EFFECTS OF VARIOUS SCENARIOS OF ENTRY OF DDT AND γ-HCH ON THE GLOBAL ENVIRONMENTAL FATE AS PREDICTED BY A MULTICOMPARTMENT CHEMISTRY-TRANSPORT MODEL

Shamsudheen Semeena and Gerhard Lammel

Max Planck Institute for Meteorology, Hamburg, Germany

SUMMARY

Various scenarios of DDT and γ-HCH global emissions of the years 1970-1990 have been used to study the sensitivity of the multicompartmental fate of these substances towards location and mode of entry during the first two years upon entry. A multicompartment chemistry-transport model with 3.75°*3.75° horizontal resolution has been used, based on an atmospheric general circulation model.

γ-HCH is expected to be the more mobile but less persistent substance. Persistence in the total environment, $\tau_{overall}$, ranged from 1.5-1.8 years for the DDT and from 0.6-1.2 years for the γ-HCH scenarios. Compartmental distributions and residence times were found to be strongly influenced by the scenario of entry. Emissions in the tropics rather than in mid latitudes and application to vegetation rather than to the soil tend to enhance the mobility and to limit the persistence.

The changing geographic application pattern of DDT in 1970-1990, which was caused by the phasing out in many countries during this period, went along with significant changes in the environmental fate of DDT: the number of completed atmospheric cycles ('hops') increased and the residence times in the ground compartments decreased correspondingly. The north-south shift in the application pattern, which occurred in this time period, was expected to have given rise to increased dispersion over the globe.

KEYWORDS: Multicompartment modelling, environmental fate, long-range transport potential, mode of entry, persistent organic pollutants, air pollution.

INTRODUCTION

Research on multicompartmental xenobiotics in the environment is motivated by fundamental interest and by transboundary regulatory needs. Much less than chemical transformations and mass exchange processes between phases of the same compartment (e.g., atmospheric and aquatic chemistries), we understand the mass exchange processes between compartments and how substance properties interfere. As a consequence of adverse effects on the organism-level in aquatic and terrestrial ecosystems and furthermore, stimulated by risks for human health mediated through the food chain risks from persistent xenobiotics need to be managed [1, 2]. This in turn demands in first place for criteria to classify substances according to their environmental exposure. Exposure in time and space is predictable in principle as being the result of the substance physico-chemical properties, its usage patterns and the geospheric transport patterns, both in time and space [3, 5]. Models which are georeferenced and capable to reproduce the transports on global scale have been hardly used so far [6, 7].

With simulations of the environmental fate upon various scenarios of pesticide application, we address and aim to quantify the sensitivity of long-range transport and compartmental distribution (hence, total environmental persistence) towards time, location and mode of entry. We selected two persistent organic pollutants which undergo long-range transport (e.g., Iwata and Baily [8, 9]), the insecticides DDT (1,1,1-trichloro-2,2-di-(p-chlorophenyl)-ethane) and γ-HCH (γ-hexachlorocyclohexane), which are both subject to regulations according to international chemicals legislation (UNEP Stockholm POPs convention, POPs protocol of the UN-ECE LRTAP convention, besides other). These two chemical substances differ considerably in their properties, however, DDT is merely volatile, merely water soluble and lipophilic, while γ-HCH is considerably volatile, water soluble and only moderately lipophilic. This is the first effort to study the environmental fate of these compounds on the global scale with a transport model.

METHODS

Model structure

We used a four-compartment (air, soil, vegetation, ocean) global dynamic model which is based on a general circulation model of the atmosphere (19 vertical levels; ECHAM4 [12, 13]). Transports occurred only in the atmosphere. Soil, vegetation and the ocean mixed layer were represented as two-dimensional compartments (no vertical resolution). The soil's vertical dimension was not specified, yet the maximum soil water depth is georeferenced. The vegetation is represented as surface only - no uptake, but application, deposition and (re-)volatilisation. The depth of the ocean mixed layer is spatially resolved and seasonally varying and was based on the results of a run of a general circulation model of the ocean [14]. Cloud processing, dry and wet deposition and tropospheric chemistry of gaseous and particulate trace substances including simple cloudwater chemistry and cloudwater acidity is represented [15]. Parameterisations used to describe the intra- and intercompartmental processes of mass exchange and conversion are listed in Table 1. These have been recently described in detail [7]. The physico-chemical properties of substances and degradation data have been taken from Moltmann et al. [16] and Finizio et al. [17].

Some of these data are in particular uncertain as they are based on various reported values which significantly differed from each other, or even had to be estimated. For example, no hydroxyl reaction rate coefficient of DDT has ever been measured; only one value for degradation of DDT in the ocean was reported as halftime of 56 days, which, given the many findings of DDT in ocean water in remote areas, may rather reflect an upper estimate than a best guess.

Emission data

We used no prescribed emissions but prescribed agricultural applications of the insecticides to vegetation and soil, while the emissions into air were determined by local weather and day-time, or from application areas, or as re-emission upon atmospheric deposition.

The DDT and γ-HCH application distributions used were taken from a data set of global agricultural usage of DDT and γ-HCH, which we compiled for the years from 1947 to 1990. γ-HCH was entered with the usage of technical HCH (15%) or lindane (99%). These data were based on statistical data regarding insecticide consumption in agriculture which were reported country-wise to FAO [29] and on other published data [30-33]. The countrywise data were scaled with the intensity of the cropland distribution within the country and distributed over the global grid space. 1°*1° cropland distribution data [32, 34] had been used for this purpose. The extrapolation would systematically suppress small-scale isolated cropland areas, which are represented in the 1°*1° distribution but are too small

TABLE 1
Features of intra- and intercompartmental mass exchange and conversion processes.

Process	Process description	Parameter representation
Partitioning between gas-phase and atmospheric particulate matter, θ	Assumed to be determined by absorption into organic matter, empirically based on the octanol-air partition coefficient, K_{oa} [1] [18] prescribed spatially and temporally variable aerosol concentrations	Diagnostic
Chemical degradation in the atmosphere.	Reaction with hydroxyl radical, similar in the gaseous and particulate-bound state; prescribed spatially and temporally variable oxidant concentrations [19]	Prognostic
Degradation in soils, in vegetation and in the ocean	Overall first-order rates, assumed to double per 10 K temperature increase [2]	Prognostic
Partitioning in soils	Phase equilibrium in 3-phase soil system [20], temperature dependent, soil hydrology represented by bucket model [12]	Diagnostic
Volatilisation from soils	Loss of gaseous substance from the soil pore space using an empirically derived rate from pesticide application studies [20]	Prognostic
Volatilisation from vegetation	Loss of gaseous substance from plant surfaces using an empirically derived rate from pesticide application studies [21]	Prognostic
Flux of trace substances from the ocean to the atmosphere	Two-film model [22], temperature dependent	Prognostic
Atmospheric dry deposition	Fixed deposition velocities vdep for gaseous molecules [3] [23] and according to the particle mass median diameter for particulate-bound molecules	Prognostic
Atmospheric wet deposition	In-cloud and below-cloud scavenging from stratiform and convective clouds according to water solubility (gaseous molecule) and wet-scavenging coefficient, ε [4] (particulate-bound molecule)	Prognostic

[1] $c_{gas} / (c_{gas} + c_{particulate}) = \theta = [1 / (K_p\ c_{TSP}) +1]^{-1}$; $\log K_p = 0.55 * \log K_{oa} - 8.23$; particulate matter concentration c_{TSP} (cm^{-3}), gas-particle equilibrium constant K_p. Temperature dependence of θ assumed to be similar to polycyclic aromatic hydrocarbons [24].

[2] according to recommendations [25] besides others; $k_{soil} = k_{vegetation}$; in the case of γ-HCH the contribution of the hydration reaction to the degradation in ocean water is accounted for, too [26]

[3] dry deposition velocities are 1.3 and 1.38 cm s^{-1} over land and 0.08 and 1.38 cm s^{-1} over sea for DDT and γ-HCH, respectively (based on [27, 28])
[4] ε = 1.0 and 0.1 for in-cloud and below-cloud scavenging, respectively

to be represented in the grid. In such cases, grid cells were added manually into the field (e.g., one grid cell was added in Saudi Arabia, one in Oman and a few in North African countries). Due to the overlapping of grid cells over more than one country, the data of those countries were added together and allocated to the country which occupies the largest portion of the grid cell. For example, the data of Gambia and Guinea Bissau were added to these of Senegal, these of Trinidad and Tobago to those of Venezuela, these of Luxembourg to those of Germany, the Malta-data to the data of Italy, and these for Austria were distributed equally among those of Switzerland, Slovenia, Italy and Czechoslovakia. Zero values were given to those countries where no data was available or countries where the values were too small (e.g. Brazil in the case of DDT and Japan and Mexico in the case of γ-HCH). Linearly interpolated data was used to fill the gaps in cases of countries where data was missing in between the years.

For this simulation, we have used data of the years 1966-1970 and 1976-1980 to produce a 5-year mean data for DDT experiments (DG7020, DG8020; Table 2). For γ-HCH experiments we used the data of 1990 for DDT (DG9020) and of 1980. For the application of DG9020, only India was to mention, whereas the amounts applied in other countries were assumed to be negligible.

TABLE 2
Scenarios of DDT and γ-HCH entry into the environment (for geographic distributions cf. Fig. 1).

Substance	Scenario acronym	Geographic coverage	Year	Application flux (t a^{-1})	Months of non-zero emission	% of applied amounts received by soil / vegetation
DDT	DG7020	Global	1970	35326	Feb.-Oct. [1]	20 / 80
	DG8020		1980	7669		
	DG9020		1990	4118		
γ-HCH	LG8020	Global	1980	18061	Feb.-Oct. [1]	20 / 80
	LN8020	30°N-90°N		12673		
	LN8060					60 / 40
	LT8020	90°S-30°N		5388		20 / 80

[1] cf. Fig. 2

a)

b)

c)

d)

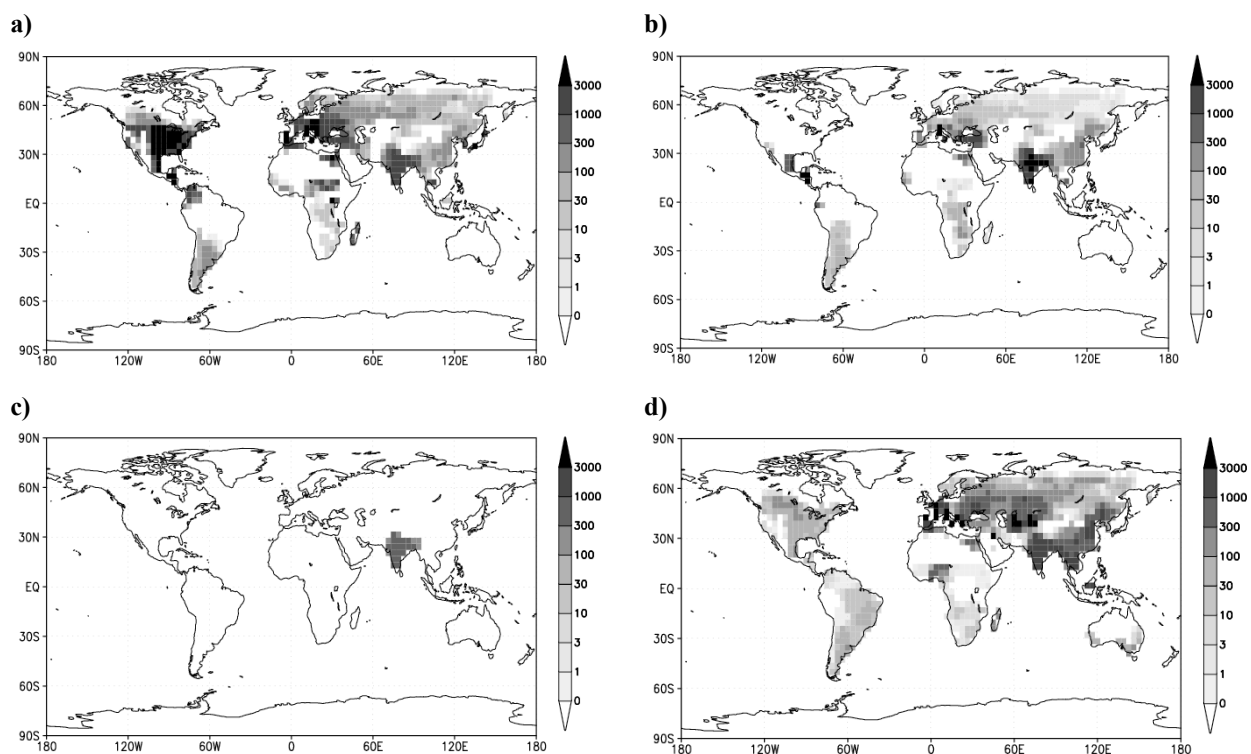**FIGURE 1 - Geographic distributions of applications of DDT scenarios
(a.) DG7020, (b.) DG8020, (c.) DG9020) and (d.) γ-HCH (LG8020) (t a^{-1} gridcell^{-1}).**

a)

b)

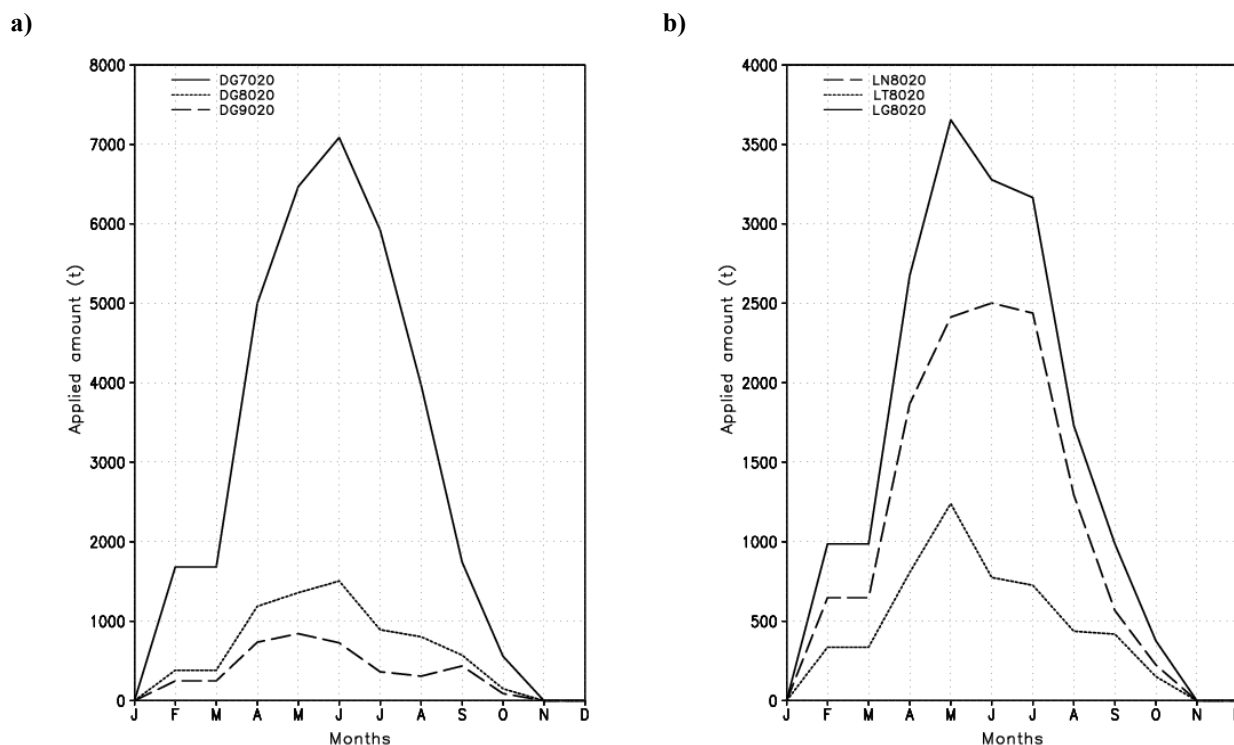**FIGURE 2**
**Temporal application patterns of (a.) DDT and (b.) γ-HCH scenarios
to the global vegetation and soil (t). The pattern is identical everywhere.**

Model run initialisation

The model was run with a 30-min. time step and a ca. 3.75°*3.75° (T30) horizontal resolution in all compartments. Model runs were performed with 15 years of physical spin-up, i.e. simulation of atmospheric dynamics prior to the entry of the substances. Then, from February until October of the 16th year, the substances were introduced into receptor compartments assuming seasonally variable applications (Table 2, Fig. 1 and 2). The application pattern remained the same in the consecutive years of the model runs, and we reported on results of the second year of application (Section 3). The second year upon entry was the first one with the substances being in the environment throughout the entire year (e.g. January - December). The various scenarios were exposed to the identical climate.

We selected the scenarios to address questions on the environmental fate of the substances. We were particularly interested in the fate of the same substance when changing over time (DG scenarios) and in changing as a function of geographic entry (LN8020 vs. LT8020) or of mode of entry (LN8020 vs. LT8060). We further were

interested in the fate of two substances under the same scenario of application (at least time and mode of entry-DG8020 vs. the sum of the scenarios LN8020 and LT8020; G, N and T stands for global, northern and tropic latitudes respectively). The amount and distribution of γ-HCH applied globally is given by the sum of the scenarios split at 30°N: LN8020 + LT8020 = LG8020. The temporal application pattern in the simulations was not uniform, but limited to the daylight hours with no rain in order to come closer to agricultural reality. Furthermore, a seasonality was included with maximum in April to July: each 20% of the amounts that were applied in one year have been distributed over the daylight hours of April-July, and each 5% over the daylight hours of February, March, August and September. Non-zero precipitation during a day-light time step (30 min.) in each grid cell caused a delayed application during the next 'dry' day-light time step in the same grid cell. Due to this rule, the application in the model world was from February-October (Fig. 2)

RESULTS

Compartmental distributions and residence times

The compartmental burdens and intercompartmental mass fluxes of DDT upon 1980 emissions are shown in Fig. 3a. According to the entry scenario, in total 7665 t a^{-1} of DDT entered the environment through application to the vegetation (spraying on crop plants) and to the soil as 80:20. Upon volatilisation from vegetation and soil, the atmosphere and, upon subsequent deposition processes, the ocean as well experienced uptake in the period of study (second year upon entry). The atmosphere experienced the largest turnover: 17311 t a^{-1} of the received substances (volatilisations, sum of arrows to the atmosphere) correspond to an annual average burden of 246 t, i.e. the annual mean atmospheric residence time would be $\tau_{atmosphere} = 0.0142$ a (ca. 5 days) in steady state. Steady state is not fulfilled however, but there is a compartmental net uptake of 81 t a^{-1} between January and December. The residence time, limited by all compartmental first-order loss processes under non-steady state condition, can be derived from the mass conservation equation:

$$\Delta c/\Delta t = E - c / \tau$$

$$\tau = c / (E - \Delta c/\Delta t)$$

When c is the compartmental burden, E the sum of import fluxes to the compartment and $\Delta c/\Delta t$ the net uptake (81 t a^{-1}), then $\tau_{atmosphere}$ is 0.0143 a. Most of it leaves the atmosphere through the deposition processes while the chemical degradation accounts only for ca. 2.5 % of the losses (405 t a^{-1}). The atmospheric turnover exceeds the input into the environment by 109%. That means that the average DDT molecule undergoes 2.09 cycles of emission into and deposition from the atmosphere (number of completed hops). The turnover rates in other compartments were lower with corresponding mean residence times of 0.30 a, 0.50 a and 0.020 a (ca. 7 days) in the soil, vegetation and in the ocean surface mixed layer respectively (see also Table 5). The compartmental residence times are influenced by the corresponding halftimes towards degradation, ca. 6 a in soil and vegetation (assumed to be equal [35]) and 56 d in the ocean (values for 273 K). A significant fraction (39%) of the entered substance is depleted (sum of arrows to degradation, 2908 t a^{-1}) and it is predicted that this happens mainly in the ocean (1748 t a^{-1}). Another significant fraction, in total 62% (sum of compartmental uptakes, 4761 t a^{-1}), is added to the compartmental burdens. The residence time with respect to the sum of all decreases - i.e., the overall environmental residence time limited by the sum of all first-order final decreases during a period Δt, $\tau_{overall}$, can be derived accordingly from the mass conservation equation with c now representing the sum of the burdens in air, soil, vegetation and ocean surface layer (7510 t for DDT under DG8020), E the flux of entry into the multicompartmental system (application, 7665 t a^{-1}), and $\Delta c/\Delta t$ the change of burden of the multicompartmental system during Δt (from December-January, 3527 t a^{-1}). Only first-order final decreases are given in the system. This calculation delivers $\tau_{overall} = 1.8$ a as the annual mean value in the second year upon entry. Various but similar definitions have been used by modelling approaches for $\tau_{overall}$ [36].

The accumulation of DDT in the total environment is predicted to be concentrated in the soils and vegetation. These compartments take up 1250 and 2150 t a^{-1} respectively, while the atmosphere and the ocean only take up 888 and 473 t a^{-1}. A net uptake of 62% of the entered amount, far from zero, reminds us that DDT in its second year upon entry is of course still far from compartmental equilibrium. Another substance's fate simulated is the loss to the deep sea: in the model, this loss is given by the seasonal narrowing of the ocean surface mixed layer and means a final removal from the mass exchanging compartments. This process was the fate for 16% of the substances (1234 t a^{-1}).

In the case of γ-HCH environmental fate upon 1980 emissions (Fig. 3b), the atmosphere experienced the largest turnover too: 47292 t a^{-1} of received substances corresponds to an annual average burden of 413 t, which means an annual mean atmospheric residence time (t_{air}) of 0.009 a (ca. 3 days). This shorter lifetime compared to ca. 5 d of DDT is reflecting the differences in hydroxyl reaction rate coefficients: $1.0 * 10^{-13}$ cm^{-3} molec^{-1} s^{-1} for DDT (estimated) and $1.9 * 10^{-13}$ cm^{-3} molec^{-1} s^{-1} for γ-HCH [37], and in susceptibility to wet deposition, which is larger for the more water soluble γ-HCH. The effect of the latter difference is more significant: despite an assumed more rapid chemical degradation, an even higher fraction of atmospheric γ-HCH was lost through the deposition processes than in the case of DDT, with the chemical degradation accounting for only ≈ 2.9% of the γ-HCH atmospheric decrease (43863 t a^{-1}).

The mean residence times of γ-HCH in the soil, vegetation and in the ocean surface mixed layer are 0.40 a, 0.065 a and 0.32 a respectively. For $\tau_{overall}$, we found 0.93 a - i.e. ca. half of the corresponding value for DDT. The compartmental residence times correspond with degradation rates of $2.9 * 10^{-8}$ s^{-1} in soil and vegetation (assumed to be equal), and with $3.7 * 10^{-9}$ s^{-1} in the ocean (at 273 K). A significant fraction (42%) of the entered substance was depleted and it is predicted that this occurs mainly in the soils (20%). The rest is added to the environment and is almost evenly distributed between air, soil, vegetation and ocean.

For γ-HCH as well as for DDT, it was found that the burdens are subject to a significant seasonality in all compartments: in the global oceans surface mixed layer, only 633 t γ-HCH and 25 t of DDT were more stored at

the end of the year compared to the beginning of the year (numbers are marked with Δ, Fig. 3) despite an annual mean uptake of 3933 t and 473 t respectively. This is not surprising regarding the temporal application pattern and the compartmental residence times. It indicates that the seasonal amplitude must have been very significant. The seasonalities of the soils and vegetation burdens are less pronounced. The differences were caused by the geographic distributions and seasonalities of DDT emissions, depositions and temperatures in these compartments.

a)
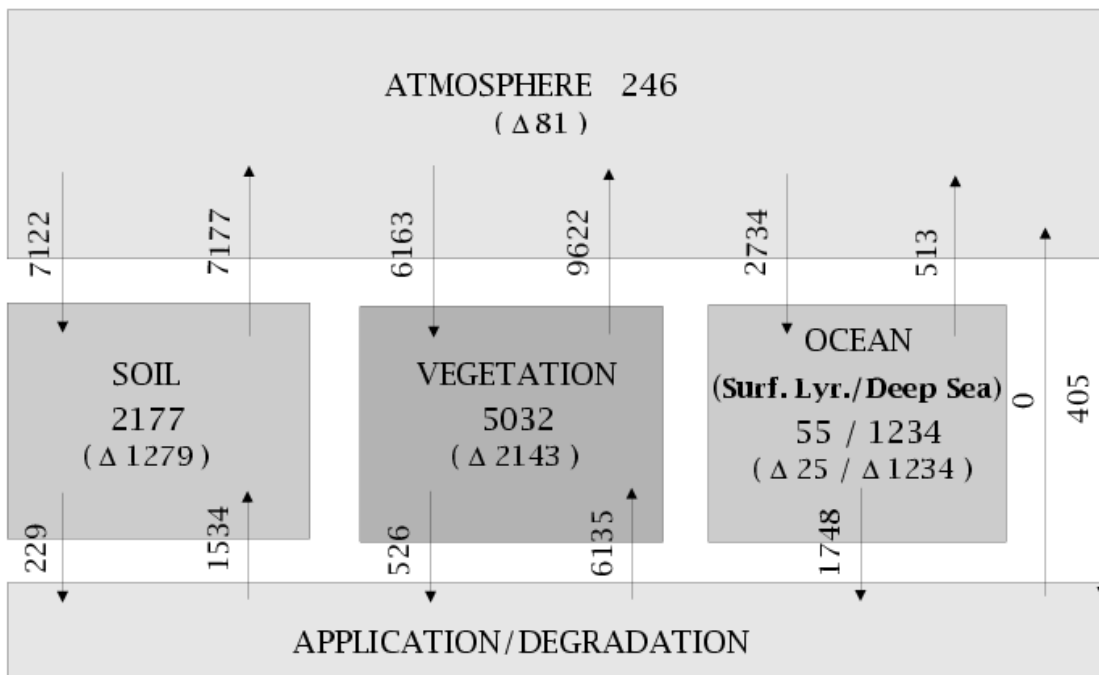
b)
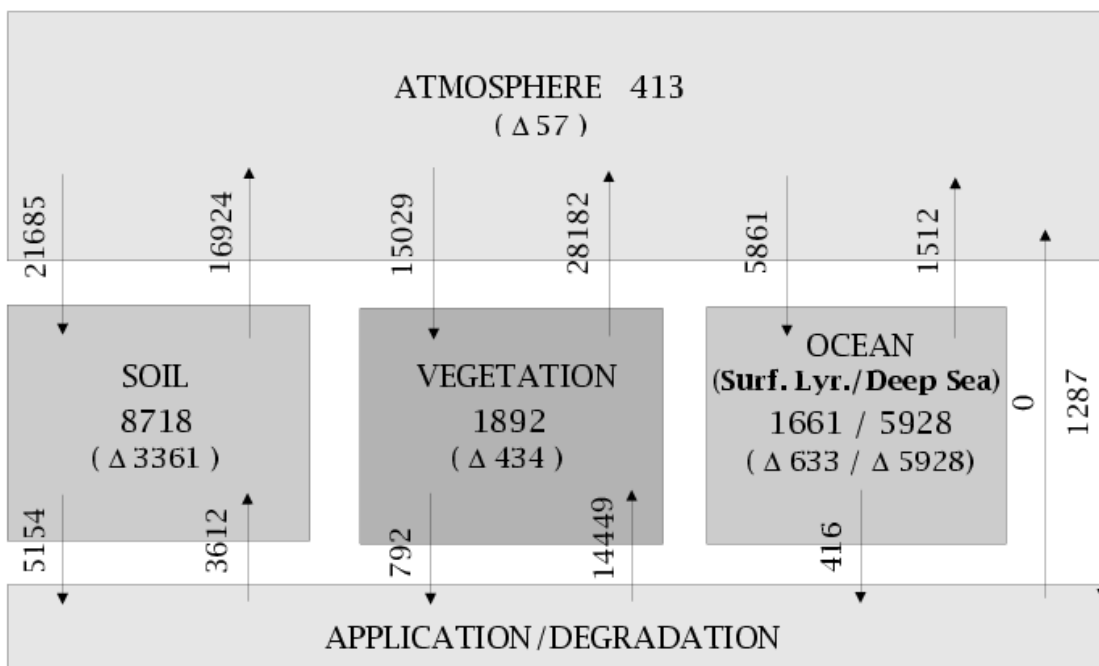
FIGURE 3 - Global environmental fate of (a.) DDT and (b.) γ-HCH upon 1980 applications (scenarios DG8020 and LG8020): mass exchange fluxes between compartments (arrows), and compartmental budgets in the form 'burden (Δ change)'. All values are given in t or t a⁻¹ and are annual means except values of change (Δ), which are defined as December mean - January mean.

TABLE 3 - Compartmental distributions: annual mean burdens in the second year upon entry. Cf. Table 2 for amounts entried into the environment.

Substance	Scenario	Total environment (t)	Air (%)	Soil (%)	Vegetation (%)	Ocean mixed layer (%)	Deep sea (%)
DDT	DG7020	54512	1.5	21.4	48.2	0.4	28.5
	DG8020	8744	2.8	24.9	57.6	0.6	14.1
	DG9020	4582	3.7	19.7	58.3	0.7	17.7
γ-HCH	LG8020	18611	2.2	46.8	10.2	8.9	31.9
	LN8020	13589	1.8	52.4	11.6	6.4	27.8
	LN8060	13641	1.4	61.6	8.4	5.2	23.4
	LT8020	5022	3.5	31.7	6.2	15.8	42.8

TABLE 4 - Compartmental residence times (d) and mean number of completed atmospheric cycles ᵃ (numbers in brackets) in the second year upon entry.

Substance	Scenario	Total environment	Air	Soil	Vegetation	Ocean mixed layer
DDT	DG7020	547	4.4 (1.8)	146	188	9.5
	DG8020	662	5.2 (2.1)	108	181	7.4
	DG9020	538	5.4 (2.6)	65	150	6.7
γ-HCH	LG8020	341	3.2 (2.4)	145	24	116
	LN8020	397	2.8 (2.2)	168	30	120
	LN8060	437	2.7 (1.9)	169	33	119
	LT8020	231	3.9 (2.7)	91	11	112

ᵃ Derived as: atmospheric total deposition flux divided by total application flux

Most of the substances were stored in soils and vegetation, 69-82% of DDT and 38-70% of γ-HCH under the various scenarios (Table 3). Only for LT8020 the ocean is more important reflecting the smaller land area fraction south of 30°N. The soils are more prominent for γ-HCH and the vegetation is more prominent for DDT. The difference in vapour pressures (0.034 and 2.9 mPa at 25°C) caused γ-HCH to volatilise more rapidly from the vegetation surfaces than DDT, in such a way that the residence time of DDT upon application and later on atmospheric deposition into this compartment was longer. The large fraction stored in soils is somewhat contra-intuitive, because the lipophilic tendencies of DDT and γ-HCH (K_{ow} = $1.55 * 10^6$ and $3.98 * 10^3$, respectively) would suggest DDT to be more sticky to soils. However, it is not only the lipophilicity which prevents volatilisation from soil but also solubility in soil water. γ-HCH is water soluble to a significant extent while DDT is practically insoluble (s = 7.4 and 0.034 mg l⁻¹ at 25°C). The change in mode of entry from vegetation to soil - from 80:20 to 40:60 - reduced the fraction of γ-HCH stored in vegetation upon applications in 1980 from 11.6 to 8.4% and enhanced the fraction stored in soil from 52.4 to 61.6%. In total, 52 t γ-HCH or 0.4% more were in the system. The corresponding change in total environmental residence time increased by 10%; 1.2 instead of 1.1 a (Table 4).

The fractions distributed over atmosphere and ocean were 2.8 and 14.7% in the case of DDT (DG8020), and 2.2 and 40.8% in the case of γ-HCH (LG8020). These numbers reflect again the large difference in water solubility. In consequence, the atmospheric wet deposition for γ-HCH is more important, because the ocean receives more and re-volatilisation from the ocean is suppressed and vice versa for DDT. The higher partitioning of γ-HCH to the ocean is furthermore related to a slower degradation in water.

A change in mode of entry of γ-HCH, i.e. shift of application split to vegetation and soils from 80:20 to 60:40, affects the substance mobility as volatilisation from vegetation occurs more frequently than from (moist) soils: the combined volatilisation from soils and vegetation reduced by 14%; less substance is transferred into the atmosphere (burden is 1.4 instead of 1.8%) and into the ocean (burden is 28.6 instead of 34.2%, cf. also Fig. 4b). The mean number of atmospheric cycles completed reduced from 2.2 to 1.9 (Table 4). The predicted overall effect is a by 10% increased environmental residence time. This result

is not influenced by the compartmental degradation rate as we assumed; the degradation of the substance in soil and vegetation obey the same time-law.

Persistence of γ-HCH is strongly influenced by the location of entry - northern mid latitudes (LN8020) vs. tropics (LT8020): the warmer tropics push more of the substance into the atmosphere (Table 3). Therefore, substance's mobility is enhanced and persistence is suppressed, because the atmosphere is this compartment with the most rapid degradation. The residence times in the ground compartments are reduced, because we assumed enhanced degradation resulting from higher temperatures. The effective residence time in air is, however, longer in the tropics due to a larger number of completed atmospheric cycles, 2.7 instead of 2.2 (Table 4). Obviously, the higher tendency to volatilise in the warmer climate over-

compensates for the more effective atmospheric sink processes in the tropics (precipitation frequency).

The seasonal patterns of the atmospheric burdens (Fig. 4a, c) reflect the superposition of the seasonalities of the application (maximum around June, Fig. 2) and of the air temperature, which drives volatilisation from the ground surfaces and obviously caused a delay of about one month. As a consequence of the short residence time, degradation in the atmosphere (Fig. 5a, c) is in phase with the burden. The same applies for the DDT burden in the ocean mixed layer with the consequence, however, that the time needed for atmospheric transport and deposition and slower degradation to the application pattern is delayed by one more month ($k_{air}^{(0)} = 5.2*10^{-8}$ s^{-1}, $k_{ocean}^{(0)} = 5.9*10^{-7}$ s^{-1} for average conditions, i.e. $c_{OH} = 0.52 * 10^6$ cm^{-3} and $T_{ocean} = 15°C$; Fig. 4b, 5b). Together with the absolute
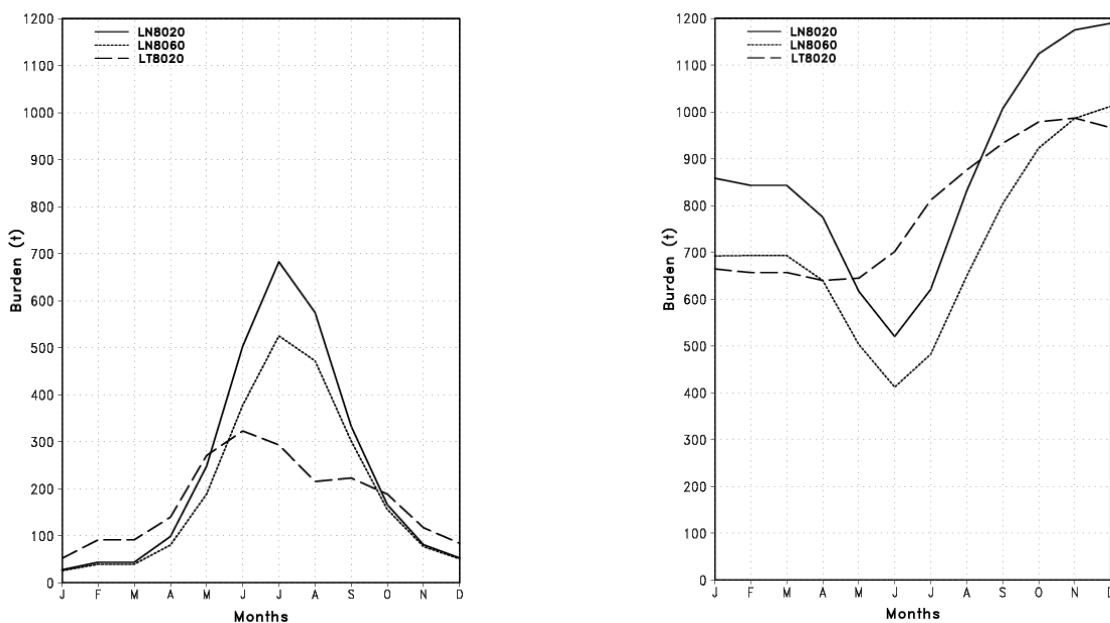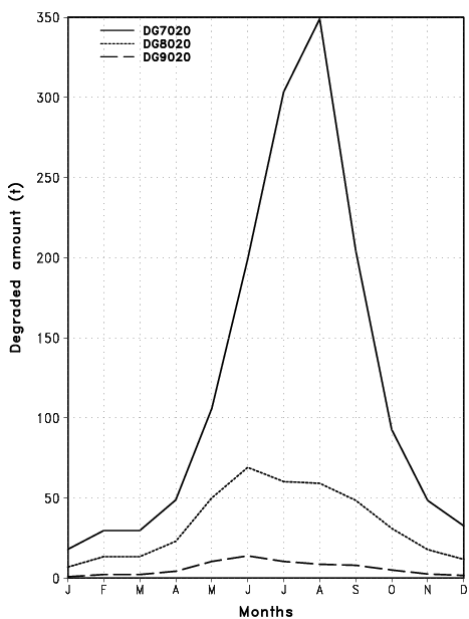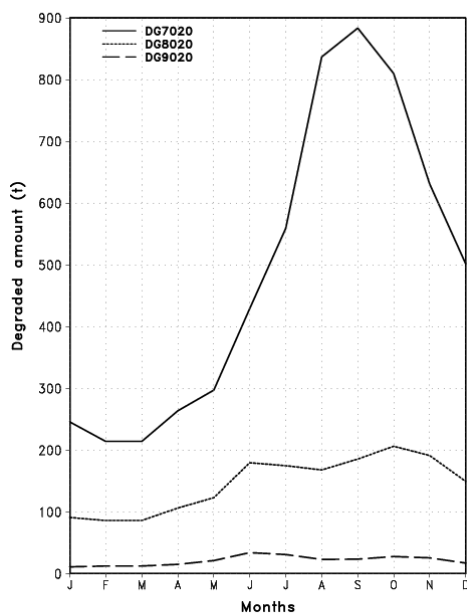
a)

b)

c)

d)

a)

b)
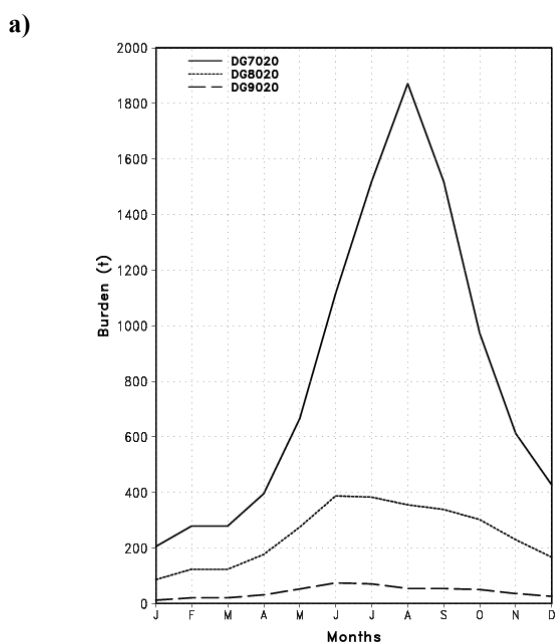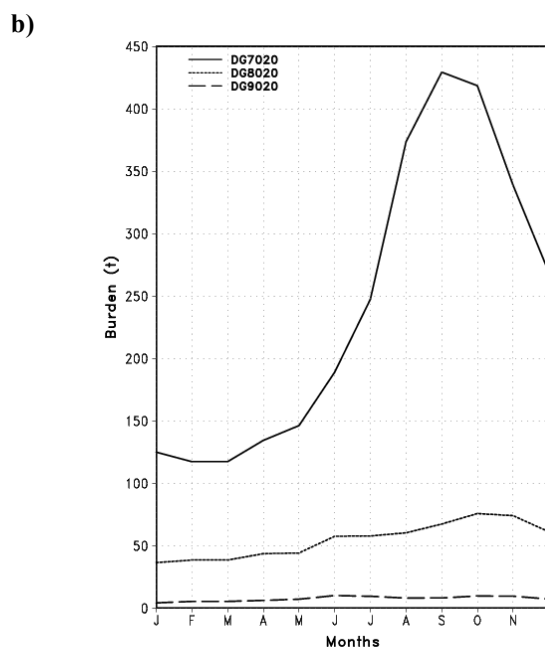
FIGURE 4
Seasonal variation of compartmental distributions: monthly mean values of the burdens in (a., c.) the atmosphere
and (b., d.) the ocean surface mixed layer of (a., b.) DDT and (c., d.) γ-HCH under the various application scenarios.
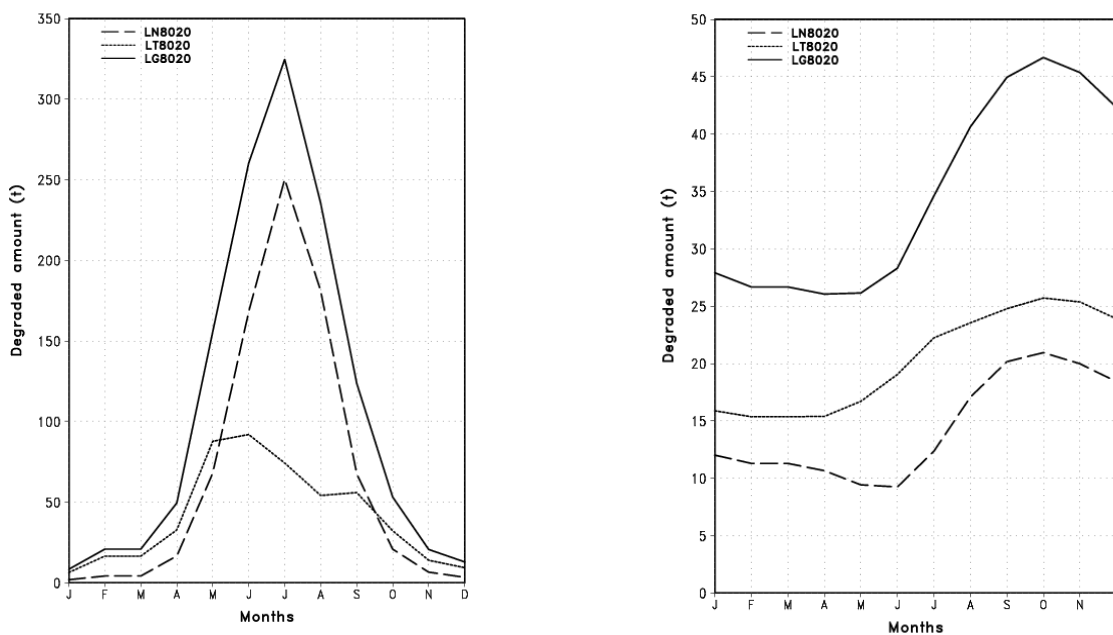

c)

d)

FIGURE 5 - Seasonal variation of compartmental losses: monthly mean values of the (a., c.) atmospheric and (b., d.) oceanic degradation of (a., b.) DDT and (c., d.) γ-HCH under the various application scenarios (kg s^{-1}).

amounts, the annual amplitudes of the atmospheric and oceanic DDT burdens are also expected to shrink from DG7020 to DG8020 and to DG9020 (Fig. 4a). This is because the sink terms do balance the smaller sources more rapidly (emission upon application and deposition for the atmosphere and the ocean). There is also a difference between the annual maximum in air of the emissions from August, 1970, in comparison to the emissions from June, 1980-1990. This was caused by the change of the gravity centre of the applications from northern mid-latitudes in 1970 (44°N, see Table 5) to the subtropics in 1980-1990

(29°-27°N): the atmospheric degradation is more efficient in the tropics than in the mid latitudes (24-h and annual mean hydroxyl radical, OH, concentrations are $0.70 * 10^6$ and $0.46 * 10^6$ cm^{-3} respectively).

The same is seen for the atmospheric γ-HCH burden upon emissions in the mid latitudes and in the tropics (Fig. 4c): northern and tropical scenarios are out of phase due to the difference (level and seasonal variations) in OH.
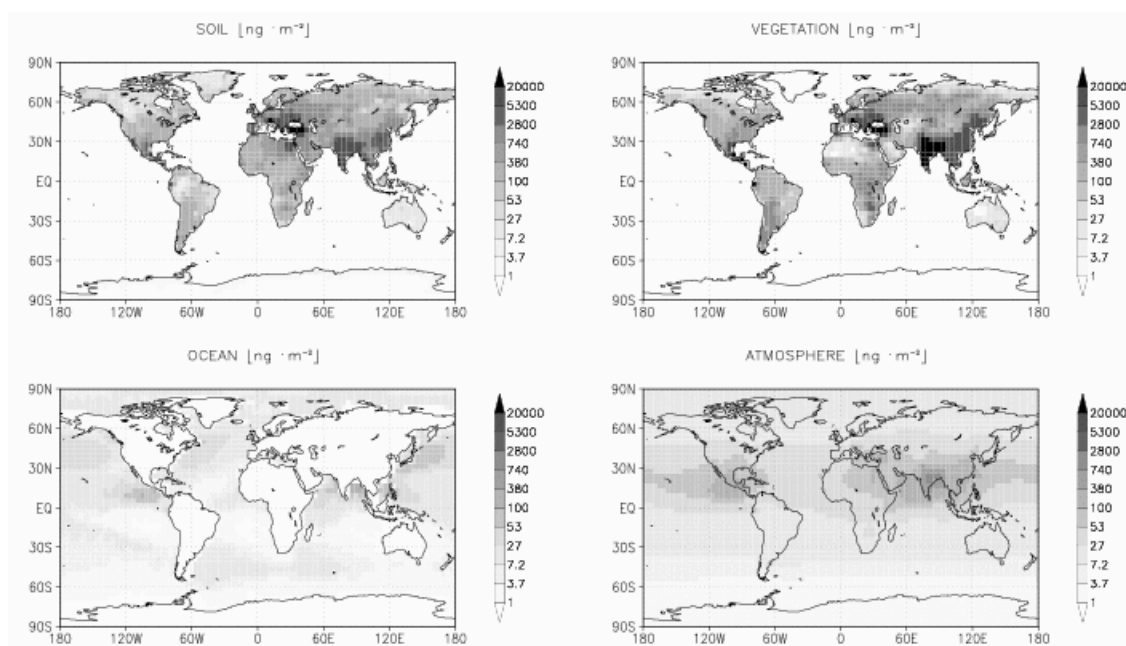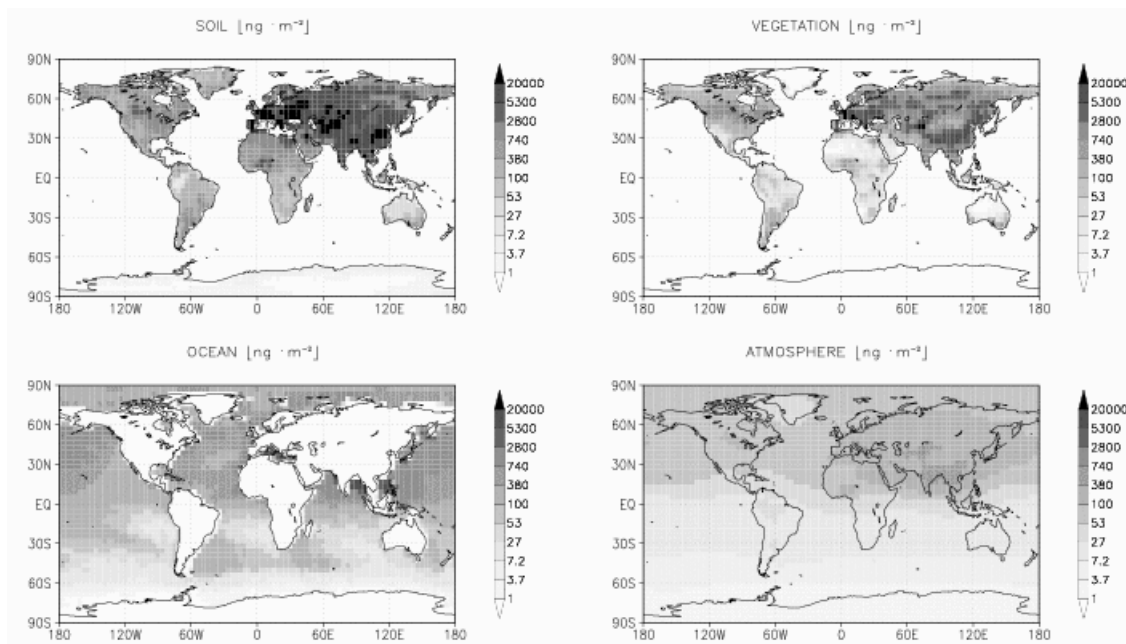
FIGURE 6
Geographic distributions in the individual compartments for (a.) DDT (DG8020)
and (b.) γ-HCH upon 1980 applications (LG8020). Annual mean values (ng m⁻²).

supply. A second and smaller seasonal maximum in September under the LT8020 scenario indicates the impact of a southern winter (mid latitudes) and of a precipitation minimum in the area of the most dense γ-HCH application in the tropics (i.e. India). The oceanic burden of γ-HCH is dominated by the superposition of atmospheric deposition, volatilisation loss and loss to the deep sea: degradation accounts for only a small fraction (Fig. 2b, 5d). The more volatile γ-HCH is lost significantly to the air in the warm season. In the LT8020 scenario, the seasonal warming of the tropical and southern hemispheric waters is in average less pronounced and is out of phase with the application pattern. This results in a steady uptake throughout the year with a cease in the southern summer months (Fig.

4d). In phase with the temperature variation, is the depth variation of the surface mixed layer: the thinning of the mixed layer occurs in spring (the depth goes down by half in the northern hemisphere between February and July) and is most pronounced in mid to high latitudes (maxima at 50-70°).

Geographic distributions

The geographic distributions demonstrate the long-range transport potential of the substances studied. The distribution in soil resembles most closely the applications (Fig. 1b, 1d). But also soils far from the areas of application are affected such as North America including the Arctic archipelago and Greenland, desert regions of North Africa, Central Asia and Australia, and northern parts of South America (in the case of DDT, which was not applied there; Fig. 1b). As to DDT, the distribution in vegetation was distorted in the direction of prevailing winds in some regions: Southeast and East Asia are obviously largely impacted by substance application in India, and applications in Europe affect most parts of European Russia. The patterns of the two substances' distribution in the oceans are similar with high concentrations in oceanic downwind regions of North America (western parts of the North Atlantic), of East Asia (western and central areas of the North Pacific), of southern parts of South America and Africa, as well as in the seas adjacent to the Indian subcontinent and Southeast Asia. As DDT was not applied in the USA and Canada according to DG8020, the oceanic DDT concentration maximum in the western North Atlantic is remarkable. A DDT plume stretching out from Central America into the eastern Pacific, and a γ-HCH plume in the Atlantic ocean west of the western African coast can obviously be explained by transport in trade wind systems from upwind source areas. The atmospheric distributions (Fig. 6) reveal that the substances are globally distributed reaching also the Arctic, but not the Antarctic. The total environmental distribution of DDT is shown in Fig.7; the DDT and γ-HCH zonal distributions in Fig. 8.

Sequential distributions upon applications of DDT in 1970, 1980 and 1990 indicate that significantly less must have been contributed to the total environmental burden of DDT during the more recent years. This more recently introduced substance is, however, despite the limited region of application still globally distributed and contributing, for example, to contamination of East Africa, the Mediterranean and as far as northern parts of South America, the eastern USA and even the Arctic (Fig. 7c). As a general conclusion, it is expected that the DDT load, which enters areas adjacent to application areas (e.g. Scandinavia in 1980, Myanmar and Thailand in 1990), is expected to be almost as high or even higher (Ethiopia and Somalia in 1980) as in the source areas of the region (central Europe, India and central Africa, respectively; Figures 1 and 5).

a)

b)

c)
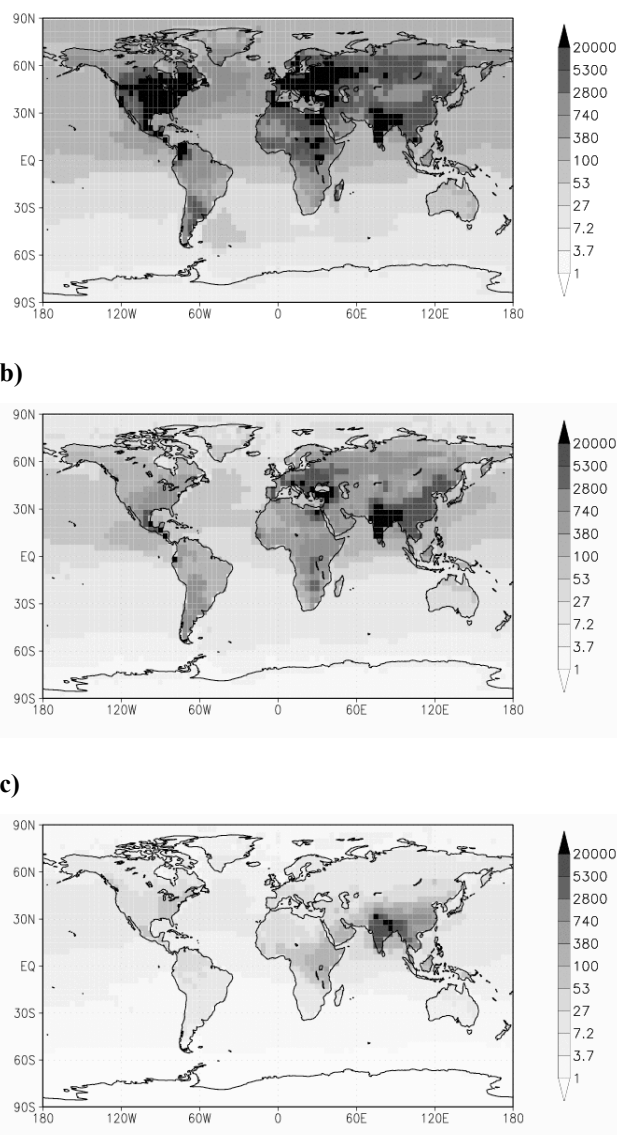
FIGURE 7
Geographic distribution of DDT in the total environment for (a.) 1970, (b.) 1980 and (c.) 1990: annual mean values (ng m^{-2}), application scenarios DG7020, DG8020 and DG9020 respectively.

Zonal distributions

We were in particular interested in migrations of the distributions in north-south direction (Fig. 8, Table 5), because the observations of xenobiotics in the Arctic and Antarctic are the most striking evidence in terms of persistence and long-range transport.

Of course, the burdens of the substances after some time elapsed since entry are zonally wider distributed than upon application. For the second year upon entry, we found that the distances between the 5%ile and 95%ile of the cumulative zonal distributions increased by 43% (from 34.1° to 48.7°) in the case of DDT (DG8020) and by 82% (from 48.0° to 88.4°) in the case of γ-HCH (Table 5). 5% of the total environmental burden of this insecticide is ex-

pected in latitudes north of 61°N while 5% were ap- plied north of 50°N. The transports made even the centre of gravity to shift somewhat towards south (≈ 3°). This com- parison reveals γ-HCH to be the more mobile substance on global scale. γ-HCH applied > 30°N contributes signifi- cantly to the burden of this substance as far south as ≈ 10°N and, in opposite direction, γ-HCH applied south of 30°N is expected to reach even > 60°N (Fig. 8b). 3.4% of γ-HCH found in the Arctic (total environment, > 66°N) originates from south of 30°N. The widening of the zonal distribution was less pronounced for DDT upon the 1970 emissions (from 40.0° to 44.7°, i.e. by 12%) which were centred significantly more north (40.9° under DG7020, but 26.9° under DG8020). The zonal distributions are very different, not only in level but also in shape and number of maxima (Fig. 8a). The northern tailing of the DG8020 zonal distribution is going beyond 60°N (Fig. 8a). The

dispersion of the DDT plume originating from India (DG9020) is still quite significant in absolute numbers (24.6°) as well as relative to actual application upon entry - spread of the zonal distribution by 40%. The model though, predicts DDT also to reach the Arctic. The annual mean near-ground atmospheric concentrations of DDT in the Arctic (> 66°N) are predicted to drop down from 7.3 pg m^{-3} to 0.52 upon DG7020, and to 0.03 pg m^{-3} upon DG8020 and DG9020. These values can be compared with those observed in the Canadian Arctic in 1993-94 (0.14 to 0.16 pg m^{-3}, [10]) and in the European Arctic, Spitsbergen, in 1998 (0.11 to 1.6 pg m^{-3}, [11]). Much of the burden in recent years have been caused to emissions before 1990 but were not simulated. The seasonality predicted for DG9020 compares well with what has been observed in 1993-94 (May to Sept. and Oct. to April: 1.0-1.1 pg m^{-3}) and in 1998 (1.1 pg m^{-3}; predicted value: 1.3 pg m^{-3}).
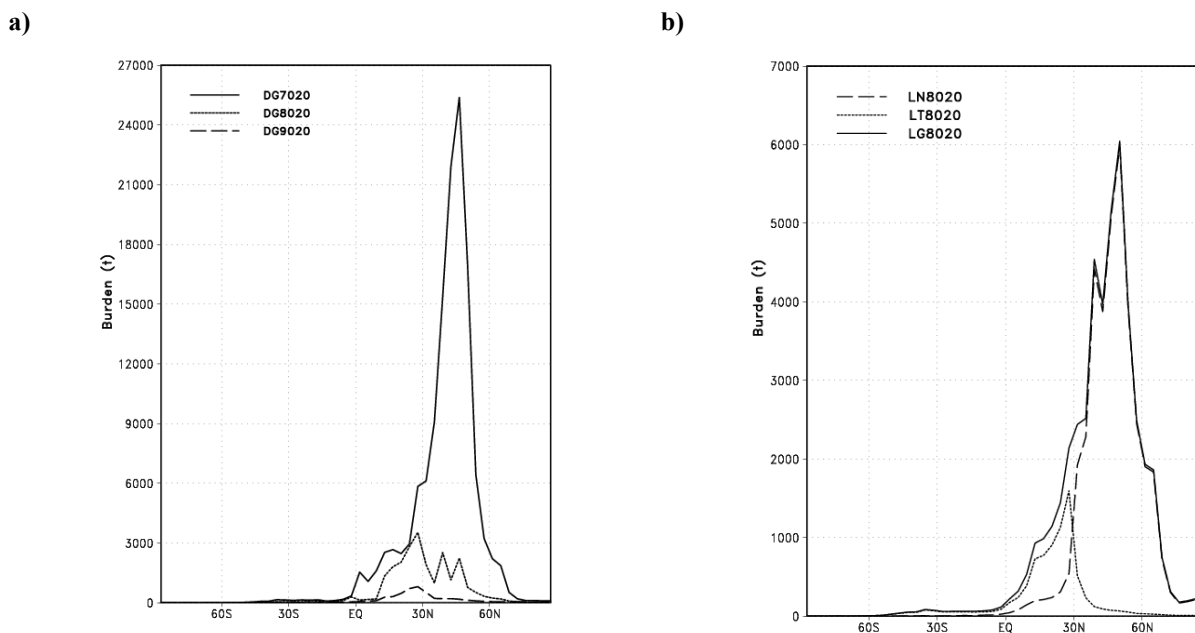
a)

b)

FIGURE 8 - Zonal distributions of the total environmental burden of
(a.) DDT (application scenarios DG7020, DG8020 and DG9020) and
(b.) γ-HCH (LG8020): zonally averaged and annual mean values (ng m^{-2}).

TABLE 5
Characteristics of the latitudinal distributions of the total environmental burden of DDT (application scenarios DG7020, DG8020 and DG9020) and γ-HCH (LG8020): 5, 50 and 95%iles (lat05, lat50 and lat95, respectively) of the cumulative zonal distribution of the geographical 2D projection, running from 90°S to 90°N during the second year (annual mean) and at the time of entry into the environment (in brackets, cf. Fig. 1).

Substance	Scenario	lat05	lat50	lat95
DDT	DG7020	11.6°N (12.4°N)	43.5°N (40.9°N)	56.3°N (52.4°N)
	DG8020	4.6°N (13.9°N)	28.9°N (26.9°N)	53.3°N (48.0°N)
	DG9020	12.8°N (14.8°N)	27.1°N (25.7°N)	37.4°N (33.0°N)
γ-HCH	LG8020	27.4°S (2.1°N)	27.7°N (31.0°N)	61.0°N (50.1°N)

Environmental fate of DDT changing historically

As a consequence of the historic change of the geographic application pattern of DDT, increasingly more of this substance was stored in the atmosphere: from 1.5 to 2.8% in 1970, and to 3.7% in 1980 and 1990 (Table 3). The fraction stored by the ocean was the highest (28.9%) upon emissions in 1970 and lower upon emissions in 1980 and 1990 (14.7 and 18.4%, respectively). The cycling of DDT molecules through the atmosphere increased from 1.8 to 2.1 and 2.6 as completed hops for the average molecule. This tendency corresponds with an increase in atmospheric residence time from 4.4 to 5.2 and 5.4 d. Consequently, the residence times in the ground compartments decreased over time: mean residence times for molecules emitted under the 1970, 1980 and 1990 scenarios were 0.40, 0.30 and 0.18 a in the soil; 0.51, 0.50 and 0.41 a in the vegetation; and 0.026, 0.020 and 0.018 a in the ocean mixed surface layer. The overall environmental residence time (disregarding the storage in deep sea) changed in parallel from 1.5 to 1.8 a and back to 1.5 a.

Such trends are the consequences of the globally prevailing precipitation and large-scale circulation patterns, but above all of the application in different regions and during different time periods; the most significant change of the geographical application pattern from 1970 to 1980 (Fig. 1a, b) is the cease of application in the USA (mostly eastern parts) and in Europe. Most of what has been applied in the USA will be ending up in the Atlantic ocean. In 1990, DDT was applied in India (according to DG9020, Fig. 1c), which experiences precipitation only in the southwestern part from June until September, while the other parts of the country, during the rest of the application period, will stay without precipitation. Precipitation limits most effectively the atmospheric residence time and hence, reduces the fraction of the substance stored in the air. The same process may explain the reduced atmospheric fraction of substances when stepping from 1970 to 1980 emissions: application in relatively dry subtropic areas became more prominent while application in humid temperate climate became less prominent (Fig. 1, Table 5).

CONCLUSIONS

We studied the environmental fate of DDT and γ-HCH during the first two years upon entry into the environment with the focus on the effect of various scenarios of pesticide application. As the amounts entered were the same in consecutive years of the model run and the time periods spanned by the historic usage of the substances studied (starting in the 1940s) were not considered, the scenarios are significantly artificial and do not aim to simulate historic processes. Validation through comparison with observational data is not possible. We neglected ocean transports which are expected to be significant for long-range transport of persistent substances on a time scale of 5-10 years and beyond. The conclusions drawn from the results are limited to the relative effects as being forced by the selected scenarios. As being influenced by the climate, multicompartmental fate is also subjected to interannual variability, an aspect also not covered by this study.

As a more general conclusion, we found that long-range transport and compartmental distribution (hence, total environmental persistence) are significantly sensitive towards mode and location of entry. The influence of the latter could only be appropriately addressed by using a complex transport model. We did not explicitly study the influence of time of entry. We expect however, sensitivity to season and even to day-time of application due to seasonal and diurnal variabilities of atmospheric loss processes, availability of oxidants and precipitation in most regions of the world.

In our simulations, γ-HCH is predicted to be the more mobile but less persistent substance. The difference lies in a factor of two of the total environmental residence time and is however not significant, considering the large uncertainties in data describing the physico-chemical properties of substances. Mobility is obviously determined by the substances' physico-chemical properties, but also by the geographic application pattern: in the warmer tropics, the mobility of substances is enhanced, whereas persistence is suppressed. We assumed a faster degradation in the ground compartments at higher temperatures. The high sensitivity of the multicompartmental fate to the temperature dependence emphasises the need to improve the respective knowledge. We also found that the zonal dispersion of DDT would be more efficient upon application to the subtropics than upon earlier applications that had been centred in the mid latitudes. The mobility of substances and their persistence are also a matter of mode of entry with application to vegetation. The latter favours mobility and decreases persistence of substances rather than soil does.

The so-called long-range transport of substances in the environment is a notion of the changes that geographic distributions of substances undergo from the time of entry under the influence of the geospheric transport. Diffuse sources together with representing areas of entry will be most common, but pointed emissions may occur as well. The change of these distributions and plumes over time is complex and influenced by location, season, daytime, weather and mode of entry. These features have also been addressed by using more generic models, e.g. [38]. Furthermore, the persistence of a substance is also determined by those features. In order to characterise environmental exposure in space and time as a contribution to risk assessment, scenario-specific ranges of values of indicators for long-range transport and persistence have to be allocated to substances. Such indicators should be low-dimensional (ideally numbers), but still be able to cover the complexity of geo- and time-referenced systems.

ACKNOWLEDGEMENTS

REFERENCES

[1] Vallack, H.W., Bakker, D.J., Brandt, I., Brorström-Lundén, E., Brouwer, A., Bull, K.R., Gough, K., Guardans, R., Holoubek, I., Jansson, B., Koch, R., Kuylenstierna, J., Lecloux, A., Mackay, D., McCutcheon, P., Mocarelli, P. and Taalman, R.D.F. (1998) Controlling persistent organic pollutants – what next ? Environ. Toxicol. Pharamacol. 6, 143-175

[2] Steinhäuser, K.G. (2001) Environmental risks of chemicals and genetically modified organisms: A comparison. Environ. Sci. Poll. Res. 8, 120-126

[3] GSF-Projektgruppe - Gesellschaft für Strahlen- und Umweltforschung München, Projektgruppe "Umweltgefährdungspotentiale von Chemikalien" (ed.) (1986) Environmental Modelling for Priority Setting among Existing Chemicals. Ecomed, Landsberg, Germany

[4] Klecka, G., Boethling, B., Franklin, J., Graham, D., Grady, L., Howard, P.H., Kannan, K., Larson, R.J., Mackay, D., Muir, D. and van de Meent, D. (eds.) (2000) Criteria for Persistence and Long-Range Transport of Chemicals in the Environment, SETAC Press, Pensacola, USA

[5] Lammel, G. (2002) Systematische Exploration stoffbezogener Umweltproblematiken - Beispiel Atmosphäre. Umweltwiss. Schadstofforschung 13, 245-253

[6] Koziol, A. and Pudykiewicz, J.A. (2001) Global scale environmental transport of persistent organic pollutants. Chemosphere 45, 1181-1200

[7] Lammel, G., Feichter, J. and Leip, A. (2001) Long-range transport and global distribution of semivolatile organic compounds: A case study on two modern agrochemicals. Report Max Planck Institute for Meteorology No. 324, Hamburg, Germany, 44 pp.

[8] Iwata, H., Tanabe, S., Sakai, N. and Tatsukawa, R. (1983) Distribution of persistent organochlorines in the oceanic air and surface seawater and the role of ocean on their global transport and fate. Environ. Sci. Technol. 27, 1080-1098

[9] Bailey, R., Barrie, L.A., Halsall, C.J., Fellin, P. and Muir, D.C.G. (2000) Atmospheric organochlorine pesticides in the western Canadian Arctic: Evidence of transpacific transport. J. Geophys. Res. 105, 11805-11811

[10] Macdonald, R.W., Barrie, L.A., Bidleman, T.F., Diamond, M.L., Gregor, D.J., Semkin, R.G., Strachan, W.M.J.,Li, Y.F., Wania, F., Alaee, M., Alexeeva, L.B., Backus, S.M., Bailey, R., Bewers, J.M., Gobeil, C., Halsall, C.J., Harner, T., Hoff, J.T., Jantunen, L.M.M., Lockhart, W.L., Mackay, D., Muir, D.C.G., Pudykiewicz, J., Reimer, K.J., Smith, J.N., Stern, G.A., Schroeder, W.H., Wagemann, R. and Yunker, M.B. (2000) Contaminants in the Canadian Arctic: 5 years of progress in understanding sources, occurrence and pathways. Science Total Environ. 254, 93-234

[11] Berg, T., Hjellbrekke, A.G. and Larsen, A. (2000) Heavy metals and POPs within the EMEP region 1998, Report EMEP/CCC No. 2/2000, Norwegian Institute for Air Research, Kjeller, Norway, 94 pp.

[12] Roeckner, E., Oberhuber, J.M., Bacher, A., Christoph, M. and Kirchner, I. (1996) ENSO variability and atmospheric response in a global coupled atmosphere-ocean GCM. Clim. Dyn. 12, 737-754.

[13] Roeckner, E., Bengtsson, L., Feichter, J., Lelieveld, J. and Rodhe, H. (1999) Transient climate change simulations with a coupled atmosphere-ocean GCM including the tropospheric sulfur cycle. J. Clim.12, 3004-3032

[14] Drijfhout, S.S., Heinze, M., Latif M. and Maier-Reimer, E. (1996) Mean circulation and internal variability in an ocean primitive equation model. J. Phys. Oceanogr. 26, 559–580.

[15] Feichter, J., Kjellström, E., Rodhe, H., Dentener, F.J., Lelieveld, J. and Roelofs, G.J. (1996) Simulation of the tropospheric sulfur cycle in a global climate model. Atmos. Environ. 30, 1693-1707

[16] Klöpffer, W. and Schmidt, E. (2001) A multimedia load model for the Baltic Sea. Environ. Sci. Pollut. Res. 8, 180-188.

[17] Moltmann, J.F., Küppers, K., Knacker, T., Klöpffer, W., Schmidt, E. and Renner, I. (1999) Verteilung persistenter Chemikalien in marinen Ökosystemen. Final Report to Federal Environment Agency (UBA), Berlin, Research Project No. 29725528, ECT GmbH, Försheim, Germany, 155 pp.

[18] Finizio, A., Mackay, D., Bidleman, T. and Harner, T. (1997): Octanol-air partition coefficient as a predictor of partitioning of semi-volatile organic chemicals to aerosols. Atmos. Environ. 31, 2289-2296

[19] Roelofs, G.J., Lelieveld, J. and van Dorland, R. (1997) A three-dimensional chemistry/general circulation model simulation of anthropogenically derived ozone in the troposphere and its radiative climate forcing. J. Geophys. Res. 102, 23389-23401

[20] Smit, A.A.M.F.R., Leistra, M. and van den Berg, F. (1997) Estimation method for the volatilisation of pesticides from fallow soil. Environmental Planning Bureau series 2, DLO Winand Staring Centre, Wageningen, the Netherlands

[21] Smit, A.A.M.F.R., Leistra, M. and van den Berg, F. (1998) Estimation mehod for the volatilisation of pesticides from plants. Environmental Planning Bureau series 4, DLO Winand Staring Centre, Wageningen, the Netherlands

[22] Wania, F., Persson, J., di Guardo, A. and McLachlan, M. (2000) The POPCYCLING-Baltic model – a non-steady state multicompartment mass balance model of the fate of persistent organic pollutants in the Baltic Sea environment. Norwegian Institute for Air Research Report No. NILU OR 10/2000, Kjeller, Norway.

[23] Slinn, W.G.N. (1982) Prediction for particle deposition to vegetative canopies. Atmos. Environ. 16, 1785-1794

[24] Pankow, J.F. (1991) Common γ-intercept and single compound regressions of gas-particle partitioning data vs. 1/T. Atmos. Environ. 25A, 2229-2239

[25] TGD (1996) Technical Guidance Document in Support of The Commissions Directive 93/67/EEC on Risk Assessment for the Notified Substances and the Commission Regulation (EC) 1488/94 on Risk Assessment for Existing Substances. European Chemicals Bureau, Ispra, Italy

[26] Ngabe, B., Bidleman, T.F. and Falconer, R.L. (1993) Base hydrolysis of α- and γ-hexachlorocyclohexanes. Environ. Sci. Technol. 27, 1930-1933

[27] Tucker, W.A. (1983) Estimation of dry deposition velocity and scavenging ratio for organic chemicals. In: Precipitation scavenging, dry deposition and re-suspension (Pruppacher, H.R., Semonin, R.G. and Slinn W.G.N., eds.), Vol. 2, Elsevier, New York, pp. 1243-1257

[28] Tucker, W.A. and Nelken, L.H. (1990) Diffusion coefficients in air and water. In: Handbook of chemical property estimation methods (Lyman, W.J., Reehl, W.F. and Rosenblatt, D.H., eds.), American Chemical Society, Washington, pp. 17.1–17.25

[29] FAO - UN Food and Agricultural Organization (1947-1989) Statistical data on insecticide consumption. FAO, Rome

[30] FAO - UN Food and Agricultural Organization (1947-1988) Production Yearbooks. FAO, Rome

[31] WHO - World Health Organization (1989) Environmental Health Criteria – 83. DDT and its derivatives in environmental effects. World Health Organization, Geneva, Switzerland

[32] Li, Y.F., McMillan, A. and Scholtz, M.T. (1996) Global hexachlorocyclohexane usage with 1°*1° longitude/latitude resolution, Environ. Sci. Technol. 30, 3525-3533

[33] Breivik, K., Pacyna, J.M. and Muench, J. (1999) Use of α-, β- and γ-hexachlorocyclohexane in Europe 1970-1996. Sci. Total Environ. 239, 151-163

[34] Li, Y. F. (1999) Global gridded technical hexachlorocyclohexane usage inventories using a global cropland as a surrogate. J. Geophys. Res. 104, 23785-23797

[35] Hornsby, A.G., Wauchope, D.R. and Herner, A.E. (1996) Pesticide Properties in the Environment. Springer, New York

[36] Pennington, D.W. (2001) An evaluation of chemical persistence screening approaches. Chemosphere 44, 1617-1631

[37] Brubaker, W.W., and Hites, R.A. (1998) OH reaction kinetics of gas-phase α- and γ-hexachlorocyclohexane and hexachlorobenzene. Environ. Sci. Technol. 32, 766-769.

[38] Scheringer, M., Wegmann, F., Fenner, K. and Hungerbühler, K. (2000) Investigation of the cold condensation of persistent organic pollutants with a global multimedia fate model. Environ. Sci. Technol. 34, 1842-1850

CORRESPONDING AUTHOR

G. Lammel
Max-Planck-Institut für Meteorologie
Bundesstr. 55
20146 Hamburg – GERMANY

e-mail : lammel@dkrz.de