The significance of the grasshopper effect on the atmospheric distribution of persistent organic substances

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[1] Slowly degradable, semivolatile organic compounds (SOCs) may undergo more than one volatilization-transport-deposition cycle through the atmosphere (multi-hopping). The significance of this process for the potential for long-range transport (LRT) is addressed for the first time. We use a multicompartment model which in turn is based on a general circulation model. The results suggest that both transport by single-hopping and multi-hopping contribute significantly to LRT of DDT and γ-HCH (lindane) and to accumulation in high latitudes. A larger fraction of the molecules transported by multi-hopping than of the molecules transported by single-hopping is deposited to the world's oceans. Multi-hopping prevails in the boundary layer far from the source regions. However, single-hopping contributes an almost equal amount to the deposition of DDT and γ-HCH in the Arctic. **Citation:** Semeena, V. S., and G. Lammel (2005), The significance of the grasshopper effect on the atmospheric distribution of persistent organic substances, *Geophys. Res. Lett.*, *32*, L07804, doi:10.1029/2004GL022229.

1. Introduction

[2] Semivolatile organic compounds (SOCs) may undergo more than one cycle through the atmosphere (multi-hopping or 'grasshopper effect'), because their vapor pressure is such that ambient temperatures allow for atmospheric condensed as well as gaseous states and low degradability prevents them from rapid breakdown at the ground (land or ocean) upon atmospheric deposition. The potential for several volatilisation-transport-deposition cycles makes the global environmental exposure particularly difficult to assess. Unlike in the case of single-hopping pollutants, such as the classical air pollutants (e.g., sulfur dioxide), it is not only the spatial and temporal emission patterns, the atmospheric oxidants distribution and the actual weather which determine the distribution and fate, but, additionally, the ground conditions and their spatial and temporal variabilities i.e., the retaining capacity influenced by temperature, water availability and organic matter content come into play. Furthermore, also the spatial substance usage patterns may contribute to the horizontal and vertical gradients of the substances' dispersion. The role of these various influences on distribution and fate remains to be elucidated.

[3] It has been hypothesized that accumulation in cold environments ('cold condensation') and large-scale fractionation of similar substances are controlled by the substance's vapor pressure [*Wania and Mackay*, 1993]. It is well established that large-scale atmospheric transport to high latitudes is quite efficient. E.g., in high latitudes of the northern hemisphere the 'Arctic haze' phenomenon is caused by rapid transport (within a few days in late winter and early spring) of polluted air from mid latitudes into the European Arctic [*Shaw and Khalil*, 1989].

[4] Global distribution of chemicals was studied by multimedia (multicompartment) models which account for the volatilisation tendencies of SOCs and for the retaining capacities of ground compartments under simplifying scenarios, such as temporally invariant and/or zonally averaged temperatures, depositions and transport efficiencies [*Scheringer and Wania*, 2003, and references therein]. The meridional gradients predicted are consistent with the cold condensation hypothesis. As the statistics and geographic distribution of transport patterns are not captured by these models, the grasshopper effect can better be addressed by a multicompartment model which encompasses an atmospheric transport model.

2. Methodology
2.1. Model Description and Substance Properties

[5] We used for the first time a multicompartment model which comprises an atmosphere general circulation model (AGCM), to study the large-scale transport and distributions of SOCs. The processes in the model have been described previously [*Lammel et al.*, 2001; *Semeena and Lammel*, 2003]. Ground compartments (soil top layer and vegetation surfaces) and the ocean surface mixed layer are coupled as single-layer compartments to the AGCM. Inter- and intra-compartmental mass exchange processes of SOCs comprise volatilization, transport, atmospheric wet and dry deposition, transfer to the deep sea, dissolution in cloudwater, and partitioning to aerosol particles (adsorption only, following Junge). Air-sea exchange is parameterized following the two-film model. The depth of the ocean mixed layer is spatially resolved and seasonally varying. SOC transfer to the deep sea is represented as consequence of the seasonal variation of the mixed layer depth: The substances dissolved in the lower part of the mixed layer are considered to be lost to the deep sea when the mixing depth decreases in spring [cf. *Lammel et al.*, 2001]. Suspended particulate matter in ocean is neglected. For the here reported simulations the model was used with the AGCM ECHAM, version 5 [*Roeckner et al.*, 2003] and with modifications regarding dry deposition of gaseous molecules (now resistance scheme) and the aerosol module (now

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Table 1. Physico-Chemical Properties of the Compounds Used[a]

	γ-HCH	DDT
Water solubility (298 K) [mg l^{-1}]	7.4	3.4×10^{-3}
Enthalpy of solution ΔH_{sol} [kJ mol^{-1}]	27	27
Saturation vapor pressure p [Pa] (298 K)	2.9×10^{-3}	3.4×10^{-5}
Enthalpy of vaporization ΔH_{vap} [kJ mol^{-1}]	115	115
Octanol-water partitioning coefficient K_{ow} [−]	3.98×10^3	1.55×10^6
OH reaction rate constant k_{OH} [cm^3 molec^{-1} s^{-1}]	1.9×10^{-13}	1.0×10^{-13}
$\Delta E/R$ of OH reaction [K^{-1}]	−1710	−1300
Degradation rate in ocean water k_{ocean} [s^{-1}] (298 K)	2.3×10^{-8}	0
Degradation rate in soil k_{soil} [s^{-1}] (298 K)	2.0×10^{-8}	4.1×10^{-9}

[a]Data sources are available through the authors.

dynamic sources, microphysics and size-dependent sinks using a preliminary version of the aerosol sub-model HAM) [cf. *Stier et al.*, 2004].

[6] Two SOCs with very different properties are studied, p,p′-DDT (1,1,1-trichloro-2,2-di-(p-chlorophenyl)-ethane) and γ-HCH (γ-hexachlorocyclohexane or lindane). Because of environmental and human health risks these insecticides were banned from agricultural usage in most countries between 1972 and 1992 (DDT) or many countries since 1990 (γ-HCH). Due to their persistence and LRT potential, these substances are ubiquitous in the global environment, with downward trends in air and other compartments in recent years.

[7] The physico-chemical properties and environmental degradation rates for DDT and γ-HCH for this study (Table 1) are taken from the literature [cf. *Rippen*, 2000; *Klöpffer and Schmidt*, 2001]. DDT has a higher affinity to soils and a lower vapor pressure and water solubility than γ-HCH. As some substance properties are not known, assumptions had to be made on the temperature dependencies (degradation in ocean, soils and on vegetation assumed to double per 10 K temperature increase) and degradation rate coefficients for DDT (0 in ocean, $k_{OH}^{(2)} = 1 \times 10^{-13}$ cm^3/molec/s). No degradation of the aerosol particle-bound molecules and of those dissolved in cloud-water was assumed. The degradation rates in soils were also adopted for the vegetation compartment.

2.2. Model Experiments and Substance Entry

[8] Ten year simulations of a test run and a control run were performed. In the test run, the SOC is precluded from re-volatilisation upon atmospheric deposition to land surfaces or the ocean by setting the re-volatilization rate to zero (single-hopping transport mode). The mass balance is still closed. In the control experiment, the SOC is allowed to undergo re-volatilisation (multi-hopping transport mode) according to substance properties and local conditions (or degradation in the ground compartment). The fraction transported by multi-hopping (FMH) of the SOC is accessible by subtraction of the test run output fields from the control run output fields. The temporal, vertical and horizontal resolutions of the runs were 30 min, 19 levels (within 1000–10 hPa) and ca. $2.8° \times 2.8°$ (i.e., T42), respectively. The scenarios describe 1980 usage of the chemicals. The geographic distributions of the application of the two insecticides in the world's agriculture are based on country-level FAO data scaled with the crop density distribution ($1° \times 1°$) [*Semeena and Lammel*, 2003]. In 1980, γ-HCH and DDT were applied in all major agricultural economies,

except for several European countries, Australia, Brazil, Canada and the US which had phased out DDT by that time. The latitudinal center of gravity (COG, as derived from a zonal distribution) [*Leip and Lammel*, 2004] of DDT application was at 25°N. The global usage patterns of γ-HCH in 1980 can be considered as representative of most globally used pesticides and will not deviate tremendously from the emission pattern of industrial chemicals (latitudinal COG at 39°N). Without a geographic differentiation, we assume application to take place continuously, Jan–Dec over ten years, day and night. The applied amounts are assumed to be distributed 20% to soil and 80% to vegetation surfaces. The SOCs enter the air by later volatilization from vegetation surfaces and soils.

[9] The spatial pattern of volatilization of the substance transported by single-hopping is determined by the usage
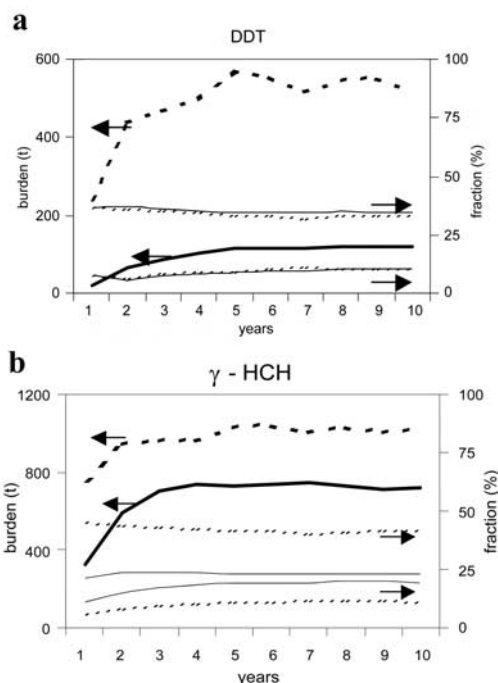

Figure 1. Temporal trends of the global atmospheric burdens (bold lines, left y-axis) transported by multi-hopping (full line) and single-hopping (dotted line) (t) and fractions of these burdens (%) in the boundary layer (750–1000 hPa, upper thin lines, right y-axis) and in the stratosphere (10–100 hPa, lower thin lines, right y-axis). Annual means.
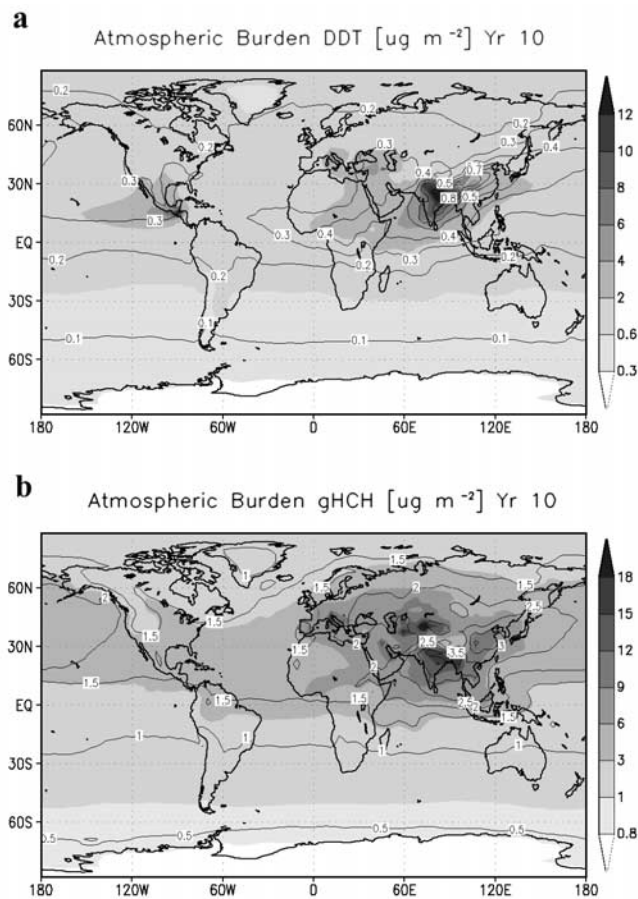
Figure 2. Atmospheric burdens (μg m^{-2}) of the substances transported by multi-hopping or single-hopping (shades) and multi-hopping only (isolines). Mean of the 10th simulated year.

pattern only, while the spatial pattern of volatilization in the control run reflects the superposition of usage, deposition and degradation patterns. The model experiment is artificial as it neglects some temporary SOC reservoirs (land and sea ice, vegetation, except its surfaces) and does not represent any historic situation. Model-predicted air concentrations were compared to observations at remote sites in the 1980s and discrepancies mostly within a factor of three and up to one order of magnitude were found.

3. Results

[10] Due to the fast turnover in the atmosphere and vegetation surfaces compartments, quasi-steady-state is reached in these compartments within 3–6 years, while the soil and ocean compartments are still filling, because of the large capacities and relatively slow turnover. In the 10th year of the control run, 3, 53, and 43% of the global burden of DDT and 7, 40, and 53% of γ-HCH are stored in air, on terrestrial surfaces (vegetation plus soils) and in the ocean surface layer, respectively. The vertical distributions in the atmosphere stabilize after 5 years from the initialization of the simulation (Figure 1). The burden of γ-HCH residing in the stratosphere reaches quasi-steady-state 1–2 years later than in the atmosphere as a whole (Figure 1b). This is

in accordance with the understanding that the age of air is 1–5 years at 100–10 hPa and mostly <1 year below (maxima in high latitudes) [*Manzini and Feichter*, 1999]: 15% of each γ-HCH and DDT are found in heights corresponding to <110 hPa and 41% of γ-HCH and 32% of DDT in heights <300 hPa. There are no photochemical sinks as partitioning to aerosols is almost complete there and we do assume zero reactivity for molecules in the particulate phase. The global mean atmospheric lifetimes are 23 days for DDT and 21 days for γ-HCH. The mean number of completed volatilization-transport-deposition cycles is 1.0 for DDT and 1.8 for γ-HCH. These numbers are low, because a significant fraction does not enter the atmosphere but remains and is degraded at the ground. The reason for the higher hopping frequency of γ-HCH is its higher susceptibility to wash-out in combination with its higher tendency to re-enter the atmosphere (higher vapor pressure and less efficiently sorbed to organic matter in soils than DDT).

[11] Re-volatilisation originates mostly from soil surfaces (50–60%). Allowing for multi-hopping increases air concentrations in particular within and downwind of the source regions (Figure 2). Concentrations more than double (FMH > 0.5) in the boundary layer of the mid and high latitudes (>50°N and >30°S for DDT and >60°N and >20°S for γ-HCH; Figures 3b and 3d). This seems to confirm the common perception that SOCs in the Arctic and Antarctic boundary layer reached there mostly by multi-hopping. However, up to half of the boundary layer reservoirs in high latitudes and for DDT even more of the stratospheric reservoir is fed from single-hops. A quantification of the tendencies of the substance distributions to spread from the areas of application (indicators not detailed here) [see *Leip and Lammel*, 2004] shows that under quasi-steady-state conditions transport by single-hopping contributes more than transport by multi-hopping to this spreading. For the shares of the global atmospheric burdens found in the
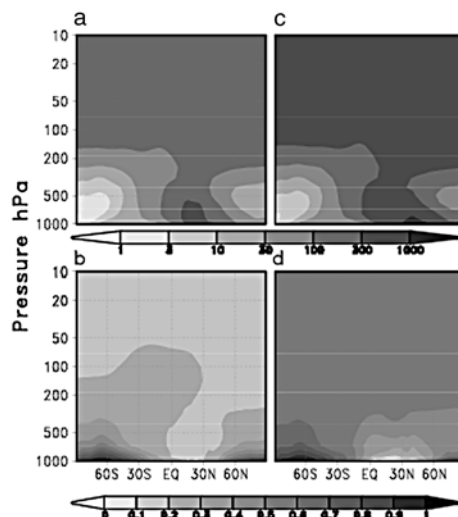

Figure 3. Zonally averaged global atmospheric distributions of (a, b) DDT and (c, d) γ-HCH, (a, c) transported by multi-hopping or single-hopping and (b, d) multi-hopping fraction (FMH). Mean mass mixing ratios in the 10th year.

Table 2. Values Characterizing the Distributions of DDT and γ-HCH in the Global Atmosphere[a]

	DDT		γ-HCH	
	Multi-hopping	Single-hopping	Multi-hopping	Single-hopping
Total burden (t)	120	520	700	1000
Burden in the Arctic/Antarctic (t)	8.2/2.6	22/9.9	63/19	53/14
Burden in the boundary layer/stratosphere (t)	42/18	172/78	161/140	420/110
Total depositions (t)	2310	6540	18990	16010
Deposition to sea (%)	56	37	40	33
Deposition in the Arctic/Antarctic (t)	370/49	347/7.2	3040/33	2720/11
Ratio of depositions in the Arctic and Antarctic over their area share[b]	2.3	0.7	2.1	2.1

[a]Annual sums or mean values for the 10th year. Boundary layer: 750–1000 hPa, stratosphere: 10–100 hPa. Arctic and Antarctic: 66.5°N–90°N, 66.5°S–90°S.

[b]8% of the globe's area is located >66.5°N or >66.5°S.

Arctic or Antarctic it is found that 48% of DDT and 46% of γ-HCH deposited in the Arctic and 13% of DDT and 8% of γ-HCH deposited in the Antarctic are transported by single-hopping (Table 2; for the global depositions, the single-hopping fractions are 46% for DDT and 74% for γ-HCH). Obviously, the polar regions can be reached via single-hops from mid latitudes and equatorial regions. The ratio of the fraction of the depositions to the Arctic and Antarctic and the corresponding area fractions of these regions is >1 − except for DDT transported by single-hopping (Table 2). These values imply that γ-HCH's global distribution is predicted to follow cold condensation when transported by both single- and multi-hopping while DDT's is predicted to follow only when transported by multi-hopping. The world oceans receive a higher share of the depositions of the substances being transported by multi-hopping than by single-hopping (Table 2). In consequence, multi-hopping significantly changes the multicompartmental distribution and tends to increase the total environmental residence time. As any long-lived tracer with sources exclusively at ground level, SOCs are lifted in tropical latitudes into the stratosphere (and higher). 15% of both substances are found in 10–100 hPa. In the height of the tropopause and stratosphere of the mid to high latitudes the FMH is preserved during transport due to lack of mixing from below. Sinking occurs in the polar regions, and in sub-tropical tropopause breaks [e.g., *Manzini and Feichter*, 1999]. A larger fraction of γ-HCH (54% of the substance residing above the 500 hPa level) than DDT (18%) is introduced into the free troposphere due to multi-hopping and then distributed into higher altitudes and poleward. Every precipitation event which an air parcel undergoes, causes some fraction of the SOC, maybe tiny but non-zero, to be washed out and later re-volatilized into then advected air and, hence, contributes to multihopping transport of the substance. Over the continents, this effect is more pronounced for the more water soluble and more readily volatilizing γ-HCH. In addition, the region where multi-hopping dominates γ-HCH transport, unlike in the case of DDT, encompasses large semi-arid areas of central Asia (longer atmospheric lifetime).

4. Discussion and Conclusions

[12] The significance of the grasshopper effect for LRT was studied for the first time. For this purpose we used a multicompartment model with a built-in atmosphere GCM. The model results suggest that both atmospheric transport by single-hopping as well as multi-hopping significantly contribute to the LRT of DDT and γ-HCH and, in particular, to the transport from low and mid latitudes to the Arctic and Antarctic. However, we are aware that the predicted FMH is subject to the choice of processes captured by the parametrisations of mass exchange at the ground. For instance, the FMH would be higher if volatilisation from soil would capture bioturbation and it would be lower if vegetation-to-air transfer would include transport from inside the leaf to its surface. In the boundary layer, the multi-hopping molecules prevail only close to the ground in the mid to high latitudes – where all field studies which focused on the 'global distillation' and 'cold condensation' mechanisms took place so far [see *Wania and Mackay*, 1993, and references therein]. Above, the FMH is expected to be high in the case of substances which are more water soluble and more volatile (high vapor pressure) (such as γ-HCH) and low for opposite properties (such as DDT).

[13] In a quantitative sense, the results are limited to the two SOCs and the very usage patterns studied, because SOC's fate on large spatial scales (including its tendency to undergo more than one volatilization-transport-deposition cycle) depends strongly on both the substance properties [*Beyer et al.*, 2000] and the location and time of entry [*Leip and Lammel*, 2004]. Furthermore, the LRT potential may be overestimated as the atmospheric lifetime in general and in the free troposphere is not well known for SOCs, because gas-particle partitioning is not well understood and we assumed gas-particle partitioning to be explained by adsorption only and zero degradability of particle-bound molecules. Any other parameterization of the gas-particle partitioning (e.g., accounting for absorption into the organic matter matrix) or non-zero photochemical degradability of the particle-bound molecules would lead to enhanced degradability and, in turn, reduce the spatial range.

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