

Inter-Congener Variability in the Global Dynamics of Polychlorinated Biphenyls: A Message from Finely-Advanced Transboundary Environmental Model (FATE)

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Abstract—The Finely-Advanced Transboundary Environmental model (FATE) was developed and used in the assessments of inter-congener variability of the fate of polychlorinated biphenyls (PCBs). FATE is capable of predicting the global dynamics of eleven PCB congeners with chlorine atoms from 1 to 8. In this study, we run the FATE for seven PCBs congeners (IUPAC No., 28, 52, 101, 118, 138, 153, and 180), for the years of the past 80 years (1931–2010), and discussed three-dimensional distributions of the selected PCBs congeners in the global atmosphere and the oceans. Our model results suggested that the meridional and the vertical distributions of PCBs in the atmosphere and the oceans are distinctly different between congeners. The PCBs with higher chlorination were more preferably transported to the subtropical to tropical atmosphere and the oceans, to the lower to middle parts of the troposphere, and to the deep oceans than the lower chlorinated congeners. These results suggest that the long-range transport potential of PCBs increase with increasing the number of chlorine. We found that the degradations in the atmosphere and the oceans are the key processes to explain the inter-congener variability of PCBs three-dimensional distributions.

Keywords: Finely-Advanced Transboundary Environmental model (FATE), polychlorinated biphenyls (PCBs), global distribution, inter-congener variability

INTRODUCTION

Persistent organic pollutants (POPs), which are highly bioaccumulative and adversely affective to human and ecosystem health, are prone to be transported to remote regions, such as the Arctic. The Long Range Transport Potential (LRTP) has been widely recognized as one of a major metric of the POPs transboundary dynamics, and is known to be differed among POPs species according to their wide variety of physicochemical properties. Because comprehensive global scale monitoring in the environmental compartments are scarce, multi-media fate models have been commonly used for the LRTP

assessments (e.g., Fenner *et al.*, 2005). On the other hand, most of these models are coarsely segmented, and have traditionally implemented rather simplified transport processes, and therefore, are not feasible for use in detailed LRTP assessments such as the inter-species/congener variability of POPs three-dimensional distributions in the environment.

Our research group has developed the Finely-Advanced Transboundary Environmental model (FATE; Kawai and Handoh, 2009; Kawai *et al.*, 2010). FATE is forced by realistic climate data and computes highly-resolved three dimensional transboundary transports of POPs in the atmosphere and the oceans. In this study, we run the FATE for seven PCBs congeners (IUPAC No., 28, 52, 101, 118, 138, 153, and 180), and discussed the inter-congener variability of PCBs three-dimensional distributions in the global atmosphere and the oceans.

MATERIALS AND METHODS

FATE is a global multi-compartment model capable of predicting POPs biogeochemical cycles across the five environmental compartments (i.e., atmosphere, oceans, soil, vegetation, and cryosphere). The model is forced by several global data and computes abiotic and biotic processes to predict POPs loads, sinks and fluxes in the environment. Some of these data and model processes have been described in the elsewhere (Kawai and Handoh, 2009; Kawai *et al.*, 2010) so that we will provide the briefly summary of the model in the followings.

Abiotic transport processes

In the atmosphere and the oceans, three-dimensional advection and diffusion equation is solved, with spatial resolutions of $2.5^\circ \times 2.5^\circ \times 27$ σ -layers in the atmosphere, and $0.5^\circ \times 0.5^\circ \times 54$ layers in the oceans, respectively. For advection, the modified Clowrey/Botts' advection scheme with 4th order accuracy (Li and Chang, 1996) is used. For vertical diffusion, computationally-cheap boundary layer models based on the non-local K -profile parameterization is used in the atmosphere and the ocean: These models are YSU-PBL (Hong and Noh, 2006) for the atmosphere and KPP (Large *et al.*, 1994) for the ocean, respectively. In the surface soil (0–30 cm), one-dimensional advection (i.e., infiltration) and diffusion (i.e., molecular diffusion and bioturbation) equation is solved (McLachlan *et al.*, 2002). Then, POPs transport to deep layer in soil is calculated in the model. Inter-compartment transfers are governed by dry and wet depositions, and the molecular and turbulent diffusions of POPs in gaseous phase. Dry deposition velocity of aerosol particles and the bulk transfer velocity of gaseous POPs in the atmospheric surface layer are parameterized by an aerosol size-resolving model of Giorgi (1986) and the Monin-Obukhov Similarity Theory with stability corrections (e.g., Brutsaert, 1982), respectively.

Biological processes

In FATE, POPs bioconcentration in primary producers (i.e., terrestrial

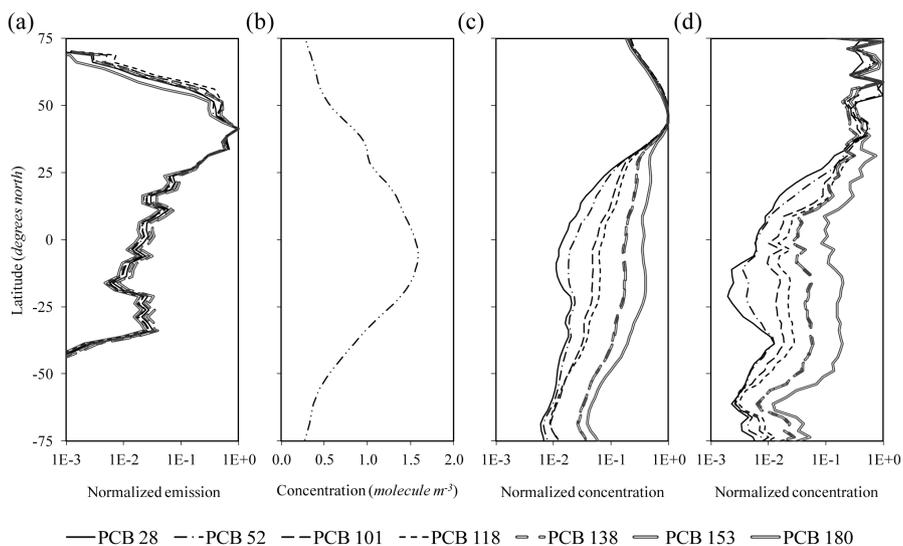


Fig. 1. Zonally-averaged meridional distributions of (a) PCBs historical emission (1931–2010), (b) *OH*-radical concentration in the atmosphere, and (c) and (d) the modeled PCBs concentrations in the atmosphere and the oceans, respectively. Annual mean results for the year 2010 are shown. The emissions and the concentrations are normalized by the maximum values.

vegetation and marine phytoplankton) are considered. Vegetation-air partitioning coefficient (i.e., bioconcentration factor) is parameterized as functions of Octanol-air partitioning coefficient and plant functional types as commonly assumed (e.g., McLachlan and Horstmann, 1998). For Bioconcentration in marine phytoplankton, we used a two-compartment model of Dachs *et al.* (1999), in which POPs adsorption/desorption to/from phytoplankton cell, uptake/depuration in phytoplankton matrix, and dilution by phytoplankton growth are taken into account. The POPs taken up by the phytoplankton detritus is exported directly to the ocean bottom. Phytoplankton biomass and growth rate, which are used in solving this process model, are estimated from the SeaWiFS-based satellite data and by the Carbon-based production model (Behrenfeld *et al.*, 2005).

Degradations and phase partitions

Degradations in compartments other than the atmosphere are calculated by the simplest first order equation, $dC_q/dt = k_q C_q$, with C_q the POPs concentration in all phases and k_q the degradation rate constant for compartment q . In the atmosphere, we assumed that the *OH*-radical reaction is dominated, and the second order degradation equation, $dC_A/dt = k_A C_A [OH]$, is solved, where subscript A and $[OH]$ represent the atmosphere and the *OH*-radical concentration, respectively. $[OH]$ is not a constant value but varies temporally and spatially. We used monthly values of the three-dimensional climatological $[OH]$ (Spivakovsky

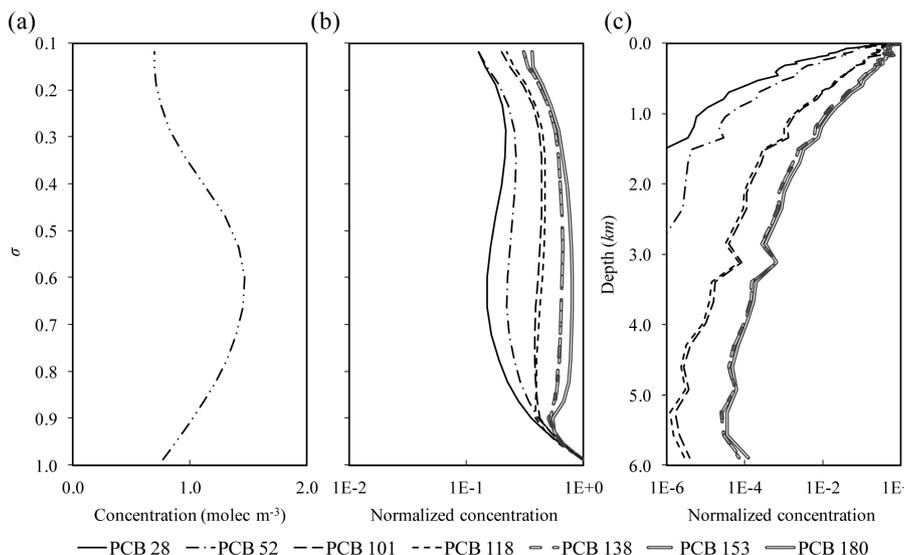


Fig. 2. Globally-averaged vertical distributions of (a) the *OH*-radical concentration in the atmosphere, and (b) and (c) the modeled PCBs concentrations in the atmosphere and the oceans, respectively. Concentrations are normalized by the maximum values.

et al., 2000).

In the atmosphere, gaseous and aerosol particle-bounded phases are considered. Partitioning into these two phases is parameterized by the model of Junge and Pankow (e.g., Bidleman, 1988). In soil, four phases, gaseous, dissolved in water, sorbed on and dissolved in the organic carbon phases are considered. Partitions into these phases are simply calculated by the partitioning coefficients between these phases.

Simulation settings and data used

We run the FATE for seven PCBs congeners (IUPAC No., 28, 52, 101, 118, 138, 153, and 180) for the years 1931–2010. The meteorological data (i.e., velocities, temperatures, precipitation, heat and radiation fluxes, and wind stresses) we have employed in the simulations are NCEP/NCAR reanalysis I. We used 6-hourly reanalysis data for the years 1948–2010, and 6-hourly climatological data (i.e., long-term mean of the reanalysis data) for the years 1931–1947. For oceanic forcing data (i.e., velocities, temperature, and salinity), we used model outputs from OFES (OGCM for Earth Simulator) 50-years simulation (climatology run; Masumoto *et al.*, 2004). For PCBs emission, we used a “high scenario” of the Breviks’ inventory (Brevik *et al.*, 2007). The congener-specific pre-fixed model parameters were determined based on the values given in literatures: We referred Li *et al.* (2003) for partitioning coefficients, Anderson and Hites (1996) for

Table 1. Degradation rate constants and half-lives of selected PCBs congeners in the atmosphere and the ocean.

	Degradation rate constants ($k_{A,O}$)		Half-lives ($t_{1/2,A,O}$)	
	Atmosphere (298 K)* ($\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$)	Ocean (s^{-1})	Atmosphere** (h)	Ocean (h)
PCB28	1.37×10^{-12}	3.50×10^{-8}	121	5500
PCB52	0.86×10^{-12}	1.93×10^{-8}	193	10000
PCB101	0.54×10^{-12}	0.62×10^{-8}	307	31000
PCB118	0.54×10^{-12}	0.62×10^{-8}	307	31000
PCB138	0.34×10^{-12}	0.35×10^{-8}	488	55000
PCB153	0.34×10^{-12}	0.35×10^{-8}	488	55000
PCB180	0.21×10^{-12}	0.35×10^{-8}	790	55000

* k_A is temperature-dependent, and the values at 298 (K) are shown.

**Global annual mean $[OH]$, 1.16×10^6 (molec cm^{-3} ; Spivakovsky *et al.*, 2000), is used in the calculation of $t_{1/2,A}$ from $k_{A(298K)}$.

degradation rate constants for the atmosphere, Wania and Daly (2002) for degradation rate constants for water and soil, Schwarzenbach *et al.* (1993) for PCBs molecular diffusivity in the air and the water, and Dachs *et al.* (1999) for parameters for bioconcentration in phytoplankton, respectively.

RESULTS AND DISCUSSIONS

We investigated the zonally-averaged meridional distributions and the globally-averaged vertical distributions of PCBs concentrations in the atmosphere and the oceans. Here, we discussed the annual mean results for the year 2010. Figure 1 shows the zonally-averaged meridional distributions of (a) PCBs historical emission (1931–2010), (b) the $[OH]$, and (c) and (d) the FATE-predicted PCBs concentrations in the atmosphere (from surface to the tropopause) and the oceans (from sea surface to 6065 m depth), respectively. The amount of PCBs emission differed significantly between congeners. Therefore, the historical emission and the concentrations were normalized by the maximum values. The results indicated that PCBs were more preferably transported to subtropical to tropical regions as the number of chlorine increased. Because the atmosphere and ocean interact with each other, the normalized concentrations in the atmosphere did not differ so much from those in the oceans. The most distinct inter-congener variability was found in the tropical regions in the southern hemisphere (*ca.* around 25°S). Figure 2 shows the globally-averaged vertical distributions of (a) the $[OH]$, and (b) and (c) the FATE-predicted PCBs concentrations in the atmosphere and the oceans. Similarly, concentrations were normalized by the maximum values. Within the atmospheric boundary layer where intense vertical mixing occurs, PCBs showed similar vertical distributions. On the other hand,

PCBs concentrations showed distinct differences in the rest of the troposphere, with relatively higher concentrations in the higher chlorinated congeners. In the oceans, PCBs concentrations were decreased with depth, and showed more significant inter-congener variability than in the atmosphere. Such decreasing rates with depth became small as the number of chlorine increased.

Because the spatial distributions of the normalized emission were similar between PCBs congeners (Fig. 1(a)), the inter-congener variability of PCBs concentrations could be attributed to the congener-specific pre-fixed parameters and the related model processes. Among a number of possible factors, we believe that the PCBs degradations in the atmosphere are the most important processes for the inter-congener variability of PCBs spatial distributions, because degradation half-lives in the atmosphere, which are highly variable among PCBs congeners (Table 1), are generally shorter than those in the other compartments. In fact, in the region of significant inter-congener variability of PCBs concentrations (i.e., tropical regions in the southern hemisphere and around the middle parts of the troposphere) showed the highest annual mean $[OH]$ (Figs. 1(b) and 2(a)). The relationship between the time scale of the ocean circulation and the PCBs persistency in the oceans could be another important factor. Typically, the time scales of the surface ocean circulation such as the subtropical gyre and the Meridional Overturning Circulation (MOC) are decadal scale and thousands of years, respectively. Because such time scales are generally longer than the PCBs half-lives in the oceans ($t_{1/2,O}$; Table 1), differences in $t_{1/2,O}$ have substantial impacts on the differences in LRTP in the oceans. That is, PCBs congeners with longer $t_{1/2,O}$ (i.e., highly chlorinated congeners) are more likely to be transported to remote regions, such as the tropical oceans and the deep ocean, by the ocean circulations.

In this study, we discussed spatial distributions of seven PCBs congeners, and concluded that the degradations in the atmosphere and the oceans are the key processes for PCBs global distributions. However, it should be noted that the degradation rates we used in this study have significant uncertainty. Such parametric uncertainties should be assessed using alternative method such as Bayesian uncertainty and sensitivity analyses (Handoh and Kawai, 2010).

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