Science of the Total Environment 569–570 (2016) 159–167

Contents lists available at ScienceDirect

Science of the Total Environment

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

Modeling short-term concentration fluctuations of semi-volatile pollutants in the soil–plant–atmosphere system

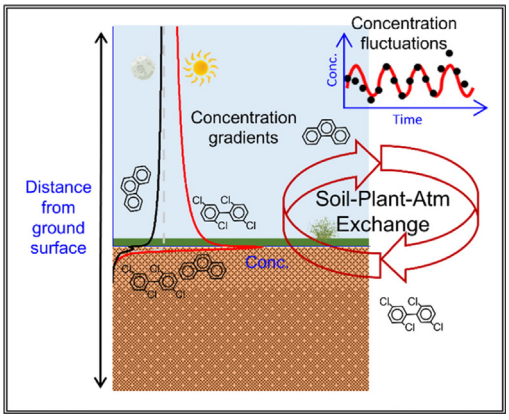
Zhongwen Bao [a,*], Christina M. Haberer [a], Uli Maier [b], Barbara Beckingham [c], Richard T. Amos [d], Peter Grathwohl [a]

[a] Department of Geosciences, University of Tübingen, Hölderlinstr. 12, 72074 Tübingen, Germany
[b] Geoscience Centre, Georg-August-Universität Göttingen, Goldschmidtstr. 3, 37077 Göttingen, Germany
[c] Department of Geology and Environmental Geosciences, College of Charleston, 202 Calhoun Street, Charleston, SC 29041, United States
[d] Department of Earth Sciences, Carleton University, 1125 Colonel By Drive, Ottawa, ON K1S 5B6, Canada

HIGHLIGHTS

- Diurnal temperature changes cycle semi-volatile pollutants in the environment.
- Soils cannot cause significant diurnal atmospheric concentration fluctuations.
- Plants strongly affect short-term atmospheric pollution.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 1 March 2016
Received in revised form 15 June 2016
Accepted 15 June 2016
Available online xxxx

Editor: D. Barcelo

Keywords:
Soil and atmosphere pollution
Plants
Diurnal temperature changes
Photochemical transformation
Numerical modeling

ABSTRACT

Temperature changes can drive cycling of semi-volatile pollutants between different environmental compartments (e.g. atmosphere, soil, plants). To evaluate the impact of daily temperature changes on atmospheric concentration fluctuations we employed a physically based model coupling soil, plants and the atmosphere, which accounts for heat transport, effective gas diffusion, sorption and biodegradation in the soil as well as eddy diffusion and photochemical oxidation in the atmospheric boundary layer of varying heights. The model results suggest that temperature-driven re-volatilization and uptake in soils cannot fully explain significant diurnal concentration fluctuations of atmospheric pollutants as for example observed for polychlorinated biphenyls (PCBs). This holds even for relatively low water contents (high gas diffusivity) and high sorption capacity of the topsoil (high organic carbon content and high pollutant concentration in the topsoil). Observed concentration fluctuations, however, can be easily matched if a rapidly-exchanging environmental compartment, such as a plant layer, is introduced. At elevated temperatures, plants release organic pollutants, which are rapidly distributed in the atmosphere by eddy diffusion. For photosensitive compounds, e.g. some polycyclic aromatic hydrocarbons (PAHs), decreasing atmospheric concentrations would be expected during daytime for the bare soil scenario. This decline is buffered by a plant layer, which acts as a ground-level reservoir. The modeling results

* Corresponding author.
E-mail address: zhongwen.bao@uni-tuebingen.de (Z. Bao).

http://dx.doi.org/10.1016/j.scitotenv.2016.06.117

emphasize the importance of a rapidly-exchanging compartment above ground to explain short-term atmospheric concentration fluctuations.

1. Introduction

Semi-volatile organic compounds (SVOCs), for example polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs), have been released into the environment by various anthropogenic activities and are now widely distributed. Soils represent a terrestrial reservoir for legacy SVOCs and may (temporarily) act as secondary sources, re-volatilizing pollutants to the atmosphere due to changes in land use (Komprda et al., 2013), reduced anthropogenic emissions (Jones and de Voogt, 1999; Kurt-Karakus et al., 2006; Bao et al., 2015), and temperature changes. Re-volatilization happens due to changes in seasons and climate on the long term (Lamon et al., 2009; Ma and Cao, 2010; Ma et al., 2011; Komprda et al., 2013) or because of the diurnal cycle of solar radiation in the short term (Wallace and Hites, 1996; Lee et al., 1998; Gouin et al., 2002; Totten et al., 2002; Mandalakis et al., 2003; MacLeod et al., 2007; Gasic et al., 2009; Morselli et al., 2011); both are relevant for the environmental fate of SVOCs because they may influence volatilization rates from soils. Plants may play an important role as short-term sources and sinks of semi-volatile pollutants in the atmosphere depending on species and growing seasons (Buckley, 1982; Jones et al., 1992; Simonich and Hites, 1994a, 1994b, 1995; Kömp and McLachlan, 1997; Böhme et al., 1999; McLachlan, 1999; Hung et al., 2001; Moeckel et al., 2001; Barber et al., 2003, 2004; Terzaghi et al., 2015).

Commonly, numerical models are used to investigate temperature-driven soil–plant–atmosphere exchange of SVOCs by simulating sorption and diffusion in soils, partitioning to plants, and the temperature dependence of these processes (Cousins et al., 1999; Prevedouros et al., 2000; Hung et al., 2001; Scholtz et al., 2002a, 2002b; Dalla Valle et al., 2004; MacLeod and Mackay, 2004; van den Berg and Leistra, 2004; Wegmann et al., 2004; MacLeod et al., 2007; Gasic et al., 2009; Collins and Finnegan, 2010; Morselli et al., 2011; Garcia et al., 2014; Loizeau et al., 2014; Trapp, 2015; Bao et al., 2015; Lichiheb et al., 2016). For instance, several models (i.e. Cousins et al., 1999; Scholtz et al., 2002a, 2002b; Gasic et al., 2009; Loizeau et al., 2014; Bao et al., 2015) have addressed soil-atmosphere exchange of SVOCs (two compartments; without plants) considering integrated physico-chemical parameters. Previous studies (i.e. MacLeod et al., 2007; Gasic et al., 2009; Morselli et al., 2011) have identified controls (such as temperature, local atmospheric stability, hydroxyl radical concentrations, and source type) for short-term concentration fluctuations of SVOCs in the atmosphere. In addition, numerical models describing plant uptake of SVOCs from soils and the atmosphere have been developed (Trapp and Matthies, 1995; Trapp, 2002, 2007, 2015; Trapp and Eggen, 2013), the development of which eventually facilitated numerical investigations of plant uptake of organic pollutants in the soil–plant–atmosphere system (van den Berg and Leistra, 2004; Collins and Finnegan, 2010; Lichiheb et al., 2016). However, relevance of plant-atmosphere partitioning compared to soil-atmosphere partitioning has hardly been explored with respect to short-term atmospheric concentration fluctuations. Moreover, steep and dynamic temperature-dependent concentration gradients of SVOCs may form in the lower part of the atmospheric boundary layer and topsoils, depending on the source-sink function of soils and plants as well as meteorological conditions. Although such concentration gradients have been observed in several studies (Farrar et al., 2005; Tao et al., 2007; Zhang et al., 2011), fluxes in the soil–plant–atmosphere system so far have not been addressed in numerical studies in detail. In fact, semi-volatile pollutants usually have been assumed to be well mixed within the atmosphere (Lee et al., 1998).

In this study, therefore, we extended a previous version of a numerical model MIN3P (Bao et al., 2015) to consider the impact of time- and depth-dependent temperature changes as well as photochemical oxidation in the atmosphere on short-term concentration fluctuations of SVOCs in the soil–plant–atmosphere system, using PCB-52 and phenanthrene as model compounds. We focus on a grassland or agricultural-type system, and do not include a forest canopy. We use the model results and comparison to observed daily concentration fluctuations of PCB-52 found in the literature (Lee et al., 1998) to elucidate sources and processes, which are relevant for atmospheric concentration fluctuations and cross-compartmental concentration gradients in a quantitative way.

2. Model setup and numerical methods

2.1. Model compounds

PCB-52 and phenanthrene were chosen as model compounds. PCB-52 was selected because it is fairly resistant to photochemical oxidation in the atmosphere (with atmospheric half-life times ranging from 3 to 120 days for all PCB congeners, and 62.5 days for PCB-52 specifically, Sinkkonen and Paasivirta, 2000). Phenanthrene was selected for comparison because of similar physicochemical properties and its photosensitivity, with a much shorter atmospheric half-life of 5.6 h (Atkinson and Arey, 1994). The relevant physicochemical properties of the two compounds (e.g. thermodynamic properties, half-lives, and diffusion and partitioning coefficients) are summarized in Table S1 (Supporting information, SI).

2.2. Conceptual model

The conceptual model used to simulate the soil–plant–atmosphere fluxes of SVOCs driven by diurnal temperature changes is shown in Fig. 1. It accounts for two distinct soil horizons (high organic carbon topsoil and sandy subsoil), a plant layer, and the atmospheric boundary layer with varying heights. Fig. 1 additionally shows how diurnal temperature changes in the atmosphere propagate into the soil over a time period of 1.5 days. For the sake of simplicity, we assumed a sinusoidal temperature change with the minimum and maximum daily temperatures at 3 am and 3 pm, respectively.

Changes in temperature over a day result in changes in the height of the atmospheric boundary layer as well as in vertical mixing. In fact, even under fair weather conditions the height of the atmospheric boundary layer still exhibits strong diurnal changes (Stull, 2000). During daytime, solar radiation leads to surface warming, and hence to the formation of convective thermal eddies that influence mass transport of atmospheric pollutants. Due to turbulence, the atmospheric boundary layer may reach heights of thousands of meters and eddy diffusion is the dominating mass transport process. At night the height of the atmospheric boundary layer decreases due to an inverse temperature field (i.e., increasing temperature with increasing height), caused by radiative cooling of surface air. In the model, the atmospheric boundary layer was simplified with a thickness of 1000 m during daytime and 100 m at night.

The plant layer may act as potential source-sink term at ground level for atmospheric concentration fluctuations, the parameterization of which depends on the species, total biomass, leaf area, age, and effective lipid content (or sorption capacity). Root uptake of pollutants from soils was not considered for the short-term diurnal simulations but may play a role for seasonal fluxes of pollutants. The focus was placed on the ground-level plant layer and the influence of the amount of plant layer that, in terms of quantity of biomass per square meter, varies significantly with dependence on the types of land cover, site-specific