Research Articles

Multicompartmental Fate of Persistent Substances

Comparison of predictions from multi-media box models and a multicompartment chemistry-atmospheric transport model

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Abstract

Background, Aim and Scope. Modelling of the fate of environmental chemicals can be done by relatively simple multi-media box models or using complex atmospheric transport models. It was the aim of this work to compare the results obtained for both types of models using a small set of non-ionic and non-polar or moderately polar organic chemicals, known to be distributed over long distances.

Materials and Methods. Predictions of multimedia exposure models of different types, namely three multimedia mass-balance box models (MBMs), two in the steady state and one in the non-steady state mode, and one non-steady state multicompartment chemistry-atmospheric transport model (MCTM), are compared for the first time. The models used are SimpleBox, Chemrange, the MPI-MBM and the MPI-MCTM. The target parameters addressed are compartmental distributions (i.e. mass fractions in the compartments), overall environmental residence time (i.e. overall persistence and eventually including other final sinks, such as loss to the deep sea) and a measure for the long-range transport potential. These are derived for atrazine, benz-[a]-pyrene, DDT, α and γ-hexachlorocyclohexane, methyl parathion and various modes of substance entry into the model world.

Results and Discussion. Compartmental distributions in steady state were compared. Steady state needed 2–10 years to be established in the MCTM. The highest fraction of the substances in air is predicted by the MCTM. Accordingly, the other models predict longer substance persistence in most cases. The results suggest that temperature affects the compartmental distribution more in the box models, while it is only one among many climate factors acting in the transport model. The representation of final sinks in the models, e.g. burial in the sediment, is key for model-based compartmental distribution and persistence predictions. There is a tendency of MBMs to overestimate substance sinks in air and to underestimate atmospheric transport velocity as a consequence of the neglection of the temporal and spatial variabilities of these parameters. Therefore, the long-range transport potential in air derived from MCTM simulations exceeds the one from Chemrange in most cases and least for substances which undergo slow degradation in air.

Conclusions and Perspectives. MBMs should be improved such as to ascertain that the significance of the atmosphere for the multicompartmental cycling is not systematically underestimated. Both types of models should be improved such as to cover degradation in air in the particle-bound state and transport via ocean currents. A detailed understanding of the deviations observed in this work and elsewhere should be gained and multimedia fate box models could then be 'tuned in' to match better the results of comprehensive multicompartmental transport models.

Keywords: Exposure analysis; fate; long-range transport; multimedia box models; multicompartmental models; persistence

Introduction

Substances which reside in and are transferred across the boundaries of various environmental media (so-called multicompartmental substances) recently became an object of scientific research for two reasons, namely multicompartmental cycling is a challenge for fundamental science and, as far as pollutants are concerned, its understanding is necessary in the context of risk assessment regarding the effects for organisms, ecosystems and through food chains for human health (e.g. Vallack et al. 1998, Klecka et al. 2000). Multimedia mass-balance box models (MBMs) have been used to predict the overall persistence, multicompartmental distribution and long-range transport potential of non-polar organic substances, e.g. persistent organic pollutants (Mackay 2001, Scheringer and Wania 2003). In these models, substances are exchanged between the environmental compartments, either assuming that the thermodynamic equilibria are instantaneously established or that the transfer is described by mass transfer kinetics. By linking the multicompartment boxes to each other, these models have also been used to mimic substance fate in regional to global environments which are characterized by temperature and other gradients, e.g. to address the hypothesis of global scale 'distillation' (Wania and Mackay 1993). Despite a considerably varying degree of complexity in this type of modelling, all of these have in common that transport in air and ocean are represented by mean exchange rate coefficients taken to be constant in time and representative for an entire region. No sub-grid scale parameterisations are used to capture environmental features. Furthermore, due to their generic nature, the degree of detailedness within individual boxes is very limited. Nevertheless, such models have been validated by real-world data (Macdonald et al. 2000, Breivik and Wania 2002, Muir et al. 2004). Being handy and of reduced complexity, they are suitable for decision making contexts, e.g. substance screening for environmental risk assessment or substance design.

It is only since recently that environmental transport and fate of multicompartmental substances have been studied using transport models, which had been developed in the geo-sciences decades ago and had been applied for the study of air pollution, in oceanography and in climate research (Strand and Hov 1996, Koziol and Pudykiewicz 2001, Lammel et al. 2001, Malanichev et al. 2004). These models capture the stochastic and deterministic features of fluid transport in air and water, e.g. the large-scale weather patterns and their seasonality. Sub-grid scale parameterisations capture additional features, e.g. cloudiness. In the context of various types of application, the atmosphere and ocean dynamics of such models have been validated. The diversity and temporal dynamics of the environmental media are represented and geo-referenced. Spatial resolution and the time scale of such simulations may be computationally limited. Once the substance specific processes were captured, such models should in principle provide the best available tools for the study of multicompartmental substances.

Here, we report on a first attempt to intercompare multicompartment models of these two types. Parameters characterizing environmental fate as predicted by three multimedia box models and one model which is based on an atmosphere general circulation model are compared for various persistent substances and different modes of entry.

1 Methodology

1.1 Models used

In this study, four models have been used: three multimedia fate box models, SimpleBox 2.0 (Brandes et al. 1996), Chemrange 1.0 (Held 2001, Scheringer et al. 2001) and MPI-MBM (Lammel 2004) and one dynamic, geo-referenced multicompartment-atmospheric transport model, MCTM (Lammel et al. 2001, Semeena and Lammel 2003, Semeena et al. 2005). Unlike the MCTM and the MPI-MBM, SimpleBox and Chemrange both calculate under the steady-state assumption (so-called 'level III' fugacity models, Mackay 2001), i.e. constancy with time or all time derivatives are zero. SimpleBox simulates a continental and a regional box for three zones of the globe as well as for two boxes. Chemrange simulates transport in a ring of boxes aligned around the globe. MPI-MBM is a non-steady-state zero-dimensional model (so-called 'level IV'). The MCTM is used in 2 versions, i.e. based on the atmospheric general circulation model (AGCM) ECHAM4, 19 vertical levels and T30 horizontal resolution (i.e. 3.5°x3.5°), and ECHAM5, 19 vertical levels and T42 horizontal resolution (i.e. 2.8°x2.8°). In the latter version it is coupled to a fully dynamic, modal aerosol model, HAM. Many relevant features of the AGCM have been extensively evaluated, namely the large-scale atmospheric dynamics (Cess et al. 1990), the tracer transport and distributions (Roelofs et al. 2001, Textor et al. 2005) and the aerosol dynamics and distributions (Stier et al. 2005). The most fundamental features of the models used are listed in **Table 1**. The parameterisation of intra- and intercompartmental mass exchange and conversion processes is similar for most parts, but differs substantially for the atmosphere, as the MCTM considers emissions of substances applied in agriculture to be determined by the local conditions (including those of the soil), processing of substances by several types of clouds and aerosols, wet and dry deposition, with the latter being determined by atmospheric turbulence and surface resistances. Partitioning between gas and particles in air is predicted according to the Junge approach (Junge 1977) in the MCTM (most scenarios), SimpleBox and the MPI-MBM. In the Junge approach, partitioning is determined by vapour pressure which captures adsorption and implies that absorptive properties are the same for the sorbing phase and the sorbate. An absorption model (Finizio et al. 1997) was used in Chemrange and in the MCTM for DDT and γ-HCH. The reaction rate of the adsorbed molecule with the OH radical is assumed to be zero. The mean OH radical abundances in the arctic, temperate and tropic regions of the SimpleBox and MCTM models are 0.40, 0.47, and 0.70 x 10^6 cm^{-3}, respectively.

Air-surface exchange is parameterised as based on the two-film model (Whitman 1923) using fugacity formulation (e.g. Wania et al. 2000) in most of the cases, i.e. for air-sea exchange in all models and for air-soil exchange in SimpleBox and Chemrange. However, in the MPI-MBM and the MCTM models, the dry deposition flux of gaseous trace substances from the atmosphere to the ocean is calculated using fixed (MPI-MBM) or calculated dry deposition velocities (according to a resistance scheme, MCTM). While the state of the atmosphere is represented only by temperature and wind velocity in the two-film model and the parameterisation follows empiric relationships based on inorganic trace gases (cf. Schwarzenbach et al. 2002), additional atmospheric (stability, turbulence) and surface (e.g. roughness, leaf area) features are consistently considered in the resistance model. The usage of a fixed dry deposition velocity, set to the supposedly temporal mean value, neglects the temporal variability of the state of the atmosphere.

Air-soil exchange in MCTM and MPI-MBM is described by an empirically derived parameterisation of volatilisation of pesticides (Smit et al. 1997) following establishment of thermodynamic equilibrium in the three-phase system soil. Another empirically derived parameterisation (Smit et al. 1998) is used for description of volatilisation from vegetation surfaces in these models. Vegetation is not considered in the SimpleBox and Chemrange simulations.

Apart from chemical degradation, burial in the deep sea (MCTM) or in sediments (SimpleBox) are considered as final losses to the model environments. Therefore, even un-

Table 1: Fundamental features of the models used, i.e. SimpleBox 2.0 (Brandes et al. 1996), Chemrange 1.0 (Held 2001, Scheringer et al. 2001), MPI-MBM (Lammel 2004) and MCTM (Lammel et al. 2001, Semeena and Lammel 2003)

Model		SimpleBox 2.0	Chemrange 1.0	MPI-MBM	MCTM
Geometry of model world		Various boxes (Arctic/Temperate/Tropic/Continental)	Ring of boxes around the globe	1 box, 4 compartments	3D atmosphere general circulation model, single-layer ground compartments
Compart-ments	Air	1000 m well-mixed, fixed temperature (–10/12/25/12°C), precipitation rate (250/700/1300/700 mm a^{-1}), aerosol surface (6x10-8 cm^{-1})	Transport by fixed rate reflecting Eddy diffusion	well-mixed of varying height, temperature (–10/12/25/12°C), precipitation frequency 0.33 d^{-1}, aerosol surface (1x10–10 cm^{-1})	1000–10 hPa (19 levels), temperature, cloud formation, various forms of precipitation, aerosol particles (dynamic microphysics, 4 size modes) according to local conditions
	Ocean	1000 m (1) mixed layer, 5 mg/l suspended particulate matter	Transport by fixed rate reflecting Eddy diffusion	mixed layer, no suspended particulate matter	80 (25–600) m mixed layer geographically and monthly varying, deep ocean
	Ocean sediment	3 cm	None	None	Not explicitly, but as a sink to the ocean compartment
	Soil	2% organic fraction		2% organic fraction	0–200 kg m^{-3} organic fraction, 9 classes (2)
	Vegetation	None	None	None	Vegetation surface only, specific surface area 1 m^2 m^{-2}
	Ice	None	None	None	Represented, but not as own compartment: substance deposited is budgeted to ocean water (sea ice) or soil (Greenland, Antarctica)
	Freshwater	3 m mixed layer, 25 mg L^{-1} suspended particulate matter (3)	None	None (3)	None
	Freshwater sediment	4% organic fraction	None	None	None
Exchange processes	Air-ocean	Wet deposition and dry particle deposition: fixed rates Gaseous: Diffusive, 2-film model (Schwarzenbach et al. 2002)		Wet and dry deposition: fixed rates Gaseous volatilisation: Diffusive, 2-film model (Schwarzenbach et al. 2002)	
	Air-soil	Wet deposition and dry particle deposition: fixed rates Gaseous: Diffusive, 2-film model (Mackay and Paterson 1991)		Wet and dry deposition: fixed rates Gaseous volatilisation: Equilibrium (gas/ soil-water/ soil organic matter) + empirically derived volatilisation rate (Smit et al. 1997)	Wet deposition and dry particle deposition: Detailed, variable Gaseous dry deposition: resistance scheme Gaseous volatilisation: Equilibrium (gas/ soil-water/ soil organic matter) + empirically derived volatilisation rate (Smit et al. 1997)
	Air-vegetation	None		Wet and dry deposition: fixed rates Gaseous volatilisation: empirically derived volatilisation rate (Smit et al. 1998)	Wet deposition and dry particle deposition: Detailed, variable Gaseous dry deposition: resistance scheme Gaseous volatilisation: empirically derived volatilisation rate (Smit et al. 1998)
	Air gas/particle	Adsorption (Junge 1977)			
Transport processes	Air	Between zones: diffusive, fixed	Diffusive, fixed	None	General circulation, variable in time and space
	Ocean	Between zones: diffusive, fixed	Diffusive, fixed	None	No advection, only loss to deep sea
	Rivers	Runoff	None	None	None
Horizontal resolution		None or 3 latitudinal zones	< 1 m (numerically)	None	ca. 100 km (2.8°)
Time step		(Steady-state)	(Steady-state)	< 1 s	20 min

(1) 200 m in the continental box
(2) Batjes 1996
(3) in the continental box only

der the assumption of no substance degradation (assumed for DDT; cf. Table 2), steady-state conditions can be reached in the ocean surface mixed layer of SimpleBox and MCTM. No final losses other than chemical degradation are considered by Chemrange1.0 and MPI-MBM.

There are deviations from reality in the assumptions in all models used in this work. Obviously, many simplifications are inherent to any type of model. We note that transport by ocean currents are neglected, that the OH radical concentrations are probably (currently accepted knowledge, Spivakovsky et al. 2000) higher in the temperate and zonal regions (should read ca. 0.73 and 1.70x10^6 instead of 0.47 and 0.70x10^6 cm^{-3}) and lower in the high latitude zone (should read ca. 0.16x10^6 instead of 0.40x10^6 cm^{-3}) than assumed in our simulations, and that degradation in air in the particle-bound state, neglected too, might be significant (Atkinson et al. 1999).

1.2 Substance scenarios

Model runs were made for 1,1,1-trichloro-2,2-di-(*p*-chlorophenyl)-ethane (*p*,*p*'-DDT), α and γ-hexachlorocyclorhexane (HCH), benzo-[a]-pyrene (BaP), 2-chloro-4-ethylamino-6-isopropylamino-s-triazine (atrazine, atr) and methyl parathion (mep). For the latter two pesticides, we studied two sets of physicochemical properties, i.e. designing scenarios which reflect a low and a high estimate for mobility in the environment, in order to account for data uncertainty (atr-low, atr-high, mep-low, mep-high). As the atmosphere is the only mobile compartment in the MCTM, we consider any change in model parameters which enhances the atmospheric residence time or increases the atmospheric source term of the substance to represent a change towards increased mobility. The mode of entry into the environment influences strongly the environmental fate. The substance properties and entry scenarios are listed in **Tables 2** and **3**, respectively.

1.3 Basis of comparison between models

SimpleBox calculates environmental concentrations in the compartments of a regional (0.08x10^6 km^2), a continental (Europe, 7.1x10^6 km^2, 50% area fraction of water) and 3 boxes of latitudinal zones of area fractions 16.7, 33.3 and 50.0%, standing for the arctic, temperate, and tropic zones of the globe. Different (constant) temperatures are allocated to these boxes, namely –10, 12 and 25°C. The same mean temperatures are chosen for the MPI-MBM simulations. The area fractions of water and bare soil in the MPI-MBM simulations, however, as well as the ocean surface mixed layer depth are taken as given in the MCTM. The atmospheric hydroxyl radical concentrations in all MBMs is identical with the values in the MCTM. MCTM results to compare with are taken from 5 zones divided by the 57th and 30th parallels with somewhat different area fractions of water (**Table 4**).

Table 2: Physicochemical properties of the compounds used for the model calculations

	γ-HCH	**α-HCH**	**DDT**	**Methyl-parathion**	**Atrazine**		**BaP**
					low mobility	**high mobility**	
Water solubility (298 K) [mg L^{-1}]	7.4 (1)	2.0 (1)	3.4x10^{-3} (1)	60	33 (2,3)		1.82x10^{-3} (4,5)
Enthalpy of solution ΔH_{sol} [kJ mol^{-1}]	27 (6)	27 (6)	27 (6)	27 (6)	25.6		27 (6)
Saturation vapour pressure p [Pa] (298 K)	2.9x10^{-3} (1,7)	6.0x10^{-3} (1,7)	3.4x10^{-5} (1)	3.8x10^{-3}	3.85x10^{-5} (2)		7.0x10^{-7} (1)
Enthalpy of vaporisation ΔH_{vap} [kJ mol^{-1}]	115 (6)	115 (6)	118 (6)	95	146 (6)		122.5
Octanol-water partitioning coefficient K_{ow} [–]	3.98x10^3 (1)	5.89x10^3 (1)	1.55x10^6 (1, 8)	1.0x10^3	630 (1, 9)	160 (1, 10)	1.35x10^6 (4)
OH reaction rate constant k_{OH} [cm^3 molec^{-1} s^{-1}]	1.9x10^{-13} (11)	3.8x10^{-13} (11,21)	1.0x10^{-13} (6)	1.67x10^{-11}	1.4x10^{-11} (12)		1.5x10^{-10} (13)
NO_3 reaction rate constant k_{NO3} [cm^3 molec^{-1} s^{-1}]	0	0	0	0	0.75x10^{-16}		0
ΔE/R of OH reaction [K^{-1}]	–1710 (1)	–1347 (1)	–1300 (6)	0	0		–1300
ΔE/R of NO_3 reaction [K^{-1}]	0	0	0	0	0		0
Degradation rate in ocean water k_{ocean} [s^{-1}] (298 K) (14)	2.3x10^{-8} (15,16)	3.1x10^{-8} (15,16,17)	0	3.3x10^{-7}	8.0x10^{-7} (9,15,16)	1.6x10^{-8} (5,15,16)	3.1x10^{-8}
Degradation rate in freshwater $k_{freshater}$ [s^{-1}] (298 K) (14)	2.3x10^{-7} (18)	3.1x10^{-7} (18)	0	Not applicable	8.0x10^{-6} (18)	1.6x10^{-7} (18)	0
Degradation rate in soil and sediment k_{soil} [s^{-1}] (298 K) (14)	2.0x10^{-8} (2)	2.0x10^{-8} (19)	4.1x10^{-9} (2)	1.3x10^{-7}	5.0x10^{-7} (2,20)	8.7x10^{-8} (1,10,21)	7.7x10^{-8} (1,20)

(1) Rippen 2000
(2) Hornsby et al. 1996
(3) at 295.65 K
(4) at 288 K
(6) estimated
(7) Harner et al. 1999
(8) mean value
(9) selected higher value of a range of values found
(10) selected lower value of a range of values found
(11) Brubaker and Hites 1998
(12) lower and upper estimate, respectively, to account for the uncertainty (cf. 14 * 10^{-12} cm^3 molec^{-1} s^{-1}, based on an extrapolation from a high-temperature measurement; Klöpffer and Kohl 1990)
(13) estimated; SRC 2000
(14) It is assumed that a doubling of the degradation rate is caused by each 10 K temperature increase. Such a dependency is justified by the acceleration of biodegradation in soils by temperature and recommended (TGD 1996)
(15) the contribution of the hydration reaction (Ngabe et al. 1993, Widmer et al. 1993) to the degradation in ocean water is accounted for by addition of two rates
(16) it is assumed that biodegradation is a factor of 10 slower in ocean water than in freshwater (Moltmann et al. 1999)
(17) arithmetic mean of the rates of two enantiomers, assuming a racemate
(18) following TGD, 1996, recommended value for 'inherently biodegradable'
(19) following DFG 1982, which stated that the degradation behaviour of α-HCH is similar to γ-HCH. Other sources (Rippen 2000, Bachmann et al. 1989) report unplausible, higher rates.
(20) extrapolated to 298 K assuming (14) and a mean soil temperature of 285 K
(21) 1.5 * 10^{-12} for the MCTM

Table 3: Substance scenarios of substance entry into the environment

Substance	Scenario acronym	Geographic coverage, year	Simulated years (1)	Application flux (t a^{-1}) (1)	Months of non-zero emission	% of applied amounts received by air / soil / vegetation (2)
α-HCH	A7C10	Various countries (3)	2	2880	Jan–Dec	0 / 10 / 90
γ-HCH	LG8020	global 1980 (4)	2	18061	Feb–Oct	0 / 20 / 80
	LN8020	30°N-90°N 1980 (4)		12673		
	LT8020	90°S-30°N 1980 (4)		5388		
	LG80HM	global 1980 (4)	10	19824	Jan–Dec	
DDT	DG80HM	global 1980 (4)	10	9002	Jan–Dec	0 / 20 / 80
	DG90HM	India 1990 (4)		4466		
	D7C05	Various countries (3)	2	2880	Jan–Dec	0 / 5 / 95
MeP	MLJADD	global 1995 (5)	10	71463	Jul–Aug	0.5 / 30 / 69.5
	MHJADD			87240		10 / 10 / 80
Atr	LMDD			200996	May	0.5 / 99.5 / 0
	LYDD				Jan–Dec	0.5 / 89.5 / 10
	HMDD			267521	May	15 / 85 / 0
	HYDD				Jan–Dec	15 / 77 / 8
BaP	PAH4	Europe, Russia 1990 (6)	10	1047	Jan–Dec	100 / 0 / 0

(1) not relevant for MBM application
(2) vegetation and soil are not distinguished in the MBMs
(3) Finland, France, Turkey, China, Indonesia, Zambia, Argentina; see Leip and Lammel 2004, for details
(4) see Semeena and Lammel 2003, for details
(5) see Lammel et al. 2001, for details
(6) country-level data (Münch and Axenfeld 1990) scaled with crop density

Table 4: Zonal division of world in the models. n.d. = not defined

		SimpleBox		MPI-MBM		MCTM	
		Area fraction of world (%)	Area fraction of water (%)	Area fraction of world (%)	Area fraction of water (%)	Area fraction of world (%)	Area fraction of water (%)
Arctic (57–90°) (1)	Northern	16.7	60	n.d.	52.4	7.3	52.4
	Southern			n.d.	73.2	7.3	73.2
Temperate (30–57°) (1)	Northern	33.3	50	n.d.	47.8	18.2	47.8
	Southern			n.d.	86.3	18.2	86.3
Tropic (0–30°) (1)		50.0	70	n.d.	75.9	49.0	75.9

(1) not geo-referenced in the MBMs

1.4 Parameters to be compared

1.4.1 Compartmental distributions

The fractions of total environmental burdens stored in the various compartments are compared according to the various model predictions. In the case of non-steady state models (MCTM and MPI–MBM), the results are taken from the last year of the runs (cf. Table 5, column 4).

1.4.2 Persistence

Persistence has been recognized as the central criterion in the environmental assessment of organic chemicals by Frische et al. (1982) and further elaborated by Klöpffer (1994) and Scheringer (2002). Scheringer also included the long-range transport in his analysis (see Section 1.4.3). Verbal definitions of persistence, e.g. 'The persistence of a substance is the result of either the absence or inefficiency of sinks or the inability of a substance to reach a potential sink' (Klöpffer et al. 1982, Klöpffer 1994), do not lead directly to the quantification desirable for comparing the persistence of different substances or the same substance under different input conditions. Quantification can be obtained by multimedia modelling. Mackay (2001) proposed a simple equation to be used for well-defined parts of the environment, e.g. lakes, in steady state conditions:

$$\tau = m / E \qquad (1)$$

where τ is the residence time, m is the amount of the chemical in steady state, and E is the input rate, identical with the removal rate under steady state. In a lake, τ is determined by transfer (e.g. advection) processes without chemical transformation and by chemical degradation. Only this latter process is interesting for quantifying the persistence, since transfer processes only shift the position of a molecule.

In a global environment, chemical reaction is the only mode of disappearance and the input rate in Eq. 1 is identical with the chemical reaction rate (averaged over all compartments). Thus, a chemical without any sink (transformation reaction) cannot reach equilibrium and accumulates as long as the input occurs.[1] However, this is a rare case for organic chemicals. For the vast majority of organic substances, Eq. 1 may be used for estimating the persistence, knowing that –as pointed out correctly by Mackay (2001) – the lifetime calculated is due to an average of many degradation reactions or may be dominated by one sink (e.g. biodegradation in soil, if most of the substance resides in surface soil in steady state).

An equation very similar to (1) has also been used by Scheringer (1996, 2002) and Klöpffer and Schmidt (2003) in order to determine quantitatively the persistence from the results of the ring-model Chemrange 1.0/2.1 and SimpleBox 2.0. It should be noted that τ does not correspond to a first-order chemical lifetime (reciprocal of a first-order rate constant), but rather to an 'equivalence time' which may contain a non-first order tailing that may be due to a small fraction of the substance residing, e.g. in the sediment.

The overall environmental residence time, τ_{res}, is given by **Eq. 2**.

$$\tau_{res}(t) = m(t) / F_{sink}(t) \qquad (2a)$$

$$F_{sink}(t) = \sum_j \frac{\Delta m_j}{\Delta t} + k_{loss\ to\ deep\ sea} \cdot m(t) \qquad (2b)$$

with m(t) being the total environmental burden at time t, $F_{sink}(t)$ the sum of all ultimate sinks to the system (t a^{-1}), i.e. the sum of chemical degradation processes, $\Delta m_j/\Delta t$, in compartment j and other 'exits' from the model world (here, loss to the deep sea). $k_{loss\ to\ deep\ sea}$ is dependent on a compartmental burden, the ocean surface mixed layer burden. In the MCTM, it is also dependent on location and season (Lammel et al. 2001) and, hence, time dependent as well. The term overall persistence, $\tau_{overall}$, is not used here as it should be reserved to resistance to degradation processes only, while some of the models used here consider an additional final sink (e.g. loss to the deep sea). Δt denotes the time interval from which the change in mass, Δm, is taken.

It is, however, of interest to address persistence also under on-going emissions, i.e. before complete phase-out. This scenario is more realistic for most of the substances under consideration, even for banned ones regarding the fact that even after the implementation of restrictions legal exceptions, leakages from inadequate storage and disposal, and unlawful usage might cause continued emissions. Therefore, the definition of overall persistence, $\tau_{overall}$, was extended to conditions of on-going emissions (Leip and Lammel 2004). Similar to the case of zero emissions, overall residence time, τ_{res}, is limited by all compartmental first-order loss processes under non-steady state as well as pseudo-steady state conditions and can be approximated from the mass conservation equation (**Eq. 3**):

$$\Delta m/\Delta t \approx E(t) - m(t) / \tau_{res}(t) \qquad (3a)$$

$$\tau_{res}(t) \approx m(t) / (E(t) - \Delta m/\Delta t) \qquad (3b)$$

with E(t) being the source term to the system (emission or application flux) and $\Delta m/\Delta t$ the net uptake (t a^{-1}). So defined, overall residence time refers to a specific time interval Δt taken at time t after entry. It is pseudo-steady state rather than pure steady state, because seasonal and other short-term variabilities prevent a compartmental distribution constant in time. In order to avoid biases due to the seasonal and higher frequent variabilities in the model world, we chose t in steps of entire years and use $\Delta t = 1$ a. Hence, $\tau_{res}(t)$ for year 10 of the simulation is derived from Δt = 10a–9a.

For pesticide release into soil (and vegetation), it is found that it increases with time before pseudo-steady state (as for filling compartments m_j, increases) and then reaches a (quasi-) constant value (see Section 2.2). This results from compartmental re-distribution under the influence of varying compartmental residence times.

For values of τ_{res} as derived from MCTM and –MBM, output equation (2) is used. The same values are obtained when using equation (1), which for most substances, however, cannot be solved analytically, but requires a numeric solution.

1.4.3 Long-range transport potential

Spatial Range, SR, in Chemrange is derived in a scenario of a continuous point emission and refers to the distance encompassing 95% of the mass in the compartments air, ocean surface layer and soil under steady-state conditions upon (meridional) transport in both air and ocean (Scheringer 1996, Scheringer et al. 2001). From MCTM results, we use the indicators meridional and zonal spreadings, *MS*, *ZS*, under scenarios of (a) regional scale (country scale) and (b) global scale continuous emissions. The *MS (ZS)* (Leip and Lammel 2004) of a distribution are defined as the changes of the distance of the 5% fringes of the plume in west-east (north-south) direction relative to t_0 (time of entry): $MS = MW(t) - MW(t_0)$, $MW = lon_{95} - lon_{05}$ and $ZS = ZW(t) - ZW(t_0)$, $ZW = lat_{95} - lat_{05}$. Hereby, lon_{95}, lon_{05}, lat_{95} and lat_{05} denote the 95th and 5th percentiles, respectively, of the meridional (zonal) cumulative distribution. Hence, while *Spatial Range* encompasses 95% of the mass, *MS* encompasses only 90%. Furthermore, for the ocean surface mixed layer compartment, higher values for the long-range transport (LRT) indicator are expected from the Chemrange results, because oceanic transport is not considered in the MCTM (note, however, that atmospheric transport is, on the average, much faster than are oceanic currents).

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[1] For practical reasons, most models allow burying in the sediment as a sink or loss to the deep sea is considered as an ultimate sink.

2 Results and Discussion

2.1 Effectiveness of mass transfer between compartments

All models predict that the distributions of α-HCH, γ-HCH and DDT over the compartments are largely to water and to the soils (or soil plus vegetation for those models which consider a vegetation compartment; **Table 5**). For all scenarios, the highest fractions in air are predicted by the MCTM.

In the non-steady state simulations, the substances are transferred slowly from the compartments of entry, soil and vegetation, to the ocean, visible in Table 5a for the distribution of γ-HCH after 2 (LG8020, cf. Table 5a) and 10 years (LG80HM). Pseudo-steady state is reached by γ-HCH within ca. 10 years according to the MCTM simulation (cf. Fig. 1c). Transfer to ocean is less effective in the MPI-MBM simulation (cf. Table 5a). This is mostly due to the lack of one loss process to the total environmental burden, i.e. transfer to the deep sea. The deep sea has received three times more than stored in all other compartments within 10 years in the MCTM simulation. For water soluble substances such as atrazine, the shift to the ocean is expectedly even more effective. In the MCTM simulation, > 98% are found in the ocean under all atrazine scenarios when the deep ocean is included in the budget. A shift of most of atrazine to the

Table 5: Results: compartmental distributions (a) globally, (b) for zones (% in air / % in ocean water / % in soil and vegetation)

a)

Substance	Scenario acronym	SimpleBox 2.0	Chemrange	MPI-MBM (1)	MCTM
α-HCH	A7C10	5x10^{-3} / 1 / 99 (2) 0.2 / 20 / 80 (3)	2 / 5/ 93	1 / 6 / 93	1–11 / 6–47 / 47–92
γ-HCH	LG8020	1x10^{-3} / 2 / 98 (2) 0.1 / 29 / 71 (3)	1 / 12 / 87	0.7 / 4 / 95	3 / 13 / 84
	LG80HM			0.2 / 8 / 92	7 / 42 / 51
DDT	DG80HM	5x10^{-2} / 17 / 83	0.3 / 1 / 98	0.07 / 2 / 98	5 / 12 / 83
	DG90HM				6 / 12 / 82
	D7C05			0.1 / 0.6 / 99	3–23 / 3–17 / 63–95
MeP	MLJADD	–	–	0.04 / 1.5 / 98	20 / 53 / 27
	MHJADD			0.2 / 7 / 93	21 / 25 / 54
Atr	LMDD	3x10^{-4} / 2 / 98	4x10^{-4} / 5 / 95	4x10^{-3} / 0.02 / 100	1 / 0.3 / 99
	LYDD			6x10^{-3} / 0.02 / 100	0.7 / 0.5 / 99
	HMDD	8x10^{-4} / 60 / 40	8x10^{-4} / 74 / 26	4x10^{-3} / 0.01 / 100	2 / 29 / 69
	HYDD			7x10^{-3} / 0.02 / 100	2 / 29 / 69
BaP	PAH4	2x10^{-2} / 10 / 90.5	0.3 / 96 / 3	8x10^{-4} / 0.03 / 100	92 / 0.3 / 8 (4)

(1) results assuming the same (and fixed) atmospheric mixing depth as in Chemrange
(2) entry split 100/0/0 (air/water/soil), i.e. deviating from scenario (see Table 4)
(3) entry split 70/20/10 (air/water/soil), i.e. deviating from scenario (see Table 4)
(4) emissions in Europe and Siberia only

(b)

Substance	Zone	Scenario acronym	SimpleBox 2.0	MPI-MBM	MCTM
Atr Low mobility	N high lat.	LMDD	5x10^{-8} / 100 / 0.2	3x10^{-8} /9x10^{-6} /100	23 / 22 / 51
		LYDD		2x10^{-5}/ 4x10^{-4}/ 100	16 / 23 / 61
	N mid lat.	LMDD	7x10^{-5} / 1 / 99	3x10^{-4}/ 6x10^{-3}/ 100	0.3 / 0.2 / 99
		LYDD		3x10^{-4}/ 9x10^{-3}/ 100	0.3 / 0.3 / 99
	Tropics	LMDD	4x10^{-4} / 1 / 99	–	1 / 0.2 / 99
		LYDD		0.3 / 13 / 87	2 / 0.4 / 98
	S mid lat.	LMDD	–	3x10^{-4} / 0.01 / 100	1 / 2 / 97
		LYDD		3x10^{-4} / 0.02 / 100	3 / 6 / 91
	S high lat.	LMDD	–	3x10^{-8}/ 1x10^{-6}/ 100	33 / 66 / 1
		LYDD		5x10^{-7}/ 2x10^{-5}/ 100	32 / 67 / 1
Atr High mobility	N high lat.	HMDD	4x10^{-9} / 99 / 0.02	3x10^{-8} /7x10^{-6} /100	2 / 67 / 31
		HYDD		2x10^{-4} /5x10^{-3}/ 100	2 / 66 / 32
	N mid lat.	HMDD	0.02 / 50 / 50	3x10^{-4}/ 5x10^{-3}/ 100	1 / 0.2 / 99
		HYDD		4x10^{-3} / 0.07 / 100	0.8 / 19 / 80
	Tropics	HMDD	2x10^{-3} / 57 / 43	–	4 / 21 / 75
		HYDD		0.3 / 14 / 86	4 / 23 / 73
	S mid lat.	HMDD	–	3x10^{-4}/ 9x10^{-3}/ 100	1 / 84 / 14
		HYDD		4x10^{-4} / 0.01 /100	1 / 85 / 13
	S high lat.	HMDD	–	3x10^{-8} / 1x10^{-6}/100	1.5 / 98 / 0
		HYDD		5x10^{-7} / 2x10^{-4}/100	1.7 / 98 / 0.2

water compartment is predicted by SimpleBox and Chemrange only under the high mobility scenarios, predicting 60% and 74% in ocean water, respectively. Note that SimpleBox is the only model which considers transfer from soil to ocean (river runoff). If effective, this process should be reflected in the burdens of these compartments in particular for water soluble substances such as atrazine, which is not the case.

Volatilisation from soil is another process which limits the shift from soil to water. Retention in soil is high for substances with high K_{ow}. K_{ow} is lower under the Atr-high than under the Atr-low scenario (cf. Table 2), which is reflected in a significant shift of the burden to the ocean in the SimpleBox and Chemrange simulations, but not in the MPI-MBM simulation. Phase partitioning in the soil multiphase system, as in the other MBMs, is considered to limit volatilisation in the MPI-MBM, but it is mediated by an empiric parameterisation (Smit et al. 1997) of loss of the gaseous fraction from the pore space. This fraction is extremely low (p is only $3.85\text{x}10^{-5}$ Pa, cf. Table 2) and limits escape from soil effectively. The same parameterisation is used in the MCTM, but the statistics of soil conditions varying in both time and location produce another volatilisation rate, expectedly not represented by the arithmetic mean of the conditions.

2.2 Substance fractions stored in air

Overall, MBMs predict a smaller fraction of the total environmental burden to reside in air than the MCTM (cf. Table 5). The reason could be in air or sources to air over a lifetime. The latter is unlikely, as the same parameterisations are used in the MPI-MBM and MCTM (cf. Table 1). More likely, MBMs transfer mass faster from air to soil. For example, SimpleBox simulations were performed under scenarios with release mostly or completely into air for α and γ-HCH (see footnotes 2 and 3 in Table 5a). Again, the mass is predominantly found in the soils. We speculate that the MBMs overestimate atmospheric sinks using continuous precipitation instead of intermittent (underestimate of the atmospheric fraction; Hertwich 2001) and constant OH radical concentration instead of fluctuating (underestimate of the atmospheric fraction; Lammel 2004). Also, we suggest that dry particle deposition is overestimated in MBMs: The particle deposition velocity used corresponds to particles of size close to the mass median size of many aerosols (ca. 3 µm; Mackay 2001), while the mass size distribution of semivolatile substances is expected to follow the surface size distribution of aerosols, which peaks between 0.2 and 1 µm (Jaenicke 1988). Particle deposition is calculated for 4 size modes separately in the MCTM (Stier et al. 2005). Wet deposition of gaseous substance might be overestimated in MBMs, too. On the other hand MBMs neglect scavenging of gaseous molecules by snow which is more efficient than by rain (Lei and Wania 2004). The effect of the different treatment of atmospheric deposition processes to be clarified, however, requires quantification on the individual mass transfer process level, which was not a subject of this study.

2.3 Overall environmental residence time

The overall residence time for the models used refers to a scenario of continuous emission. While the Chemrange and SimpleBox models simulate distribution and degradation under steady-state conditions, overall residence time from MPI-MBM and the MCTM simulations are determined before establishment of steady-state conditions (pseudo-steady-state in the case of the MCTM, which generates its own interannual climate variability) for some of the substance scenarios and compartments (e.g. MCTM: Atrazine under the high mobility scenario, lindane and DDT in soil, **Fig. 1**).

The representation of final sinks in the models, e.g. burial in the sediment, is expectedly a key for model-based overall residence time prediction and, hence, for the interpretation of related discrepancies (e.g. Scheringer et al. 2004). While the MCTM and SimpleBox considered burial in the deep sea and in the sediments, respectively, no such final sink was considered in the MPI-MBM or Chemrange1.0 (but in Chemrange2.1).

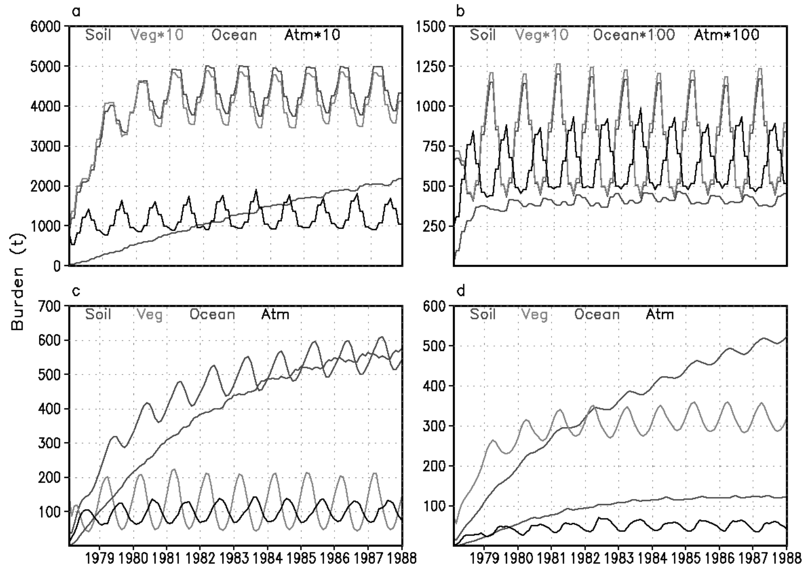

Fig. 1: Change of compartmental burdens over time (10 years) in the MCTM simulations of atrazine (a. AHYDD , b. ALYDD), lindane (c. LG80HM) and DDT (d. DG80HM)

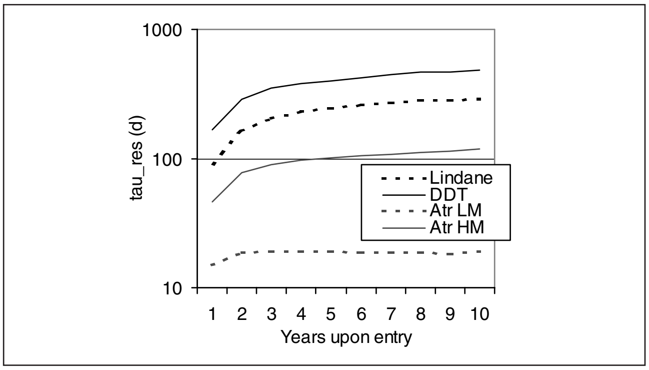

Fig. 2: Change of persistence over time (10 years) in the MCTM simulations of atrazine (scenarios ALJDDD, AHJDDD), lindane (LG80HM) and DDT (DG80HM)

Overall residence time values reflect the compartmental distribution. As the MCTM predicts the highest partitioning to air (Section 2.1), the τ_{res} values predicted by the MCTM are accordingly lower than for the other models.

γ-HCH. The total environmental persistence as derived from Chemrange and SimpleBox simulations, 549 and 503 d, respectively, exceed slightly the range spanned by values for overall residence time derived from the MCTM: This range is 162–287 d for the years 2–10 upon entry. As persistence is increasing with time elapsed since entry and is approaching pseudo-steady state according to the MCTM prediction (**Fig. 2**), this discrepancy is expected to decrease in later years of substance fate. The MPI-MBM predicts 62–194 d for this time period, which is considerably less.

DDT. The persistence as derived from Chemrange and SimpleBox simulations, 2670 and 2307 d, respectively, exceed the values for persistence derived from the MCTM: This range is 288 and 485 d for global emissions of DDT in years 2 and 10 upon entry, and is 317–1527 d for the second year upon entry from various locations around the globe (**Table 6**; 7 selected countries; Leip and Lammel 2004). The geographic distribution of the usage pattern matters and may imply an additional uncertainty, 10–15% as based on the usage patterns of 1980 and 1990 (cf. Table 6). The MPI-MBM predicts 50 and 132 d for years 2 and 10, respectively, and between 21 and 85 d for various climatic zones (**Fig. 3**). These values are lower than the values predicted by the other MBMs, because persistence from MPI-MBM simulations reflects states prior to establishment of steady-state.

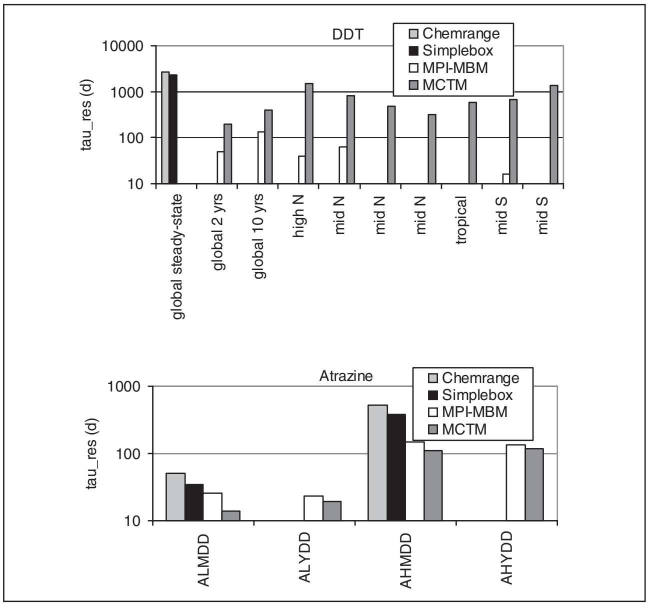

Fig. 3: Values for total environmental residence time of DDT and atrazine derived from the models SimpleBox, Chemrange (steady state), MPI-MBM and MCTM (non-steady state) under scenarios of global and, for DDT, also regional usage (country-scale; FIN = Finland, F = France, TR = Turkey, CN = China, RI = Indonesia, ZAM = Zambia, RA = Argentina). Simulation time: see Table 3

Table 6: Results: Overall residence time (d)

Substance	Scenario acronym	SimpleBox	Chemrange	MPI-MBM	MCTM
γ-HCH	LG8020	503 425 (8)	549 (7) 495 (8)	26	341
	LG80HM			104	287
DDT	DG80HM	2307 (5)	2670 (5)	132	485
	DG90HM				430
	D7C05			21–85 (1)	317–1527
MeP	MLJADD	–	–	1.0	3.7
	MHJADD			76	62
Atr	LMDD	34	51	26 (18–81) (1)	14
	LYDD			23 (16–73) (2)	19
	HMDD	373	530	149 (101–469) (1)	110
	HYDD			135 (4.4–422) (2)	117
BaP	PAH4	(2017) (6)	56 213 (6)	151 (3)	510 (4)

(1) Temperatures covered: T = 263-288 K
(2) Temperatures covered: T = 263-298 K
(3) Temperature and hydroxyl radical concentration representative for mid latitudes
(4) Emissions from Europe and Siberia only
(5) Calculated for 70/20/10 (soil/air/water), Chemrange 2.1: 2312 d (Klöpffer and Schmidt 2003)
(6) Calculated for 50/50/0 (soil/air/water), Chemrange 2.1: 228 d (Klöpffer and Schmidt 2003)
(7) Calculated for 100/0/0 (soil/air/water), Chemrange 1.0
(8) Calculated for 70/20/10 (soil/air/water), Chemrange 2.1: 503 d (Klöpffer and Schmidt 2003)

Atrazine and methyl parathion. The persistence of atrazine as derived from Chemrange1.0 simulations, 51 d under low mobility and 530 d under the high mobility scenario, exceeds the respective values for persistence derived from the MCTM by a factor of 2.5–5. Under a slightly different release scenario, air/soil/vegetation = 20%/70%/10% instead of 15%/85%/0%, Chemrange1.0 predicts 321 d (Klöpffer and Schmidt 2003). Similar values are predicted by SimpleBox. Each of the two values from the MCTM are compared with one value from the MBMs here, as the mode of entry had been varied, too, in MCTM simulations, namely allocating what is applied to 'soil' and partly (10%) to vegetation. This variation, however, has only a minor influence (explains less than a factor of 1.5). The MPI-MBM are somewhat higher, 15–90%, than the MCTM persistence values. Here, a range of results is also given as corresponding to a range of temperatures (cf. Table 6, Fig. 3).

Between the two models studying methyl parathion persistence, MPI-MBM and MCTM, a discrepancy by a factor of 3 is predicted for the persistence of methyl parathion under the low mobility scenario, while a good agreement, 76 and 62 d, is found under the high mobility scenario.

BaP: A large discrepancy is found between the Chemrange and MPI-MBM (56 d and 151 d, respectively) and the other models which predict a higher persistence, 510 d and even 2017 d by MCTM and SimpleBox, respectively. This is only partly explained by the differences in the compartmental distribution (Section 2.1) and might be related to compartments with zero degradability, Arctic soil (large volume) and sediment in SimpleBox, while residence in sediments is neglected for derivation of the overall residence time in Chemrange (see also discussion in Klöpffer and Schmidt 2003).

2.4 Effect of climate

Atrazine compartmental distributions were studied for different climatic zones (cf. Table 5b). Again, the highest fraction in air is predicted by the MCTM. The effect of climate on the distributions is less pronounced for the MBMs which consider temperature and ground surface fractions (land, sea, soil, etc.) than for the MCTM which covers geo-referenced and temporally varying distributions of these parameters and, in addition, the large scale atmospheric dynamics and its temporal statistics and some more ground surfaces' features (Section 1.1). Accordingly, there are also differences between similar climatic zones on the two hemispheres. For example, under the high mobility scenarios, most of the burden is predicted to be stored in the ocean water of the S mid latitudes but in the soils of the N mid latitudes. This is obviously an effect of the very different land-sea distribution. The suppressed escape from the compartments of entry limits this effect to a few percent under the low mobility scenarios. Note, however, that according to the SimpleBox simulation, the effect of a temperature change from 285 to 298 K (mid latitudes to tropics) pushes 9% of the burden from water into soils, while the MPI-MBM predicts 14% to be shifted from ocean water to soil and vegetation and the MCTM 3 and 4% from ocean water to air and soils and vegetation, respectively. This suggests that temperature affects distribution more in the box models, while temperature is only one among many climate factors acting in the transport model. For a tropic climate, the MPI-MBM predicts transfer of a significant fraction from the compartments of entry to water and a similar distribution than the MCTM under the high mobility scenario. This result is explained by the ground surface distribution assumptions, namely 100% vegetation and no (bare) soil area on land in the tropics. Therefore, volatilisation into air from soil is not occurring and the parameterisation (see above) cannot influence the distribution. The practical non-existence of soils in the N (SimpleBox) and S high latitudes (MCTM) forces the distribution to air and ocean water alone. The MCTM predicts that a third of the burden which reached (via air) the S high latitudes is stored in air and two thirds have been deposited to ocean water.

2.5 Long-range transport potential

The values for *MS* (MCTM) in air and ocean exceed those for *SR* (Chemrange) in most cases (**Table 7**). For HCHs, the indicators for the LRT potential in air, however, are in good agreement. The agreement found for α-HCH (*SR* falls into the respective range spanned by the values for *MS* which vary by a factor of 4; **Fig. 4a**, cf. Table 7) is biased, because lifetime in air with respect to degradation is considerably shorter in the MCTM: The OH radical reaction rate constants deviate by a factor of 4 (footnote 21 in Table 2).

Table 7: Results: Long-range transport potential indicators

Substance	Scenario acronym	*Spatial Range* (km) from Chemrange			*MS* (km) from MCTM			
		Air	Ocean	Soil	Air	Ocean	Soil	Vegetation
α-HCH	A7C10	18600	24400	4x10^{-3}	7700–30370	5410–23840	2070–4540	790–6070
γ-HCH	LG80HM	18800	10000	4x10^{-3}	20908	17053	6603	2544
DDT	DG80HM	22000	21600	2880	12695	14960	728	433
	DG90HM				30151	26882	10422	1597
	D7C05				18770–34930	11750–30970	5820–24880	450–6390
Atr	LMDD	1320	680	4x10^{-3}	13785	11198	–704	–1771
	LYDD				10229	4998	–2735	–2742
	HMDD	1320	4800	4x10^{-3}	13707	11528	–328	–1070
	HYDD				10488	5588	–2506	–2587
BaP	PAH4	1000	12000	1000	9864	10194	2512	2310

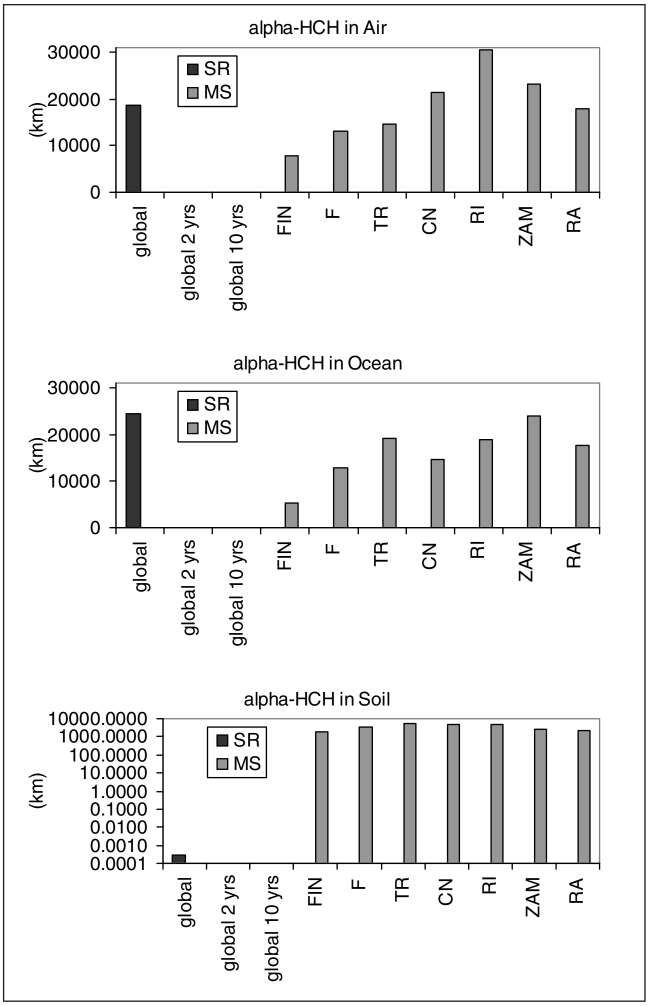

Fig. 4: Indicator values for the long-range transport potential of α-HCH in meridional direction in (a) air, (b) ocean water and (c) soil, *Spatial Range* (*SR*; Chemrange) and *Meridional Spreading* (*MS*; MCTM), for various years upon entry under scenarios of regional usage (country-scale; FIN = Finland, F = France, TR = Turkey, CN = China, RI = Indonesia, ZAM = Zambia, RA = Argentina)

The *SR* values of α-HCH do not fall into the ranges of respective *MS* values in ocean and soil. The predicted *SR* in soils is 0.004 km, while 2070–4500 km (**Fig. 4c**, cf. Table 7) and 790–4500 km are predicted for MS_{soil} an $MS_{vegetation}$, respectively. The indicators address different processes, though: In Chemrange transport in ocean and soil are considered, but SR is still dominated by transport in air (and subsequent deposition to the ocean or soil surfaces), while in the MCTM it is the change of distribution in ocean or soil as a consequence of transport only in air. Shorter transports in soil, as measured by *SR*, result from small substance fractions released into air (typically $\leq 5\%$, cf. Table 3). Despite a 15% release into air, atrazine under the HMDD scenario is still less transported. Interestingly, however, despite zero release into air, DDT is predicted to undergo LRT (*SR* = 2880 km). Obviously, Chemrange mobilises DDT from soil more efficiently than HCH and atrazine, probably as a consequence of differences in vapour pressure and water solubility (cf. Table 2).

For DDT Chemrange predictions of the LRT potential comes closest to the MCTM prediction: The values for *SR* (Chemrange) in atmosphere and ocean (surface layer) fall into the respective ranges spanned by the values for *MS* (MCTM) (**Fig. 5a,b**, cf. Table 7). These vary by a factor of 2 and 3 in the atmosphere and ocean, respectively. However, the values for *SR* in soils are significantly lower and outside the range spanned by MS_{soil} or $MS_{vegetation}$ (**Fig. 5c**). These vary by a factor of 4 and 12 in the soils and vegetation (surfaces), respectively. This agreement might be related to the fact that no effect of neglecting the hydroxyl radical fluctuations is expected for DDT (Lammel 2004), which is probably a consequence of the slow degradation rate (cf. Table 2).

LRT in air of the two non-volatile substances atrazine and BaP is dramatically less efficient, i.e. one order of magnitude, according to Chemrange prediction than according to the MCTM prediction (cf. Table 7). The variabilities of volatilisation from soil determining conditions in the MCTM may give raise to significant volatilisation as opposed to uniform environmental conditions in the box model. Obviously, lifetime in air as predicted by Chemrange is limited by deposition processes only, while the difference in degradation in air for atr-high vs. atr-low does not translate into any difference in transport length (1320 km in both cases, cf. Table 7).

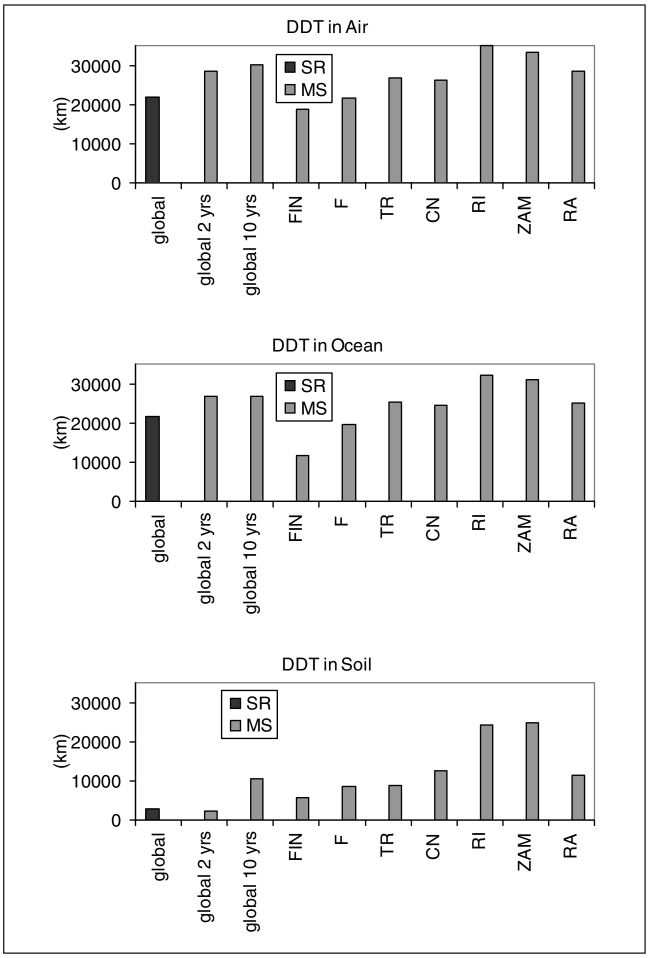

Fig. 5: Indicator values for the long-range transport potential of DDT in meridional direction in (a) air, (b) ocean water and (c) soil, *Spatial Range* (*SR*; Chemrange) and *Meridional Spreading* (*MS*; MCTM), for various years upon entry under scenarios of global and regional usage (country-scale; FIN = Finland, F = France, TR = Turkey, CN = China, RI = Indonesia, ZAM = Zambia, RA = Argentina)

In general, multimedia fate box models should underestimate the LRT potential because they underestimate the fraction residing in air (see Section 1.1). Furthermore, the representation of transports is very different: While transport in Chemrange is represented by a fixed macroscopic or eddy diffusion coefficient, corresponding to a typical tropospheric intrahemispheric mixing time (taken as 1 month; Scheringer 1996), the MCTM simulates the large-scale dynamics and its typical velocities in the boundary layer, free troposphere and the lower stratosphere. Some of these transports aloft are significantly faster than the typical tropospheric, intrahemispheric mixing. The latter, however, can substantially exceed 1 month. The agreement of LRT potential in air predicted for DDT and HCH suggests that it is degradation in air (not limiting for these substances) which might dominate the discrepancy. Overall, the consequence of neglecting the temporal and spatial variabilities of climate parameters (precipitation, oxidant concentration, wind speed) seems to be an underestimate of the significance of the atmosphere for the multicompartmental cycling.

Agreement between MBMs with respect to the LRT potential was reported to be very good with regard to ranking substances, but deviations up to a factor of 20 are to be expected for quantification of the LRT potential (Muir et al. 2004). Here, we found discrepancies for the predictions of the LRT potential in air typically within a factor of 2 for HCH and DDT, but up to a factor of 10 in the case of the non-volatile substances atrazine and BaP.

3 Overall Conclusions and Perspectives

There is a tendency of MBMs to overestimate substance sinks in air and to underestimate atmospheric transport velocity as a consequence of the neglection of the temporal and spatial variabilities of these parameters.

MBMs should be improved in order to ascertain that the significance of the atmosphere for the multicompartmental cycling is not systematically underestimated. It has been stressed that simple strategies are at hand to account for at least some of the temporal variabilities of the atmospheric environment (Hertwich 2001, Lammel 2004). The spatial and temporal variabilities of transport efficiency in air, i.e. wind speed or tropospheric intrahemispheric mixing time, should also be addressed.

In future research, a detailed understanding of the deviations observed in this work and elsewhere should be gained. The easy-to-use, rapid box models could be 'tuned in' to better match the results of the comprehensive MCTM. This elaborate model, however, should also be adapted to better suit the needs for modelling persistent, water soluble compounds for which the transport in rivers and oceans may be more important than the transport in the atmosphere. Box models will continue to play an important role for rapid screening of the great number of potentially persistent organic pollutants (POPs) and other persistent chemicals to be identified within REACH. Since observational data from remote areas – the direct proof for long-range transport - will be available only for few substances, MCTM may play the role of a standard to be applied for characteristic representatives of chemical groups.

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