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Indicators for persistence and long-range transport potential as derived from multicompartment chemistry–transport modelling

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"Capsule": *Multicompartment chemistry–transport models can be used to better assess persistence and long-range atmospheric transport potential.*

Abstract

Total environmental and compartmental residence times as a measure for persistence as well as indicators for long-range transport potential (LRTP) have been derived from global geo-referenced modelling and LRTP is characterized in two geographic directions for the first time. A dynamic multicompartment chemistry–transport model (MCTM) was used to study the fate of the insecticides DDT and α-hexachlorocyclohexane (α-HCH) during the first 2 years upon entry. The indicators for LRTP were defined such as to address the tendencies of substance distributions to migrate ('plume displacement', PD) and to spread into remote areas ('spatial spreading', SS). The indicators deliver values as function of time upon entry. With the aim to address the effect of location of entry on environmental fate, scenarios of emission from the territories of seven countries were studied. It was found that the effect of location of entry on the spatial scale of countries (400–4000 km) is significant for the compartmental distribution and the inter-compartmental mass exchange fluxes (e.g., number of atmospheric cycles, 'hops'). Location of entry introduces uncertainties in the order of a factor of 5 for the total environmental residence time, $\tau_{overall}$, and a factor of 5–20 for *PD* and *SS*. For the 2nd year upon entry into the environment, $\tau_{overall} = 317$–1527 days are predicted for DDT and 101–463 days for α-HCH. The influence of location of entry does affect the substance ranking, i.e. we cannot simply state that DDT is more persistent than α-HCH, but for one scenario studied, application in China, the opposite is predicted. Precipitation patterns proved to be significant, besides other climate parameters, for atmospheric residence time. Integration of the location of entry in chemicals risk assessments is therefore recommended. In general, persistence and some indicators for LRTP, pertinent to their definition, refer to the fate of a large fraction, e.g., 63% ($= 1-1/e$) or 90%, but not the total substance burden. The choice of this fraction may have the consequence of a normative step which defines the spatial and temporal extensions of a related chemicals risk assessment and may affect substance ranking.
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1. Introduction

Many slowly degradable (or 'persistent') organic substances are subject to long-range atmospheric transport. An obvious pre-condition for that is partitioning into air to a significant extent. As degradation of organic molecules in the gaseous state is usually quite rapid (in the order of days, with some exceptions, e.g., the totally halogenated compounds) it is a specific range of vapour pressure which characterizes these slowly degradable organics which are subject to long-range atmospheric transport, i.e., the semivolatile organic compounds (SOCs). These, obviously, partition significantly to more than one environmental compartment (multicompartmental substances). In air they partly partition to the aerosol's particulate phase. SOCs' fate in the environment is a complex and high-dimensional phenomenon, incompletely understood: Compartmental distribution adds to

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Nomenclature

COG	Centre of gravity
d_W, d_E, d_N, d_S	Range of the substance's distribution into the four directions
lat_{05}, lat_{50}, lat_{95}	Characteristic locations: 5, 50 and 95 percentiles of the cumulative zonal distributions
lon_{05}, lon_{50}, lon_{95}	Characteristic locations: 5, 50 and 95 percentiles of the cumulative meridional distributions
LRTP	Long-range transport potential
MCTM	Multicompartment chemistry-transport model
NOH	Number of atmospheric deposition and subsequent re-volatilization cycles (number of 'hops')
PD	Plume displacement
S	Spatial scale
SOC	Semivolatile organic compound
SS	Spatial spreading
ZD	Zonal displacement
ZS	Zonal spreading
ZW	Zonal width
MW	Meridional width

three-dimensional geographic distribution, both variable in time.

While the investigation of a substance's fate is intrinsic to environmental science, the characterization of environmental exposure by indicators is motivated from outside the science: assessment of substances in the context of chemicals and risk politics needs not only to address detrimental effects to the ecosystems and the food chain, but also the spatial and temporal extents of environmental exposure (Korte et al., 1970). Indicators are respective low-dimensional measures (ideally zero-dimensional numbers). In prosecution of the precautionary principle and as suggested by systematic deficiencies of effect-based evaluation procedures substances and emission/usage scenarios should be assessed in terms of environmental threat or hazard (Berg and Scheringer, 1994). Indicators for persistence (P) and long-range transport potential (LRTP) have been introduced and used based on evaluative 0–2 dimensional multimedia mass balance models, (Klöpffer, 1994; Scheringer et al., 2001 and references therein). These models do not aim to describe three-dimensional transport and fate referenced in time and space but are meant to unravel more general aspects and assist substance evaluation e.g., by delivering substance rankings (Wania and

Mackay, 1999). In contrast, more facets of environmental fate are covered by 3D georeferenced multicompartment chemistry–transport models (MCTM). For example, the LRTP can be characterized in three spatial dimensions and as influenced by the location (climate, geographic features), time (daytime, season, historic year) and mode of entry. Persistence and LRTP was hardly addressed using 3D models, so far.

It is the purpose of this study to extend model-based assessment of environmental exposure to multicompartmental substances to geo-referenced 3D models. We use a dynamic (non-steady state), geo-referenced multicompartment chemistry–transport model (MCTM) with high spatial and temporal resolutions (described in Section 2.1), introduce a set of indicators suitable for in principle any SOC and emission/usage scenario (Section 2.3) and characterize the LRTP of two SOCs, DDT (1,1,1-trichloro-2,2-di-(*p*-chlorophenyl)-ethane) and α-HCH (α-hexachlorocyclohexane), for the first time in two spatial dimensions on the global scale (Section 3). Using our MCTM for the study of the multicompartmental fate of DDT and γ-HCH usage in global agriculture it was found (Semeena and Lammel, in press) that location of entry has a significant influence. Therefore, in the present study we include a more systematic analysis of the effect of location of entry.

2. Methods

2.1. Model used

The model used is a MCTM which has recently been applied to the description of the environmental fate of pesticides (Lammel et al. 2001; Semeena and Lammel, 2003). In the present state of model development it comprises atmosphere (3D), vegetation, soils and ocean (each in 2D distribution of single layer boxes). It is based on a general circulation model of the atmosphere, a 'climate model' using 19 vertical levels from 1000 to 10 hPa (ECHAM4; Roeckner et al., 1996, 1999). Without external physical forcings such models generate a realistic interannual climate variability. Tracer transports are only represented in the atmosphere, which is a three-phase system (gas, particles, cloudwater), with the mass exchange between them being controlled by instantaneous equilibria. Degradation is controlled by the hydroxyl and nitrate radical concentrations (3D fields varying each month and with time of day). Deposition of the gaseous molecules to ground surfaces is described by fixed deposition velocities. Soil, vegetation and the ocean mixed layer are represented as two-dimensional compartments (no vertical resolution). The soil's vertical dimension is not specified, yet the maximum soil water depth is geo-referenced. The transfer of water within the soil is calculated using a bucket-type approach. Biota

are represented as vegetation which covers a fraction of the continental grid cells. The vegetation is represented as surface only (no uptake but application and deposition and (re-)volatilization). Volatilization from soil and vegetation is assumed to obey an exponential time-law. A parameterization is used which is based on the experimental determination of losses of a large variety of pesticides under field and laboratory conditions (Smit et al., 1997, 1998). The depth of the well-mixed surface layer of the ocean is locally and seasonally varying and is based on information taken from a 3D ocean global circulation model run. For distinguishing between the surface layer and the underlying deep ocean we used a threshold of a water density of $+0.2$ kg·m^{-3} (Drijfhout et al., 1996). The global annual mean depth is 80.2 m with maximum yearly amplitudes at 60 °N where the depth of the surface layer is varying between 190 m and 600 m. No river runoff, which in reality transfers mass from the vegetation and soil compartments to the ocean compartment, is considered. Cloud processing, dry and wet deposition and tropospheric chemistry of gaseous and particulate trace substances including simple cloudwater chemistry and cloudwater acidity is represented (Feichter et al., 1996). The model describes degradation processes in the compartments and volatilisation processes from the ground compartments into the atmosphere as first-order processes. Parameterisations used to describe the intra-and intercompartmental processes of mass exchange and conversion are listed in Table 1.

2.2. Substances studied

For this study we selected two persistent organic pollutants which undergo long-range transport (e.g. Iwata et al., 1983; Bailey et al., 2000), but have different properties with respect to their environmental behaviour and are subject to regulation under international chemicals legislation (UNEP Stockholm Convention, UN-ECE Convention on Long-Range Transboundary Air Pollution, beside other): the insecticides DDT and α-HCH. While DDT is a lipophilic substance and hardly volatile, α-HCH is considerably water soluble and volatile (Table 2). The substance physico-chemical and degradation data have been selected in a critical review (Klöpffer and Schmidt, 2001) and are listed in Table 1. Some of these data are in particular uncertain as they had to be based on various reported values significantly differing from each other, or even had to be estimated. For example, no hydroxyl reaction rate coefficient of DDT has ever been measured. For α-HCH, both degradation and hydrolysis are considered in the model to occur in the ocean compartment. No degradation rate of DDT in the ocean has been determined. Given the many findings of DDT in ocean water in remote areas, we adapt $k_{ocean}=0$ here.

2.3. Development of indicators

2.3.1. Purpose

Indicators should be able to condense information of environmental fate yet realistically describing the major characteristics of substances. Our choice of indicators is lead by the aims to

- characterize the potential for persistence and LRTP of slowly degradable xenobiotics quantitatively;
- address substance behaviour in individual environmental compartments as well as in the total environment; and
- reflect the temporal evolution of the substance–environment interaction by the time-dependence of the indicators' values.

Out of the many facets of the spatial dimension of the environmental fate of substances, such as migration distance and velocity, shape and extension of distribution, we select two major characteristics:

- The tendency to spread from the areas of entry into a larger geographical distribution by direct atmospheric transport or by multiple cycles of atmospheric deposition and subsequent volatilisation ('hops'). We address this tendency by measuring the difference between a characteristic distance of the geographical distribution (Spatial Scale, S, definition see below) at the time of entry and a second, later time. This indicator will be called Spatial Spreading, SS. The mean number of hops (NOH) a substance is undergoing is determined as the ratio of the total deposited mass and the total applied mass (Lammel et al., 2001).
- The tendency of a plume or distribution to migrate, e.g., into remote regions. We address this tendency by determining the distance between the *centre of gravity* (COG, definition see below) of the geographical distribution at the time of entry and at a second, later time. This indicator will be called Plume Displacement, PD.

Note that this set of spatial indicators, SS and PD, will not be able to cover all facets of the spatial dimension of the environmental fate. The multicompartmental aspects can be addressed at least partly by applying these indicators to individual compartments. Moreover, intermediate steps of the derivation procedures (below) will deliver several other quantities, which are suitable to reveal and characterize additional aspects of the spatial dimension of environmental fate. These are characteristic locations such as the COG, measures of distribution extensions in one and two directions, i.e., *zonal and*

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 an empirical relationship between vapor pressure, aerosol surface and adsorbed fraction (Junge, 1977)	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 (Roelofs et al., 1997)	Prognostic
Degradation in soils, on vegetation and in the ocean	Overall first-order rates, assumed to double per 10 K temperature increase[a]	Prognostic
Oceanic sedimentation	Based on the movement of the mixed surface layer. Decreasing height: the fraction of mass now assumed to be below the surface layer is considered to be lost to the deep ocean. Increasing depth: dilution of the pesticides with constant total mass.	Diagnostic
Partitioning in soils	Phase equilibrium in three-phase soil system (Smit et al., 1997), temperature dependent, soil hydrology represented by bucket model (Roeckner et al., 1996)	Diagnostic
Volatilization from soils	Loss of gaseous substance from the soil pore space using an empirically derived rate from pesticide application studies (Smit et al., 1997)	Prognostic
Volatilization from vegetation	Loss of gaseous substance from plant surfaces using an empirically derived rate from pesticide application studies (Smit et al., 1998)	Prognostic
Flux of trace substances from the ocean to the atmosphere	Two-film model (Wania and Mackay, 1995), temperature dependent	Prognostic
Atmospheric dry deposition	Fixed deposition velocities v_{dep} for gaseous molecules[b] (Slinn, 1982) 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[c] (particulate-bound molecule)	Prognostic

[a] According to recommendations (EC, 1996) besides others; $k_{soil} = k_{vegetation}$; in the case of α-HCH the contribution of the hydrolysis reaction to the degradation in ocean water is accounted for, too (Ngabe et al., 1993).

[b] Dry deposition velocities are 0.38 cm s^{-1} over land for both insecticides and 0 and 0.38 cm s^{-1} over sea for DDT and α-HCH, respectively (based on Tucker, 1983; Tucker and Nelken, 1990).

[c] $\epsilon = 1.0$ and 0.1 for in-cloud and below-cloud scavenging, respectively.

Table 2
Substance parameters used for α-HCH and DDT (298 K)

	Unit	α-HCH	DDT
Degradation rate constant in soil and vegetation	s^{-1}	5.7×10^{-9}	4.0×10^{-9}
Equilibrium constant octanol–water		5890	1.55×10^{6}
Degradation rate constant in ocean	s^{-1}	1.3×10^{-8}	0
Hydrolysis rate constant	s^{-1}	3.8×10^{-9}	0
Vapour pressure	mPa	3.0×10^{-3}	2.5×10^{-5}
Enthalpy of vapourization	KJ mol^{-1}	115	118
Water solubility	μmol L^{-1}	26	9.6×10^{-3}
Enthalpy of solution	KJ mol^{-1}	27	27
OH reaction rate coefficient	cm^{-3} molec^{-1} s^{-1}	1.5×10^{-12}	0.14×10^{-12}
NO$_3$ reaction rate coefficient	cm^{-3} molec^{-1} s^{-1}	2.9×10^{-17}[b]	1.0×10^{-18}[a]
Factor E/R in van't-Hoff form of temperature dependent OH reaction rate	K	−1347	0

Data sources: Klöpffer and Schmidt (2001).

[a] Estimated.

[b] Based on QSAR (Sabljic and Güsten, 1990).

meridional widths (ZW, MW) and *spatial scale (S)*, respectively.

As major characteristics of the temporal dimension of the environmental fate of substances we consider the tendency to resist removal processes with the risk of re-accumulation at remote places (total environmental residence time, $\tau_{overall}$). Again, the multicompartmental aspects can be addressed by applying this indicator to individual compartments.

Furthermore, τ as well as SS and PD?address the dynamics of fate, because they are dependent on the time interval elapsed since entry of the substance into

the environment. Note also that the indicators, as mentioned before, are also dependent on the emission/application scenario, namely time profile of emission (e.g., singular emission pulse or continuous emission), location, time and mode of entry. They are applicable to all scenarios of entry, be it point or wide spread area sources. This study is limited to scenarios of continuous emission from area sources of local to regional scale (described in Section 2.4).

2.3.2. Indicators for persistence

Persistence reflects the tendency of the chemical to resist final sink processes in the multicompartmental system.

In our model system the mass balance equation for the total environmental burden, m, is given by:

$$dm/dt = Q - k_{overall}\, m \tag{1}$$

with the source term Q (application in agriculture) and loss term $k_{overall}m$ which contains the compartmental degradation rate coefficients multiplied with the compartmental burdens and the loss rate to the deep sea (first order in the ocean surface mixed layer concentration). We consider loss to the deep sea to be a final sink to the environment.

In our scenarios with continuous input of pesticide an analytical solution to Eq. (1) exist only for the special cases of steady-state conditions ($dm/dt=0$) or for very long-lived substances ($k\Delta t < 0.001$), which both do not apply in the present case and for reasonable Δt. However, replacing dm/dt by $\Delta m/\Delta t$ in any chosen time interval Δt, Eq. (1) can be transformed into:

$$k_{overall} = D/m = 1/\tau_{overall} \tag{2}$$

with D being the time-averaged (over Δt) overall sink term or depletion rate of the substance from the environment and $\tau_{overall}$ the total environmental residence time or overall persistence (Klöpffer, 1994). So defined persistence refers to a specific time interval Δt after entry.

We, furthermore, define persistences in the individual compartments, τ_i (i = soil, vegetation, ocean, atmosphere). These are given by the compartmental residence times and are limited by the compartmental loss processes e.g., degradation and volatilisation for soil, and degradation and deposition processes for the atmosphere. Accordingly, k_i reflects the combined sinks to the compartment and the source terms Q_i the sum of all sources to compartment i e.g., application and atmospheric deposition for soil and volatilisation from ground compartments for the atmosphere.

2.3.3. Indicators for the long-range transport potential

The substance's *zonal* and *meridional* distributions are defined by the total mass of substance in one meridional band of grid cells and given as a function of latitude (zonal distribution) or in one zonal band and given as a function of longitude (meridional distribution). The *cumulative zonal* and *meridional distributions* are then used to localize some characteristic points in the distributions: the centre of gravity and the 5 and 95 percentiles of the zonal and meridional distributions. The *centre of gravity* (COG) is given by the longitude lon_{50} and the latitude lat_{50} that are defined as the median of the zonal and meridional cumulative distributions, respectively. Fifty per cent of the mass are found north and southwards of lat_{50}, and in the hemispheres east and westwards of lon_{50}. The 5 and 95 of percentiles of the latitudinal cumulative distribution encompass the latitudes containing 90% of the substance's total mass in the environment. Accordingly, the 5 and 95 percentiles of the meridional cumulative distribution encompass the longitudes that contain 90% of its total environmental mass (90% interquantile distances of the geographic distribution).

The calculation of the zonal cumulative distribution is straightforward, using the north pole or the south pole as a reference point. When summing over the meridional distribution, complications may arise when the substance plume is moving beyond the reference meridian: If, for example, a relatively uniform plume is moving eastwards over any chosen reference meridian, the COG remains stable nonetheless the movement of the plume. When 50% of the mass is east of the reference meridian, the COG would be determined at the eastern edge of the plume, and in the next moment at the western edge of the plume, if more than 50% of the mass is west of the reference meridian. To overcome this problem, a dynamic reference meridian has to be used, that follows the movement of the cloud. Its location was determined in each time step as the absolute minimum in the meridional distribution of mass contained in 25 meridional slices—from 45° west to 45° east of each longitude. The number of 25 slices was chosen as a compromise between too narrow bands that bear the risk of ambiguity and too broad bands that may level out the distribution.

Characteristic locations are used to calculate the range of the substance into the four directions, namely the distances between the COG (lat_{50}/lon_{50}) and the 5 and the 95 percentiles of the zonal and the meridional distributions:

$$\begin{aligned} d_N &= lat_{95} - lat_{50} \\ d_S &= lat_{50} - lat_{05} \\ d_W &= lon_{50} - lon_{05} \\ d_E &= lon_{95} - lon_{50} \end{aligned} \tag{3}$$

Distances, a, between two locations, A (lat_A/lon_A) and B (lat_B/lon_B), on the globe are calculated based on the cosine theorem of a side:

$$\cos\{a\} = \sin\{\text{lat}_A\} \times \sin\{\text{lat}_B\}$$
$$+ \cos\{\text{lat}_A\} \times \cos\{\text{lat}_B\} \times \cos\{-\text{lon}_A\} \quad (4)$$

The *zonal*, ZW, and *meridional width*, MW, of the plume/distribution are defined as the distances of the 5% fringes of the plume in north–south and west–east direction, respectively:

$$\text{ZW} = d_N + d_S$$
$$\text{MW} = d_W + d_E \quad (5)$$

The added value of reporting ZW (or MW) is due to interest in meridional (or zonal) transport rather than interest in the distribution area extension. We define the half of the geometric mean of ZW and MW as the *spatial scale*, S:

$$\text{S} = 0.5 \times (\text{ZW} \times \text{MW})^{0.5} \quad (6)$$

S is equally sensitive to (relative) changes of ZW and MW, hence, weighs zonal and meridional transports equally. Spatial scale S as well as characteristic locations of distributions, such as COG, are time dependent quantities. Their change in time will be illustrated in Section 3.1. As announced above, the time-dependent (dynamic) indicators *spatial spreading* (*SS*) and *plume displacement* (*PD*) are derived as differences between each two time-dependent values of S and COG, respectively:

$$\text{SS} = \text{S}(t) - \text{S}(t_0) \quad (7)$$

$$\text{PD} = \text{COG}(t) - \text{COG}(t_0) \quad (8)$$

Similarly, for the characterization of zonal extensions only, the *zonal spreading* (ZS) and the *zonal displacement* (ZD) can be derived using the ZW and the zonal 50%il (lat$_{50}$), respectively:

$$\text{ZS} = \text{ZW}(t) - \text{ZW}(t_0) \quad (9)$$

$$\text{ZD} = \text{lat50}(t) - \text{lat50}(t_0) \quad (10)$$

Note that according to the definitions made in Eq. (3), with S, SS and ZS we refer to 90% of the environmental burden and neglect the LRTP of the remaining 10%. Indicators referring to individual compartments are defined in the same way as the indicators referring to the total environment with the exception of compartments where $m_0 = 0$ (then not defined).

2.3.4. Potential vs. effective long-range transport potential

The spatial indicators derived so far disregard the absolute amount of substance present in the environment and thus characterize for $t > t_0$ the potential spatial mobility a substance undergoes within $\Delta t = t - t_0$. During Δt, a significant fraction of the applied mass might have been degraded. Therefore, the *effective* mobility is smaller for substances with a shorter lifetime in the environment. We account for this fact defining effective indicators for long-range transport potential by multiplying the potential indicators with the fraction of mass that is present at time t (m) relative to the total mass present at time t_0 (m_0) and applied during the time Δt ($Q\Delta t$):

$$I_{\text{eff}} = I_{\text{pot}} \times \frac{m}{m_0 + Q \times \Delta t} \quad (11)$$

where I stands for any indicator. Note that I_{pot} as disregarding the absolute amount of substance present is an intensive substance (environmental) property while I_{eff} is an extensive substance property. For application of indicators in regulatory contexts I_{pot} should be related to hazard, I_{eff} to risk assessment (in terms of PEC and PNEC i.e., predicted environmental concentration and predicted no-effect concentration data).

2.4. Scenarios of substance entry into the environment

We chose to compare scenarios where the two model substances—DDT and α-HCH—were brought into the environment at seven places characterizing different conditions, in geographic position and continentality. For the sake of intuition, the pesticides were applied uniformly over the territories of seven countries, namely Finland, France, Turkey, China, Indonesia, Zambia, and Argentina. For Argentina, however, we restricted application of the pesticides to the region north of 47° S assuming the arable land to be concentrated there. The quantity of pesticide applied was constant for all emission scenarios in all months throughout the year (240 t month^{-1}). We neglect application seasons here. The temporal distribution within individual months, however, was not necessarily uniform but to some extent dependent on the local conditions: In agriculture pesticides will preferentially be applied during daytime and according to the weather conditions, which are both factors significantly affecting the volatilization and other sink processes of the chemicals (Kurtz, 1990). Hence, in the model simulation pesticides are applied only during daytime and in time steps (30 min) without precipitation in the gridcell. Under these conditions, every gridcell receives an amount of substance that was calculated beforehand on the basis of the total mass to be applied in the country, the total country's territory (north of 47° S in the case of Argentina) and the total number of time steps during daylight. In the case of a precipitation event, the not-applied amount of substance accumulates and is entried delayed, namely during the first dry time step at daytime which follows.

The pesticides were introduced to the receptor compartments in fixed ratios. This so-called mode of entry was soil:vegetation = 5:95 for DDT and 10:90 for α-HCH.

With that differentiation between the two insectides we try to account for the broad application spectrum of HCH (BCPC, 1997). The amount of substance lost directly to air during application was assumed to be zero.

A characterization of the application scenarios with the above-defined indicators is given in Fig. 1 and Table 3.

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 January of the 16th year, the tracers, distinguishable for the seven countries were introduced into the receptor compartments. The application pattern remained the same in consecutive years of the model runs and we report on results of the 2nd year of application (Section 3).

3. Results

The compartmental burdens and intercompartmental mass exchange fluxes of substances, which are entered into the environment with a constant rate and from the same sources, may achieve 'equilibrium', i.e., steady-state conditions after some time. Because of the natural cycles (day, year) we do not expect fixed concentration levels but fixed amplitudes and phase lengths. On the time-scale of decades we may neglect changes in climate with good reason, but even so we should call it quasi-steady-state conditions because inter-annual climate variability will prevent total periodicity and impress some 'noise'. The time needed to achieve quasi-steady-state conditions is determined by the compartmental degradation rates and their spatial distributions. With respect to the compartmental distribution and if we consider burial in the deep sea to be a final (irreversible) sink to the system, for POPs such as DDT and α-HCH we may expect this state beyond a decade or so upon entry into the environment (based on studies using generic models, e.g., Wania and Mackay, 1995). Note that it is an open and important question whether quasi-steady-state conditions with respect to the spatial patterns eventually need even much more or endless time to be established ('cold condensation' hypothesis; Wania and Mackay, 1993).

First we illustrate the dynamics of environmental fate over a short period (2 years) and then characterize it based on annual mean indicator values.
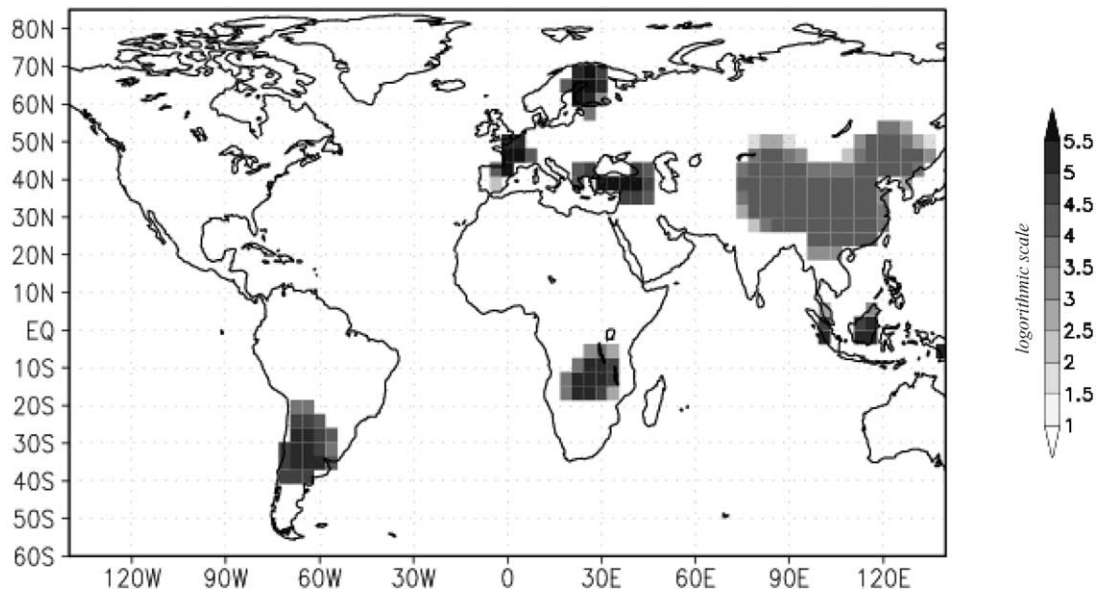

Fig. 1. Application of pesticide in the seven application scenarios.

Table 3
Distribution characteristics of the pesticides upon application (t_0)

	Finland	France	Turkey	China	Indonesia	Zambia	Argentina
Spatial Scale, S [km]	323	368	548	1610	1070	580	734
Zonal Width, ZW [km]	1070	1060	856	2610	1050	1100	1730
Meridional Width, MW [km]	390	508	1400	3970	4370	1230	1240
Zonal 50%il, lat_{50} [°N]	66.0	48.3	40.9	37.5	0.3	−11.1	−29.9
Meridional 50%il, lon_{50} [°E]	30.7	6.6	42.1	108.0	120.0	33.1	300.0

3.1. Evolution of environmental fate

According to the seasonality of temperature (temperature dependent degradation rates), oxidant abundances (atmospheric decay) and other environmental parameters the compartmental distribution undergoes seasonal changes. For example, a 1 and 11% of DDT applied in Finland and Indonesia, respectively, are stored in the air in the annual mean of the second year of simulated pesticide fate (Table 4). The corresponding seasonal amplitudes [defined as (max−min)/mean, monthly resolution] are 220 and 40%, however. The amplitudes of total environmental burdens are 50 and 40%, respectively. By presenting results of the evolution of indicators for long-range transport, illustratively for the Spatial Scale S of pesticides applied in Finland, China, and Argentina (Fig. 2), we want to shed some light on the susceptibility of the environmental behaviour of DDT and α-HCH towards interannual variations of seasonality and on the time scale the environment needs to adapt to the continuous input of pesticides.

The distribution extensions, as determined by S, are larger for DDT than for α-HCH. We will come to that point later (Section 3.2). The extensions are minimal in summer in the case of DDT (Fig. 2b, all three countries) and α-HCH when applied in Finland (Fig. 2a), but no unambiguous seasonality is predicted for α-HCH when applied in China or Argentina. Furthermore, the development of the HCH cloud suggests that a quasi steady-state with respect to the distribution extension is reached already after some (3–4) months of substance entry. Note, that this occurs prior to α-HCH reaches quasi-steady-state conditions with respect to compartmental distribution in the environment. For DDT, however, no stabilization of the cloud's geometry is

Table 4
Compartmental distribution of α-HCH (a) and DDT (b) as annual mean in the 2nd year upon entry into the environment

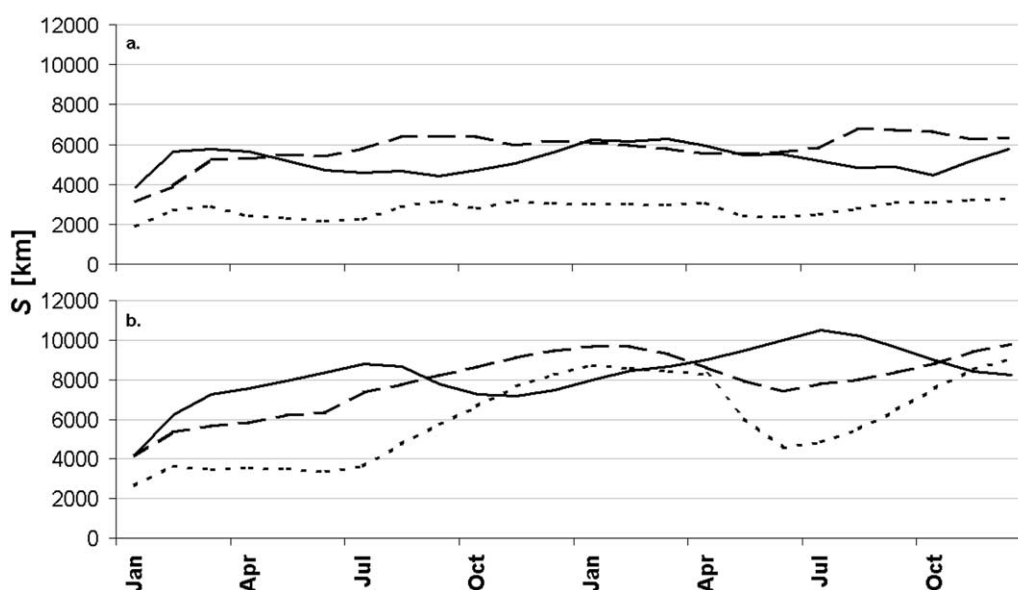|	Finland	France	Turkey	China	Indonesia	Zambia	Argentina
(a) α-HCH							
Soil	53	68	68	52	49	53	32
Vegetation	36	24	23	37	8	18	15
Ocean	10	6	6	9	32	22	47
Atmosphere	1	2	3	3	11	8	5
(b) DDT							
Soil	4	7	12	8	4	4	5
Vegetation	91	82	70	78	59	69	65
Ocean	3	5	7	5	14	11	17
Atmosphere	3	6	12	9	23	16	13

Fig. 2. Change over time of spatial scale (S [km]) during the first 24 months (monthly resolution) after entry into the environment of α-HCH (a) and DDT (b) following application in Finland (dotted line), China (broken line) and Argentina (bold line).

apparent after two years of pesticide application and a higher LRTP is expected for DDT in the 3rd year upon entry.

The COG of the total environmental burden moves seasonally only little in north–south direction with largest zonal shifts of 2.4 and 2.1° for DDT applied in China and Argentina, respectively. Note that continuous entry in the region of origin will necessarily suppress the (geographical) mobility of the substances' distributions. For α-HCH these shifts are most pronounced when applied in Indonesia (2.0°) and Zambia (1.1°). Among the individual compartmental burdens highest seasonal mobility is found for the fraction of the substance stored in the ocean: for DDT the seasonal shift of the COG_{ocean} is predicted to be between 14° (France) and 21° (Turkey). The shift of the $COG_{vegetation}$ is largest when entried in China, 3.2°, compared with 0.1–0.2° for all other entry scenarios. Obviously, the north–south movement of the 5% and 1% fringes of the pesticide distributions are more pronounced. For example, the northern and southern 5% fringes of the zonal distribution of DDT move by 0° and 10° (Finland), 12° and 25° (Argentina) and 8° and 31° (Turkey) throughout the year. Accordingly, also other characteristic locations, and indicators derived from these, show seasonal variabilities.

What do we expect for the evolution of indicators for persistence? As quasi-steady-state conditions are not expected to be achieved in the 2nd year but $dm/dt > 0$, the compartmental distribution will change to increasingly larger fractions of the burden in those compartments where degradation is slow. Therefore, D in the 3rd year will be smaller than D in the 2nd year, hence, $\tau_{overall}$ is increasing in this phase of the environmental fate [cf. Eq. (2)]. This has to be kept in mind for the discussion of values for $\tau_{overall}$.

3.2. Effects of location of entry on substance distribution

We find that the compartmental distribution of the substances is strongly dependent on location of entry (Table 4). For example, the atmospheric fraction varies by about an order of magnitude for the various application scenarios (1–11% for α-HCH and 3–23% for DDT). Using the same model, for entry of DDT in India and global usages as of 1970 and 1980, but with a somewhat different mode of entry (vegetation: soil = 80:20 instead of 95:5) atmospheric fractions of 3.7, 1.5 and 2.8%, respectively, were found (Semeena and Lammel, 2003). This, again, emphasizes the significance of mode of entry.

Relatively more DDT than α-HCH is predicted to reside in the atmosphere (Table 4) despite a smaller source term (corresponding to a low vapour pressure, cf. Table 2). This is caused by more efficient sinks for α-HCH (deposition and degradation, corresponding to dry deposition velocity over sea, water solubility and hydroxyl radical reaction rate coefficient, cf. Tables 2 and 3). In fact, deposition is more important than degradation as the α-HCH total deposition flux exceeds the DDT total deposition flux by 120% (mean of the seven scenarios). Obviously, the larger particulate-bound fraction of DDT, favouring deposition processes, cannot compensate for this difference.
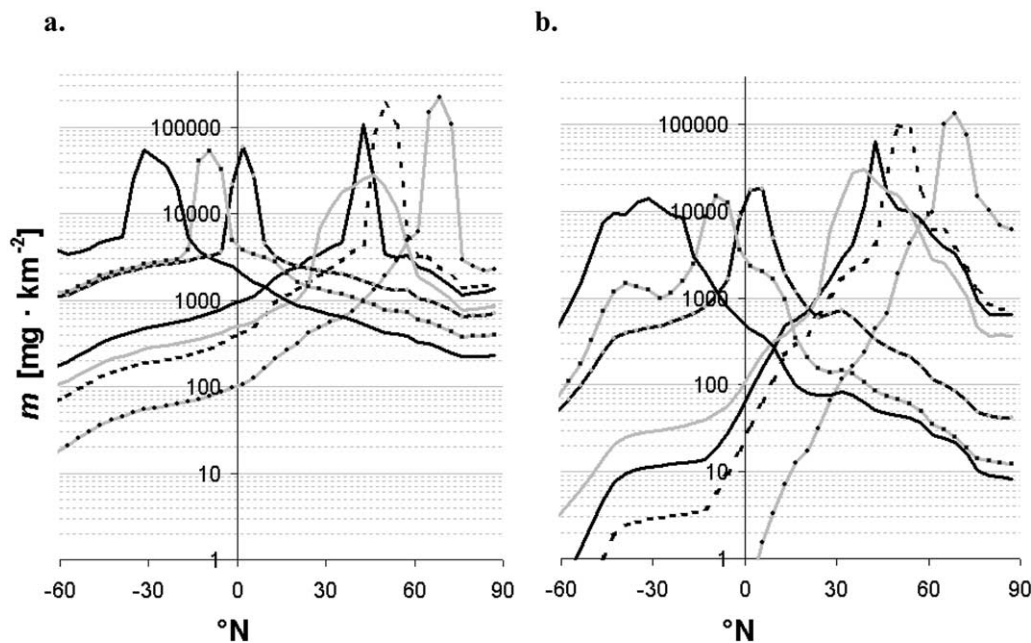

Fig. 3. Zonal distribution of the total environmental burdens of α-HCH (a) and DDT (b) under the various scenarios of entry (from south to north: Argentina, Zambia, Indonesia, China, Turkey, France and Finland). Annual mean of the 2nd year.

The zonal distributions (Fig. 3) show the effect of latitude of application/emission as well as of the substance. The zonal distributions of DDT are smoother than those of α-HCH in the latitudes of entry and in their vicinity. The north–south extension of the countries of origin can still be recognized. However, in the latitudes far from entry it is found that zonal gradients are steeper for DDT indicating more efficient LRT in meridional direction of α-HCH. Obviously, a larger fraction of DDT remains in the latitudinal band of entry while more HCH reaches remote latitudes. Quantification by the zonal spreading, ZS, as referring to the 90% interquantile distance, however, identifies DDT distributions to spread more in meridional direction than the respective α-HCH distributions (for all country scenarios

except of Finland). With increasing interquantile distance (e.g., using the 98% interquantile instead of the 90% interquantile), the difference in the ZS of the two substances is increasing. In the case of Finland, we even observe a switch in the substance ranking: ZS_{98} is larger for DDT (5200 km) than for α-HCH (3800 km). As a message from this analysis we note that substance ranking when based on LRTP indicators which refer to a chosen fraction of the environmental burden in principle can be sensitive to the size of this fraction.

Due to atmospheric transport and input into ground compartments, the zonal distributions peak within the latitudinal band of the countries of origin but sometimes are significantly distorted. For example, the maximum of the zonal distribution of α-HCH originating
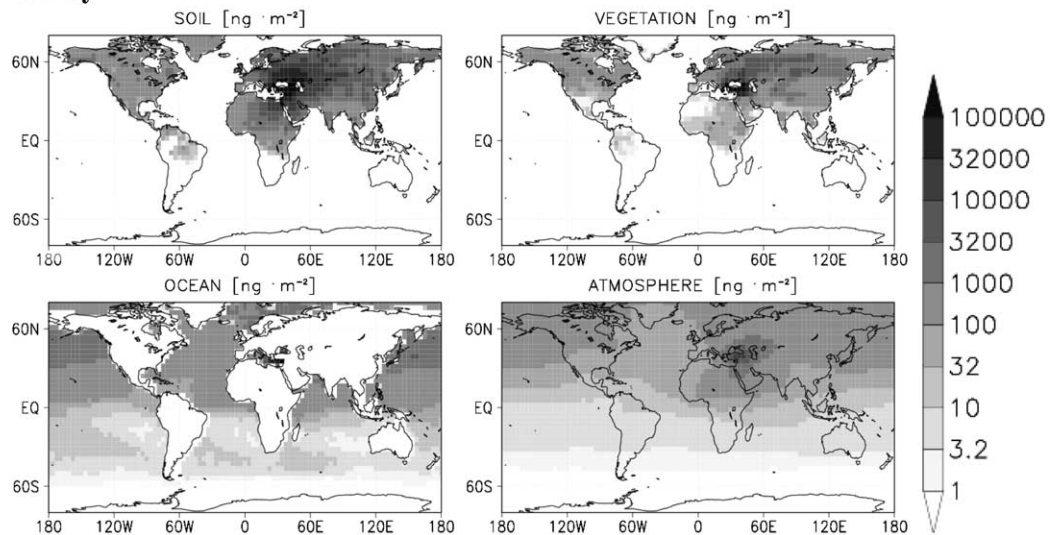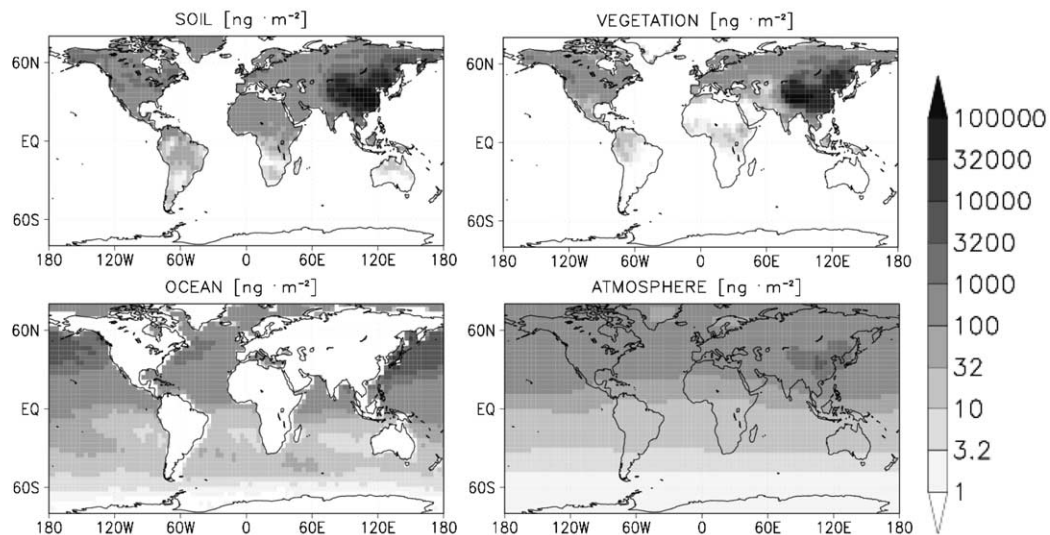

Fig. 4. Effect of longitudinal position of α-HCH application: distribution of α-HCH in thesoil, vegetation, ocean and atmosphere for the Turkey (a) and China (b) application scenarios. Annual mean of the 2nd year. Note the logarithmic scales.

from Chinese territorium is located at 47° N (corresponding to North China) while the zonal distribution of DDT peaks at 36° N (corresponding to South China). Especially if the area of entry is close to oceans (in the prevailing wind direction) the difference in the tailing of the plume between the two substances is most pronounced. This reflects the impact of the substance properties (degradation rates in air and water, water solubility, besides other). Comparing the environmental distribution of α-HCH and DDT along the north–south transect of entry of substance into the model world, it is possible to assess the impact of continentality of the source region. Generally, the plumes of HCH are larger compared to DDT, as HCH is the substance with higher potential to environmental mobility (e.g., Semeena and Lammel, 2003). High water solubility of α-HCH makes the ocean an important receptor of pesticide (see Table 4). In the case of the Argentina scenario, this results in a long tailing of the α-HCH plume east of Argentina, which is not observed for the less water soluble DDT and in the application scenarios of the northern hemisphere.

Geographical distributions are subject to the large-scale atmospheric transportation patterns. This becomes obvious when comparing the plumes spreading from two individual countries located in the same latitudinal band, i.e., Turkey (centred around 41° N) and China (38° N, Table 3, Fig. 4: a plume originating in China spreads eastward without leaving the latitudinal band. It is mainly the precipitation frequency in the East Asian subtropics, which limits τ_{air} and, hence, the plume's extension. In contrast, a plume originating on Turkish territory is spreading more rapidly eastward as precipitation in the region is a less effective sink. Time-resolved analysis shows that beginning in June, however, this plume's dispersion is influenced by northeasterly winds in the region, which belong to the seasonal monsoon low. As a consequence, parts of the plume are transported in the latitudinal bands dominated by easterly winds (trade wind zone) and deposited to ground compartments there. The zonal distribution of the substances in air (not shown) has two maxima, one at 5–10° N besides the one at the latitudes of origin. Removal by rain is 33% less in the region's dry climate than when originating in China. Hence, α-HCH and DDT originating from Turkish territory are dispersed over a larger region (Western Asia, South Asia, North Africa) compared with when originating from Chinese territory (Pacific and North America, but with less zonal dispersion). This is quantified as values of SS (Fig. 5c, d). On temporal scales of seasons and above, meridional transport in the boundary layer is more
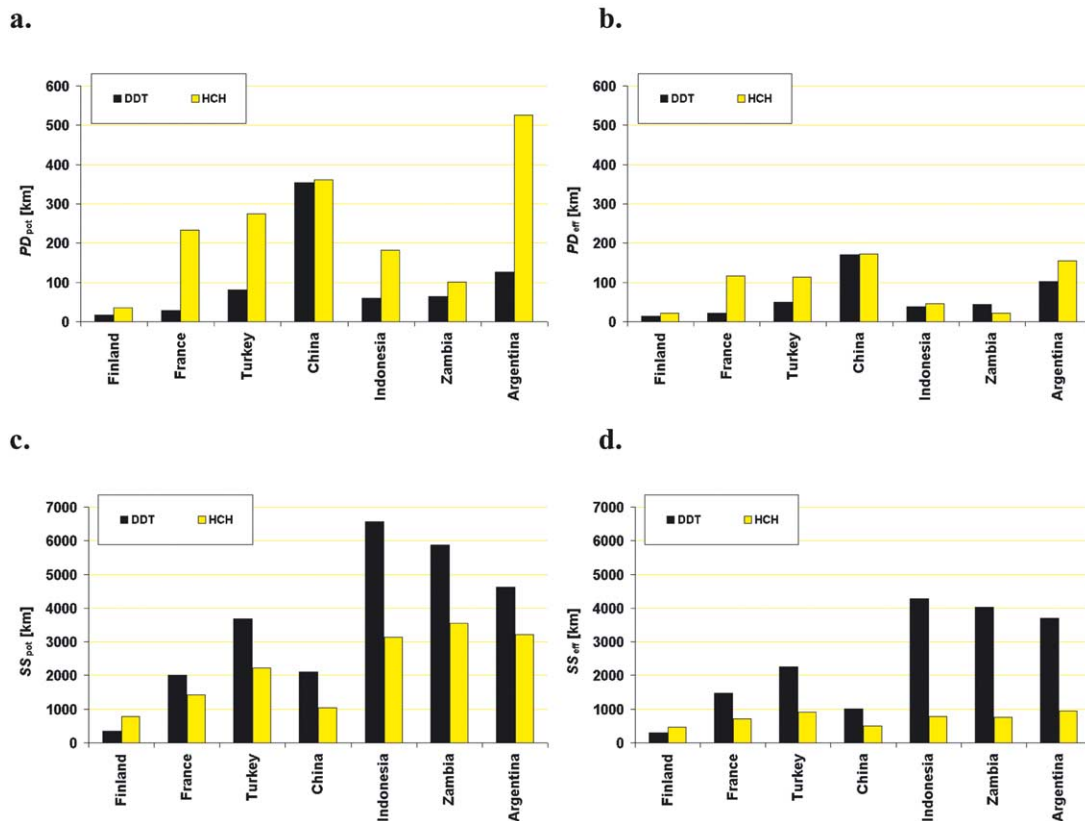

Fig. 5. Indicators for spatial dimensions of (a, c) potential and (b, d) effective total environmental fate of DDT and α-HCH. (a, b) Plume displacement, PD, and (c, d) spatial spreading, SS. Annual mean [km] of the 2nd year upon entry. For m_0 [cf. Eq. (11)] the amount applied until mid of the 2nd year was taken.

effective in the monsoon region compared with other regions of the same latitudinal band. Note that at least on the regional scale (a few hundreds to a few thousands of km) such large-scale circulation features (other examples are the central Asian and North American winter highs; Lahey et al., 1960) imply significant deviations from the mean meridional transport efficiency and question the validity of spatial averaging of the dynamics. Climatic zone models e.g. (Wania and Mackay, 1995; Scheringer et al., 2000), assess long-range transport assuming well-mixed latitudinal bands connected by zonally-averaged macro-diffusion coefficients.

3.3. Potential and effective long-range transport potential

The LRTP of DDT and α-HCH upon entry in various countries is predicted to vary significantly. Values of PD_{pot} and SS_{pot} of the total environmental burden fall into a range spanned by a factor of 21 and 19 for DDT and 15 and 5 for α-HCH, respectively (Fig. 5). For most scenarios and for both substances the distribution extensions are largest in air, second to largest in ocean, then rank soil and vegetation. The only exceptions of this order are: Distribution in ocean is larger than in air for α-HCH entried in Turkey and Zambia, in the vegetation compartment larger than in soil for α-HCH entried in Indonesia and in the soil compartment larger than in ocean for DDT entried in Zambia.

Due to substance decay ($m/m_0 < 1$), values of indicators addressing effective fate are always smaller than when addressing potential fate (Fig. 5a–d). DDT distributions show in all entry scenarios a stronger tendency to spread but migrate less far than the corresponding α-HCH distributions. Note that substance ranking as based on SS, as mentioned above for ZS, may be sensitive to the choice of characteristic locations, if differences in degradation dynamics cause differences in spatial concentration gradients. As substance degradation is influenced by the local climate (temperature, precipitation frequency, besides other), values of m/m_0 and, hence, the emission scenario rankings delivered by various indicators are affected: For DDT it is found that the SS ranking, showing distributions originating from Indonesia with the highest and from Finland with the lowest tendency to spread, is almost preserved. Only France and China change their positions. For α-HCH the influence of the local weather is obviously more significant. However, the impact of location of entry of α-HCH on the effective environmental fate is less pronounced than on the potential environmental fate. Obviously, differences in decay of α-HCH in various climates compensate for the differences in transports (as measured by SS and PD). The reason for this finding is that atmospheric transports tend to be more significant in the tropics.

In contrast, the migration of the entire distribution (plume, addressed by *PD*) is suggested to be potentially fastest for α-HCH applied in Argentina but effectively slower than for this pesticide applied in China. This is caused by the effective deposition of α-HCH into the ocean where a large amount of mass is temporarily stored (47% for application in Argentina vs. 9% for application in China). Despite high overall degradation rates of α-HCH in the Argentina scenario, the substance does not undergo transport in the ocean. Thus, the gradient of environmental burden of α-HCH is steep in the vicinity of Argentina and concentrations are low far from the source region. The latter are included in the derivation of the indicators of potential, but not in the derivation of the indicators of effective environmental fate.

The comparison of the emission scenario rankings for the indicators PD and SS show that these are indeed independent indicators: In the case of DDT, highest PD values are found for application in Argentina and China and lowest in France and Finland, while Indonesia and Zambia rank highest and Finland lowest when SS is measured (both addressing the potential fate). In the case of α-HCH, the by far highest PD values is found for application in Argentina and the lowest for Finland, while, again, Zambia and Indonesia rank highest and Finland lowest when *SS* is measured (both, again, addressing the potential fate). The ranking of emission scenarios is also completely different for PD and SS when the effective environmental fate is addressed.

3.4. On the relation between long-range transport potential and persistence

The values for $\tau_{overall}$ (annual mean of the second year) span a factor of 4.8 for DDT (range 317–1527 days) and 4.6 for α-HCH (range 101–463 days), respectively, for the various locations of entry (Fig. 6). The differences between the various scenarios in total environmental residence times are influenced by both
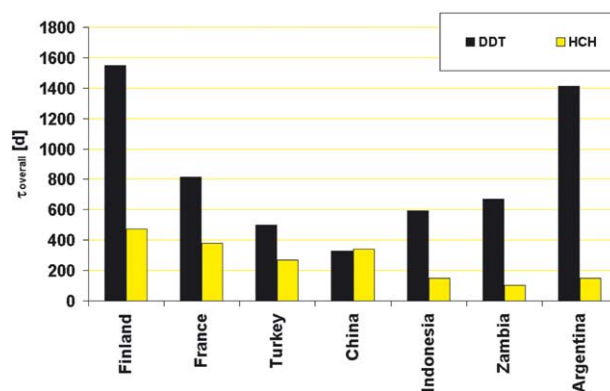
Fig. 6. Indicators for the temporal dimension of multicompartmental fate of DDT and α-HCH, total environmental residence time, $\tau_{overall}$. Annual mean for the 2nd year upon entry into the environment.

differences in the compartmental distributions and residence times. Residence times in the ground compartments are strongly influenced by temperature. For the various scenarios, values for τ_{soil} of DDT and α-HCH span factors of 3 and 20, respectively. Residence time in air is limited by oxidant availability, precipitation and other and values for τ_{air} vary by factors of 3 and 1.5 for DDT and α-HCH. Obviously, the influence of location of entry is so strong, such that we cannot simply state that DDT is more persistent than α-HCH: With small difference between the two values, the opposite persistence ranking is predicted for application of the two substances in China ($\tau_{overall}$ = 317 and 331 days). Persistence for application in other countries from the same or adjacent climate zones, Turkey and Indonesia, is expected to be higher, because a larger fraction ends up in the ocean with no degradation assumed to happen there (cf. Table 2). However, a large fraction of pesticides volatilising from ground surfaces in China does not reach the downwind seas because of degradation in the atmosphere. Wet deposition is less significant there, because of the low solubility of DDT. Considering the distribution of cropland in this country, we note that our emission scenario—spatial uniform distribution—is artificial and does not simulate agricultural application in China well. Identifying 'China' we here refer to the geographic locations encompassed by the national borders.

Atmospheric cycles ('hopping') will usually reduce the accumulated residence time in the ground compartments, because degradation in the atmosphere will be faster than in the ground compartment. Exceptions may occur for night-time hopping (which can be months in high latitudes), as degradation is much slower in the dark.

As intercompartmental mass exchange is influenced by local weather, the NOH should vary between the scenarios, too. We obtain a value around 1 for α-HCH independently of the application region (Table 5). With the notion that the cycling of substance through the compartments resembles a simple two-phase multiple equilibration process, a mean NOH of one implies a partitioning coefficient of 0.5 which leaves 10% of the mass undergoing two cycles and 3% of mass undergoing four or more cycles. A larger range of *NOH* is predicted for DDT, ranging from 0.8 (Finland and China) to ⩾2 (Indonesia and Argentina). Thus, it is predicted that 5% of DDT applied in Indonesia and Argentina will undergo five or more atmospheric cycles. While the reason for the low NOH for entry in Finland

can be explained by cold temperatures restricting re-volatilization (low vapour pressure), the reason for the low value in the case of China might be due to the high percentage of substance being predicted in the atmosphere, which enhances the overall depletion rate (lowest $\tau_{overall}$). High temperatures and relatively high deposition rates explain the high NOH under the Indonesia and Argentina scenarios. *NOH* values of 2.6 for entry in India and 1.8–2.1 for global usage was found under a somewhat different mode of entry (vegetation: soil = 80:20 instead of 95:5; Semeena and Lammel, 2003).

Likewise, water solubility plays a role determining the lifetime of α-HCH in the ocean, which ranges around 2 months for application in France, Turkey, China, and Indonesia, while a double residence time is predicted for application for Finland (temperature effect) and Zambia and Argentina (deposition effect). No residence time in the ocean surface mixed layer can be calculated for DDT, since this compartment is in the state of filling (source term is larger than sink term).

It is found that geographic distributions of the more persistent substance, DDT, show a higher tendency to spread (Fig. 7 a) but a lesser tendency to migrate (Fig. 7b). The first finding is plausible as transports can sustain spreading longer for substances residing longer in the environment. The latter finding means that as a transport-efficiency-weighted and time-weighted mean the mobile fraction of the DDT burden is smaller than the mobile fraction of α-HCH. This is somewhat contra-intuitive considering the higher fraction of DDT residing in the atmosphere (Table 4). However, a large atmospheric fraction favours not only transport but also degradation and, as mentioned above, more α-HCH is deposited to the ground compartments than DDT. Even if more DDT may have entered the mobile compartment (the atmosphere) it is α-HCH of which a higher fraction survives the atmospheric cycling, ends up in remote areas and adds to shift the COG.

For the various scenarios, i.e., location of entry, but for the same substance there is a significant scatter in Fig. 7. This scatter reflects the differences in compartmental distributions, i.e., high spreading tendencies are expected for significant fractions of the burden in those compartments where degradation is relatively fast. This should lead to point distributions in Fig. 7a aligned from high SS and low $\tau_{overall}$ to low SS and high $\tau_{overall}$. Deviations from this behaviour i.e., particularly low and

Table 5
Mean number of atmospheric cycles ('hops', NOH) during the 2nd year for DDT and α-HCH as determined from the ratio of total mass deposited to total mass applied during the 2nd year

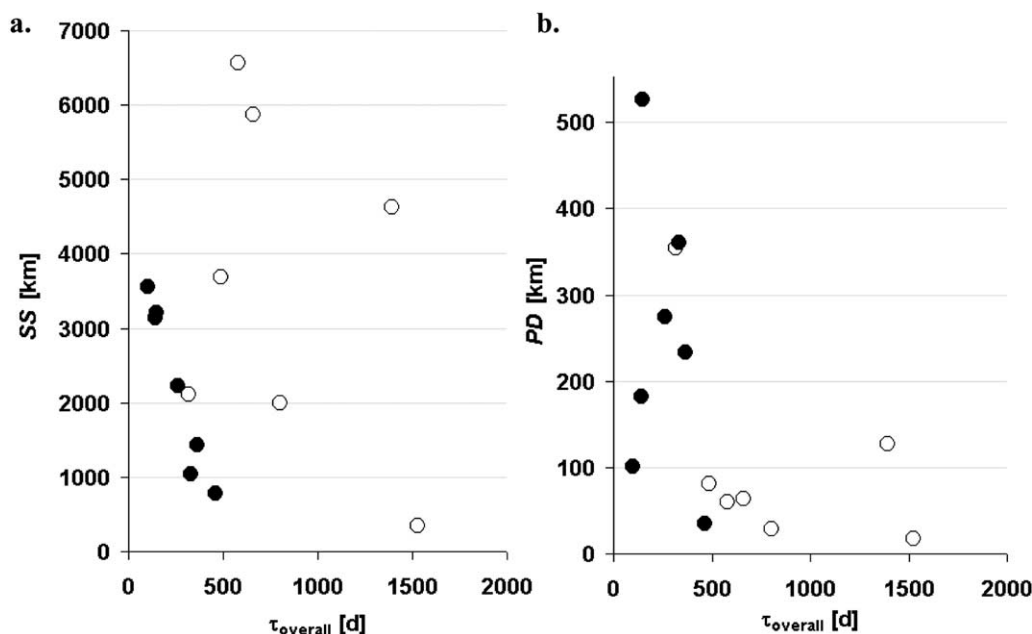|	Finland	France	Turkey	China	Indonesia	Zambia	Argentina
(a) α-HCH	1.0	1.1	1.2	1.1	1.0	1.0	1.0
(b) DDT	0.8	1.3	1.5	0.8	2.0	1.7	2.2

Fig. 7. Relation between indicators for the spatial and the temporal dimensions, spatial spreading, SS, and $\tau_{overall}$ (a) and plume displacement, PD, and $\tau_{overall}$ (b) for DDT (open circles) and α-HCH (full circles). Annual mean for the 2nd year upon entry into the environment. Indicators for potential environmental fate in both cases.

high persistences, are found for DDT scenarios which correspond to either minimal partitioning to the ocean in a warm climate (China, discussed above, negative deviation from the mean behaviour) or to maximal partitioning to the ocean (Argentina, positive deviation), respectively.

4. Discussion

Total environmental and compartmental residence times as well as a set of indicators which addresses the spatial dimension of environmental fate i.e., the change of the location and extension of substance distributions over time, have been derived from results of a dynamic model and applied to characterize persistence and LRTP of two organochlorines. We did not address the entire environmental fate of persistent substances but limited our study to one year only, the second year upon entry into the environment i.e., before quasi-steady-state was achieved. Therefore, snapshots of persistence and LRTP are provided, which allow for relative comparisons (substance and location of entry rankings) but not for characterization of the entire substances' fates. With the aim to simulate close to reality we studied emission scenarios of continuous emission and did not address emission pulses. We neglected the seasonality of agricultural application, however.

The application of the indicators showed that these are appropriate to characterize the environmental fate of SOCs in individual compartments as well as the total environment. Tendencies of distributions to migrate and

to spread into remote areas can be addressed separately by the indicators spatial spreading and plume displacement as a function of time. SS and PD are independent of each other. The consideration of substance decay allows to derive measures useful in the context of hazard and risk assessment, namely indicators for potential and effective, respectively, environmental fate.

In general and as a consequence of the transport velocities and degradation dynamics in the various compartments, the geographic distributions of total environmental substance burden under conditions of continuous entry are expected to exhibit bell-like shapes with the maximum in the area of entry and decreasing concentrations with increasing distance—the 'bell' shaped by a sequence of gradients. As a result, a small or even tiny fraction of the burden will be very mobile while most of the burden will be significantly less mobile (cf. Section 3.2). Substance ranking as based on LRTP indicators which address a chosen fraction of the environmental burden, such as when referring to the 90% interquantile distance, will be sensitive to the size of this fraction. Also in the temporal dimension, persistence as indicated by the time elapsed until $m_0/2$ or m_0/e remain may hide small fractions subject to very or even extremely slow degradation.

It was the prime aim of this study to present and apply for the first time a set of indicators for environmental exposure based on a geo-referenced, 3D MCTM. LRTP was addressed for the first time in more than one spatial dimensions on the global scale. The main results gained on the occasion of studying the fate of the SOCs DDT and α-HCH were:

(1) The environmental fate of the two studied SOCs is very different (compartmental distributions, inter-compartmental mass exchange fluxes, persistence and LRTP). The more complex a fate model is, the more can the many facets of fate be studied, e.g., various aspects of LRTP and regional features. Although in principle achievable and valuable, we did not include information about vertical distribution in the atmosphere, ocean or soil into the characterization of the (geographical) substance distributions, but exploited two-dimensional distribution projections, only.

(2) We found that persistence and LRTP are both strongly dependent on location of entry. Even in the same latitudinal position the longitudinal location matters. The effect of location of entry on the level of countries is significant for the compartmental distribution and inter-compartmental mass exchange fluxes (NOH, besides other) and introduces uncertainties on the order of a factor of 5 for τ_{overall} and 5–20 for indicators of LRTP, respectively. We expect even stronger effects for entry in different seasons (according to the local vegetation period). On the level of hemispheres a factor of 2 for τ_{overall} still remains (for γ-HCH; Semeena and Lammel, 2003). The significance of local climate is, of course, substance specific. At least in part of the subtropics and tropics e.g., in the East Asian subtropics, it is the precipitation frequency which limits τ_{air}. The same was found in a study for atmospheric sulfur species (Roelofs et al., 2001): τ_{air} of sulfate is 2.8 days in June–August in Southeast Asia, but 3.7 days in Europe and 4.0 days in North America (mean of nine transport models). We note that atmospheric residence times and, hence, the assessment of LRTP, will be deficient when based on non-georeferenced models, such as most multimedia mass-balance models, which fail to adequately account for precipitation frequency. One false conclusion would be an overestimation of the influence of temperature on LRTP (cf. Beyer et al., 2003). On longer time scales, the effects of location of entry might level out to some extent. On the other hand, the influence of oceanic transports, then becoming relevant, too (neglected in this study), might introduce additional forcing to segregate distributions of various location of origin.

(3) Using a 3D model and respective indicators it was confirmed that long-range transport potential and persistence of two organochlorines are independent (Fig. 7). It was, furthermore, found that even prior to reach quasi-steady-state conditions in the environment with respect to the compartmental distribution and total burden, at least the spatial dimension i.e., the spreading of α-HCH distributions in the total environment had reached quasi-steady-state. The impact of location of entry of α-HCH on the effective environmental fate is less pronounced than on the

potential environmental fate, because differences in persistence in various climates seem to compensate for differences in LRTP (as related to circulation patterns in the tropics). These findings, also, emphasize the independence of the spatial and temporal dimensions of fate. The general independence of LRTP and persistence has been hypothesized and studied earlier using an evaluative model (Scheringer, 1996).

Insights gained into the fate of DDT and α-HCH were not the focus of this study. Longer simulations are necessary and transports in the ocean and, eventually, in rivers are necessary model features to be included, too, for an adequate description of persistent substances' environmental fate. We, furthermore, emphasize that these necessarily have to be considered to be preliminary as long as important substance properties used as input data (degradation rates, in particular) are very uncertain. Substance and emission/usage scenario indicators as derived from MCTMs (such as presented here) have not been compared with indicators for persistence (Pennington, 2001) and LRTP (van Pul et al., 1998; Scheringer et al., 2001) based on evaluative multimedia modelling. Such a systematic comparison is desirable as it could provide a means for validation of the evaluative models, which due to their generic nature cannot be directly validated by observational data (OECD, 2002). On the other hand, the transport part of atmospheric models has been validated independently (e.g., Roelofs et al., 2001), while intracompartmental substance transformation and intercompartmental mass exchange processes are formulated in both model types in a similar way (e.g., air/sea and air/soil exchanges) or are formulated closer to reality in the MCTM (e.g., cloud processing). Comparability, however, is not straightforward: Some indicators are model dependent and differences in model design (compartments included, spatial and temporal resolution, etc.) will strongly influence model results and, hence, the values delivered by even the same indicator (e.g., Wania and Dugani, 2003). Here, we characterized persistence for a phase of the fate of substances prior to achievement of quasi-steady-state (namely the 2nd year). These values cannot directly be compared to results for steady-state conditions. When studying the fate of α-HCH using a high-resolved non-steady-state climatic zone model (Scheringer et al., 2000), the zonal width referring to the 95% interquantile distance of the total environmental burden was predicted to 67° upon entry at 30° N and to 38° upon entry at the equator by the climatic zone model, while our results (ZW referring to the 90% interquantile distance) are 32, 29 and 41° for entry in the territories of Turkey, China and Indonesia, respectively. While small differences could be attributed to the difference in definition, we feel that a significant difference for the effect of moving from the equator to the mid-latitudes is

found between the predictions of the two models. One significant reason for these discrepancies certainly is the variability of precipitation and circulation patterns, not resolved in generic models. A more systematic comparison of indicators from both model types is in work (Klöpffer and Schmidt, 2003) and will be the focus of a future communication.

5. Conclusions

The long-range transport potential of multi-compartmental substances is a multidimensional phenomenon, which merits to be studied by temporally and spatially resolved models. Adequate characterization requires the use of more than one indicator for LRTP. These, together with the indicator for persistence's temporal evolution allow for characterization of environmental fate in space and time. The here presented study of a number of entry scenarios differing in geographic location demonstrated that the effect of location of entry on persistence and LRTP is significant and turns numbers for persistence and LRTP indicators into ranges. Location of entry, therefore, should be considered in substance assessments. Sometimes it is implied that average environmental conditions are sufficient for substance hazard or risk assessment. We note that, in general, averaging can never cover the real diversity, that it may lead to systematic deviations from reality (Lammel, this issue) and, furthermore, cannot guarantee to lead to conservative results i.e., to estimate at the safe end of the uncertainty range, because the interaction of parameters is not trivial and not necessarily intuitive.

In general, indicators for persistence and LRTP, pertinent to their definition, refer to the fate of a large fraction, e.g., 90%, but not the total substance burden. Due to the complexity of transport and degradation dynamics, deviations from first-order exponential decay with increasing distance from entry in space and time are not the exception but the rule. The spatial distribution and degradation dynamics of the fraction of the burden not addressed by the indicator cannot be extrapolated from the characterization of the fate of the majority of the burden. Therefore, the choice of a fraction of the burden to refer to may have the consequence of a normative step which defines the spatial and temporal extensions of a related chemicals risk assessment, similar to what is practised in the critical loads / critical levels concept (Nilsson and Grennfelt, 1988; Nagel and Gregor, 1999).

Acknowledgements

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