-range Transboundary Air Pollution (CLRTAP) (Gusev et al., 2010).

Several incremental modifications have been made to the BETR Global model since 2005, including changes to the model algorithms and updates of the model's database of environmental characteristics. Among the most important modifications of the model since 2005 are; 1) the introduction of seasonally-variable hydroxyl radical fields in the atmosphere, 2) algorithms to account for the intermittent nature of contaminant scavenging by rainfall in both steady-state and dynamic calculations, and 3) improvements in the efficiency of solving the system of mass balance equations.

Our purpose here is to introduce two new software implementations of the BETR Global model, BETR Global V.2.0, and BETR-Research, that incorporate these changesand are being made publically available for direct download. BETR Global 2.0 is coded in Visual Basic for Applications (VBA) as an add-on for Microsoft Excel, and is based on the same code-base as the original 2005 version. Recently, the model has been re-implemented in Python as "BETR-Research", which is more accessible for model modifications and thus more versatile, but is lacking the graphical user-interface of the VBA version. During the development of BETR-Research a thorough code-review was performed, which increased the quality and validity of both BETR implementations. We illustrate the new version of the model using a case study of the global fate and transport of decamethylcyclopentasiloxane (D5), which can be replicated using the VBA version of BETR Global 2.0 by following the tutorial on the BETR Global website (http://sites.google.com/site/betrglobal/home). The BETR-Research Python implementation of the model can be downloaded from http:// betrs.sourceforge.net.

2. Model Software and Formulation

The BETR modeling framework allows geographically-explicit contaminant fate models to be assembled by linking a set of regional fugacity-based multimedia mass-balance models together. The fugacity concept is described in detail by Mackay (2001), and the general structure of models based on the BETR framework is described by MacLeod et al. (2001). The BETR Global parameterization of the framework describes the global environment on a $15^o \times 15^o$ grid as a set of 288 multimedia regions linked by flows of air and water. Within each region the model calculates the distributions of chemicals in, and between seven bulk environmental compartments: 1) upper air, representing the free troposphere, 2) lower air, representing the boundary layer of the troposphere, 3) vegetation, 4) fresh water, 5) ocean water, 6) soil and 7) freshwater sediments. Transport of chemicals between regions is modeled in the upper air, lower air, freshwater and ocean water compartments.

The mass balance of the chemical pollutant is modeled by a system of partial differential equations, with one equationdescribing sources, transport and degradation in each compartment. Spatial derivatives are approximated using two-point upwind differencing to yield a system of ordinary differential equations. These equations can be solved either for 1) steady-state conditions in which constant emissions are balanced by removal process, or 2) non-steady-state scenarios in which emissions and rates of removal processes vary in time. The VBA version solves the model

equations using Euler's method with an adaptive time-step selected to ensure numerical stability, whereas the Python version uses the backward differentiation formula as implemented in VODE (Brown et al., 1989). Typical computing time using BETR Global 2.0 is less than 1 minute for a steady-state calculation, and approximately 8 minutes per year of simulation time in a non-steady-state calculation. BETR-Research is about 20 times faster on the same hardware, taking about 24 seconds to integrate one year of simulation time, and multiple calculations can be run in parallel on desktop computers with multi-core processors.

Input data required to run the model are 1) physico-chemical properties of the chemical of interest (i.e. equilibrium partition coefficients between air and water, water and octanol, and octanol and air), 2) estimates of degradation half-lives of the chemical in each bulk model compartment, and 3) spatially-explicit emission estimates. The model calculates fugacities and chemical concentrations in the multimedia global environment, and transport fluxes between regions and between compartments in each region.

3. Environmental Database

The BETR Global model includes a database of information about the global environment used in model calculations. The environmental parameters in the database have been selected to represent long-term average conditions. Some environmental parameters are fixed values derived from GIS databases, such as the area of each region, and the fractions of the surface covered by soil, vegetation, and water. Other parameters, such as temperature, atmospheric hydroxyl radical concentrations, and air- and water-flow rates between regions, are specified as monthly averages. In non-steady-state model calculations, chemical transport and transformation rates are changed every month of model time to reflect conditions appropriate for that month. Multi-year model simulations repeat the same cycle of environmental conditions. Thus the model describes monthly, but not inter-annual, variability in environmental conditions in non-steady-state calculations, and long-term average conditions in steady-state calculations. More details about the environmental database can be found on the BETR Global website (http://sites.google.com/site/betrglobal/home)

4. Range of Applicability

Like all models that use two-point upwind differencing to approximate the derivative of concentrations in space, BETR Global overestimates transport of chemicals due to numerical diffusion (Warren et al., 2009). The extent of overestimation is largest when steep concentration

gradients exist at spatial scales smaller than the model regions. This can occur, for example, shortly after emission from a point source into an uncontaminated environment, or for substances with half-lives in air and water that are short relative to the residence times of air and water in the model regions. Warren et al. (2009) argue that overestimation of transport due to numerical diffusion will generally not introduce significant errors if less than 25% of the inventory of a chemical in air or water is removed in a model region. We also note that the extent of overestimation of transport will be reduced considerably if sources to air and ocean water are spatially diffuse at sub-region and multi-region scales. This is often the case for persistent substances used in global commerce and especially for ocean water when loadings are predominantly by deposition from the atmosphere. Residence times of air and water in each BETR Global grid cell are variable, however average values imply that the model can be generally applied to chemicals with atmospheric residence times greater than 180 h (7.5 d), and oceanic residence times greater than 30,000 h (1250 d) without significantly overestimating the extent of transport.

Caution should be used when interpreting model results for substances with residence times in air and water approaching these values.

5. Illustrative Application to Decamethylcyclopentasiloxane (D5)

As an illustration of the BETR Global model, we applied the model to describe the fate and transport of decamethylcyclopentasiloxane (D5, CAS#: 541-02-6) in the global environment. This case study is very similar to a recent study using the Danish Eulerian Hemisperic Model (DEHM) (McLachlan et al., 2010). Here we provide only a summary of the input data and model results for the D5 case study. A detailed tutorial that guides users through these calculations using the BETR Global 2.0 is available (http://sites.google.com/site/betrglobal/home).

5.1 Properties of D5

D5 is highly hydrophobic and volatile. It has a rate constant for reaction with hydroxyl radicals in the atmosphere that corresponds to a global-average half-life of 10 days in air. We have used the property data for D5 selected by Gouin (2010) as input to the BETR Global model for this case study.

5.2 Estimates of D5 emissions

D5 is widely used as a solvent in personal care products, and emissions to the environment are believed to be predominantly by volatilization to air (McLachlan et al., 2010; Brooke et al., 2009). Here, estimated emissions to air of 20 million kg y^{-1} globally based on the emission estimates made in the risk assessment of D5 conducted by the Environment Agency of England and Wales (Brooke et al., 2009). In the absence of specific information about the global geographic distribution of D5 use, we allocated emissions spatially according to the distribution of light emissions at night, as suggested by von Waldow et al. (2010), to weight emissions toward densely populated regions of industrialized countries where use of personal care products containing D5 is assumed to be highest.

5.3. Monitoring data

McLachlan et al. (2010) reported the first extensive set of monitoring data describing concentrations of D5 in ambient air. They measured D5 at a rural site (59.31N 15.49E) near Örebro, Sweden from January 19, 2009 to June 15, 2009.

5.4 Model application and results

The steady-state mass balance for the global environment calculated by BETR Global indicates that D5 is sufficiently volatile that its fate and transport is dominated by atmospheric processes. At steady-state, greater than 75% of the global inventory of D5 is found in the atmosphere, with most of the remainder in soils. Removal of D5 from the global environment is dominated by hydroxyl radical degradation in air (99.9% of removal from the global system). The modeled overall residence time of D5 in the global environment was 31.6 days. This indicates that results of non-steady-state calculations are insensitive to emissions that occur more than a few months earlier. In this illustrative case study, we used the model software to set initial inventories of D5 in all model compartments at the values calculated for steady-state conditions, then ran the non-steady-state model for two years. Model results for the second year of the simulation were considered to be illustrative of monthly variability in concentrations.

These model results are compared to D5 concentrations measured at 59.31° N 15.49° E (McLachlan et al., 2010) in Figure 1. The monitoring site lies near the intersection of boundaries between four BETR regions. The model results in Figure 1 are for the region immediately to the

north of the site. Modeled concentrations of D5 in the region to the south are a factor of 2 higher because this model region includes more source regions, but have a very similar temporal trend. They are represented by the upper boundary of the illustrative uncertainty range of a factor of 2 that is shown in Figure 1.
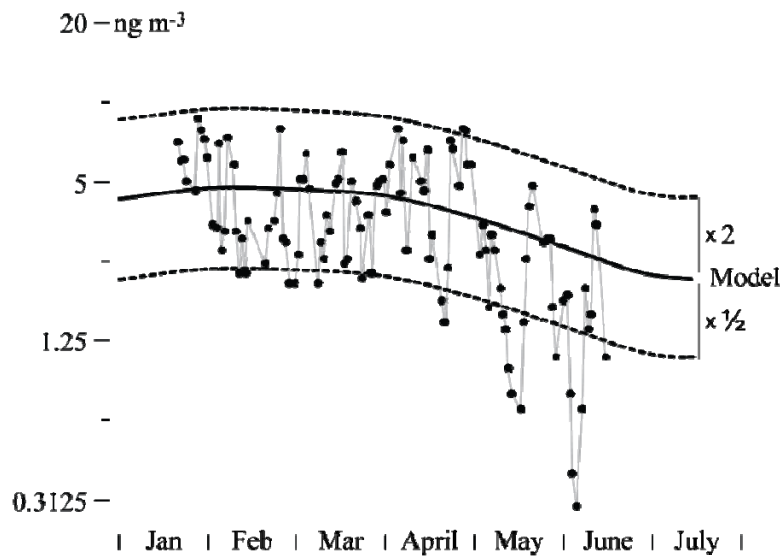
Figure 1: Comparison of measured concentrations (solid circles) of D5 in air at …rebro, Sweden (59.31°N 15.49°E) measured daily in the first half of 2009 (McLachlan et al., 2010) and concentrations calculated with BETR Global (solid line). The dashed lines represent a factor of two uncertainty around the model result.

The non-steady-state BETR Global calculation describes the absolute level and intra-year trend of the monitoring data very well (Figure 1). The decrease in modeled concentrations between March and July is attributable to concurrent increases in Northern Hemisphere hydroxyl radical concentrations. Because the model's environmental database describes variability at a monthly resolution, the day-to-day variability in the measurement data is not represented by the model.

Variability in hydroxyl radical concentrations controls both spatial and temporal variability in modeled concentrations of D5 in the atmosphere. In February, when hydroxyl radical concentrations are low, concentrations of D5 in the atmosphere vary by less than a factor of 3 over a large area that includes the North Pole (Figure 2A). In August, when hydroxyl radical concentrations are high in the Northern Hemisphere, D5 concentration gradients between regions of highest emissions in North America and Europe and more remote areas are relatively steep

(Figure 2B). Based on their modeling with DEHM, McLachlan et al. (2010) also concluded that variability in hydroxyl radical concentrations controlled variability in concentrations of D5 in the atmosphere.
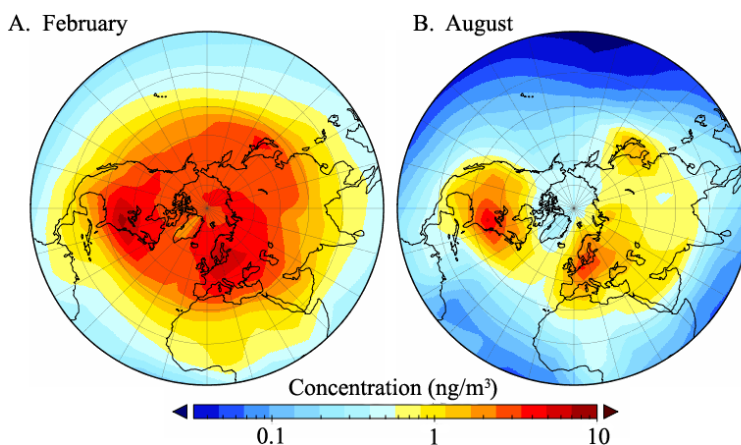

Figure 2: Modeled concentrations of D5 in boundary layer air in the Northern Hemisphere during (A) February and (B) August, 2009.

6. Conclusions

BETR Global 2.0 and BETR-Research are now available for public download and use on conventional desktop computers. BETR Global 2.0 has a graphical user interface, while BETR-Research is more computationally efficient and the code is more amenable to modification. Both versions of the model can be applied to analyze the global-scale fate and transport of persistent organic pollutants at a process-level, and to evaluate global mass budgets based on emission estimates and physico-chemical properties of chemicals.

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