Cycling of DDT in the global environment 1950–2002: World ocean returns the pollutant

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[1]   The global distribution and fate of the insecticide DDT was modeled for the first time using a spatially resolved global multicompartment chemistry-transport model comprising a 3D coupled atmosphere and ocean GCM, coupled to 2D vegetation surfaces and top soils. DDT enters the model environment as a pesticide in agriculture only. Final sinks of DDT in the total environment are degradation in air (hydroxyl radical reaction), on vegetation surfaces, in ocean sediments and soils. The process resolution of the ocean compartment, i.e., either a fixed or variable size and sinking velocity of suspended particles, has almost no effect on the large-scale cycling and fate of DDT. The residence times in various ocean basins were declining but varied regionally. The global ocean absorbed until 1977 and since then has been losing DDT, while large sea areas are still accumulating the pollutant. The main sink is volatilization to the atmosphere. In 1990, the year when emissions ceased, 292 kt of DDT were deposited to the global ocean, 301 kt were volatilized, and 41 kt were exported from the surface layer to the deeper levels. The sea region that has been representing the most significant (secondary) DDT source is the western N Atlantic (Gulf stream and N Atlantic Drift regions). It has been a source since approximately 1970. Also large parts of the tropical ocean and the southern mid-latitude ocean have turned net volatilizational (i.e., volatilization flux > deposition flux) during the 1980s. Despite the emissions migrating southward as a consequence of substance ban in mid latitudes, the geographic distribution of the contaminant (and, hence, environmental exposure) has been migrating steadily northward since the 1960s. **Citation:** Stemmler, I., and G. Lammel (2009), Cycling of DDT in the global environment 1950–2002: World ocean returns the pollutant, *Geophys. Res. Lett.*, *36*, L24602, doi:10.1029/2009GL041340.

1. Introduction

[2]   Apart from environmental conditions (including ocean dynamics and the status of the marine biosphere), the capacity of the ocean surface layer to store organic trace contaminants is regulated by their water and – because of suspended particulate matter - organic solubilities, partial pressure and the level of pre-contamination of the seawater. Organochlorides have been uptaken by the world ocean for decades. Saturation and subsequently reversal of the air-sea gas-exchange has been observed in the open ocean for hexachlorocyclohexane (HCH) in northern mid and high latitudes [*Bidleman et al.*, 1995; *Lakaschus et al.*, 2002], but so far not for any other organic contaminant with exclusively anthropogenic sources.

[3]   DDT is an insecticide which was first applied in the late 1940s and until the 1970s in large amounts in agriculture worldwide, approximately 1.5 Tg [*United Nations Environment Programme* (*UNEP*), 2003]. After its persistence and toxicity to wildlife (upon bioaccumulation along food chains) had been discovered [*Carson*, 1962], it was substituted in mid-latitude and later in low-latitude agricultures. Accordingly, the substance has been reported to decline in air and soils, but is thought to still accumulate in the ocean and in sediments [*UNEP*, 2003]. Due to its persistence DDT continues to cycle between compartments and also to be primary emitted, as an impurity of a substitute pesticide, dicofol [*Qiu et al.*, 2005], and since a number of Asian and African countries reserve the right of its application for malaria control.

[4]   Transport in ocean and atmosphere and fluxes between these compartments are essential to understand global cycling of contaminants. It was the aim of this modeling study to follow the global fate and both the geographic and compartmental distributions of a high-volume production chemical from the early years upon first release until far beyond the peak application years.

2. Methods
2.1. Model Description

[5]   The multicompartment chemistry-transport model MPI-MCTM is based on the three-dimensional coupled atmosphere-ocean general circulation model ECHAM5-HAM/MPIOM-HAMOCC [*Roeckner et al.*, 2003; *Marsland et al.*, 2003]. It includes two-dimensional top soils and vegetation surfaces. An aerosol module (HAM [*Stier et al.*, 2005]) is embedded in the atmosphere and a biogeochemistry module (HAMOCC5 [*Maier-Reimer et al.*, 2005]) is embedded in the ocean. HAMOCC uses a nutrient-phytoplankton-zooplankton-detritus ecosystem model [*Six and Maier-Reimer*, 1996; *Maier-Reimer et al.*, 2005], and a carbon chemistry formulation following *Maier-Reimer* [1993]. The model offers two ways of defining gravitational sinking of detritus, i.e., constant sinking with 5 m d^{-1}, and particle-size dependent sinking. In the latter case aggregation of marine snow from phytoplankton and detritus produces a temporally and spatially varying size distribution and corresponding sinking velocities [*Kriest*, 2002; *Maier-Reimer et al.*, 2005].

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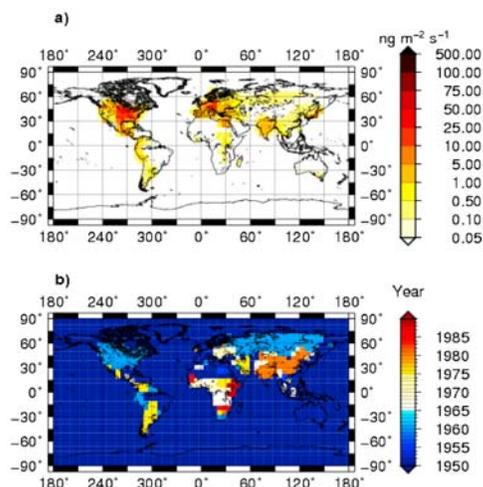
Figure 1. DDT emissions: accumulated application in agriculture (a) 1950–1990 and (b) year of peak application.

[6] Chemicals are cycling in atmosphere (gas, water and particle phase), ocean (dissolved, colloidal, particulate phase), and soil and vegetation surfaces. Cycling includes chemical degradation and mass exchange processes, which have been described previously [*Semeena et al.*, 2006; *Guglielmo et al.*, 2009]. In the ocean, in addition to advection and diffusion, chemicals in the particulate phase are subject to gravitational settling at the same velocity as detritus.

2.2. Emissions

[7] DDT application estimates for this study were adapted from a compilation of global agricultural usage 1950–1990 [*Semeena and Lammel*, 2003]. The emissions were compiled from data reported by member states to the UN Food and Agricultural Organisation (FAO), scaled with a $1° \times 1°$ cropland distribution. The total inventory of p,p'-DDT is approximately 1.2×10^6 t (see Figures 1 and S1[1] for annual application rates). Other DDT usage, such as malaria control or illegal use are ignored (due to data availability and/or quality). The emissions do not resolve any diel or seasonal cycles.

2.3. Model Experiments

[8] A resolution of about 5° (T21) and 19 vertical levels from 1000–10 hPa in the atmosphere with a time step of 40 min, and a nominal resolution of 3° in the ocean with a time step of 144 min were used. The ocean model uses an orthogonal curvilinear C-grid with one pole located over Greenland and the other over Antarctica. The model ocean has 40 vertical levels with level thickness increasing with depth. Eight levels are within the upper 90 m and 20 levels are within the upper 600 m. The coupling time step between atmosphere and ocean was 1 day. In the experiment, DDT was introduced following the agricultural applications during 1950–1990 using a split upon entry of 20% to soil and 80% to vegetation. No primary emissions in the period 1991–2002 were considered.

[9] The chemical DDT is characterized by a low vapor pressure and water solubility and a medium lipophilicity (Table S1). Degradation of the DDT in the environmental compartments is notoriously slow and is set to zero in seawater. DDT removal from the model environment is by degradation in soil only, represented as a first-order process ($4.05 \cdot 10^{-9}$ s^{-1} at 298 K [*Hornsby et al.*, 1996]) and assumed to double per 10 K temperature increase.

3. Results and Discussion

[10] The temporal evolution of the DDT burden in all environmental compartments follows the pattern of the applications (Figure S1), partly with significant delay (Table 1). Offsets from the application peak reflect the residence time of DDT in the compartments, which is shortest in the atmosphere (7.3 days), and longest in the ocean (23.7 years). The global ocean loses mass since 1977. Sinks for DDT in the model ocean are volatilization and degradation in sediment. Volatilization was found to be the dominant sink process: after 30 and 40 years, respectively, loss in the sediment still accounts for only 3.8 and 5.5% of total loss, respectively.

[11] The distribution of DDT in seawater shows a spatio-temporal pattern, which is far from reflecting the application pattern in the neighbouring continental regions. Obviously, sea currents and other features influencing residence time in seawater are involved. Thereby, neighboring regions, e.g., in the Atlantic Ocean, behave differently (Figure 2a), obviously in response to the environmental conditions, such as surface temperature, currents and deep water formation, and atmospheric deposition patterns. The Equatorial Ocean, as well as parts of the Arctic Ocean, and the Gulf Stream (including the North Atlantic Drift) region do not reach a maximum in burden until 1990, but still continue to accumulate DDT. Due to low mean sea surface temperatures volatilization is reduced in the Arctic Ocean, and DDT sources (deposition and inflow) dominate. The vertical stratification of DDT is defined by export with sinking particulate matter, and water movements (including deep water formation and upwelling). Both are spatially and temporally highly variable, but in general downward water movements dominate the removal of DDT from surface waters [*Guglielmo et al.*, 2009]. Globally, in the ocean below 100 m DDT mass is increasing continuously. This process significantly slowed down since the 1970s (Figure 2b). 76.0, 101.1, and 101.2 kt of DDT had been stored below 100 m of depth since the years 1970, 1980 and 1990, respectively. The surface ocean reaches a maximum DDT load in the late 1970s and early 1980s. A significant amount of DDT is not exported into the deep ocean, but returned to the atmosphere.

[12] The DDT volatilization flux from the global ocean was 2472 kt/year in 1970 but 301 kt/year in 1990. The total amount returned from the global ocean since the peak year

Table 1. DDT Dynamics in Environmental Compartments[a]

	Emissions	Atmosphere	Ocean	Soil	Vegetation
Year of peak burden	1960	1961	1977	1973	1966
Residence time [a]	-	0.02	23.70	14.93	1.20

[a]Global means were used.
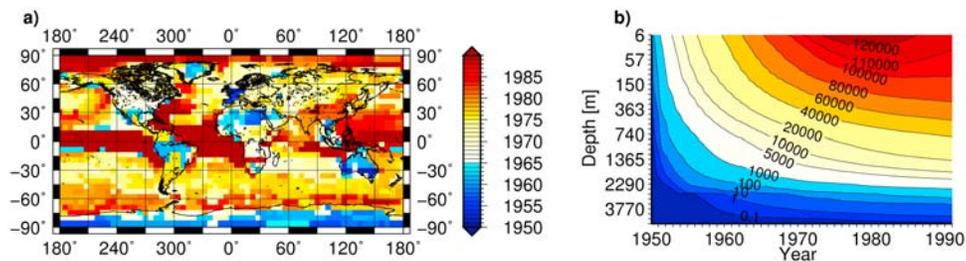
Figure 2. DDT in the global environment: (a) year of peak burden and (b) vertical distribution in the global ocean integrated from the sea bottom upward.

1977 was 13.4 kt until 1990. In 1990 292 kt were deposited to the ocean, 301 kt were volatilized, and 41 kt were exported from the ocean surface layer (i.e., ≤90 m depth) to the deeper levels. Outgassing of DDT started in the Atlantic ocean in the 1970s (Figure 3b), and was strongest in the extension of the Gulf Stream close to the mouth of the St Lawrence river. The Pacific ocean starts to return DDT to the atmosphere only 20 years after the Atlantic ocean, in the 1990s. The reason for the delay between the oceans is the much earlier application peak on American soils upwind with regard to the oceanic regions (Figure 1) in the 1950s, in contrast to the application peak in Asia in the 1980s (not shown). Large parts of the tropical ocean and the southern mid-latitude (so-called 'roaring fourties') turned net-volatilizational, i.e., volatilization flux exceeded deposition flux, in the 1980s. In general, in remote areas, regions with strong mean wind speed turn net-volatilizational earlier than regions with lower mean wind speeds (Figure 3b).

[13] The spatial pattern of net deposition in 2002 (Figure 3a) is obviously determined by prevailing environmental conditions, whereas the application pattern (Figure 1a) is not dominant anymore. This was different in 1990, when the net deposition pattern over land was still dominated by the spatial distribution of the applications in the 1980s. In regions of high DDT usage, such as India, large parts of Europe, and western Africa, the surface fluxes were net volatilizational. The model identifies the highest net volatilization fluxes in the year 2002 in the Northern Atlantic ocean, whereas over India, Europe and West Africa, deposition and volatilization are near equilibrium. Expectedly, ignored primary sources (health programs/malaria control, leakage from improper storage, illegal use) cause a modified spatial pattern in recent years.

[14] The residence time of DDT was derived for several oceanic regions from storage, volatilization, degradation in sediment, and advection out of the region. It was found to be strongly spatially and temporally variable (Table 2). Longest residence times are found in the Arctic, (1–7 a) and Southern Ocean (0.13–2.4 a), where deposition is favoured over volatilization due to cold mean surface temperatures. Short residence times are found in the Indian Ocean (0.04–1.0 a). These values are much lower than the residence time of DDT in the total compartment (23.7 a, Table 1), because the individual sea regions are small compared to the global ocean (Figure S2), and advection contributes to DDT turnover. Driven mainly by the decreasing deposition flux, the long-term trend is that the residence time of DDT is decreasing over time.

[15] DDT distribution in the total environment has been migrating slowly northward. The centre of gravity (COG, corresponding to the 50th percentile of the cumulative distribution function in zonal direction [Leip and Lammel, 2004]) of the total environmental burden of DDT was located at 47.4, 48.5, 50.0 and 53.0°N in 1960, 1970, 1980 and 1990, respectively. This is not explained by the
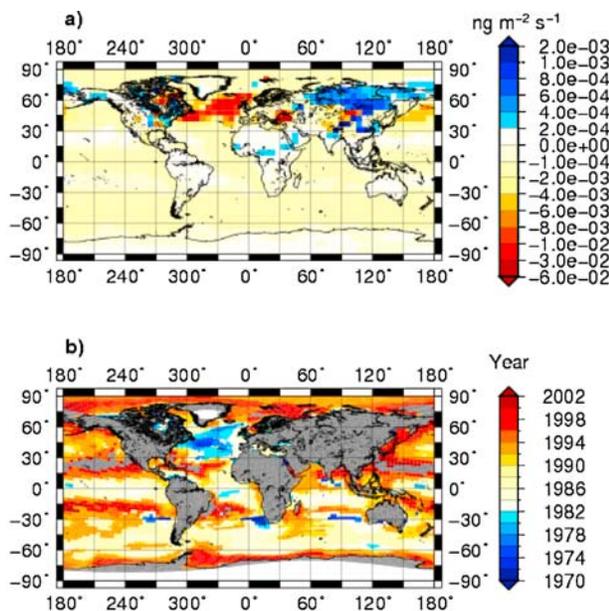
Figure 3. Net deposition: (a) annual mean in 2002 and (b) year in which the ocean turns net-volatilizational. Grey indicates no net-volatilization until 2002.

Table 2. Residence Times of DDT in Various Ocean Regions 1950–1990[a]

Region	1950	1960	1970	1980	1990
Labrador Sea, Baffin Bay, Hudson Bay	477	269	259	194	129
Norwegian Sea, Barents Sea	1090	525	491	251	156
Arctic Ocean	2592	1241	579	504	386
North Atlantic	172	103	86	63	50
Central Atlantic	84	37	39	47	62
South Atlantic	317	113	68	51	40
Indian Ocean	151	54	39	29	21
Pacific Ocean	229	73	57	46	37
Southern Ocean	893	165	98	70	50

[a]Residence times are in [d].

emissions which were located more southerly and, in contrary, moved further southward (COG at 43.1 and 42.7, 29.8 and 28.8°N in 1960, 1970, 1980 and 1990, respectively). Instead, it is obviously a consequence of the substance mobility, which is driven by atmospheric and oceanic transports and by repeated cycles through the atmosphere before final removal by degradation or transfer to the deep sea, the so-called grasshopper effect [*Wania and Mackay*, 1993; *Semeena and Lammel*, 2005; *Jurado and Dachs*, 2008; *Guglielmo et al.*, 2009].

[16] Due to lack of monitoring data before the early 1990s, validation of these model results is hardly possible. No observational data have been collected in most open ocean regions since decades. Oversaturation and reversal of the air-sea exchange had been observed previously for an other organochlorine pesticide, HCH, with respect to the isomer α-HCH in the Bering and Chukchi Sea between 1988 and 1993 [*Bidleman et al.*, 1995], in the North Atlantic off the Norwegian coast and in the Southern Ocean by 1999/2000 [*Lakaschus et al.*, 2002] and with respect to the isomer γ-HCH in the North Atlantic off the Norwegian coast [*Lakaschus et al.*, 2002], but not for polychlorinated biphenyls in the North Atlantic and Arctic Oceans [*Gioia et al.*, 2008]. The historic usage of technical HCH, PCB and DDT was by and large in phase [*Lohmann et al.*, 2007]. Both DDT and PCB are less water-soluble, more lipophilic (and, therefore, do partition more efficient to organic phases suspended in seawater) and less volatile than HCH, such that substantial differences of the cycling in the marine environment and the time reversal of air-sea exchange is expected.

4. Conclusions

[17] The results of a global long-term simulation of DDT cycling using historical application data suggest that until the 1970s the ocean acted as a global sink of DDT. But vertical export of DDT into the deep ocean was not sufficiently effective to compensate for high atmospheric deposition as a consequence of intense usage of the pesticide. From the end of the 1970s onwards, as a consequence of declining emissions following the ban of DDT in the different countries and, hence, depositions, parts of the ocean surface layer became oversaturated, and the net air-sea flux was reversed. This was not indicated by any study before. The decline of atmospheric levels over the ocean following the ban of DDT across countries and continents was hence superimposed by re-emissions from the ocean. To some extent, even atmospheric concentrations over the European continent may have been affected by DDT returned from the ocean via long-range transport in the atmosphere.

[18] A strong poleward migration of the contaminant's geographic distribution (and, hence, environmental exposure) is found in the northern hemisphere in agreement with previous findings, which, however, were based on simplified (non-transient) emission scenarios [*Guglielmo et al.*, 2009] or neglected oceanic transports [*Semeena et al.*, 2006].

[19] Direct evidence of DDT distribution and model validation is hampered by lack of monitoring data in the marine environment. The global cycling of DDT, due to re-entry in malaria and other vector-bourne diseases control and as impurity in a registered pesticide (dicofol), but also due to the chemodynamics in ocean and terrestrial compartments, deserves more scientific attention. Measurement campaigns should address potential source areas in the open ocean, such as the North Atlantic, and possible past influence on continental monitoring stations in Europe and the Arctic by advection from these sea regions should be studied.

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