Atmospheric Environment 96 (2014) 345–352

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Modeling global persistent organic chemicals in clouds

Xiaoxuan Mao [a], Hong Gao [a], Tao Huang [a], Lisheng Zhang [b], Jianmin Ma [a, *]

[a] College of Earth and Environmental Sciences, Key Laboratory of Western China's Environmental Systems (Ministry of Education), Lanzhou University, 222 South Tianshui Road, Lanzhou, China
[b] Lamu Environment, 41 Mountfield Crescent, Thornhill, Ontario L4J 7E9, Canada

HIGHLIGHTS

- Atmospheric partition of persistent organic chemicals was affected by cloud liquid water content and air temperature.
- Hydrophilic chemicals could be strongly partitioned onto cloud water droplets.
- Hydrophobic chemicals tended to partition onto particles.
- Clouds played an important role in global distribution of persistent organic chemicals in the atmosphere.

ARTICLE INFO

Article history:
Received 17 January 2014
Received in revised form
14 April 2014
Accepted 26 May 2014
Available online 2 August 2014

Keywords:
Clouds
Persistent organic chemicals
Atmospheric partition
Long-range atmospheric transport

ABSTRACT

A cloud model was implemented in a global atmospheric transport model to simulate cloud liquid water content and quantify the influence of clouds on gas/aqueous phase partitioning of persistent organic chemicals (POCs). Partitioning fractions of gas/aqueous and particle phases in clouds for three POCs α-hexachlorocyclohexane (α-HCH), polychlorinated biphenyl-28 (PCB-28), and PCB-138 in a cloudy atmosphere were estimated. Results show that the partition fraction of these selected chemicals depend on cloud liquid water content (LWC) and air temperature. We calculated global distribution of water droplet/ice particle–air partitioning coefficients of the three chemicals in clouds. The partition fractions at selected model grids in the Northern Hemisphere show that α-HCH, a hydrophilic chemical, is sorbed strongly onto cloud water droplets. The computed partition fractions at four selected model grids show that α-HCH tends to be sorbed onto clouds over land (source region) from summer to early fall, and over ocean from late spring to early fall. 20–60% of α-HCH is able to be sorbed to cloud waters over mid-latitude oceans during summer days. PCB-138, one of hydrophobic POCs, on the other hand, tends to be sorbed to particles in the atmosphere subject to air temperature. We also show that, on seasonal or annual average, 10–20% of averaged PCB-28 over the Northern Hemisphere could be sorbed onto clouds, leading to reduction of its gas-phase concentration in the atmosphere.

1. Introduction

Environmental fate of persistent organic chemicals (POCs) depends remarkably on their partitioning between air and condensed phases or compartments of the earth-atmosphere system, such as aerosols, rain, fog, snow, water, soil, and vegetations. The partitioning of POCs, such as HCHs, PCBs, and polybrominated diphenyl ethers (PBDEs) etc., between the gaseous and particle phases in the atmosphere has been extensively studied in recent decades (Pankow, 1987, 1994; Finizio et al., 1997; Shoeib and Harner, 2002; Cetin and Odabasi, 2008). Several gas-particle portioning adsorption/absorption models have been developed to describe the phase distribution of POCs in the global environment (Pankow, 1987; Finizio et al., 1997; Harner and Bedleman, 1998; Lohmann and Lammel, 2004). Sorption of POCs to aqueous phase (rain/snow/ice) is a more complicated process as compared with gas/particle partitioning. It has been recognized that, given its stronger sorbing capability, snow is a very efficient scavenger of organic vapors (Goss, 1997; Wania et al., 1998, 1999; Hanot and Donime, 1999; Domine et al., 2002; Cabanes et al., 2003). The sorption of organic chemicals onto water and ice surface has been also investigated (Goss, 1997; Donaldson and Anderson, 1999; Roth et al., 2002, 2004). Lei and Wania (2004) calculated equilibrium partitioning in the atmosphere to quantify and compare the capacity of rain and snow to scavenge gaseous and particle-bound organic chemicals (HCHs, PAHs, PCBs etc.) under cold and warm

* Corresponding author.
E-mail address: jianminma@lzu.edu.cn (J. Ma).

http://dx.doi.org/10.1016/j.atmosenv.2014.05.081
1352-2310/

atmospheric conditions. They demonstrated that partition of a semi-volatile organic chemical from the vapor phase to liquid water droplets, atmospheric particles and the snow surface tended to take place more frequently in a lower air temperature. Field measurements have shown that snow, ice melt water, and rainwater become increasingly the reservoirs of POCs (Finizio et al., 2006; Villa et al., 2006; Manoli et al., 2000; Grynkiewicz et al., 2001; Grynkiewicz er al., 2002; Malik et al., 2007).

Ma et al. (2013) have recently examined the POCs uptake and mobilization with clouds from a hail sample. They found that, during this hail event, approximately 7–30% of pyrene, one of polycyclic aromatic hydrocarbons (PAHs), could be sorbed into cloud water droplets and ice particles. Given huge amount of clouds in the troposphere (composing 7% of the troposphere's total volume), the sorption of POCs onto clouds may lead to substantial decline of gas-phase POCs, particularly for those water-soluble POCs in the atmosphere. Sheili and Lammel's model simulations for the atmospheric fate of polycyclic aromatic hydrocarbons have implemented a cloud model in their atmospheric transport model (2007). Franco et al. applied a cloud model to simulate the effect of clouds on atmospheric transport of neutral, ionizable substances (2011). While these studies revealed the potential effect of clouds on the environmental fate of POCs, most POCs models did not consider the effect of clouds on changes in POCs in the atmosphere and systematic investigations to the interactions between clouds and POCs remained lacking.

Due to difficulties in the routine measurement of POCs in clouds, numerical models for clouds and atmospheric transport provide a very useful tool to simulate global clouds and POCs distribution in the atmosphere and the impact of clouds on partitioning and mass balance of POCs. In particular, numerical cloud models have been widely adopted in the atmospheric science community as major approaches to simulate cloud formation, physics, and the interaction with climate change. In the present numerical study, a cloud model was implemented into a global-scale atmospheric transport model for POCs to compute global cloud liquid water content (LWC, g m^{-3}) on daily, seasonal, and annual basis, and to quantify the distribution of aqueous, particle, and gas phase POCs in clouds. The water/air, ice/air and particle/air coefficients and fractions of three selected chemicals α-HCH, PCB-28, and PCB 138 in clouds were estimated to elucidate the influences of clouds on the distribution, partition coefficients, and masses of POCs in the atmosphere.

2. Methods

2.1. CanMETOP model and model input

The Canadian Model for Environmental Transport of Organochlorine Pesticides (CanMETOP) has been used in previous numerical investigations of POCs budget in North America, China, and the globe (Ma et al., 2003; Zhang et al., 2008). Briefly, the CanMETOP is a three-dimensional atmospheric transport model coupled with a fugacity-based mass balance soil–air exchange model with three soil layers and a water–air exchange model. The distribution (partition) coefficients used to estimate interface partitions are presented in Supplementary data. Removal processes of POCs in the atmosphere include particle dry deposition calculated by a resistance approach, wet deposition estimated using 6 hourly objectively analyzed precipitation data (Kalnay et al., 1996), and degradation. Detailed CanMETOP framework is referred to as Ma et al. (2003). The horizontal coordinate was established on a spherical coordinate system with a horizontal resolution of $1^\circ \times 1^\circ$ latitude/longitude. In the vertical, a modified terrain-following coordinate is used, and the model top is 11 km with 14 levels. Six-hourly meteorological data driving the CanMETOP, including winds, air temperature, precipitation, and atmospheric pressure, were collected from the United States National Centers for Environmental Prediction (NCEP) reanalysis in 2005 (Kalnay et al., 1996).

To highlight the effect of the sorption of POCs onto clouds on their air concentrations, we examined the changes in PCB-28 atmospheric concentrations with and without cloud uptake process included. Global emission inventory of PCB-28 used $1^\circ \times 1^\circ$ latitude/longitude gridded air emission inventory developed by Breivik et al. (2002, 2007). Although the CanMETOP has been evaluated extensively by comparing modeled air concentration of toxic substances with those measured (e.g., Ma et al., 2003; Zhang et al., 2008, 2010), modeled air concentrations of PCB-28 were further verified against available monitoring data over the Great Lakes region and the Arctic. Results show good agreements between modeled and measured data (Supplemental data Fig. S1 and text).

2.2. Cloud model

The cloud model for warm clouds (Tisler and Savijarvi, 2002; Sundquist et al., 1989) was implemented into the global CanMETOP model to estimate cloud LWC. The cloud LWC is a measure of the total liquid water contained in a cloud in a vertical column of atmosphere and is estimated by the product of volumetric fraction of cloud in each model column and the LWC within the cloud (Ma et al., 2013). Considering different characteristics of cold and warm clouds under real atmosphere conditions and the change in cloud amount, an algorithm that connects cloud fraction with cloud LWC (Tisler and Savijarvi, 2002) was also applied in calculation of cloud LWC. Details for this model and clouds-POCs interactions were given in Ma et al. (2013). Using the coupled cloud and the CanMETOP model we computed the global total cloud cover from random multiple-layer cloud overlapping (Morcrette and Jakob, 1999). Results agree well with a satellite derived global cloud cover by International Satellite Cloud Climatology Project (ISCCP) (results not shown) (Rossow et al., 1996).

2.3. Distribution (partition) coefficients and fraction of POCs in clouds

To determine the interface partition of the three selected chemicals between gaseous and liquid as well as gaseous and particle phase, following Lei and Wania (2004) and Ma et al. (2013) we calculated the atmospheric distribution coefficients and fractions of the three chemicals in cloud water droplets and ice particles. Lei and Wania's approaches to estimate partition between POCs and rain/snow were applied to calculate the partition between POCs and clouds by assuming the same properties between cloud water droplet and rain droplet, and between cloud ice particles and snow. In the model we used cloud LWC to replace the constant volume fraction of rainwater in the atmosphere defined by Lei and Wania (2004). Under the assumption of phase equilibrium in the atmosphere, three atmospheric distribution coefficients $K_{rain/air}$, $K_{snow/air}$, and $K_{particle/air}$ were applied in the present study to describe the ratio of the equilibrium concentrations of the water droplets (mol m^{-3}), ice particles (mol m^{-3}), and particle phase (mol m^{-3}) to the gas phase (mol m^{-3}). To highlight the interaction of the selected chemicals with clouds, we redefine the partition coefficient $K_{rain/air}$ and $K_{snow/air}$ as $K_{cw/air}$ and $K_{ci/air}$, respectively, referred to as cloud water/air and cloud ice particle/air partition (distribution) coefficient. In computation of $K_{cw/air}$ and $K_{ci/air}$, we have assumed a radius at 1 mm for cloud droplets and a specific surface area at 0.1 m^2 g^{-1} for ice particles (Lei and Wania, 2004). It should be noted that in their study Lei and Wania considered