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Process Study on Numerical Simulation for Persistent Organic Pollutants in the East China Sea

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Abstract—A three-dimensional/high-resolution transport model for persistent organic pollutants (POPs) has been developed to investigate the dynamics of POPs in the East China Sea. The POPs model includes four compartments: POPs in air, water, phytoplankton, and detritus. Biochemical processes considered in this study are diffusive air-water exchange, phytoplankton uptake of POPs, vertical sinking of phytoplankton, detritus from phytoplankton, and vertical sinking and decomposition of detritus. The POPs model is coupled with an ocean circulation model that successfully reproduces the velocity fields to include processes of advection and diffusion. We have conducted numerical simulation for the PCB153 from the atmosphere and river. The model showed the remarkable seasonal variability in PCB153. Concentrations of dissolved and particulate PCB153 were higher in winter (January–March) and lower in summer (July–September). In coastal regions where chlorophyll *a* concentrations are higher, horizontal and vertical distributions of dissolved and particulate PCB153 concentrations were strongly affected by the effect of phytoplankton uptake. The sensitivity experiments on the dynamics of PCB153 suggested that the seasonal variability in PCB153 was mainly caused by water temperature fields. From the yearly mass balance of PCB153, most of the atmospheric input by diffusive air-water exchange were removed by horizontal advection and were accumulated to the sea bottom by vertical sinking. Massive amounts of the dissolved PCB153 from river influenced air-water and water-phytoplankton exchange processes but its impacts were confined to regions near the mouth of river.

Keywords: East China Sea, persistent organic pollutants, polychlorinated biphenyls, seasonal variability

INTRODUCTION

Global contamination by persistent organic pollutants (POPs), such as polychlorinated biphenyls (PCBs) and hexachlorocyclohexanes (HCHs), and its impact on wildlife and ecosystem have been of concern over the last decade. POPs are mainly characterized by persistence, long-range transport in the atmosphere and ocean, bioaccumulation, and toxicity. Thus understanding and quantifying the dynamics of POPs are important to assess their environmental impact and final fate. In particular, the ocean is thought to be the global reservoir and ultimate sink of POPs (Iwata *et al.*, 1993). However, the dynamics of POPs in the ocean has not yet been well understood. Numerical modeling studies (e.g., Dachs *et al.*, 1999) suggested that not only the horizontal advection and diffusion by current and turbulence but also the vertical transport of POPs by the phytoplankton, which absorbs POPs and sinks to the deep water as detritus, are important to understand their dynamics inside the ocean.

Up to now, most numerical modeling of POPs was based on a simple box model that was oriented to understand the processes. To know the spatial distribution of POPs in the ocean, a three-dimensional transport model for POPs based on realistic topography and ocean currents is necessary. Recently, Ilyina *et al.* (2006) has developed a realistic model for the POPs dynamics to investigate the fate of γ-HCH in the North Sea. In addition, global modeling studies for PCBs and DDT have been reported by Kawai *et al.* (2009) and Stemmler and Lammel (2009), respectively.

In this study, we applied the POPs modeling to the East China Sea. Why do we focus on the East China Sea? The East Asian countries are considered to be a potential source of POPs because of the enhancement of industrialization. Nevertheless, the behavior of POPs in the ocean has been poorly understood. This may be partly because the observation for POPs is limited. We have conducted the POPs observations in the East China Sea in December 2008, July 2009, and August 2010. Shimizu *et al.* (2009) reported the results in December 2008. These data may be available for the model validation. The objective of this study is to assess quantitatively the POPs dynamics in the East China Sea (ECS), a marginal sea surrounding by China, Korea, and Japan. Based on an ocean circulation model that provided flow field and turbulence parameters, we have developed a three-dimensional high-resolution transport model for the POPs, in the ECS. As the first step towards the POPs modeling in the East China Sea, we examined the seasonal variability in PCB153 from the atmosphere and river.

MODEL DESCRIPTION

The POPs model includes four compartments (Gas phase POPs, Dissolved phase POPs, Phytoplankton POPs, and Detritus POPs) that are linked by some physical and biochemical processes, as shown in Fig. 1. Gas phase POPs dissolve into the surface ocean through diffusive air-water exchange from the atmosphere to the ocean. In the ocean, a part of dissolved phase POPs are absorbed by the phytoplankton and the others are decomposed. The phytoplankton POPs is involved three processes: phytoplankton uptake, natural mortality, and vertical sinking. The natural mortality of phytoplankton transformed phytoplankton POPs into detritus POPs. A part of detritus POPs are then transported to the deep water by vertical sinking of detritus, and the others are transformed into dissolved phase POPs by decomposition. The POPs model is coupled with a three-

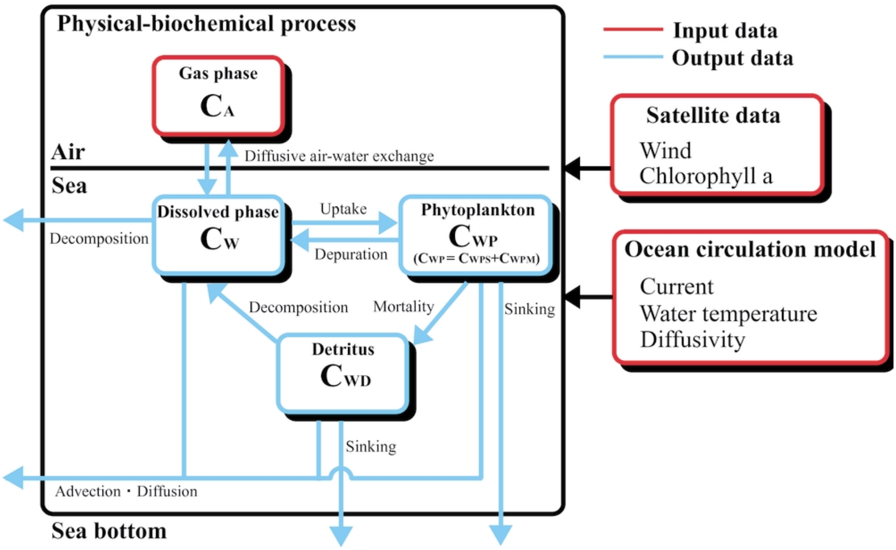

Fig. 1. Schematics of the POPs model in the East China Sea.

dimensional ocean circulation model (Guo *et al*., 2003) that is based on the Princeton Ocean Model and can reproduce well the seasonal variations of current fields in the ECS. The velocity vectors in January are shown in Fig. 2, as an example of the velocity fields in our model.

Figure 2 shows the model domain and bathymetry, which includes the East China, Yellow, and Bohai Seas. The grid size is 1/18° and there were 20 levels in the vertical. Monthly satellite chlorophyll *a* from Sea-viewing Wide Field-of-view Sensor (Sea WiFS) and wind stress from European Remote-Sensing Satellites (ERS-1 and ERS-2) are used to obtain the phytoplankton biomass and to calculate the diffusive air-water exchange flux, respectively. Target compound in this study is PCB153 that is one of the most bioaccumulation isomer of PCBs and dominant in the ecosystem of the ECS. Among initial and boundary conditions, concentrations of dissolved, phytoplankton, and detritus phase PCB153 were set to 0 pg m^{-3}, while concentrations of gas-phase PCB153 were set to 2.08 pg m^{-3} (Jaward *et al*., 2004) that is the source of POPs in our model ECS.

To investigate what is the most important factor controlling the seasonal variability in PCB153, we designed three sensitivity experiments, in which the temporal variation of only one parameter was re moved while that of the others was kept. Specifically, we removed the temporal variation in chlorophyll *a* concentration (chlorophyll-run), wind speed (wind-run), and water temperature (temperature-run), respectively.

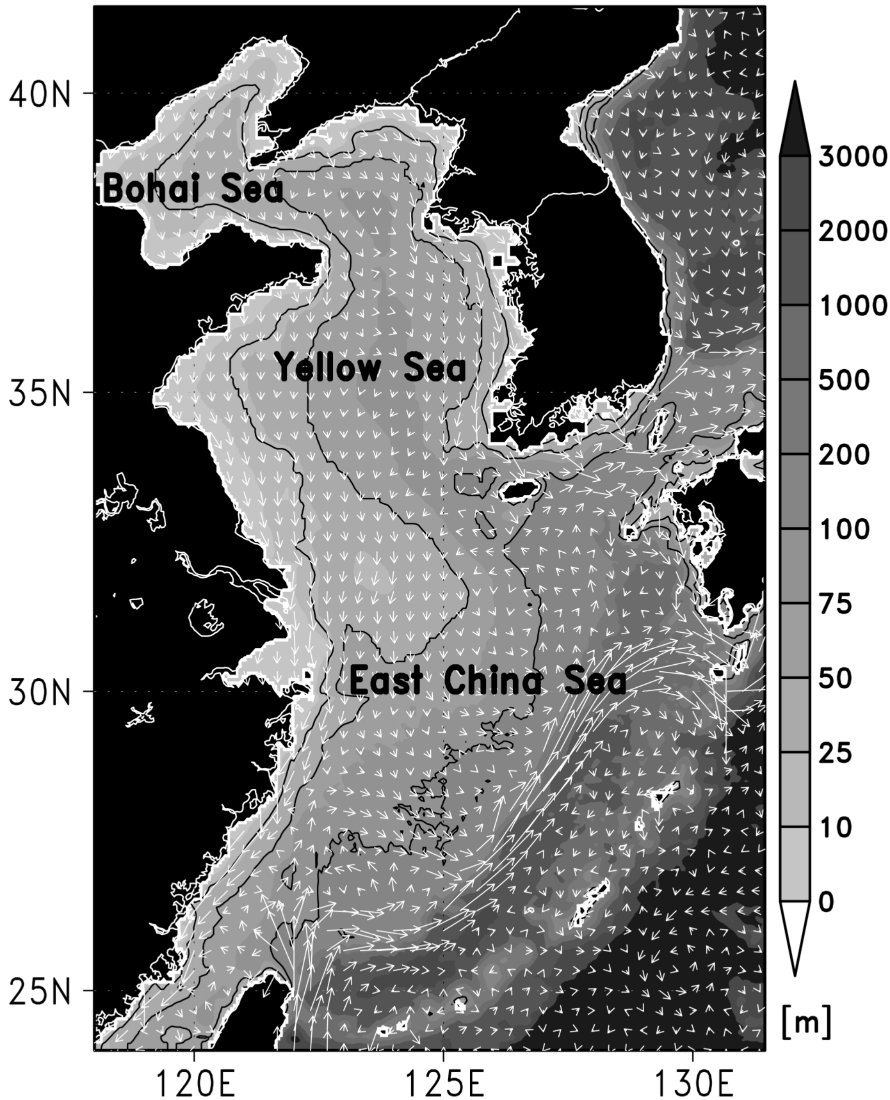

Fig. 2. Model domain and bathymetry. Velocity fields at the surface in January were superimposed by vectors. The 20, 50, and 100-m isobath were also superimposed by solid line.

RESULTS AND DISCUSSION

The model results showed a remarkable seasonal variability in dissolved and particulate PCB153 concentrations that are high in winter (January–March) and low in summer (July–September) (Fig. 3). The surface flux by diffusive air-water exchange is also higher in winter than in summer (not shown). We show the

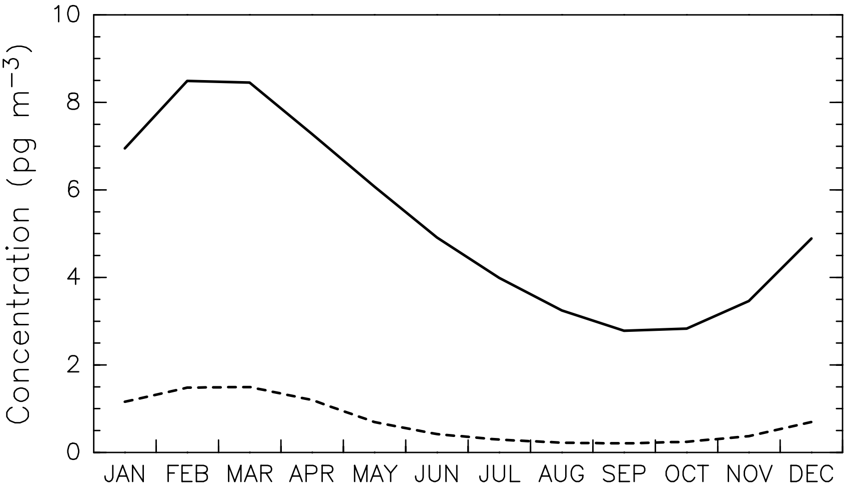

Fig. 3. Seasonal cycle of concentrations in dissolved-phase (solid line) and particulate-phase (shaded line) of PCB153, averaged for the whole modeling domain in the East China Sea.

horizontal distributions of PCB153 in February in Fig. 4.

The high surface flux area is mainly formed in coastal regions from China to Korean Peninsula (Fig. 4a). Associated with the high surface flux, concentrations of dissolved and particulate PCB153 were also higher (Figs. 4b and 4c). Interestingly, in coastal regions where concentrations of chlorophyll *a* are high, dissolved PCB153 concentrations are lower but particulate PCB153 concentrations are higher (Figs. 4b and 4c). This would be due to the uptake of dissolved phase PCB153 by phytoplankton. Consequently, the sinking flux also becomes high in coastal regions by vertical transport of particulate PCB153 (Fig. 4d).

We investigate the vertical structure of PCB153 at northern latitude of 31° (not shown). The surface flux in winter is larger in coastal regions because of stronger wind speed and lower sea-surface temperature. As a result, dissolved PCB153 concentrations become higher in coastal regions but the maximum value appears in offshore regions. This is because dissolved PCB is strongly absorbed by phytoplankton in coastal regions where the chlorophyll *a* concentration is high. In contrast, particulate PCB153 concentrations are higher at the coast. On the other hand, these features cannot be seen in summer.

To examine what is the most important factor controlling the seasonal variability in PCB153, we per formed three additional numerical experiments: chlorophyll-run, wind-run, and temperature-run. These results imply that the temporal change in water temperature fields contributes most to the seasonal variability in PCB153 (Fig. 5). This can be caused by the variation of Henry's law constants with water temperature, which results in the direct change of the surface flux and indirect change in the concentrations of dissolved and particulate PCB153. We also estimated the yearly mass balance of PCB153 in the ECS.

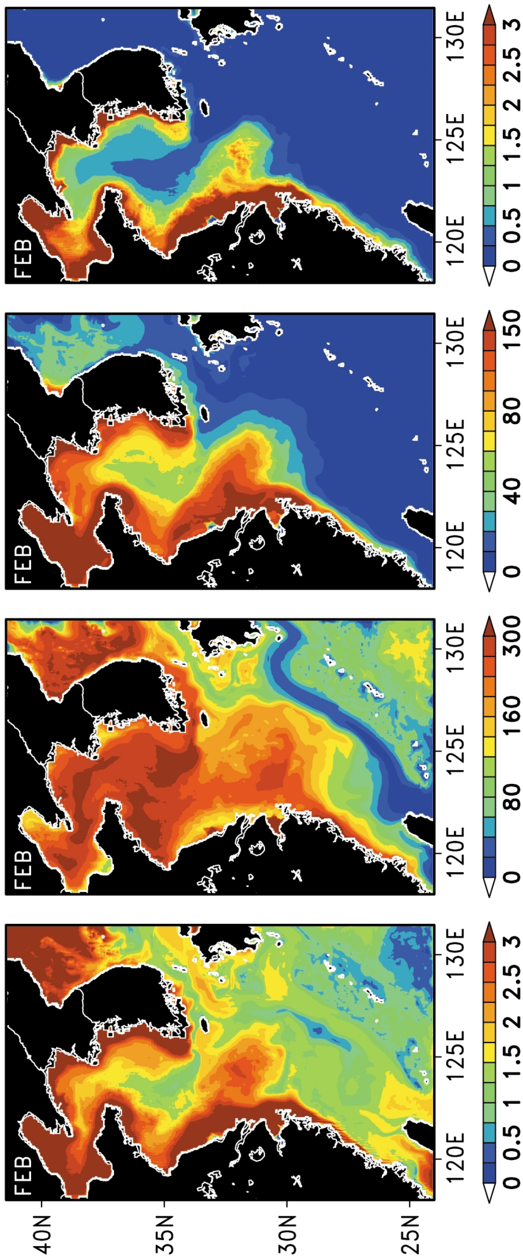

Fig. 4. Seasonal cycle of concentrations in dissolved-phase (solid line) and particulate-phase (shaded line) of PCB153, averaged for the whole modeling domain in the East China Sea.

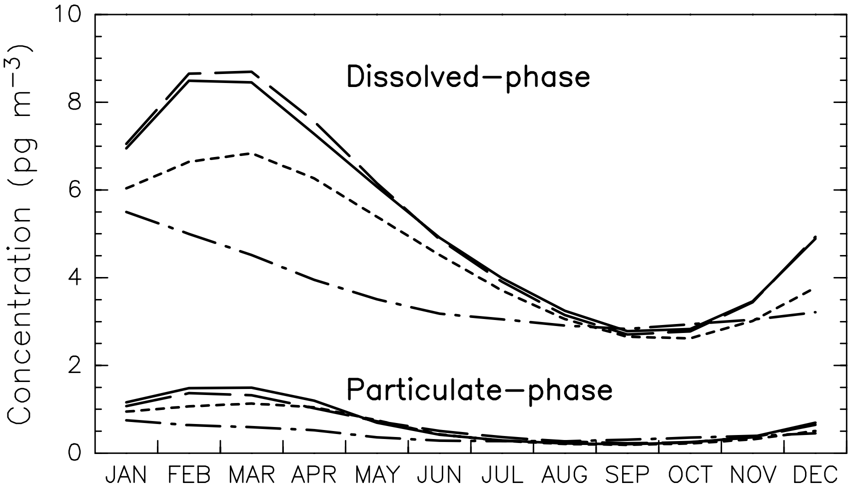

Fig. 5. Horizontal distributions of (a) the surface flux ($\times 10^{-3}$ pg $m^{-2}s^{-1}$) of PCB153 from the atmosphere to the ocean, (b) dissolved and (c) particulate PCB153 concentrations (pg m^{-3}), (d) sinking flux ($\times 10^{-3}$ pg $m^{-2}s^{-1}$) of PCB153 to sea bottom, in February.

Atmospheric input by diffusive air-water exchange was about 35 kg per year, in which 19 kg was removed by horizontal advection outside the ECS and 16 kg was accumulated to the bottom of ECS by vertical sinking. We also investigated the impact of river discharge on the PCB153 dynamics. Concentrations in the dissolved and particulate phases became high in summer associated with the increase of river discharge. However, its impact was confined to regions near the mouth of river.

CONCLUDING REMARKS

We have a three-dimensional/high-resolution transport model for persistent organic pollutants (POPs) in the East China Sea to investigate the dynamics of POPs. The model is coupled with an ocean circulation model with good reproducibility in the velocity fields. We have conducted some numerical simulation of the PCB153 from the atmosphere and river. The model revealed clear seasonal variability in PCB153. Concentrations of dissolved and particulate phase were higher in winter (January–March) but lower in summer (July–September). Sensitivity experiments imply that the seasonal variability in PCB153 is mainly caused by that in the Henr's low constant depending on water temperature. From the yearly mass balance of PCB153, most of the atmospheric input by diffusive air-water exchange were removed by horizontal advection and accumulated to the sea bottom by vertical sinking. In addition, the impact of river discharge on the behavior of the PCB153 was limited to regions near the mouth of river. This study is a first step toward the realistic simulation of the POPs transport in the East China Sea. Our future effort will take account of following effects: (1) suspended particulate matter, (2) temporal and spatial variations of the POPs concentration in the atmosphere, (3) POPs concentrations at the open boundaries, and (4) dry and wet depositions.

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