Dependence of Persistence and Long-Range Transport Potential on Gas-Particle Partitioning in Multimedia Models

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A novel approach of modeling gas-particle partitioning using polyparameter linear free energy relationships (ppLFERs) is implemented into three different multimedia box models (the OECD *P*ov and LRTP screening tool (The Tool), ChemRange, and CliMoChem) and compared to approaches based on the octanol-air partition coefficient (K_{OA}). In all three multimedia models, calculated overall persistence is not strongly influenced (differences <3%) by the gas-particle partitioning approach selected. The long-range transport potential (LRTP) is more sensitive to the choice of the gas-particle partitioning model. In CliMoChem, the LRTP of polar chemicals is higher if the ppLFER gas-particle partitioning approach is applied, with differences up to a factor of 2. Modeled concentrations of polar chemicals in Arctic air are also higher in the ppLFER version of CliMoChem. The model results obtained with the ppLFER approach are in good agreement with measured concentrations of α-HCH, methoxychlor, and trifluralin in Arctic air, whereas results from the K_{OA}-based version of the model are in some cases lower by a factor of 10−100. If the required chemical property data are available, the ppLFER approach holds considerable potential to improve the gas-particle partitioning description for polar chemicals in multimedia models.

Introduction

Screening-level environmental hazard assessments for chemicals require estimating the chemicals' persistence and long-range transport potential (*1, 2*). Several models have been developed to calculate overall persistence (*P*ov), spatial range (*R*), characteristic travel distance (CTD), and efficiency of transfer to a target in a remote region (TE) (*1, 3–5*). For most pollutants found in remote regions, long-range transport in the atmosphere is the dominant transport pathway. A key parameter that determines atmospheric long-range transport of semivolatile organic chemicals (SOCs) is gas-particle partitioning to aerosols (*6, 7*).

Roth et al. have derived polyparameter linear free energy relationships (ppLFERs) to describe gas-particle partitioning

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from partitioning experiments with volatile chemicals (*8, 9*). They have shown that a ppLFER approach results in better agreement between modeled and measured gas-particle partitioning than regressions based on the octanol-air partition coefficient (K_{OA}). Recently, we have confirmed that gas-particle partitioning and atmospheric deposition of semivolatile chemicals can be described successfully with models using ppLFERs (*10, 11*). In our approach, partitioning to all relevant components of aerosol particles is explicitly described with ppLFERs, and different atmospheric lifetimes of fine ($PM_{2.5}$) and coarse ($PM_{10-2.5}$) aerosol particles are taken into account. This combined two-particle-size ppLFER approach showed better agreement with measured deposition data in temperate regions than a K_{OA}-based sorption model that is commonly applied in multimedia models (*11*). A particular advantage of the ppLFER approach compared to K_{OA}-based models is that chemical-surface interactions of polar chemicals, such as electron acceptor and donor interactions, are considered. This is of particular importance for polar chemicals such as current-use pesticides (*12*).

In this paper we use three different multimedia contaminant fate models to analyze the impact of implementing the two-particle-size ppLFER approach on metrics of persistence and long-range transport, and on calculated concentrations of SOCs in the Arctic. We use the OECD *P*ov and LRTP Screening Tool (*4*), and the multimedia box models ChemRange (*13*) and CliMoChem (*7*). With all three models, *P*ov and long-range transport indicators (*R*, CTD) calculated with the K_{OA}-based and the ppLFER approach are compared, and differences between the two model versions are discussed. For CliMoChem, which includes region-specific information and shows the largest sensitivity to the selected gas-particle modeling approach, we explore the differences between the model versions in more detail. Furthermore, we calculate concentrations of current-use pesticides (CUPs) in the Arctic with both versions of the CliMoChem model and compare them with measurement data to explore which version of the model is in better agreement with field data.

Methods and Models

Multimedia Models. A summary of model characteristics of the three models used in this study is given in Table 1.

The Tool and ChemRange are generic models and do not contain region-specific information. The Tool is a unit-world model, whereas ChemRange consists of a loop of regions connected by transport of air and water. In contrast, CliMoChem contains region-specific information; model parameters such as amounts of water, soil, vegetation, and vegetation-covered soil, temperature, relative humidity, and hydroxyl radical concentration vary with latitude. The CliMoChem model has no spatial resolution in the east–west direction (zonally averaged) (*16*). The Tool and ChemRange yield steady-state solutions only, whereas CliMoChem can be solved either as a steady-state or time-resolved model.

In their reference version, all models describe gas-particle partitioning using regressions with K_{OA} and implicitly assume one aerosol size (see Table 1). Furthermore, no region-specific information about aerosol concentration or composition is implemented in any of the models. Therefore, additional aerosol data had to be incorporated into all three models to parametrize the ppLFER approach.

Two-Particle-Size ppLFER Aerosol Model. Polyparameter linear free energy relationships have been developed to describe sorption to a variety of environmental media (*17*). They include regression terms that represent specific molecular interactions between the sorbent and the sorbate,

TABLE 1. Multimedia Box Models Used in This Study

	spatial resolution (lat. × long.)	geographical information	default description of gas-particle partitioning	hazard indicators
OECD Pov and LRTP Screening Tool (The Tool)	1 × 1; one box	unit world, average values	$K_{PA} = 0.42 \times K_{OA}$ (14)	Pov, CTD, TE
ChemRange	$n \times 1$; closed loop, here: $n = 80$	generic average values	$\log K_P = 0.55 \times \log K_{OA} - 8.23$ (15)	Pov, R
CliMoChem	$n \times 1$; n latitudinal zones, here: $n = 10$	region-specific values based on remote sensing data	$\log K_P = 0.55 \times \log K_{OA} - 8.23$ (15)	Pov, R

K_P: aerosol-air partition coefficient (m^3 air/μg aerosol particles), K_{PA}: volumetric aerosol-air partition coefficient (m^3 air/m^3 aerosol particles), K_{OA}: octanol-air partition coefficient, Pov: overall persistence (d), CTD: characteristic travel distance (d), TE: transfer efficiency (%), R: spatial range (% of pole-to-pole distance).

such as van-der-Waals interactions, electron-acceptor, and electron-donor interactions (18–20). Recently, our research group has combined individual ppLFERs to describe simultaneously occurring sorption to different components of aerosol particles (10). Our aerosol model contains a fine fraction ($PM_{2.5}$) and a coarse fraction ($PM_{10-2.5}$) with different compositions and different dry and wet deposition velocities. For details of this approach to modeling gas-particle partitioning and aerosol deposition, the reader is referred to refs 10,11. Dry deposition velocities for the fine and the coarse fraction have been selected to be 10 m·d^{-1} and 250 m·d^{-1}, respectively, and are assumed to be independent of the geographical region (21, 22). Wet particle-associated deposition is described with the intermittent rainfall approach (23). The wet deposition velocity, v_{wet} (m·d^{-1}), depends on the geographical region and is a function of rainfall intensity and frequency:

$$v_{wet} = \left(U_{rainevent} \cdot \frac{t_{wet}}{t_{wet} + t_{dry}} \right) \cdot Q \cdot E_{scav} \qquad (1)$$

$U_{rainevent}$ (m/d) is the average rain rate during a rain event, t_{wet} (d) is the duration of a single rain event, t_{dry} (d) is the time between two rain events, and Q (dimensionless) is the scavenging ratio, which has a value of 200 000, assuming a cloud base at 200 m and a raindrop volume of 1 mm^3 (24, 25). The scavenging efficiency, E_{scav}, depends on the particle size and we assume $E_{scav} = 0.01$ for the fine particle fraction and $E_{scav} = 0.5$ for the coarse fraction (22). Additionally, the intermittent rainfall approach imposes a chemical-independent maximum value for the sum of wet particle deposition and rain washout that ensures wet deposition does not occur on a faster time scale than the frequency of rain events (11, 23).

The aerosol particle composition in the ppLFER versions of The Tool and ChemRange is based on globally averaged data. The aerosol composition in CliMoChem is based on spatially highly resolved data from the general circulation model ECHAM5-HAM (26). The particle compositions used in the model are described in section 1 of the Supporting Information.

We implemented the ppLFER approach with two particle sizes in the three multimedia models described above, and below we compare the results obtained with these new model versions with results from the reference model versions that describe gas-particle partitioning with K_{OA}-based approaches and default parameters for deposition. PpLFER parameters of the aerosol components considered (organic matter (OM), elemental carbon (EC), mineral surfaces, and sea salt) are given in ref 10.

Atmospheric Processes and Molar Fluxes. In all models, the atmospheric compartment is connected to surface compartments such as soil and water by various exchange processes (section 2 of the Supporting Information). Chemicals are deposited to surface compartments by advective processes that include dry and wet particle-associated deposition and rain washout of chemicals in gas phase. Furthermore, there is diffusive exchange between atmosphere and surface compartments, degradation by reaction with hydroxyl radicals, and interzonal exchange between the air compartments of different geographical zones (atmospheric long-range transport). The rates of these processes are quantified as molar fluxes (F (mol·s^{-1})),

$$F_i = (k_{eff,i} \cdot c \cdot V) \qquad (2)$$

where F_i is the molar flux of process i, $k_{eff,i}$ (s^{-1}) is the effective rate constant of process i, c (mol·m^{-3}) is the chemical's bulk concentration in air, and V (m^3) is the volume of the compartment. The effective rate constant, $k_{eff,i}$, of processes that only act on particle-bound chemicals, such as dry and

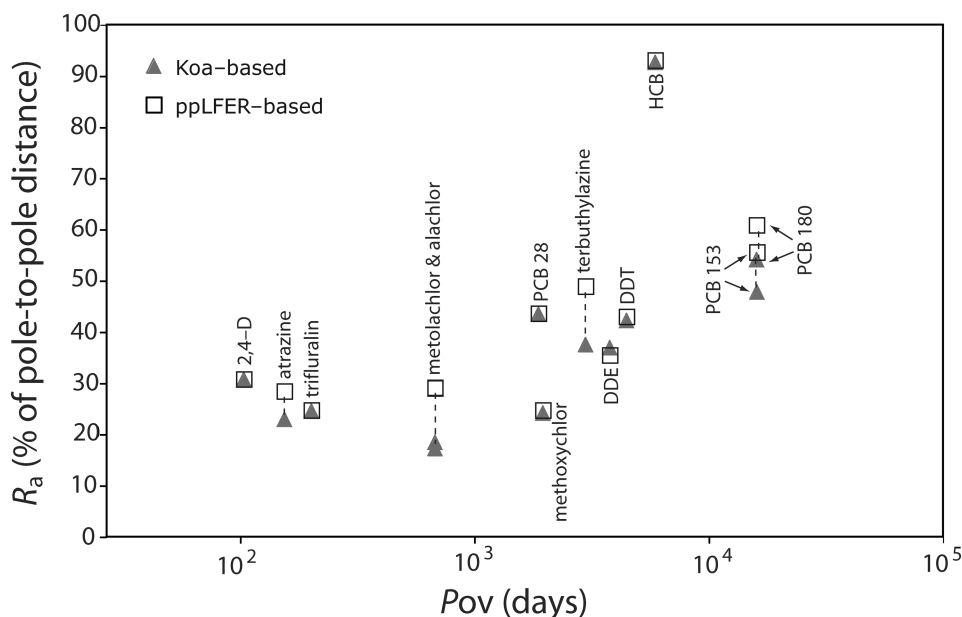**FIGURE 1. Persistence (P_{ov}, days) and atmospheric spatial range (R_a, %). Gray triangles: CliMoChem with K_{OA}-based gas-particle sorption approach. Open squares: CliMoChem with two-particle-size ppLFER sorption approach.**

wet deposition, is equal to the process rate constant multiplied by the particle-bound fraction: $k_{\text{eff},i} = k_i \cdot \Phi$. In contrast, diffusion, rain washout of the chemical in the gas phase, and atmospheric degradation only act on the fraction of chemical in the gas phase: $k_{\text{eff},i} = k_i \cdot (1 - \Phi)$. If a process acts on the particle-bound and the gaseous fraction of the chemical in the same way, as in the interzonal atmospheric exchange, the effective rate constant is equal to the process rate constant: $k_{\text{eff},i} = k_i$.

Scheringer et al. introduced a method to analyze the differences in calculated concentrations between two different model versions by analyzing molar fluxes (27). They divided the molar fluxes into two groups: group 1 includes all fluxes with different k_{eff} in the two model versions (which also includes fluxes that are present in only one of the two model versions); group 2 includes all fluxes with identical k_{eff} in both versions. In a steady-state solution the sum of all inputs into a compartment is equal to the sum of all outputs, $\Sigma F_{\text{in},i} = \Sigma F_{\text{out},i}$. This equation can be rearranged to $\Sigma F_{\text{group1}} = \Sigma F_{\text{group2}}$ and to $\Sigma \Delta F_{\text{group1}} = \Sigma \Delta F_{\text{group2}}$ for the differences between two model versions. All changes in group 2 fluxes are caused by concentration differences only, as a result of changes in fluxes of group 1, but not by changes in rate constants. Here, we further distinguish between two different kinds of group 1 fluxes: group 1A fluxes have different k_i *and* different $k_{\text{eff},i}$ in the two model versions. This group includes processes with different descriptions in the ppLFER and K_{OA}-based approach, like dry and wet particle-associated deposition. Group 1B fluxes have identical k_i but different k_{eff} because of changes in Φ in the two model versions. This group includes processes with the same description in both approaches, like rain washout, gaseous deposition, and degradation. Changes in 1A fluxes are proportional to changes in k, Φ and $c_{\text{air,bulk}}$, whereas changes in 1B fluxes are proportional to changes in $(1 - \Phi)$ and $c_{\text{air,bulk}}$.

Chemicals. To evaluate the impact of the different gas-particle partitioning approaches we selected chemicals that represent a broad range of properties, including persistent organic pollutants, such as hexachlorobenzene (HCB) and DDT, and current-use pesticides, such as terbuthylazine and trifluralin. Our selected chemicals include both nonpolar and polar SOCs. Chemical properties are given in section 3 of the Supporting Information.

Results and Discussion

Model Comparison. For all chemicals, we compared persistence and long-range transport potentials calculated with the K_{OA}-based gas-particle partitioning approach and the two-particle-size ppLFER approach in The Tool, ChemRange, and CliMoChem. Generally, P_{ov} is insensitive to changes of the aerosol parametrization in all three investigated models; the differences in P_{ov} between the K_{OA}-based and the ppLFER model versions are below 3% for all investigated chemicals.

In The Tool and in ChemRange, differences in long-range transport metrics between the model versions with the K_{OA}-based sorption approach and the two-particle-size ppLFER approach are below a factor of 1.1 for all investigated chemicals with the exception of some polar CUPs: metolachlor, alachlor, terbuthylazine, atrazine, methoxychlor, and 2,4-D show an increase in R_a between a factor of 1.1 and 1.3 in the ppLFER model version. Generally, the small differences between the K_{OA}-based and ppLFER models are due to the relatively high organic matter (OM) concentration in the aerosol, resulting from the globally averaged values of the aerosol composition used in The Tool and in ChemRange. Our previous work has shown that if OM is the dominant sorbent, differences between the two sorption approaches are small. Only in regions where other sorbents are of high importance, such as oceanic regions (sea salt) or deserts (mineral dust), larger differences are observed (11).

In CliMoChem, in contrast, the atmospheric spatial range, R_a, of some polar and nonpolar chemicals show significant differences between the ppLFER approach and the K_{OA}-based approach. Figure 1 shows R_a (in percent of the length between the poles, L) and P_{ov} calculated with CliMoChem for all investigated chemicals.

Most nonpolar chemicals show small differences in R_a, with the exception of the heavier PCBs, for which R_a is higher with the ppLFER model version. Among the polar chemicals, metolachlor, alachlor, atrazine, and terbuthylazine exhibit the biggest increase in R_a (up to a factor of 1.9) with the ppLFER sorption approach; other polar CUPs, such as 2,4-D and trifluralin, have similar R_a with both sorption approaches. R_a is a measure of the spatial distribution of a chemical's atmospheric bulk phase concentration over the different geographical zones and reflects changes in atmospheric long-range transport. To analyze the changes in R_a, we investigate
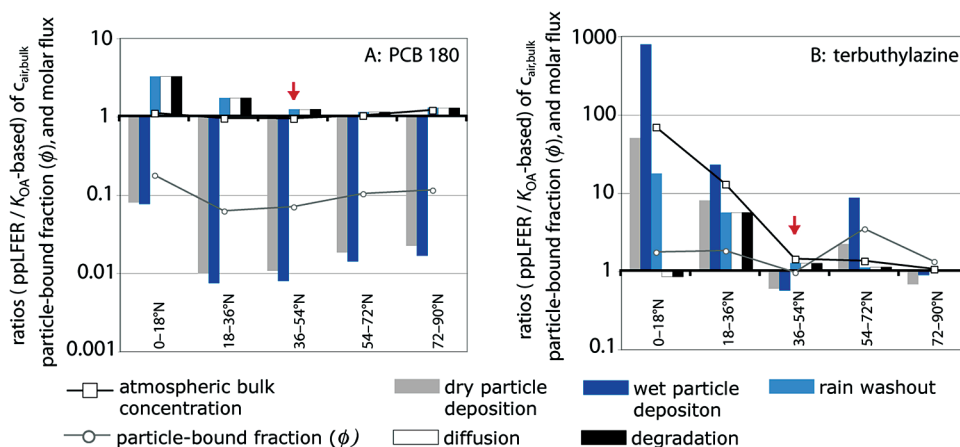
FIGURE 2. Ratio of group 1 molar fluxes, particle-bound fraction Φ and the atmospheric bulk concentration ($c_{air,bulk}$) between the ppLFER and the K_{OA}-based CliMoChem versions for the zones of the northern hemisphere (*x*-axis). (A) PCB180 and (B) terbuthylazine. Emission into temperate zone (36–54°N, red arrow).

the spatial concentration profiles and changes in molar flux in the atmospheric compartment of CliMoChem that are due to the implementation of the new two-particle-size ppLFER approach.

Flux Analysis in CliMoChem. We use steady-state solutions of the ppLFER and the K_{OA}-based versions of CliMoChem to analyze differences in molar fluxes and concentrations. A generic continuous emission into the vegetation-covered soil of the northern temperate zone (36–54°N) is assumed. We selected a nonpolar chemical, PCB180 (a heptachlorinated biphenyl), and a polar CUP, terbuthylazine, for the molar flux analysis. For both chemicals, more than 95% of the total steady-state mass is located in the northern hemisphere.

In Figure 2, ratios of group 1 molar fluxes, particle bound fraction (Φ), and bulk concentration in the air ($c_{air,bulk}$) between the ppLFER and the K_{OA}-based model versions are shown for the northern hemisphere. The value of $c_{air,bulk}$ in a given zone is determined by the net long-range transport molar flux into the atmosphere of that region. The net long-range transport molar flux to the air compartment of a given zone is the sum of net fluxes from (i) interzonal atmospheric transport and (ii) the indirect transport to the atmosphere through oceanic long-range transport and subsequent volatilization to air in the target zone. If the net long-range transport molar flux in a specific zone is higher in the ppLFER model version, the ratio of concentrations shown in Figure 2 in the zone under consideration is higher than one, whereas a lower net molar flux into the atmospheric compartment in the ppLFER model results in a ratio below one. Because the net molar flux into the air compartment of a given zone depends not only on $c_{air,bulk}$ but on several other concentrations as well (in different media in the same zone and also in the adjacent zones), the difference in the net molar flux is generally different from the difference in $c_{air,bulk}$. Conservation of mass implies, however, that a higher net flux into the air compartment of a given zone always corresponds with a higher $c_{air,bulk}$.

In the ppLFER model version, $c_{air,bulk}$ of PCB180 and terbuthylazine in the Arctic is increased by factors of 1.1 and 70, respectively (Figure 2). This means that the net long-range transport molar flux into the atmosphere of the Arctic is higher in the ppLFER model version for both chemicals, which is in agreement with the increased spatial ranges (R_a) of these chemicals (compare Figure 1).

For PCB180, the ppLFER model version yields a lower Φ than the K_{OA}-based model for all latitudinal zones in CliMoChem. The net molar flux to the Arctic (0–18°N) in the ppLFER model version is higher by a factor of 1.4. Higher

$c_{air,bulk}$ in remote regions are due to lower dry and wet particle-associated deposition, which is, in turn, attributable to lower Φ and lower deposition velocities in the two-particle-size ppLFER approach (Figure 2A). The ppLFER model version thus predicts higher concentrations of PCB180 in the gas phase, and higher degradation fluxes in air since it is assumed that only gas-phase chemical is available for reaction with hydroxyl radicals.

Terbuthylazine has, in contrast to PCB180, a higher Φ in all zones in the ppLFER model version, with the exception of the emission zone (36–54°N). However, similar to PCB180, the long-range transport molar fluxes and the concentrations in remote areas are higher in the ppLFER model version. The net atmospheric long-range transport flux into the Arctic is increased by a factor of 3. In this case, higher Φ leads to a longer residence time in air because the rate constant for degradation of gas-phase terbuthylazine by hydroxyl radicals is higher than the overall rate constant for deposition of particle-bound terbuthylazine. Therefore, in contrast to PCB180, for which atmospheric long-range transport and $c_{air,bulk}$ is limited by the rate of particle-associated deposition processes, for terbuthylazine, atmospheric long-range transport and $c_{air,bulk}$ is limited by the degradation rate of gas-phase chemical. Terbuthylazine is about 100 times more reactive with hydroxyl radicals in air than PCB180 ($k_{OH,terbuthylazine}$ = 9.5×10^{-7} cm³·molecule⁻¹·d⁻¹ (*28*) versus $k_{OH,PCB180}$ = 8.6×10^{-9} cm³·molecule⁻¹·d⁻¹ (*29*)). Additionally, higher atmospheric net long-range transport fluxes of terbuthylazine are favored by the decrease in particle-associated deposition flux in the emission zone (36–54°N, see Figure 2B). In the temperate zone, Φ has approximately the same value with both model versions due to aerosol composition, relative humidity, and chemical properties. Therefore, similar k_{eff} for degradation, rain washout and diffusion are found in this zone with both model versions. Particle-associated deposition, however, is decreased due to the decrease of the particle deposition velocity in the two-particle-size ppLFER approach (group 1A, see above). In all other zones, deposition processes are increased due to the higher concentration in the atmospheric compartment, and the higher particle-bound fraction.

Generally, the removal process that limits the overall residence time in air is the key factor that determines if the long-range transport is increased or decreased by a higher particle-associated fraction (Φ) of the chemical. For SOCs that are resistant to degradation by hydroxyl radicals, such as PCB180, particle-associated deposition processes determine the atmospheric long-range transport, whereas for more reactive chemicals that are present in the gas phase,
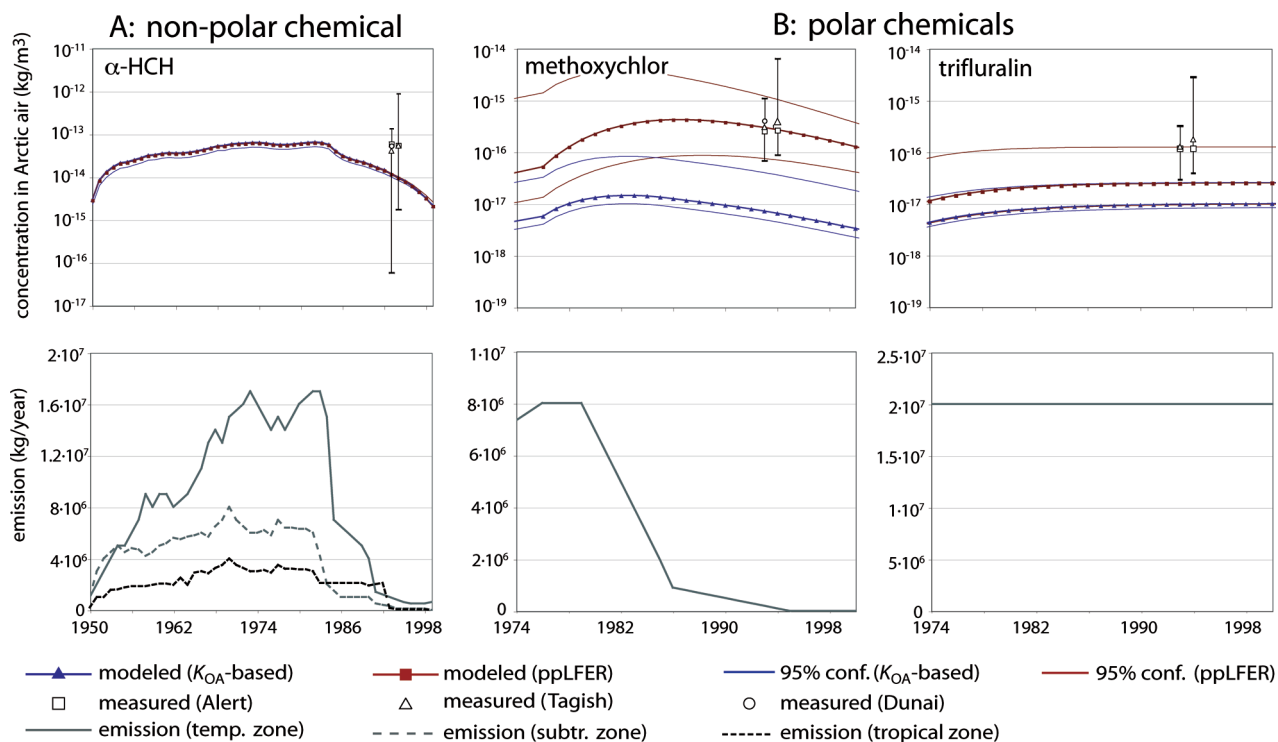
FIGURE 3. Top: measured contaminant concentrations in air at three different locations in the Arctic (Alert, Tagish, Dunai) and modeled concentrations from CliMoChem (ppLFER version) in the Arctic zone. A: α-HCH, B: methoxychlor and trifluralin. Measurement ranges and 95% confidence intervals, based on uncertainties of gas-particle partitioning, are given. Bottom: estimated historical emissions of the three chemicals.

degradation in air is the controlling process. All investigated current use pesticides (CUPs) showed a higher Φ with the ppLFER model version in most regions of the model. Because CUPs generally are relatively reactive with hydroxyl radicals in air, the net long-range transport molar fluxes of all CUPs examined in this study is increased with a higher Φ. This effect is not always visible if only the atmospheric spatial range (R_a) is considered, because R_a as an indicator of long-range transport potential is not very sensitive to changes in concentrations in remote zones if the dominating part of the chemical's mass remains in the emission zone. However, inspection of the concentration values shows that concentrations of all polar pesticides are higher in the Arctic air by a factor of 5−100 if the ppLFER model is used. Below, we compare measurements of concentrations of CUPs in the Arctic with our model results to search for empirical evidence supporting this model result.

Comparison with Field Data for Concentrations in the Arctic. The field data used for comparison with results from the CliMoChem model have to meet two important criteria: (i) emission data for the selected chemicals have to be publicly available, and (ii) the measurements have to include polar semivolatile chemicals, for which the most marked differences between the models can be expected (see above). These requirements are fulfilled by the data reported by Halsall et al. (30). Halsall et al. measured atmospheric concentrations of several organohalogen pesticides, including well-investigated compounds such as α-HCH, but also the polar herbicide trifluralin and the DDT substitute methoxychlor at different locations in the Arctic. Measurements were performed in 1993 and 1994 and yearly averaged concentrations in air were reported (30). We ran the K_{OA}-based and the ppLFER versions of CliMoChem for all three chemicals to calculate the concentrations in Arctic air. Geographically resolved emission data for α-HCH used as input to the model were taken from Wania et al. (31, 32). For methoxychlor and trifluralin we compiled emission data from various literature

sources (33–37). Detailed information about the emission estimates used here is provided in section 4 of the Supporting Information. Uncertainty ranges in the measured concentrations represent the temporal variation during the field measurements by Halsall et al. (30). In Figure 3, the average, maximum, and minimum values of the concentrations measured in air are shown. Ranges of model results represent 95% confidence intervals based on the uncertainties of the gas-particle partition coefficient, K_P. The modeled confidence intervals are derived from Monte-Carlo simulations, as described by Götz et al. (10).

For α-HCH, the modeled and measured concentrations in Arctic air agree within the ranges of the measured data, independent of the selected aerosol parametrization (Figure 3A). α-HCH is a relatively volatile chemical (Φ between 0.001 and 0.07, depending on the latitudinal zone), and therefore, there is a small range of uncertainty in model results due to uncertainty in the description of sorption to aerosols. The low influence of the aerosol model is consistent with the results for R_a obtained with a generic peak-emission, which are similar for both aerosol approaches (see Figure 1).

For the more strongly sorbing compounds, trifluralin and methoxychlor, marked differences between the K_{OA}-based and ppLFER model versions are found. In both cases, the modeled concentrations obtained with the K_{OA}-based aerosol model versions are lower than those from the ppLFER version. The lower concentration in Arctic air observed in the K_{OA}-based model version is due to the lower value of Φ in most regions and to the higher deposition velocities of the K_{OA}-based aerosol model. The modeled concentrations of trifluralin and methoxychlor in Arctic air from the ppLFER version of CliMoChem show better agreement with measured concentrations than the K_{OA}-based model version (Figure 3B). This result is in agreement with earlier studies showing that the K_{OA}-based aerosol sorption approach may underestimate sorption of polar compounds to aerosols (10, 11).

Degradation of Surface-Bound Chemicals. In the air, the most important degradation process for organic chemicals is reaction with hydroxyl radicals (*29, 38*). The modeled rate constants of hydroxyl radical degradation depend substantially on the assumption whether particle-bound chemicals are degraded or not. In multimedia models, it is often assumed that particle-bound chemicals are shielded from hydroxyl radicals and thus not degraded (*24, 39*). Under environmental conditions, it is likely that the frequency of collisions between hydroxyl radicals and surface-bound molecules is lower than for the gaseous molecules, and that reaction rates are reduced by partial shielding by the aerosol particle. However, for some chemicals it has been reported that the surface-bound fraction is degraded under laboratory conditions (*40*). Furthermore, aerosol studies show that the aerosol surface is partially oxidized by hydroxyl radicals and ozone under environmental conditions (*41*).

It is, however, not possible to derive reaction rate constants for aerosol-bound chemicals from these studies. Therefore, we evaluate the influence of our assumption that particle-sorbed chemicals are shielded from reaction with hydroxyl radicals by comparing our default scenario to an alternative scenario. In this alternative scenario we assumed the same second-order rate constant for reaction with hydroxyl radicals applied to surface-bound chemicals as in the gas phase. A detailed assessment of this scenario is presented in section 5 of the Supporting Information. Generally, including degradation of surface-bound chemicals leads to lower concentration in air for chemicals with a relatively high degradation rate constant, such as most CUPs. The modeled concentration of methoxychlor in Arctic air is lower by about a factor of 4 than with the default assumption, but is still within the variability of the measurement results presented in Figure 3B. The concentration of trifluralin in Arctic air is decreased by about a factor of 3 and is below the lower bound of the measured concentrations in Arctic air. However, assuming complete accessibility for hydroxyl radicals probably overestimates degradation. If an accessibility of 50% is assumed, trifluralin concentrations in Arctic air are still within the range of the measurements.

Environmental Significance and Recommendations for Multimedia Models. Generally, adopting the ppLFER-based gas-particle partitioning approach impacts calculated long-range transport potential and concentrations in remote regions for polar chemicals, whereas nonpolar chemicals are less affected. In generic multimedia models, such as The Tool and ChemRange, even polar chemicals show only small increases in long-range transport (below factor 1.1) if the ppLFER model version is used. Therefore, either gas-particle partitioning approach can be used in generic models to screen chemicals for their persistence and long-range transport potential (LRTP). However, our results indicate that the LRTP of some polar chemicals may be underestimated by generic multimedia models relative to nonpolar chemicals at the screening stage. In more detailed fate assessments of polar chemicals after the screening stage, we recommend using a spatially resolved multimedia model including a ppLFER approach for gas-particle partitioning.

In models with region-specific information, such as CliMoChem, there are considerable differences of LRTP between the K_{OA}-based and ppLFER-based model versions. Particularly, concentrations of polar CUPs in Arctic air are markedly higher in the ppLFER model version. The higher chemical concentrations in air calculated with the ppLFER model version for polar CUPs are in good agreement with field data. Modeled concentrations in Arctic air depend particularly on (i) the assumed emissions and (ii) atmospheric degradation. To make the agreement between measured concentrations and the K_{OA}-based model version better than for the ppLFER-based model version, global emissions would

have to be higher by about a factor of 100 for methoxychlor and a factor of 20 for trifluralin, which is unlikely (see Supporting Information, section 4). We find better agreement between measurement data and model results with the ppLFER version if no degradation of particle-surface bound chemicals is assumed. We believe that degradation of surface-bound chemicals by hydroxyl radicals is likely to be slow relative to degradation in the gas-phase because (i) it is likely that collisions with hydroxyl radicals are less frequent on the surface due to steric shielding by the aerosol particle and (ii) because collisions that do occur may not result in reaction if the potentially reactive part of the chemical is bound to the aerosol surface and thus inaccessible (*22*).

Our findings indicate a need for experimental measurements in two areas. First, a current limitation of the ppLFER approach is the availability of measured solvation parameters and limited accuracy of estimation programs such as ABSOLV (*42*) for complex chemicals. To use ppLFER-based models for a broad range of chemicals, more experimental data are needed. Second, for SOCs only few measured data are available for degradation in the gas-phase and even fewer for degradation on natural aerosol surfaces. For most SOCs, rate constants for degradation by hydroxyl radicals currently have to be estimated with the Atmospheric Oxidation Program (*43*). To reduce the uncertainty of these estimates, more measurement data of atmospheric degradation rate constants of SOCs are needed.

If the necessary chemical property data are available, the ppLFER based gas-particle partitioning model is a promising approach and has clear advantages for modeling the environmental fate of polar chemicals compared to K_{OA}-based approaches.

Supporting Information Available
Chemical properties of the investigated chemicals; aerosol composition data; emission data for α-HCH, methoxychlor and trifluralin; concentrations of methoxychlor and trifluralin in air in a scenario with degradation of the surface-bound chemicals. This information is available free of charge via the Internet at http://pubs.acs.org.

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