

## **Towards State-of-the-Art Dynamical Modelling and Risk Assessment of Persistent Organic Pollutants (POPs) in the Global Environment**

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**Abstract**—The Finely-Advanced Transboundary Environmental (FATE) model was developed to quantify the fate and transport of Persistent Organic Pollutants (POPs). The global version of the model, FATE-global, includes five environmental compartments: atmosphere, ocean, ice, soil, and vegetation. With a horizontal resolution of  $2.5^\circ \times 2.5^\circ$  and 8 vertical atmospheric layers, FATE-global incorporates advection and diffusion processes in the atmosphere, however, no horizontal transport is included in the other compartments. The abiotic processes in all compartments and the bioconcentration process in the vegetation compartment are parameterized.

A simulation was performed for polychlorinated biphenyl #153 (PCB#153) for the period 1931–2006, and the simulated monthly near-surface concentration of PCB#153 was validated against observational data at eight observational sites in Europe for the period 1994–2006. The model underestimated the near-surface PCB#153 concentration, predicting approximately 20% of the observed value, and the temporal trend of the model-predicted PCB#153 concentration at coastal sites differed significantly from that of the observational data. These drawbacks of the model may be explained by uncertainties in the emission data used for the simulation, and simplified processes in the atmosphere and ocean compartments of the model.

**Keywords:** global model, long-term model prediction, multi-compartment model, Persistent Organic Pollutants (POPs)

### INTRODUCTION

Modelling the dynamics of Persistent Organic Pollutants (POPs) is a big challenge for 21st century science, and is important for environmental risk assessments. Rapid progress has been made in the development of numerical models for POPs dynamics in recent years, and these models are capable of quantifying the long-range transport potential and the overall persistency of POPs in the environment (see review of Wania and Mackay (1999); and the model comparison studies of Shatalov *et al.* (2004, 2005) and Fenner *et al.* (2005)). However, high-resolution global models that predict the non-steady dynamics of POPs are yet to be

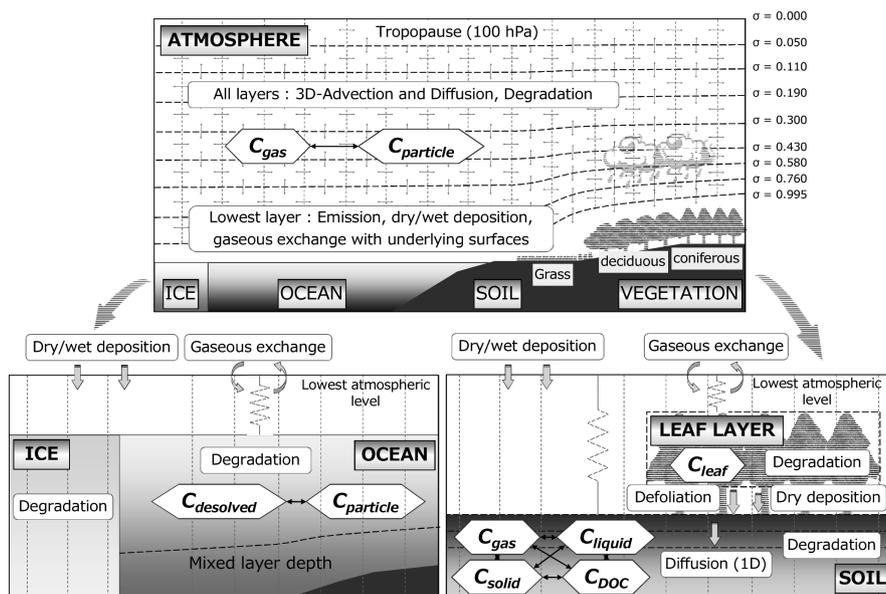


Fig. 1. Schematic diagram of the POPs FATE model, illustrating POPs partition in various phases and the processes governing POPs dynamics.

developed (e.g., Malanichev *et al.*, 2004; Leip and Lammel, 2004) and the comprehensive global-scale POPs emission inventories to be employed by such models are limited.

We have developed a space-resolving time-dependent multi-compartment model to predict the fate and transport of POPs, called the POPs FATE (Finely-Advanced Transboundary Environmental) model. The POPs FATE model is a unified multi-scale modelling system, which is capable of quantifying the long-range transboundary transports, source-receptor relationships, and persistent sinks of POPs, and is directly applicable to environmental risk assessments of POPs. Two versions of the POPs FATE model are currently under development, in order to focus on the POPs dynamics at the spatial scale of interest: one is for global assessment (FATE-global), and the other is for regional assessment (FATE-regional).

The purpose of this paper is to present the current status of FATE-global, and to validate the model against observational polychlorinated biphenyl #153 (PCB#153) datasets. In Section “Materials and Methods”, the model specifics, including the input and forcing data, and the processes considered in each of the environmental compartments are described. The results of model validation and the need for model improvement are discussed in Section “Results and Discussions”, followed by a few conclusions in Section “Conclusions”.

## MATERIALS AND METHODS

*Model description*

The FATE-global model represents POPs dynamics within and across five environmental compartments: atmosphere, ocean, ice, soil, and vegetation (Fig. 1). The horizontal resolution of the model is  $2.5^\circ \times 2.5^\circ$ . The model incorporates advection and diffusion processes in the atmosphere, however, no horizontal transport is included in the other compartments. Within a  $2.5^\circ \times 2.5^\circ$  grid, the total amount of POPs is calculated by the areal weighting of POPs contents in respective compartments. Brief descriptions of the processes associated with POPs dynamics in each environmental compartment are given in the following subsections.

*a) Atmosphere*

The atmosphere, from the mean sea-level surface to the top of the troposphere (100 hPa), is divided into 8 sigma layers ( $\sigma = 0.76, 0.58, 0.43, 0.3, 0.19, 0.11, 0.05, \text{ and } 0$ ). The model solves 3D advection and diffusion, degradation, and gas/particle partitioning processes of POPs through the depth of the troposphere. Dry and wet deposition and gaseous exchange with the underlying surfaces are calculated in the lowest atmospheric layer.

The model employs the positive definite advection scheme of Bott (1989). The vertical eddy diffusivity is parameterized by the local Richardson number, and the horizontal eddy diffusivity is determined from the horizontal deformation using the Smagorinsky first-order closure approach (Grell *et al.*, 1995). The difference of total POPs mass between the states before and after advection and diffusion calculations usually deviates from zero. The mass required to preserve conservation of mass is distributed proportionally to local POPs concentrations. For POPs partitioning processes between gaseous and particle phases, the Junge-Pankow model (Junge, 1977; Pankow, 1987) is used. This model has been widely adopted in other POPs multi-compartment modelling studies. The degradation of POPs in air is described by a second order equation that has as inputs the degradation rate constant,  $k_{\text{air}}$ , and the [OH] radical concentration. Dry and wet deposition are parameterized by the methods of Tsyro and Erdman (2000), and Atlas and Giam (1988), respectively.

The exchange of POPs between the atmosphere and the underlying compartments is formulated by a network of resistances for mass transfers. The total resistance between the atmospheric reference height ( $\sigma = 0.995$ ) and the underlying compartments,  $\gamma_T$ , is formulated as a sum of resistances below the surface,  $\gamma_M$ , and above the surface,  $\gamma_A$ . The values of are determined for each compartment, and the values of  $\gamma_A$  are estimated with the stability correction from Monin-Obukhov similarity theory (Monin and Obukhov, 1954) by assuming an analogy between mass and heat transfers.

*b) Ocean*

The ocean compartment of the current model does not include horizontal or vertical transport of POPs by ocean currents. Instead, the ocean compartment consists of a large number of boxes, each of which has a height equal to the depth

of the mixed layer and an area of  $2.5^\circ \times 2.5^\circ$ . Within each box, POPs equations for the partitioning between particle and dissolved phases and the degradation processes are solved. The degradation of POPs is modeled by a first order equation with a degradation rate constant,  $k_{\text{ocean}}$ , specific for POPs. The mass transfer resistance in the ocean,  $\gamma_M$ , is equal to the inverse of the air/water partitioning coefficient,  $1/K_{AW}$ .

*c) Ice*

The processes governing POPs in the cryosphere are largely unknown, although the areal extent of ice cover on the globe is not negligible. The current model assumes no POPs emission from the ice to the atmosphere (Wania and Mackay, 1995). However, POPs deposited to the cryosphere from the atmosphere by dry/wet deposition degrade according to the same degradation rate constant as that used for the ocean.

*d) Soil*

The soil compartment consists of 10 uniform vertical layers that range from the soil top to a depth of 30 cm; each layer is 3 cm deep. A 1-D molecular diffusion equation in the vertical direction is solved, while no hydrological processes such as infiltration or runoff are parameterized in the current model. The degradation of POPs in the soil is described by a first order equation with a degradation rate constant,  $k_{\text{soil}}$ . The partition of POPs into gaseous, solid, and dissolved phases, and the sorption of POPs to dissolved organic matter are solved in each of the soil layers. The mass transfer resistance in soil,  $\gamma_M$ , is set equal to the resistance between the gaseous phase and the other phases in the top soil layer, i.e., the model assumes that the POPs concentration below the laminar sublayer of the atmosphere is in equilibrium with the gaseous phase POPs concentration in the top soil layer.

*e) Vegetation*

The vegetation is classified into five plant functional types, evergreen broad-leaved and needle-leaved forests, deciduous broad-leaved and needle-leaved forests, and grassland. The vegetation (leaf layer) acts as a filter to POPs exchange between the atmosphere and the soil. The intake of POPs into the vegetation compartment is described by dry/wet deposition and gaseous exchange with the atmosphere. The mass transfer resistance in the leaf layer,  $\gamma_M$ , is equal to the vegetation/air partitioning coefficient (bioconcentration factor),  $K_{VA}$ . The value of  $K_{VA}$  is parameterized for each plant functional type as an exponential function of the octanol-air partition coefficient,  $K_{OA}$  (Mclachlan and Horstmann, 1998). The transport of POPs from vegetation (leaf layer) to the vegetation soil is described by defoliation. The seasonal change in defoliation rate is not considered in the current model, hence the rate is kept constant throughout the year.

*Input data*

*a) Physicochemical parameters*

The main physicochemical parameters used in the model are partitioning coefficients, degradation rate constants, and molecular diffusion coefficients.

Table 1. Physicochemical parameters for PCB#153 (Malanichev *et al.*, 2004) that are used in the model.  $R$  and  $T$  are the universal gas constant and the ambient temperature, respectively.  $T_0$  is 283.15 K.

Parameter	Symbol	Unit	Value or equation
<i>Partition coefficients</i>			
Air/Water	$K_{AW}$	—	$\frac{4.146}{RT} \exp\left[-8.347 \times 10^3 \left(\frac{1}{T} - \frac{1}{T_0}\right)\right]$
Octanol/Water	$K_{OW}$	—	$7.94 \times 10^6$
Octanol/Air	$K_{OA}$	—	$3.64 \times 10^{10} \exp\left[1.0811 \times 10^4 \left(\frac{1}{T} - \frac{1}{T_0}\right)\right]$
Organic carbon/Water	$K_{OC}$	$\text{m}^3\text{kg}^{-1}$	$3.26 \times 10^3$
Subcooled liquid vapour pressure	$P_{OL}$	Pa	$9.69 \times 10^{-5} \exp\left[-1.0995 \times 10^4 \left(\frac{1}{T} - \frac{1}{T_0}\right)\right]$
<i>Degradation rate constant</i>			
Atmosphere	$k_{\text{air}}$	$\text{cm}^3\text{molec}^{-1}\text{s}^{-1}$	$8.12 \times 10^{-11} \exp\left(\frac{1.5380 \times 10^4}{RT}\right)$
Soil	$k_{\text{soil}}$	—	$1.17 \times 10^{-9}$
Ocean	$k_{\text{ocean}}$	—	$1.60 \times 10^{-9}$
<i>Molecular diffusion coefficient</i>			
Air	$D_a$	$\text{m}^2\text{s}^{-1}$	$4.58 \times 10^{-9}$
Water	$D_w$	$\text{m}^2\text{s}^{-1}$	$5.14 \times 10^{-9}$

The specific parameters for PCB#153 are summarized in Table 1, all of which are taken from Malanichev *et al.* (2004). The coefficients for POPs phase partition (i.e.,  $K_{AW}$ ,  $K_{OW}$ ,  $K_{OA}$ , and  $K_{OC}$ ) and phase change (i.e.,  $P_{OL}$ ) depend on the ambient temperature,  $T$ . This temperature dependency is taken into account in the model.

#### b) Emission

Breivik and his colleagues have provided emission inventories (high, mid, and low scenarios) for PCBs (22 congeners) for the period 1930–2100 (Breivik *et al.*, 2002a, 2002b, 2007). Although there are large uncertainties in their emission estimates, which range over approximately two orders of magnitude (Breivik *et al.*, 2002b), their inventory is the only data currently available for global modelling studies. In this study, the high emission scenario of Breivik *et al.* (2002b, 2007) has been adopted because their emission estimates are likely underestimated (Breivik *et al.*, 2002b).

#### c) Land cover

The land cover classification data from GLC2000 (Global Landcover Classification for the year 2000) (<http://www-tem.jrc.it/glc2000>) and USGS GLCC version 2 (U.S. Geographical Survey, Global Land Cover Characterization version 2) (Loveland *et al.*, 2000) are used for the latitudes of 60°S–90°N, and for

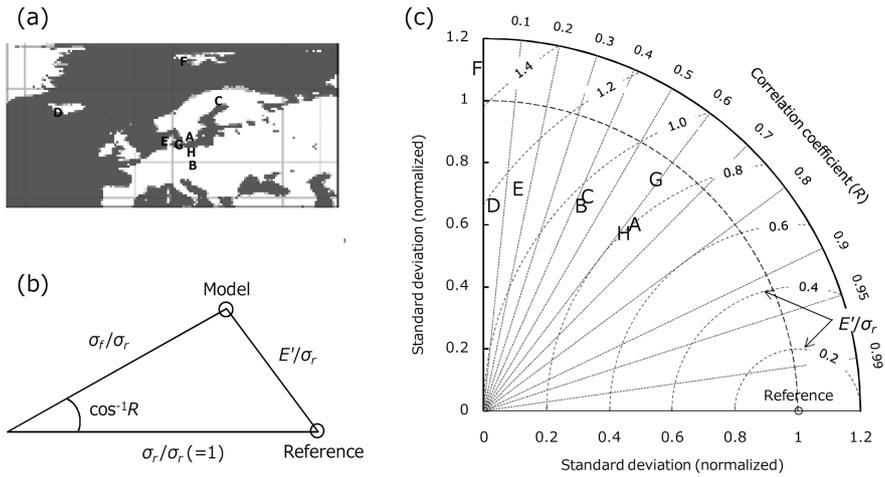


Fig. 2. (a) Geographical map showing the location of the observational stations in Europe. (b) Geometric relationship among the correlation coefficient,  $R$ , the root-mean-square error,  $E'$ , and the standard deviations of the modeled result,  $\sigma_f$ , and observed result,  $\sigma_r$ . (c) Taylor diagram summarizing and comparing the statistics of the observed and model-based values of monthly average near-surface PCB#153 concentration. The letters (A, B, ... , F) correspond to the observational sites in (a).

the rest of the world (i.e., the Southern Ocean and the Antarctic), respectively. The 23 land cover types provided by these datasets are classified into ocean, ice, bare soil, and the 5 plant functional types, in order to fit the five compartments of the model. The areal fraction of the eight model land cover types is calculated for each  $2.5^\circ \times 2.5^\circ$  horizontal grid.

#### d) Meteorology and oceanography

Five meteorological forcing variables are used as input data to the model: wind velocity, temperature, and potential temperature at each grid-point and at the reference height in the atmosphere, and temperature and precipitation at the sea-level surface. These meteorological forcing data are obtained from NCEP/NCAR (National Centers for Environmental Prediction/National Center for Atmospheric Research) Reanalysis 1 data (Kalnaya *et al.*, 1996). We prepared the long-term mean (1948–2007) 6-hourly data, which was used for the long-term simulations.

To determine the box height of the ocean compartment, the mixed layer depth is determined from the World Ocean Atlas 1998 (<http://www.nodc.noaa.gov>). The use of this dataset allows seasonally dependent estimates of the mixed layer depth.

#### Simulation settings

The model was run for the period of 1931–2006 (including a spin-up period

of 63 years) in order to simulate the PCB#153 dynamics. The time integration interval was 3 hours. Emission was assumed to be zero for the years before 1931, thus, initial concentrations of PCB#153 were set to zero in all the model compartments.

### *Observational datasets*

For model validation, we used the monthly average near-surface PCB#153 concentration data (gas and particle phase) from the European Monitoring and Evaluation Programme (EMEP) which are available online (<http://tarantula.nilu.no/projects/ccc/index.html>; e.g., Wenche and Breivik, 2008). The PCB#153 data were collected at eight observational stations in Europe (Fig. 2(a)).

Because of the limited period of the observational dataset, the model-data comparison will focus on the period of 1994–2006.

## RESULTS AND DISCUSSIONS

A single Taylor diagram (Taylor, 2000) was used to evaluate multiple aspects of the model performance with respect to the prediction of monthly average near-surface PCB#153 concentration. A Taylor diagram provides a visual summary of the three statistical variables that are most frequently used to evaluate model performance: the correlation coefficient,  $R$ ; the root-mean-square error,  $E'$ ; and the standard deviation of the model predictions  $\sigma_f$  (which is compared to the standard deviation of the observed data,  $\sigma_r$ ) (Fig. 2(c)). The geometric relationships among the three statistical variables displayed in the Taylor diagram are shown in Fig. 2(b). The statistical variables are normalized by  $\sigma_r$ , as they are site-dependent. It is important to note that each of the statistical variables is indicative of the model performance in the temporal domain.

The variability of the monthly average near-surface PCB#153 concentration predicted by the model was systematically smaller than those of the observed PCB#153 concentrations (Fig. 2(c)). Except for Site F, the ratios of  $\sigma_f/\sigma_r$  were approximately 0.8. In fact, the model underestimated the near-surface PCB#153 concentration, predicting approximately 20% of the observed value (not shown). The correlation coefficients of Sites A, B, C, G, and H were approximately 0.5, while those of Sites D, E, and F are significantly smaller than 0.5.

The above disagreement in the statistical variables between the observed and modeled PCB#153 concentration can be attributed to various factors such as certain processes not being included in the model (e.g., POPs transport by ocean currents, runoff, and infiltration), uncertainties in the emission estimates and physicochemical parameters, and insufficient spatial resolution of the model. Here, we consider two of these plausible reasons which likely account for the underestimated near-surface PCB#153 concentration. One plausible reason is the underestimation of emission. As described in Subsection “Emission”, the emission data values are subject to large uncertainties and may be smaller than the actual emission values. Another plausible reason is the vertical resolution of the atmosphere. The height of the lowest atmospheric layer in the current model

roughly coincides with that of the atmospheric boundary layer. Thus, we speculate that the model inevitably underestimates the near-surface concentration of PCB#153.

As for the sites with small correlation coefficients (i.e., D, E, and F), they are all located near the coast on the western edge of the land mass, where the near-surface concentration of PCB#153 can be influenced by oceanic advection and the overlying westerlies. However, as described in Subsection “Model description”, the ocean compartment of the current model does not incorporate advection and diffusion processes. This suggests that improvements of the ocean compartment in the model will help address the statistical disagreement between the observed and model-predicted values of the near-surface concentration of PCB#153.

## CONCLUSIONS

We presented a novel dynamic global multi-compartment model for POPs, FATE-global. The current model generally underestimated the observed values of the near-surface PCB#153 concentration (the model predicted approximately 20% of the observed value), and coastal sites exhibited a lack of correlation between the observed and model-predicted values of the monthly average near-surface PCB#153 concentration. These drawbacks of the model performance can be readily explained by the structure of the model. The FATE-global model is currently being improved and is aiming for state-of-the-art dynamical modelling and risk assessments of POPs in the global environment.

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