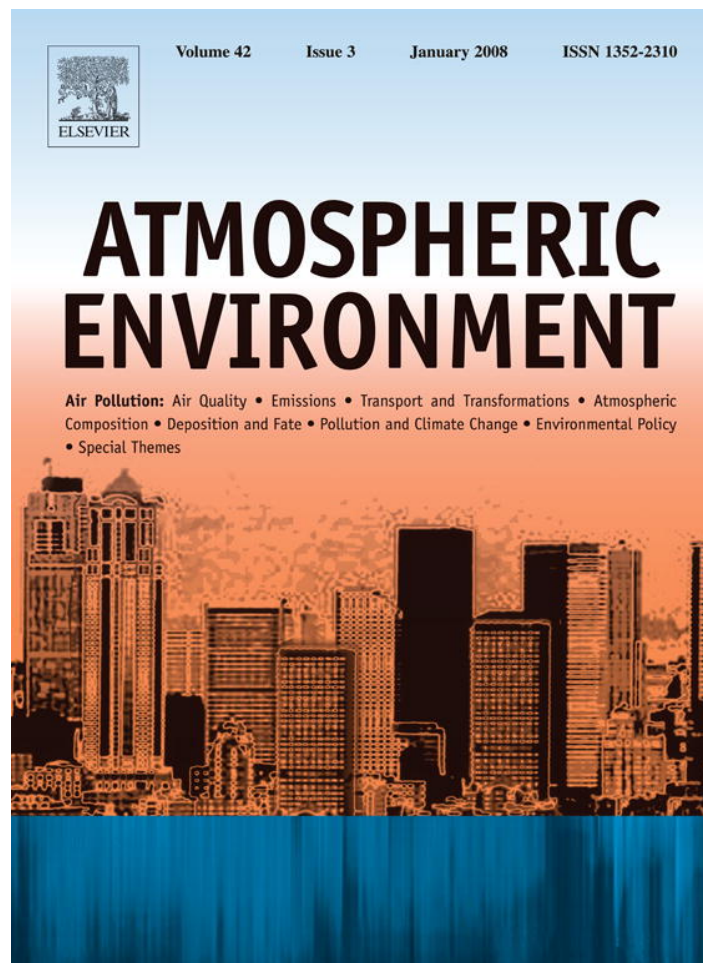


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Regional differences in gas–particle partitioning and deposition of semivolatile organic compounds on a global scale

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Abstract

Variability in gas–particle partitioning of semivolatile organic compounds (SOCs) and related atmospheric processes (particle-associated deposition, rain washout and degradation) are investigated on a global scale. Two different sorption approaches (one using the octanol–air partition coefficient, K_{OA} , and one based on poly-parameter linear free energy relationships, ppLFER) and two different atmospheric box models (unit-world and highly spatially and temporally resolved) are applied. In the unit-world model, the overall deposition and atmospheric fate of SOC calculated with the K_{OA} -based sorption approach are similar to the ones calculated with the ppLFER approach. Rain washout dominates the atmospheric removal of polar chemicals in the unit-world model while non-polar chemicals are removed mainly through degradation or particle-associated deposition. In contrast, big differences and a high sensitivity to the selected sorption approach are found in the spatially and temporally resolved model. The highly resolved geographic variability cannot be represented using the K_{OA} -based approach if aerosol components other than OM are of importance for sorption. In particular, aerosols in dry regions (desert) and regions with low OM aerosols (arctic, some oceanic regions) are more appropriately described by the ppLFER approach. With the ppLFER approach, good agreement between modeled deposition fluxes and measurement data are found for higher chlorinated PCBs and TCDD/Fs. In general, we recommend the ppLFER approach for highly resolved environmental fate models.

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1. Introduction

Atmospheric processes play an important role in the fate of semivolatile organic compounds (SOCs, Mackay and Paterson, 1991; Bennett et al., 2001;

Scheringer et al., 2003). In the atmosphere, SOC are simultaneously present in the gas phase and associated with aerosol particles (Bidleman, 1988). In contaminant fate models, partitioning of SOC to aerosol particles and removal of aerosol particles through dry deposition or rainfall are key factors determining long-range transport potential and overall persistence (Scheringer, 1997; Scheringer et al., 2003; Lohmann and Lammel, 2004). Nevertheless,

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most multimedia box models treat gas–particle partitioning and particle-associated deposition processes in a rather simplistic manner.

In chemical fate modeling, two different types of models are common: multimedia box models with relatively low spatial and temporal resolution (Mackay and Paterson, 1991; Scheringer et al., 2003); and models with high spatial and temporal resolution, based on general circulation models (GCM) (Gong et al., 2002; Semeena and Lammel, 2003; Leip and Lammel, 2004). In both types of models, gas–particle partitioning is generally described with single-parameter linear free energy relationships (spLFRs) that estimate the aerosol–air partition coefficient from vapor pressure or octanol–air partition coefficient (K_{OA}). These relationships have two important limitations. First, they are only valid within the compound class from which they have been derived (Goss and Schwarzenbach, 2002). Most spLFRs are based on sorption data for non-polar chemicals such as PCBs and PAHs, for which total sorption is assumed to be dominated by absorption into organic matter (OM, Cousins and Mackay, 2001). Other possible chemical–sorbate interactions are not explicitly considered. Second, the effect of variability in composition and properties of aerosol particles is not taken into account. In most cases the sorptive capacity of the aerosol is described in terms of OM content only.

In multimedia box models, a single aerosol particle size is often assumed and, thus, different atmospheric lifetimes of aerosol particles are not distinguished. However, the atmospheric lifetime of fine and coarse aerosol particles can differ considerably (Seinfeld and Pandis, 1998). Furthermore, average particle deposition velocities assumed for single-size aerosol particles in multimedia models often represent the deposition velocity of coarse aerosol particles, which have up to 100 times higher deposition velocities than fine particles (Seinfeld and Pandis, 1998; Mackay, 2001; Scheringer, 2002). Accordingly, particle-associated deposition may be overestimated in contemporary multimedia box models.

Recently, it has been shown that gas–particle partitioning to aerosols can be described in a more comprehensive way with polyparameter linear free energy relationships (ppLFRs), which provide a more detailed description of different sorption processes by describing aerosols in more detail (Götz et al., 2007). In particular, different aerosol sizes, components, and surface characteristics can

be specified separately. Here, we use this approach and distinguish two size fractions of atmospheric aerosols: fine (PM_{2.5}) and coarse (PM_{10–2.5}) particles (Putaud et al., 2004). This differentiation allows us to specify particle-size dependent deposition velocities and aerosol compositions.

The objectives of this paper are (i) to investigate the influence of gas–particle partitioning on atmospheric removal processes in a multimedia box model, and (ii) to investigate the global variability of gas–particle partitioning and atmospheric removal processes in a spatially highly resolved model that is representative of GCM-based models. On this basis, we make recommendations for the parameterization of sorption and aerosol related processes for different kinds of environmental fate models.

Concerning objective (i), we investigate two different sorption models (K_{OA} -based spLFR and ppLFR) and compare the results for the gas–particle partition coefficient and analyze the influence of the selected sorption model on gas–particle partitioning and deposition in a unit-world model. We use a two particle-size aerosol model, globally averaged aerosol composition, and globally averaged values for rain intensity and frequency, OH radical concentration, temperature, and relative humidity.

To address objective (ii) we explore the global variability of gas–particle partitioning and deposition velocity using a set of highly resolved box models covering the earth at a spatial resolution of 180×360 cells and a temporal resolution of 1 month. We include geo-referenced data from remote sensing for temperature, precipitation, number of rain events, relative humidity, OH-radical concentration, and data from a GCM to characterize aerosol composition and concentration. Using these data, we calculate geo-referenced gas–particle partitioning (with K_{OA} -based and ppLFR sorption models separately), deposition velocities, and rate constants for reaction with OH radicals. Furthermore, we compare modeled deposition fluxes with data from field measurements.

2. Chemicals and data sources

We investigate four different groups of SOCs: (1) polychlorinated biphenyls (PCBs), (2) polychlorinated dibenzo–dioxins and furans (PCDD/Fs), (3) DDT and DDE (DDTs), and (4) various polar current-use pesticides (CUP) such as phenylurea

herbicides, amides, and triazines. Abraham solvation parameter and K_{OA} -values of the chemicals were taken from Götz et al. (2007) and ABSOLV (Pharma-Algorithms, 2004), see Supplementary data.

Monthly rainfall rate (U_{rain} [$m d^{-1}$]), average length of rain events (t_{wet} [d]), and the average time between rain events (t_{dry} [d]) were obtained from publicly available databases (GCPC, 2007; IPCC, 2007). Data for t_{wet} and t_{dry} were available for continents only. Therefore, estimates of t_{wet} and t_{dry} over the oceans and Antarctica were made by averaging data in latitudinal bands. Temperature and concentration of OH are based on data from Spivakovsky et al. (2000).

Aerosol component concentration and relative humidity (RH) were calculated with the aerosol–climate model ECHAM5–HAM (Stier et al., 2005), in which the double-moment aerosol scheme HAM is coupled to the GCM ECHAM5. The aerosol population comprises the following major compounds: sulfate, elemental carbon, organic matter, sea salt, and dust. Its size distribution is described as the superposition of seven lognormal modes, whose evolution is dynamically controlled by aerosol microphysical processes. The data used in this paper has been computed with a special version of ECHAM5–HAM which includes a double-moment cloud microphysics scheme, and which showed good agreement with measurement data (Lohmann et al., 2007). This simulation has been performed for the year 2000, with a spatial resolution of T63 (96×192) on 31 levels, and a temporal output of 12 h. However, here we use monthly averaged values. The surface areas of the individual aerosol components such as silica or elemental carbon are not directly available, because ECHAM5–HAM calculates weight fraction of the different aerosol components. Hence, we estimated surface areas assuming that all components of the coarse fraction are individually accessible for the chemicals and that they consist of spherical particles with a mean radius of $5 \mu m$. In Fig. 1 the yearly mean of these data is given for both aerosol size fractions, fine (PM_{2.5}) and coarse (PM_{10–2.5}).

3. Methods and model description

3.1. Gas–particle partitioning

We describe gas–particle partitioning with a ppLFFER-based sorption model that includes ad-

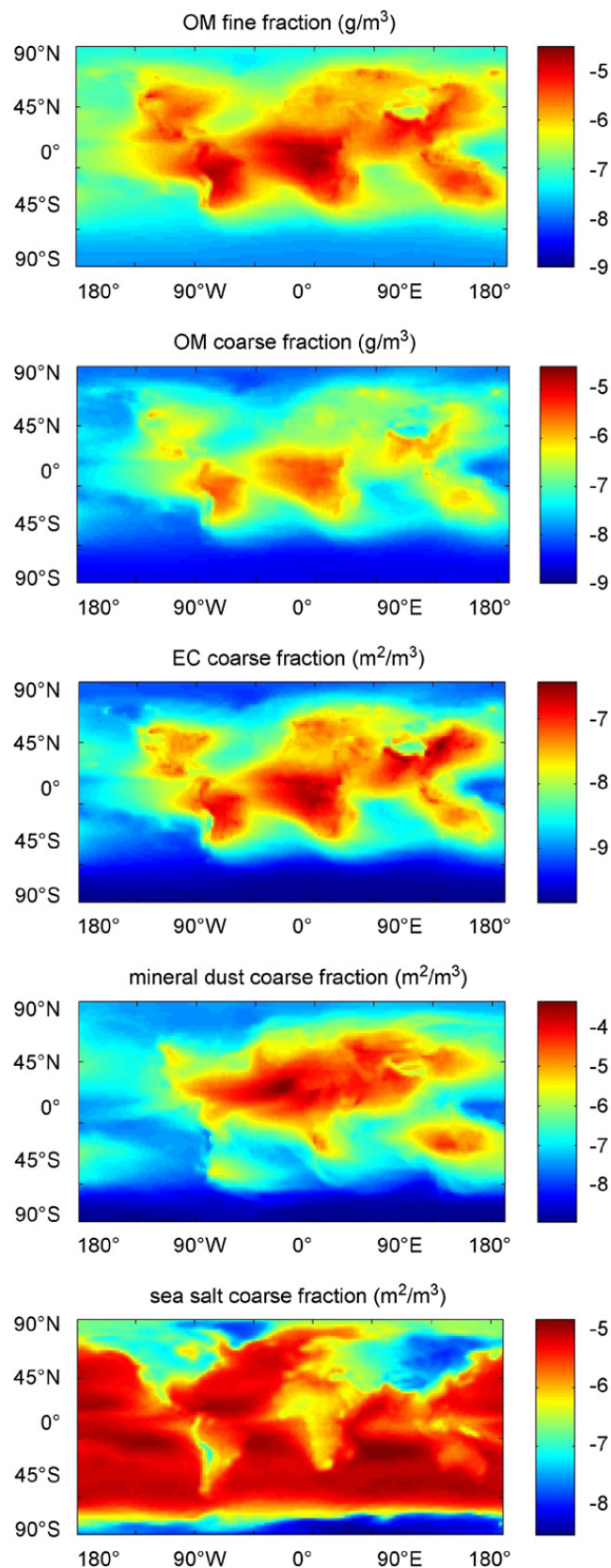


Fig. 1. Mass and surface concentration (logarithmic scale) of aerosol components in fine fraction (PM_{2.5}) and coarse fraction (PM_{10–2.5}) that contribute to the sorptive capacity of the aerosol particles for SOCs. Annual averages of year 2000. OM: organic matter, EC: elemental carbon.

sorption to different aerosol surfaces and absorption into aerosol particles, and with a K_{OA} -based sorption model. Recently, we showed that in some cases the ppLFFER-based model is preferable to K_{OA} -based models, especially for polar chemicals and for aerosol particles with low OM content as in desert or arctic environments (Götz et al., 2007). Furthermore, the ppLFFER model allows us to treat the fine and coarse aerosol particle fraction individually and to describe the deposition processes of chemicals sorbed to fine and coarse particles separately. For comparison against the ppLFFER model, we use the K_{OA} -based model of Finizio et al. (1997). Only interactions of the chemicals with OM are considered in the K_{OA} -based model.

The ratio of chemical concentration on particles [mol m^{-3} air] and in the gas phase [mol m^{-3} air] is described with the dimensionless partition coefficient K_p^* (Götz et al., 2007). The distribution of a chemical between aerosol particle and gas phase can also be described by ϕ , which is the particle bound fraction of a chemical. ϕ can be calculated from K_p^* as

$$\phi = K_p^*/(K_p^* + 1), \quad (1)$$

ϕ depends on chemical properties and a variety of system properties such as temperature, aerosol composition and concentration, and relative humidity. A detailed description of the sorption model using the ppLFFER approach, of the model's assumptions and limitations, and a systematic comparison with the K_{OA} -based sorption model has been given by Götz et al. (2007).

3.2. Atmospheric deposition processes

3.2.1. Dry deposition

Dry particle-associated deposition includes gravity and Brownian-diffusion driven settling of chemicals bound to aerosol particles. Wet particle-associated deposition is scavenging and washout of particle-bound chemicals by rain. Common multimedia-box models mostly include one particle size and have therefore one single deposition rate for dry deposition only. It is convenient to describe transfer processes with the transfer coefficient D , which has units of $\text{mol h}^{-1} \text{Pa}^{-1}$ (Mackay and Paterson, 1991). D for the dry particle-associated deposition, $D_{p,dry}$ [$\text{mol h}^{-1} \text{Pa}^{-1}$], is described as (Mackay and Paterson, 1991)

$$D_{p,dry} = Av_p Z_p U_{dry}. \quad (2)$$

Table 1
Average dry deposition velocities

Fine fraction (about 100 nm) [cm s^{-1}]	Coarse fraction (2.5–10 μm) [cm s^{-1}]	Reference
0.001–0.1 ^a	0.2–0.3	Schmel (1980)
0.01	0.05–4	Slinn et al. (1978)
0.01	0.1–0.5	Caffrey and Ondov (1998)

^aRange of values for surface roughness heights from 0.001 to 10 cm.

A [m^2] is the exchange surface area, v_p [m^3 particles m^{-3} air] the volume fraction of particles in air, Z_p [$\text{mol m}^{-3} \text{Pa}^{-1}$] the overall fugacity capacity of the aerosol particles, and U_{dry} [m h^{-1}] is the dry deposition velocity. An often used value for U_{dry} is 0.3 cm s^{-1} (10.8 m h^{-1}), which is suggested by Mackay et al. (Mackay and Paterson, 1991; Mackay, 2001). However, in a model with different size classes of aerosol particles, size-dependent deposition velocities are needed. Table 1 shows average dry deposition velocities for fine and coarse aerosol particles from the literature. We used 0.01 cm s^{-1} for the fine fraction, which is appropriate for a surface roughness height of 0.1 cm, and 0.3 cm s^{-1} for the coarse fraction.

3.2.2. Wet deposition

Commonly, in multimedia models, rain washout and wet particle-associated deposition of chemicals are modeled as continuous processes. A drawback of this approach is that unrealistically high values of rain washout and wet particle-associated deposition may occur for polar chemicals. To overcome this problem, we adapted the intermittent rainfall approach of Jolliet and Hauschild (2005), which introduces an upper limit on wet deposition, determined by the frequency and duration of rain events. We distinguish between rain washout (wet deposition of gaseous chemicals) and wet particle-associated deposition. The D -value for rain washout ($D_{g,wet}$) is

$$D_{g,wet} = A \left(U_{\text{rainevent}} \frac{t_{\text{wet}}}{t_{\text{wet}} + t_{\text{dry}}} \right) Z_{\text{raindrop}}. \quad (3)$$

A [m^2] is the surface area receiving the rainfall, $U_{\text{rainevent}}$ [m h^{-1}] is the average rain rate during a single rain event, t_{wet} [h] is the duration of a rain event, t_{dry} [h] is the time between different rain events, and Z_{raindrop} [$\text{mol m}^{-3} \text{Pa}^{-1}$] the fugacity capacity of the raindrop.

Z_{raindrop} is often assumed to be equal to the fugacity capacity of water, where $Z_{\text{water}} = Z_{\text{air}}/K_{\text{AW}}$ (Mackay and Paterson, 1991). However, in the intermittent rainfall approach, Z_{raindrop} is different from Z_{water} . If a chemical has a very low K_{AW} , Z_{water} is very high, which may lead to a chemical concentration in the raindrop that is unrealistically high, considering the limited volume of air that is accessible to a raindrop during its lifetime. Therefore, an upper limit for Z_{raindrop} has been introduced that takes the limited accessibility of air to a raindrop into account, see Eq. (4). $V_{\text{W}}/V_{\text{A}}$ is the volume fraction of raindrops in air and has a typical value of $6 \times 10^{-8} \text{ m}^3 \text{ water m}^{-3} \text{ air}$ (Joliet and Hauschild, 2005). The value for Z_{raindrop} in the intermittent rainfall approach is given as

$$Z_{\text{raindrop}} = \frac{Z_{\text{air}}}{K_{\text{AW}} + V_{\text{W}}/V_{\text{A}}}. \quad (4)$$

In addition to chemicals in the gas phase, particle-bound chemicals are also deposited by rainfall. The D -value for wet particle-associated deposition ($D_{\text{p,wet}}$) is given as

$$D_{\text{p,wet}} = Av_{\text{p}} \left(U_{\text{rainevent}} \frac{t_{\text{wet}}}{t_{\text{wet}} + t_{\text{dry}}} \right) QE_{\text{scav}} Z_{\text{p}}. \quad (5)$$

A [m^2] is the area, v_{p} [$\text{m}^3 \text{ particles/m}^3 \text{ air}$] the volume fraction of particles in air, $U_{\text{rainevent}}$ [m h^{-1}] is the average rain rate during a single rain event, t_{wet} [h] is the duration of a rain event, t_{dry} [h] is the time between different rain events, Q is the scavenging ratio, E_{scav} the scavenging efficiency, and Z_{p} [$\text{mol m}^{-3} \text{ Pa}^{-1}$] the Z -value of the aerosol particles.

The scavenging efficiency, E_{scav} , depends on the particle size. For particles with diameters smaller than $0.1 \mu\text{m}$, Brownian diffusion leads to incorporation into raindrops, whereas impaction and interception are scavenging mechanisms for large particles. A minimum in the scavenging efficiency occurs in the regime where the particles are too large to have an appreciable Brownian diffusivity yet too small to be collected effectively by either impaction or interception. For very large particles (diameter $> 20 \mu\text{m}$) and extremely small ones, the scavenging efficiency approaches unity. However, for mid-sized particles (diameter $\sim 1 \mu\text{m}$) raindrops collect only particles that are close to the center of the volume swept by the raindrop, resulting in scavenging efficiencies about 0.001 to 0.01 (Slinn, 1983; Seinfeld and Pandis 1998). In this work, we assume for the fine particle fraction $E_{\text{scav}} = 0.01$, and for the coarse

fraction 0.5 (Seinfeld and Pandis, 1998). Q is 200,000, which means that each raindrop falls through a volume of air about 200,000 times its own volume prior to landing on the surface. This value represents a cloud base at 200 m and a raindrop volume of 1 mm^3 (Mackay and Paterson, 1991; Mackay, 2001). The average rainfall intensity ($U_{\text{rainevent}}$) depends on the geographic region. We derived $U_{\text{rainevent}}$ from remote sensing data (see Section 2).

If intermittent rainfall is considered, the D -value for the total wet deposition has an upper limit. We assume for the upper limit that the chemical and the particles are removed completely from the atmosphere during rain events, and that there are rainfall events with an average duration of t_{wet} and dry periods of duration t_{dry} . Thus, we can calculate a minimum residence time (Eq. (6)) that is based on system properties only:

$$\tau_{\text{wet}}^{\text{min}} = \frac{t_{\text{dry}}}{2} \frac{t_{\text{dry}}}{t_{\text{wet}} + t_{\text{dry}}}. \quad (6)$$

With this assumption, the maximum D -value for the total wet deposition is given as

$$D_{\text{total,wet}}^{\text{max}} = V \left(\frac{2}{t_{\text{dry}}} \frac{t_{\text{wet}} + t_{\text{dry}}}{t_{\text{dry}}} \right) (Z_{\text{bulk,atmosphere}}). \quad (7)$$

Therefore, the D -value of the total wet deposition, $D_{\text{total,wet}}$, is the minimum value of Eq. (7) (upper limit for total wet deposition) and the sum of Eqs. (3) and (5) (rain washout and wet particle-associated deposition):

$$D_{\text{total,wet}} = \min[D_{\text{wet,total}}^{\text{max}}; d_{\text{g,wet}} + D_{\text{p,wet}}]. \quad (8)$$

3.3. Mass transfer coefficients

The chemical specific mass transfer coefficients (MTC, symbol k_{M} , units of m d^{-1}) are calculated from the particle deposition velocities and rain rates, which are independent of the chemicals, and the partitioning properties of the chemical (K_{AW} , ϕ). In Eqs. (9)–(11), the MTCs for dry particle-associated deposition ($k_{\text{M,dry}}$ [m d^{-1}]), rain washout ($k_{\text{M,rain}}$ [m d^{-1}]) and wet particle-associated deposition ($k_{\text{M,wet}}$ [m d^{-1}]) are given:

$$k_{\text{M,dry}} = U_{\text{dry}} \phi, \quad (9)$$

$$k_{\text{M,rain}} = U_{\text{rain}} [1/(K_{\text{AW}} + V_{\text{W}}/V_{\text{A}})(1 - \phi)], \quad (10)$$

$$k_{\text{M,wet}} = U_{\text{rain}} QE_{\text{scav}} \phi. \quad (11)$$

3.4. Atmospheric box models

We calculated atmospheric removal processes with a unit-world multimedia box model and with a global model composed of a set of spatially and temporally variable grid cells. Both models are solved as steady-state models with generic emission data. The spatially and temporally resolved model is a grid with 180×360 cells for which the environmental conditions are individually specified; in each cell, the environmental parameters change with a temporal resolution of one month. There are no horizontal transport processes in this model, i.e. atmospheric removal processes in each grid cell are calculated without outflow to or input from adjacent cells. In addition, in the grid cells there is no revolatilization of chemicals from the surface media. Consequently, the global model is a model of atmospheric removal processes that can be used to analyze deposition and degradation processes, but not for prediction of phase partitioning and long-range transport. In the unit-world model, we applied globally averaged values of the remote sensing data and the data from the ECHAM5-HAM model (see Section 2) that are used in the spatially and temporally resolved model. The global averages of the concentrations of the aerosol components in the unit-world model are: $c_{\text{OM, fine}} = 1.3 \times 10^{-6} \text{ g m}^{-3}$, $c_{\text{OM, coarse}} = 2.3 \times 10^{-7} \text{ g m}^{-3}$, $c_{\text{EC, coarse}} = 1.78 \times 10^{-7} \text{ m}^2 \text{ m}^{-3}$, $c_{\text{silica, coarse}} = 3.4 \times 10^{-6} \text{ m}^2 \text{ m}^{-3}$, $c_{\text{seasalt, coarse}} = 7 \times 10^{-6} \text{ m}^2 \text{ m}^{-3}$. The same generic emission scenario (100 mol d^{-1}) was applied to the unit-world model and all cells of the spatially resolved model.

4. Results and discussion

4.1. Unit-world model

Atmospheric removal processes considered are wet and dry particle-associated deposition, rain washout, and degradation. Results from the unit-world model are given in Fig. 2. We distinguish between three groups of chemicals according to their characteristic atmospheric removal processes: degradation, particle-associated deposition, and rain washout.

The atmospheric removal of lighter PCBs is dominated by degradation, independent of the applied sorption model. However, if the K_{OA} -based approach is used, particle-associated deposition is more important than for the ppLFER approach.

The K_{OA} -based approach yields higher aerosol–air partition coefficients for non-polar compounds if the sorptive capacity of the aerosol particles is dominated by OM, which is the case in the unit-world model (Götz et al., 2007). Generally, the importance of particle-associated deposition processes increases with increasing degree of chlorination of the PCBs. Rain washout is negligible for the lighter PCBs, which have relatively high Henry's law constants and do not partition to raindrops to a significant amount.

The atmospheric fate of heavier PCBs, TCDD/Fs, and DDTs is controlled by particle-associated deposition. Dry and wet particle-associated deposition processes are both important, with wet particle-associated deposition being higher than dry particle-associated deposition by about a factor of 2. Again, the K_{OA} -based approach tends to result in higher total particle-associated deposition than the ppLFER approach. In contrast to the general trend of increasing sorption with increasing degree of chlorination that occurs for the K_{OA} -based sorption model, PCB 155 shows low sorption and, thus, particle-associated deposition if the ppLFER sorption model is used. This is due to the relatively low value of 8.72 for the logarithm of the hexadecane–air partition coefficient of PCB155 (Abraham and Al-Hussaini, 2005) that is used in the ppLFER approach. However, this estimated value appears to be too low compared with values of similar PCBs (e.g. PCB153, $\log K_{\text{hexadecane-air}} = 9.59$); there are no measurement results available. 2,3,7,8-TCDD shows a slightly higher sorption and particle-associated deposition with the ppLFER approach, in contrast to 2,3,7,8-TCDF, which has a less pronounced electron-donor property, and PCBs with no electron-donor properties at all. This effect is attributable to the ether groups of 2,3,7,8-TCDD, which can participate in specific adsorption interactions with aerosol surfaces, which is only considered in the ppLFER approach.

The atmospheric fate of CUPs is mainly controlled by rain washout and atmospheric degradation. Therefore, the influence of the aerosol model is less significant than for particle-associated deposition controlled chemicals. However, for some CUPs, dry particle-associated deposition plays an important role. Phenylurea herbicides (isoproturon, diuron, metoxuron), propazine, and metolachlor show a significant dry coarse particle-associated deposition in the ppLFER approach that does not show up in the K_{OA} -based model. This is caused by

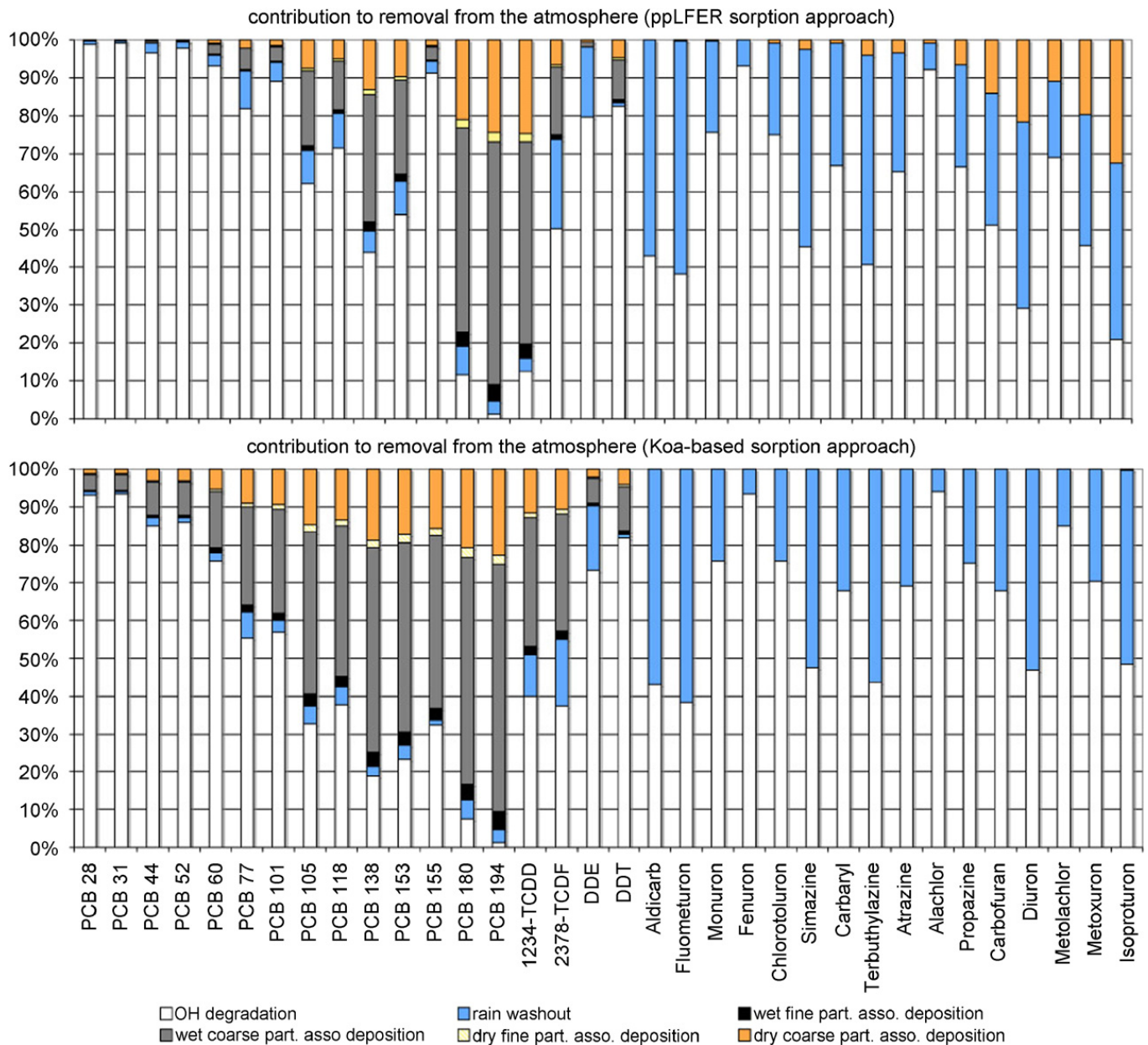


Fig. 2. Relative importance of atmospheric removal processes of different chemicals for the ppLFER and K_{OA} -based sorption model.

their strong sorption to mineral surfaces (silica, kaolinite, bentonite) in dry periods (average RH between rain events: 60%) that increases with increasing polarity of the chemicals (Goss and Eisenreich, 1996; Goss and Schwarzenbach, 2002). Mineral dusts are mainly coarse particles and, thus, settle much faster than fine particles, which contain a higher fraction of OM. Differences in deposition between the ppLFER and the K_{OA} -based model are not large in the unit-world model, however they are more important in a spatially resolved model in regions where precipitation and RH are lower, as is the case in desert, arid, or arctic regions (see

Section 4.2). Beside the deposition processes, degradation plays a major role for the removal of CUPs from the atmosphere. The highest degradation occurs for alachlor, which has a relatively high second order degradation rate constant with OH of $1.6 \times 10^{-5} \text{ d}^{-1} \text{ cm}^3$.

In summary, in a unit-world model the choice of the sorption model influences the relative importance of atmospheric removal processes significantly for particle-associated deposition controlled chemicals, and for some degradation-controlled chemicals. However, both sorption models yield similar overall atmospheric removal

rates and both are appropriate to be applied. The specific values of the atmospheric removal processes depend strongly on system parameters, such as precipitation, RH, and aerosol composition, for which global average values are used in the unit-world model.

4.2. Spatially and temporally resolved global model

To investigate the influence of sorption approach, particle deposition velocities, and rain rate on the atmospheric removal on a global scale, we use global remote sensing and GCM data as presented above, and focus on three chemicals representing the three groups defined above: PCB28 as a degradation-dominated chemical, PCB180 as particle deposition-dominated chemical, and terbuthylazine, for which atmospheric fate is controlled by rain washout.

4.2.1. Spatial and temporal variability of the particle-bound fraction, ϕ

ϕ values of PCB28, PCB180, and terbuthylazine are given in Fig. 3. PCB28 is essentially in the gas-phase in the atmosphere all over the globe. However, from October to March, up to 30% can be bound to particles in the northern hemisphere in regions with very high particulate OM concentrations and low temperature. PCB28 is a non-polar chemical and thus sorbs mainly into OM (Götz et al., 2007).

PCB180 shows strong particle binding ($\phi > 0.9$) in arctic and temperate regions, whereas ϕ is near to 0 in tropical oceanic regions. These regions have very low concentrations of particulate OM and EC, which are the main sorbents for PCB180. The affinity to sea salt is low because PCB180 is non-polar. The strong sorption to particles near the poles is due to the low temperatures, which increase

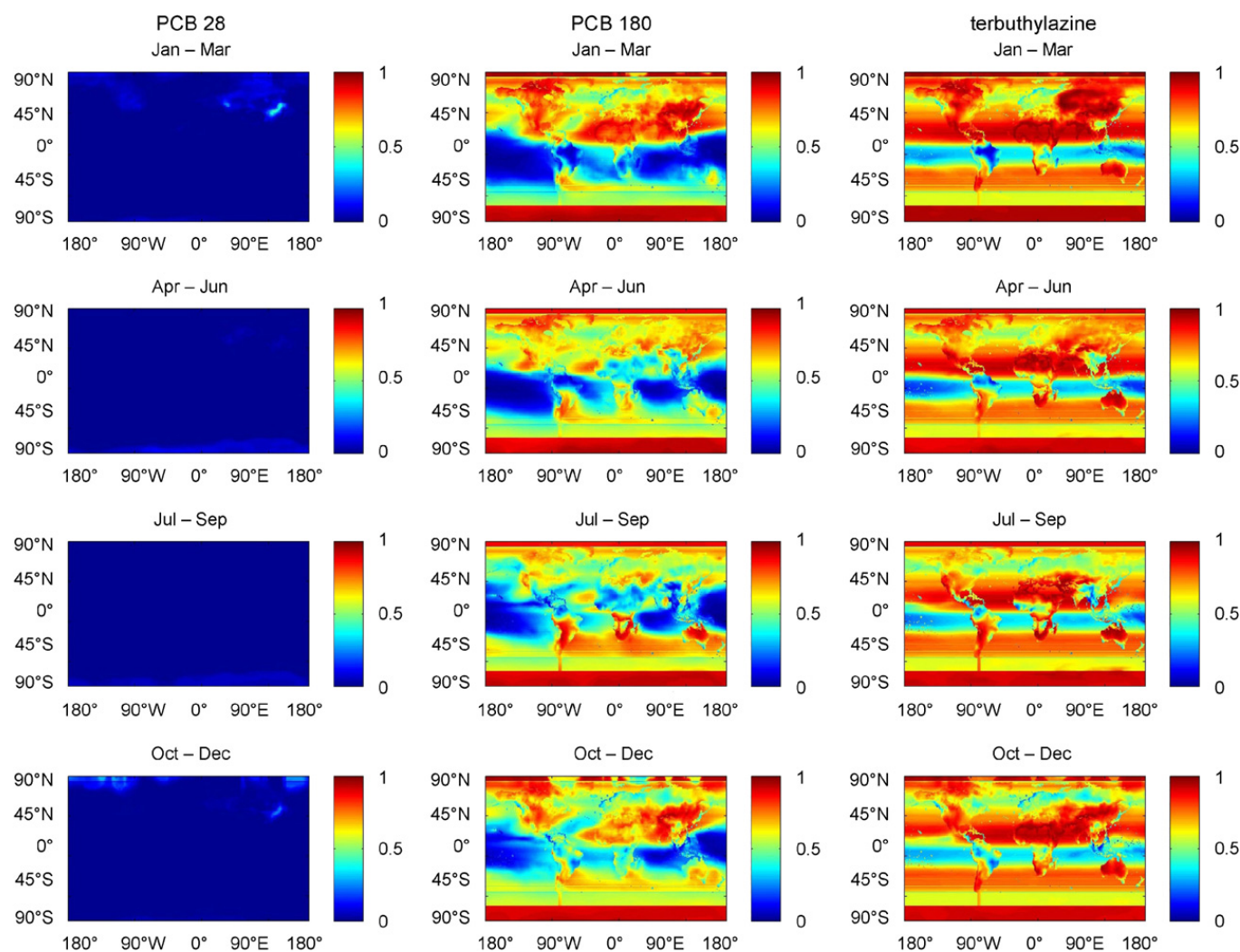


Fig. 3. Global spatially and temporally resolved ϕ calculated with the ppLFER approach for PCB28, PCB180, and terbuthylazine.

the aerosol–air partition coefficient by several orders of magnitude compared to tropical regions. As an example, with a phase transition energy (ΔU_{OA}) of $-95.2 \text{ kJ mol}^{-1}$ (Schenker et al., 2005), the K_{OA} of PCB 180 decreases approximately by a factor of 3 for every -10°C . Therefore, we observe a high ϕ in arctic regions, even when the particle concentrations are relatively low (see Fig. 1).

Terbutylazine is strongly bound to aerosol particles, except in some tropical regions. The stronger binding in oceanic regions than for PCB180 is due to the polar functional groups of terbutylazine, which are able to form H-bond interactions with polar surfaces, such as sea salt or mineral oxides. Accordingly, terbutylazine has a higher ϕ than non-polar chemicals in regions where mineral oxides and sea salt are the dominating sorbents, such as in desert or oceanic regions. The latitudinal bands of constant ϕ observed in Fig. 3 are due to dependence on temperature and values of t_{wet} and t_{dry} . The duration of the wet and dry periods influence ϕ by determining relative humidity; when relative humidity is high (set at 90% during t_{wet} ; during dry periods, relative humidity depends on the region and is derived from ECHAM-HAM5), water out-competes terbutylazine for H-bond sites on the aerosols, which affects sorption to surfaces calculated by the ppLFFER model. Uncertainties in ϕ over oceans are considerably higher than over the continents since they are based on extrapolated data (see above).

Generally, the ppLFFER-approach, which considers various aerosol particle components, results in a higher ϕ than the K_{OA} -based approach in most regions, except in regions with high concentrations of particulate OM. However, whereas PCB28 and PCB180 have similar ϕ values in both sorption models, terbutylazine has a higher ϕ if the ppLFFER approach is applied and polar surfaces such as sea salt or silica are included. The K_{OA} -based approach, which considers only particulate OM as a potential sorption phase results in ϕ -values for terbutylazine between 0.01 and 0.4, which is, independent of the geographic region, lower than with the ppLFFER approach.

The uncertainty in ϕ is directly coupled with the uncertainty of K_{p}^* (dimensionless gas–particle partitioning coefficient). In a former study (Götzt et al., 2007), we investigated the uncertainty of K_{p}^* based on uncertainty of chemical properties such as K_{OA} or $K_{\text{hexadecane/air}}$. The uncertainty analysis showed that, within the range of investigated chemicals

($10^{-3} < K_{\text{p}}^* < 10^2$), the 90% confidence intervals of K_{p}^* were in the range of a factor of 10 above and below the median K_{p}^* values. In contrast to K_{p}^* , the relative uncertainty ranges calculated for ϕ are not constant over the range of K_{p}^* values. For low ϕ -values (< 0.1), the relative uncertainty is similar to that of K_{p}^* . With higher ϕ -values, the relative uncertainty decreases strongly.

4.2.2. Particle-associated deposition

In addition to gas–particle partitioning, weather conditions strongly influence deposition of chemicals. Whereas dry particle-associated deposition is approximately independent of rainfall, rain washout and wet particle-associated deposition are directly linked to rainfall intensity and frequency. Because our model does not include land-cover information, we used average dry deposition velocities in all grid cells.

The mass transfer coefficients (MTC [m d^{-1}]) for the different deposition processes of PCB28, PCB180 and terbutylazine are given in Fig. 4. First, the dry particle-associated deposition MTC of PCB28 is between 1 and 70 m d^{-1} , and between 1 and 250 m d^{-1} for PCB 180 and terbutylazine, depending on the geographic location and point in time. These regional differences are determined by the differences in gas–particle partitioning, because the dry deposition velocity of the aerosol particles is independent of the region. Therefore, the pattern for dry particle-associated deposition in Fig. 4 directly reflects the spatial pattern of ϕ . The dry particle-associated deposition MTC is high in arctic and temperate regions because ϕ is high in these regions, see Section 4.2.1.

Wet particle-associated deposition depends, in addition to gas–particle partitioning, on the frequency and intensity of precipitation events. Generally, the spatial variability of wet deposition is higher than the variability of dry deposition due to the additional influence of precipitation. PCB28 shows very low wet particle-associated deposition in most regions, which is, compared to the other atmospheric deposition processes of PCB28, negligible. For PCB180 and terbutylazine, wet particle-associated deposition is dominant over dry particle-associated deposition processes in regions with intense rainfall and with high particle-sorption of the chemical, such as northern Europe or eastern Asia.

Rain washout of the gaseous fraction is for non-polar chemicals, such as PCB28 and PCB180, not of

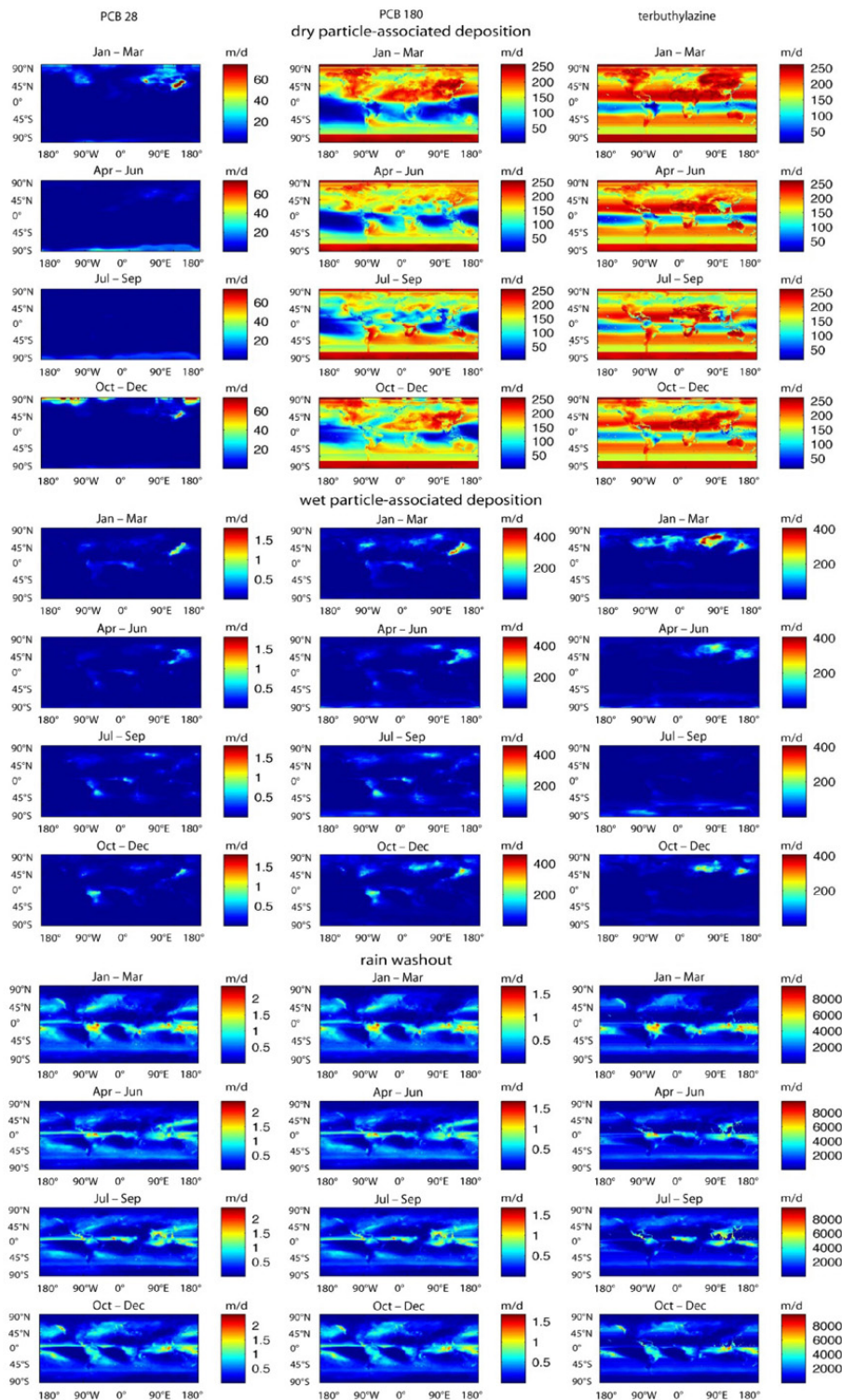


Fig. 4. Dry and wet particle-associated deposition MTCs ($k_{M,dry}$, $k_{M,wet}$, $k_{M,rain}$ [m d^{-1}]) of PCB 28, PCB 180, and terbuthylazine.

high importance for the overall deposition. In contrast, the deposition of terbuthylazine is dominated by rain washout consistent with results from the unit-world model. However, the relative importance of the different advective deposition

processes is highly dependent on the geographic region. In arctic and arid regions, dry particle-associated deposition is more important than rain washout, even for polar chemicals, such as terbuthylazine.

Generally, the MTCs for deposition are highly dependent on the geographic region for all investigated chemicals, and the spatial variability of the modeled MTCs covers several orders of magnitude. To evaluate the modeled MTCs, we compared the model results of two different geographic regions with measurement data.

4.2.3. Comparison with measurement data

From the atmospheric bulk concentration (c_{bulk} [ng m^{-3}]) of the chemical and modeled MTCs ($\sum k_{M,i}$ [m d^{-1}]) of different deposition processes i , deposition fluxes ($F_{\text{Dep,bulk}}$ [$\text{ng m}^{-2} \text{d}^{-1}$]) can be calculated as

$$F_{\text{Dep,bulk}} = c_{\text{bulk}} \sum_i k_{M,i}. \quad (12)$$

Horstmann and McLachlan (1998) and Su et al. (2007) measured deposition fluxes ($F_{\text{Dep,bulk}}$) of various SOCs in Bayreuth, Germany and southern Ontario, Canada, respectively. Additionally, they measured the chemicals' concentrations in air and on particles (c_{bulk}). The experiments of Horstmann and McLachlan (1998), and Su et al. (2007) include the same advective deposition processes that we investigated in our model: dry particle-associated deposition, wet particle-associated deposition, and rain washout. With the measured bulk concen-

tration in the atmosphere (c_{bulk}), we calculated the bulk deposition fluxes for the two regions in central Europe and southern Ontario with our modeled MTCs, and then compared them to the measurements. The MTCs were calculated for the same months in which the measurements were made; they were obtained from long-term averages of aerosol concentrations taken from remote sensing data and ECHAM5-HAM results. No specific weather and aerosol information from the two field studies were used. We included all PCBs, which were measured in both studies, and 2,3,7,8-TCDD and 2,3,7,8-TCDF, which were measured by Horstmann and McLachlan only (Fig. 5). For polar chemicals, such as terbuthylazine, no measurement data for deposition fluxes are available.

We observe good agreement of $F_{\text{Dep,bulk}}$ between the model and the measurements for PCB101, PCB138, PCB153, and PCB180 with both studies. Also 2,3,7,8-TCDD and 2,3,7,8-TCDF show a good agreement between the model and the measured values (see Fig. 5). Hence, the model reproduces the deposition fluxes and, therefore, the MTCs for the group of particle-associated deposition controlled chemicals very well.

In contrast, PCB28 and PCB52 show an apparent deviation between the modeled and the measured fluxes. The model estimates the deposition flux of PCB28 and PCB52 about two orders of

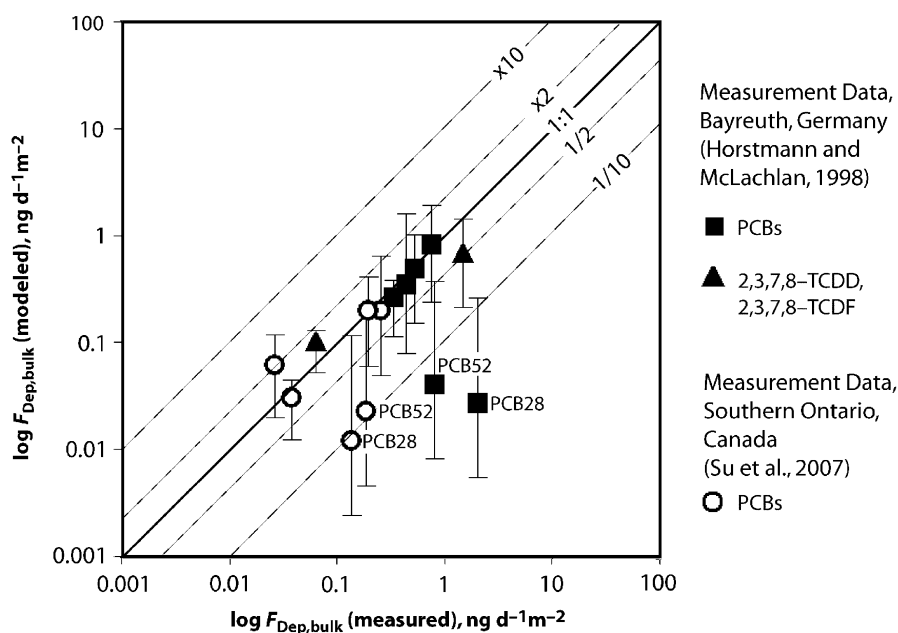


Fig. 5. Comparison of bulk deposition fluxes ($F_{\text{Dep,bulk}}$) between modeled data and measurements of Horstmann and McLachlan (1998), and Su et al. (2007). 90% confidence intervals for modeled data are given.

magnitude lower than measured data of Horstmann and McLachlan (1998), and one order of magnitude lower than the measurements of Su et al. (2007). Possible explanations are that the ϕ value estimated by the model is too low and, thus, the particle-associated deposition is underestimated, or that the measurements include for these relatively volatile chemicals additional processes other than the deposition processes included in our model. However, as mentioned above, the sensitivity of ϕ to deviations in K_p is very high for weakly sorbing chemicals. For PCB28 and PCB52, the estimation of ϕ depends mainly on the hexadecane/air partition coefficient. An increase of $\log K_{\text{hexadecane/air}}$ from 7.818 (Abraham and Al-Hussaini, 2005) to 8.318 (0.5-units) explains the discrepancy for the Su et al. (2007) data, and half of the difference for the Horstmann and McLachlan (1998) data.

For comparison, we contrasted the measured deposition fluxes with the modeled fluxes if the K_{OA} -based sorption approach is used. For all investigated chemicals, this resulted in higher discrepancies between model and measurements. For the local conditions of Bayreuth and southern Ontario, the K_{OA} -based model yields smaller fractions sorbed to coarse particles than the ppLFFER model (sorption to EC and mineral surfaces disregarded). Because the deposition velocity of coarse particles is high, a smaller fraction sorbed to coarse particles leads to a smaller deposition flux. This reduction of the deposition flux obtained with the K_{OA} -based sorption model is discernible even for chemicals of which only a small fraction is sorbed to coarse particles.

5. Conclusions and outlook

We have shown that in generic unit-world models the ppLFFER and the K_{OA} -based sorption approaches yield similar results. Differences between sorption estimations for polar chemicals (e.g. terbuthylazine) as they were observed in previous work (Götz et al., 2007), which have a high impact on the particle-associated deposition processes, did influence the overall removal only to a lesser extent because of the dominant role played by rain washout for polar chemicals. Generally, both sorption approaches are appropriate if they are applied in a unit-world model. This is because averaging of environmental parameters, such as precipitation, particulate OM, and relative

humidity, reduces discrepancies between the two models.

For spatially and temporally resolved multimedia models, in contrast, the choice of the sorption approach is crucial. Generally, we suggest that the ppLFFER approach be used in spatially highly resolved box models and GCMs, because local conditions in several regions (e.g. desert, arctic or marine environments) cannot be represented properly with the K_{OA} -based approach, which considers only OM absorption. Spatially variable parameters, such as presence of different aerosol components, relative humidity, frequency and intensity of rain events, are reflected by the ppLFFER model. Furthermore, the calculated deposition fluxes show good agreement with measured data for low-volatility SOCs. In contrast, the more volatile compounds PCB28 and PCB52 showed a significant discrepancy between modeled and measured deposition mass fluxes, which may be caused by an underestimation of the particle-bound fraction of these chemicals. However, the discrepancies between measurements and modeled data using the K_{OA} -based sorption approach are, for all investigated chemicals, higher than with the ppLFFER approach.

Generally, the complexity of the sorption description should correspond to the complexity of the description of atmospheric aerosols in environmental fate models for organic chemicals. While a simple sorption model such as the K_{OA} -based approach works well for a unit-world model, the high spatial variability of gas–particle partitioning cannot be reproduced by this approach, because sorbents other than OM are of importance in e.g. oceanic or desert regions. Therefore, for highly resolved models we recommend to use the ppLFFER approach. However, the advective bulk deposition of weakly and moderately sorbing chemicals ($\phi < 0.2$), such as PCB28 and PCB52, is estimated lower by both models than the measured data. Further research and more data from field studies will help to reduce uncertainties in models of atmospheric deposition processes and the gas–particle partition coefficient.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.atmosenv.2007.08.033](https://doi.org/10.1016/j.atmosenv.2007.08.033).

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