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Long-range Atmospheric Transport and  
Total Environmental Fate  
of Persistent Organic Pollutants  
- A Study using a General Circulation Model

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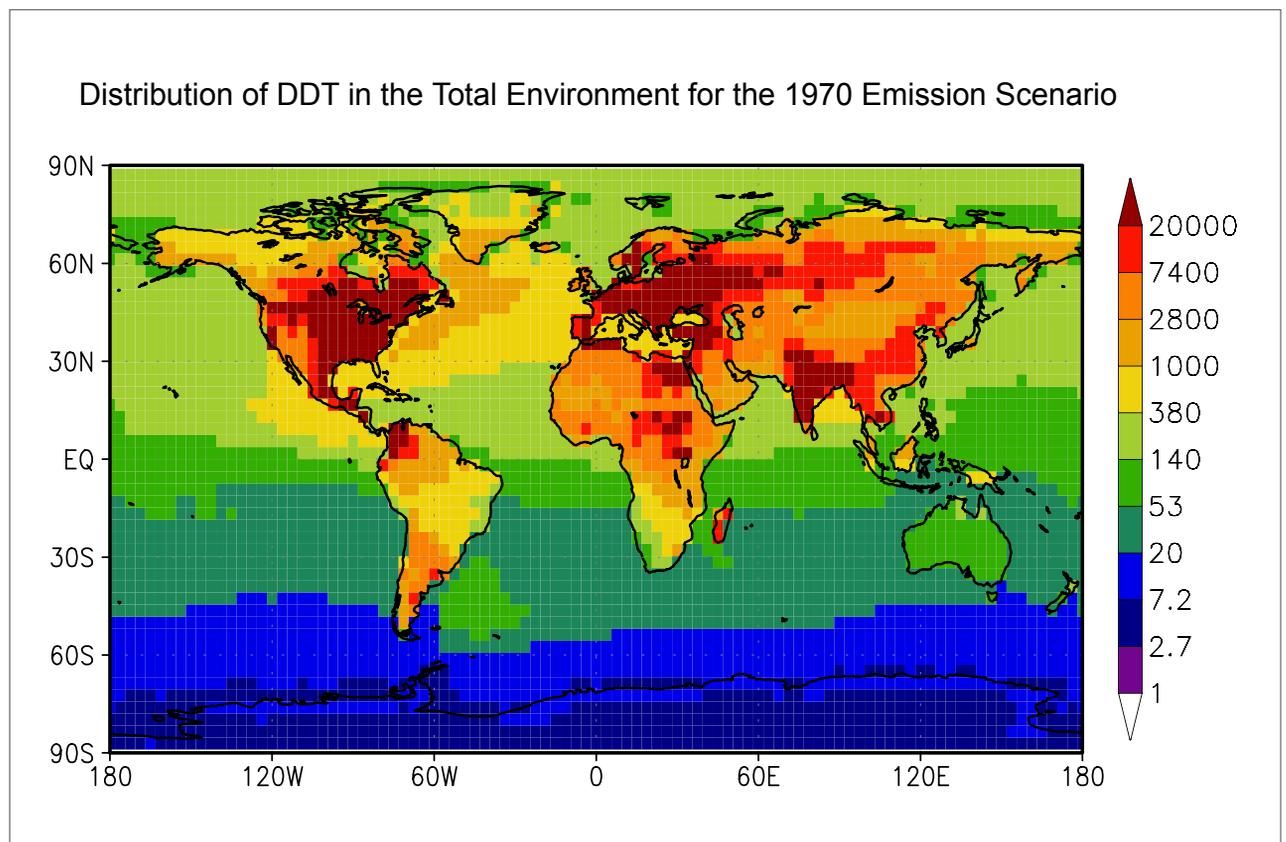
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# Long-range Atmospheric Transport and Total Environmental Fate of Persistent Organic Pollutants

## - A Study using a General Circulation Model

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Semeena Valiyaveetil Shamsudheen

Hamburg 2005



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## Abstract

Persistent bioaccumulative contaminants in pristine, remote regions like the Arctic are of great concern due to the hazard they pose to the ecosystems. These substances have been transported to the Arctic via atmosphere, ocean currents, rivers or biota (migratory birds or mammals). At least for semivolatile organic compounds on global to medium scales, long-range transport is most efficient in the atmosphere.

For the first time, a three dimensional atmosphere global general circulation model (ECHAM4 and ECHAM5), is used, to study the long-range transport of persistent organic pollutants, and their fate in the multimedia environment. ECHAM4 used a horizontal resolution of  $3.75^\circ \times 3.75^\circ$ , and ECHAM5  $2.8^\circ \times 2.8^\circ$ . Both of them use a terrain following 19 level vertical resolution, 1000 - 10 hPa. The models comprise a fully developed atmospheric compartment, soil with a 'bucket model' hydrology, two-dimensional vegetation surface and a mixed layer ocean. The transport and fate of two persistent organic pollutants, DDT and  $\gamma$ -HCH, which are subject to regulations, were studied. These two agrochemicals differ considerably in their physico-chemical properties. DDT is more lipophilic while  $\gamma$ -HCH is more hydrophilic.

Similar trends of multicompartamental behaviour were predicted by both versions of the model. Model experiments show that, while the strongest emission occurs in the tropics, the Arctic is contaminated. This long-range transport was quantified. The long-range transport potential of  $\gamma$ -HCH is higher than that of DDT. All the experiments show that DDT is more persistent than  $\gamma$ -HCH in the total environment, while  $\gamma$ -HCH is more persistent in the oceanic reservoir.

$\gamma$ -HCH seems to be more mobile (cycles more in atmosphere, i.e., 'multi-hopping') than DDT in total environment. Revolatilisation of both substances occur mostly from the soil surfaces. Even though the long-range transport potential of the 'single-hopping' event is more than that

of the 'multi-hopping' event, this study points out that a 'single-hopping' event also can move the substance from the equatorial region to polar regions, together with transport into higher altitudes. It is found that most of the multihopping occur in the boundary layer and close to the source regions. The multi-hopping fraction is found smallest in the stratosphere.

Case studies show that together with the general circulation of the atmosphere, regional weather systems play a key role in dispersing the substance regionally. Atmosphere and vegetation compartments reach quasi-steady state in three-four years, while the soil compartment shows a tendency to reach quasi-steady state in about ten years. The more hydrophobic DDT achieves quasi-steady state in ocean in six to seven years, while the hydrophilic  $\gamma$ -HCH accumulates in it.

It has been found that the fate, distribution and long-range transport are significantly influenced by the physico-chemical properties and the mode and location of entry. An emission only during non rainy days causes a shorter life-time than a daylong emission due to the fast degradation with OH radicals. This limits the tendency of the distribution to spread in the meridional or horizontal direction and hence the long-range transport potential. A faster atmospheric degradation can limit the atmospheric transport to a greater extent. An enhanced wash-out is observed with enhanced water solubility of the substance, which results in a threefold increase in deposition of  $\gamma$ -HCH over Arctic than DDT. A close inspection into the movement of mass in the environment over years shows that the mass is shifting towards north on a global scale. Mobility is also a function of the geographical location of application. A warm tropical region enhances the mobility and rather than a cold mid-latitudinal region. The DDT application maxima was shifted from north to south over the period 1970 to 1990 ( $15.2^\circ$  shift of Centre of Gravity). This corresponded to 36% increase in the long range transport potential.

An experiment with regional emission from India has shown that the monsoon winds carry the substance efficiently to the north (south-west monsoon winds) as well as to the south (north-east monsoon winds), together with a zonal spreading. Even though the emission takes place in the tropical region, the substances reach the Arctic and Antarctic. A cold terrestrial compartment over Alaska seems to support an enhanced cycling in the atmosphere together with enhanced long-range transport. Low concentrations as well as elevated concentrations in the same latitudinal zone are predicted as a consequence of regions being located leeward (such as equatorial Africa) or far off (such as the Indonesian region) of source regions.

Global modelling of persistent organic pollutants is still in its infancy. The experiments conducted were artificial with regard to emission (applied amounts). Non-reported usage of the

substances lead to an uncertainty. The application inventories used for this study were purely based on reported data and also assumed that 100% application takes place on agricultural land. This multicompartment model is incomplete in the sense that substance cycling does not include sedimentation, rivers, ice and the inner volume of biota. The oceanic compartment lacks transport due to currents. Soil-atmosphere exchange is not validated, and air-sea exchange does not contain all processes. Vegetation compartment provides only a surface for exchange with air. Due to these reasons, we cannot expect exposure modelling to predict environmental concentrations perfectly. Still the model experiments could simulate multicompartmental behaviour reasonably well. The simulated seasonality in atmospheric concentrations over continental sites of the Arctic compares reasonably well with those of observations.



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## Introduction

Since the 1960's, there has been growing concern regarding the presence of pesticides in the atmosphere. The monitoring results obtained [Bidleman *et al.*, 1990; Ballschmiter and Wittlinger, 1991; Iwata *et al.*, 1993; Davidson *et al.*, 2003; Villa *et al.*, 2003] show that traces of pesticides undergo long-range transport and can be deposited considerable distances away from the treatment areas, including remote regions such as the Arctic and Antarctic. Pesticides have been found in air, rain, cloud water, fog and snow [Nations and Hallberg, 1992; Siebers *et al.*, 1994; Simcik *et al.*, 2000]. The appearance and subsequent behaviour of pesticides in the atmosphere are complex processes and the concentrations found depend on several variables such as their volatility, photostability, formation and application technique, and extent of use. Volatility of pesticides is primarily influenced by the water solubility and the surfaces treated, e.g. soil or leaves, and by the extent to which the substance partitions to aerosols during and after application. The disappearance of pesticides from the atmosphere is due to photolysis (reactions with OH and NO<sub>3</sub> radicals), dry deposition and to deposition in rain [Unsworth *et al.*, 1999]. Pesticides which are resistant to hydrolysis and photolysis can be transported over great distances, e.g. organochlorine insecticides have been detected in the Arctic regions [Bidleman *et al.*, 1990; Harner *et al.*, 1999; Macdonald *et al.*, 2000]. Under most conditions the presence of pesticides in air, or rain water has no significant effect on non-target organisms. But one exception has been proven for both animals and humans and this is for Persistent Organic Pollutants (POPs) [UNEP, 2003].

POPs are organic compounds that, to a varying degree, resist photolytic, biological and chemical degradation. Most of them are characterised by low water solubility and high lipid (fat) solubility (called lipophilicity), leading to their bioaccumulation in fatty tissues. Furthermore many POPs are semivolatile, and hence are also known as Semivolatile Organic Compounds (SOCs).

Persistence refers to the property of a compound to remain a longer time in the environment before being broken down or degraded into other substances [Klöpffer, 1994; Malmquist *et al.*, 2003]. Semivolatility is the property to occur either in vapour phase or adsorbed to atmospheric particles, thereby facilitating long-range transport and accumulation over remote regions [UNEP, 2000]. In the aquatic environment, high lipophilicity results in the substance bioconcentration from the water into the organism. In polar regions they are more liable to bio-accumulate and be transported in the food web giving enhanced levels in fatty tissues and mother's milk [WHO, 1985; AMAP, 2003b]. Combined with environmental persistence and a resistance to biological degradation, lipophilicity also results in biomagnification along the food chain. It will be appropriate to integrate the persistence of daughter compounds (metabolites) also when assessing a compound's persistence [Kooijman *et al.*, 2002].

Many of the first generation organochlorine insecticides fall under the category of POPs (e.g. DDT). These substances are highly toxic and upon bioaccumulation may pose a hazard to wildlife (chronic effects). Organochlorine pesticides were originally manufactured due to their toxicity and the persistence, so that they can work against the pests for a longer time period, however, it was detected later that they are toxic to other non-targeted organisms too.

The possible pathways of POPs to pristine, remote regions like Arctic are atmosphere, ocean currents, large rivers and biota (migratory birds, sea mammals). In addition, the physico-chemical properties of the substances, and the time and location of their emissions decide upon the relative importance of these transport pathways. The atmosphere is the most efficient and rapid transport medium, where it takes only days to weeks for an air parcel to mix completely in the northern hemisphere [Shaw and Khalil, 1989; Barbara and Pitts, 1999], while the transport times of ocean currents are measured in years and decades [Willebrand and Anderson, 1987]. The persistence, low water solubility and high chemical and biological stability supports the potential to undergo such long-range transport to the Arctic from the warm temperate regions, resulting in longer life times in terrestrial compartments [AMAP, 2004].

In this thesis, an effort is made to understand for the first time, the long-range transport of POPs, and hence the behaviour in the receiving environmental media, using a three dimensional global atmospheric general circulation model (AGCM) [ECHAM; Roeckner *et al.*, 1996, 1999] with tracers, the sulfur cycle [Feichter *et al.*, 1996], and extended to a multicompartment model [Lammel *et al.*, 2001]. The four compartments are atmosphere, soil and vegetation surfaces and a mixed layer ocean. There is no transport in the ocean compartment, but degradation, loss to deep sea, and air-water gas exchange are included based on the standard two-film theory [Liss and Slater,

Table 1.1: Contents of the thesis chapters.

Chapter	Contents
1	Introduction
2	Properties of DDT and $\gamma$ -HCH, their global usage and compilation of application inventories.
3	Parameterisations of substance cycling used for ECHAM4 simulations.
4	Contents of the publication <i>Semeena and Lammel</i> [2003]
5	Contents of the publication <i>Semeena and Lammel</i> [2005]
6	Contents of the manuscript in preparation "Significance of the global and regional climate and of substance properties on the fate and long-range transport of persistent organic pollutants - Examples of DDT and $\gamma$ -HCH", to be submitted to <i>Atmos. Phys. Chem.</i> .
7	Conclusions and outlook.

1974] (see chapter 3). Two of the most widely used agrochemicals, DDT and  $\gamma$ -HCH, which are subject to regulation under international chemicals legislation (UNEP Stockholm POPs convention, POPs protocol of the UN-ECE LRTAP convention, besides other), are studied. Both of them are proven highly toxic to wild life. Both are non-polar, but have different physico-chemical properties. Organisation of the thesis is given in Table1.1.

Models are indispensable tools to study substance cycling and long-range transport. Several box models have been in use to understand the behaviour of persistent non-polar substances in the multimedia environment [Wania *et al.*, 2000; Scheringer *et al.*, 2002; Wania and Dugani, 2003]. Models composed of meridionally connected boxes have been used to study long-range transport in two dimensions [Mackay *et al.*, 1992a; Wania and Mackay, 1995; Scheringer *et al.*, 2002]. Atmospheric dispersion models and multicompartment regional to hemispheric [Hansen *et al.*, 2004] models are in use to investigate the environmental behaviour of persistent organochlorine pesticides [Berkowicz *et al.*, 1986]. A global study was first presented by Koziol and Pudykiewicz [2001] based on observed meteorology. However, there has been no previous study using a full fledged three-dimensional AGCM. Furthermore, unlike compartmental models such as atmospheric models, multicompartmental models are in addition, capable of addressing total environmental persistence and total environmental long-range transport potential - indicators inaccessible by observations.

Sensitivity studies for the different parameterisations can be efficiently performed with box models. The same applies to the selection of appropriate substance physico-chemical properties. But for a global scale understanding of the POPs behaviour, global AGCMs are the best tool available.

The rest of this chapter is devoted to providing a general insight about pesticides, with special emphasis on DDT and  $\gamma$ -HCH.

## 1.1 Organochlorine pesticides and their presence in the environment

Organochlorine pesticides are man-made organic chemicals composed primarily of carbon, hydrogen and chlorine, and of a unique class because of their cyclic structure, number of chlorine atoms, and low volatility. They are classified into four categories: dichlorodiphenylethers (e.g. DDT), cyclodienes, chlorinated benzenes (e.g. hexachlorobenzene, HCB), and cyclohexanes (e.g. hexachlorocyclohexane, HCH). These compounds partition to the vapour and particulate matter phases. They are usually highly halogenated, have a molecular weight of 200 to 500 g mol<sup>-1</sup> and a vapour pressure in the range 10<sup>-5</sup> - 10<sup>0</sup> Pa.

Even though these industrial chemicals have been in use as pesticides in agriculture and insecticides for domestic purposes since the 1940s, the world has become aware of the hazards of these substances only by 1962 when Carson's "Silent Spring" has been published [Carson, 1962]. The effect of pesticides and other toxic chemical pollutants on the environment and human health had been well documented before and environmental scientists were aware of the problem too. Carson synthesized this knowledge into a single image by joining the bits and pieces that everyone, scientists and the general public alike could easily understand.

The presence of pesticides in the atmosphere was first reported when there was significant usage of chlorinated products on a global scale; in particular DDT,  $\gamma$ -HCH, and dieldrin, which were found not only near the site of application but also in the polar regions [Bidleman *et al.*, 1990; Egan *et al.*, 1995; Pacyna, 1995; Harner *et al.*, 1999; Macdonald *et al.*, 2000]. Ever since then, techniques for collecting and analysing atmospheric samples for organic contaminants, from both natural and anthropogenic sources, have been developed and improved. The data show that the atmosphere can be an important transport system and sink for many organic compounds [Ballschmiter and Wittlinger, 1991]. The highest levels of pesticides are generally found close to the site of application and for a period which corresponds to the maximum application. However, these substances have been measured on every continent, representing every climate zones and geographic sectors even where significant sources can be totally excluded, such as open oceans

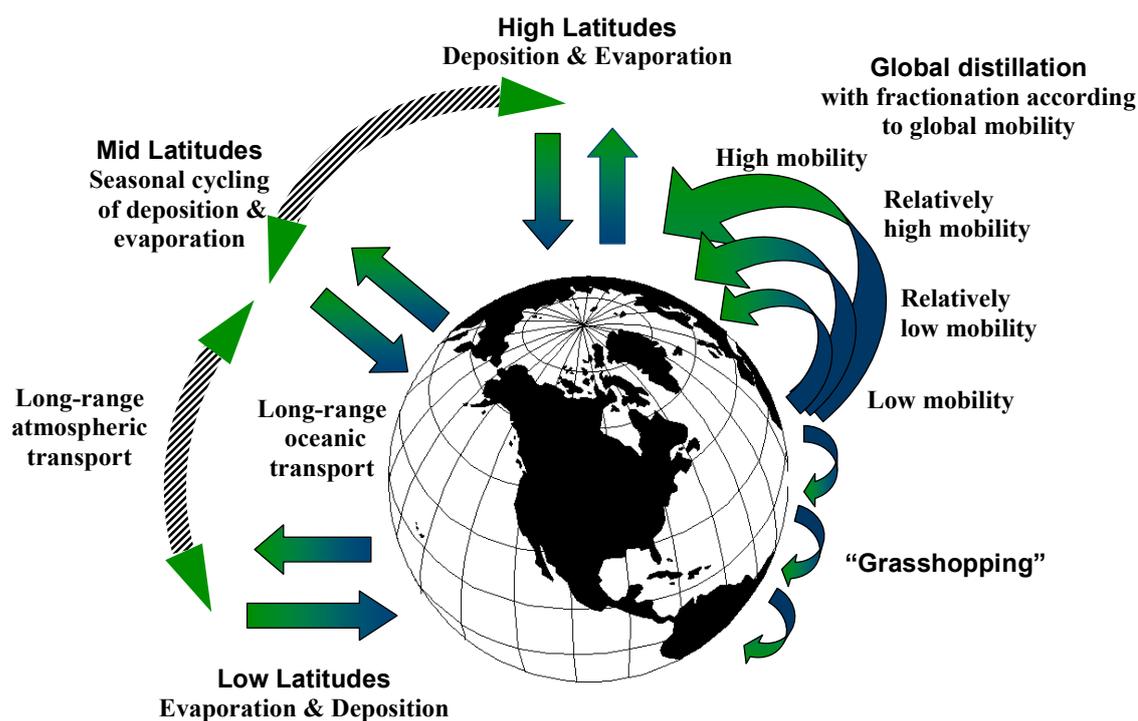


Figure 1.1: Long-range pathways of POPs (Adapted from [Wania and Mackay, 1995]).

[Tanabe *et al.*, 1982], the Arctic [Cotham and Bidleman, 1991], the deserts [Ritter *et al.*, 1995], the Antarctic [Weber and Monotone, 1990; Lohmann *et al.*, 2001; Lakaschus *et al.*, 2002], and the high mountains [Villa *et al.*, 2003]. These occurrences can only be the result of atmospheric or oceanic transport and subsequent wet or dry depositions. Evidently they are transported from low latitudes to high latitudes and hence 'cold condensation' occurs [Bidleman *et al.*, 1990; Wania and Mackay, 1993]: i.e. substances volatilise easily at higher temperature region (low latitudes) and are carried by winds until they meet cold temperature (high latitudes) to condense (Fig. 1.1). So the net effect would be transfer of the substance from warm tropics to cold poles. Because of cold condensation, Arctic waters would be formed into major sinks for organochlorines released around the world [Iwata *et al.*, 1993] and continued release of persistent, semivolatile chemicals to the environment at lower latitudes would pose a threat to the Arctic ecosystem [Li *et al.*, 1998].

As there is no central registry for the organochlorine pesticides, the information needed about the production and usage for this study were taken from different literature (who got them through personal contacts, contacts with international agencies and discussions with scientists world wide), environmental fact sheets and data banks. Voldner and Li [1995] compiled the data for the global usage of 10 pesticides from 1940s to 1990s. The estimate is given in Table 1.2. Data compiled for this model study are explained in Chapter 2.

Table 1.2: Estimate of global usage of selected organochlorine contaminants [Voldner and Li, 1995].

Organochlorines	Function	Usage time period	Estimated total global usage(Mt)
PCBs	Dielectric/ hydraulic fluid	1930-1992	1.2
DDT	Insecticide	1950-1992	2.6
		1970-1992	0.99
Toxaphene	Insecticide	1950-1992	1.33
		1970-1992	0.67
Lindane	Insecticide	1950-1992	0.72
Technical HCH	Insecticide	1948-1997	10.00
Chlordane	Insecticide	1945-1988	0.078
Aldrin	Insecticide	1950-1992	0.50
Dieldrin	Insecticide	1950-1992	0.034
Endosulfan	Insecticide	1956-1992	0.057

## 1.2 Entry of Substances into the environment

Entry of pesticides into the atmosphere can occur by several routes: drift during spray application in agriculture or forestry, volatilisation after application or from wind erosion of treated soil, spraying of insecticides in vector control (DDT played an important role in malaria control after second World War), pesticide manufacture/formulation, effluents, fumes, vapours, dust (industrial), moth proofing, protection of stored food, industrial hygiene, sanitation, insect control in buildings (commercial), local applications in home and garden, and via spilling and improper disposals [Unsworth *et al.*, 1999]. There are evidences that atmospheric transport can occur on the global scale, at least for the most stable products such as organochlorines [Ballschmitter and Wittlinger, 1991; Ballschmitter, 1992] and thus dry and wet deposition occurs on non-target areas after horizontal and vertical translocation.

Spray drift, is an important contributor to the presence of pesticides in the atmosphere close to the sources. For any pesticide, if the spray droplets are less than 100-150  $\mu\text{m}$  diameter they can be transported over long distances by air currents before they precipitate. Reports show that a significant proportion of some pesticides, disappear from the target area (soil or plants) and are present in the atmosphere immediately after application [Karthikeyan and Bhandari, 2001;

*Blight, 2002*]. Volatilisation also continues to occur a few days after application depending on the physico-chemical properties of the pesticide.

Moreover leaching to soil may occur upon pesticides application over crops. Pesticides classed as nonvolatile will be found as aerosols in the atmosphere, near the spray area and in downwind air [*Unsworth et al., 1999*]. In extreme cases soil particles containing adsorbed material can be transported over significant distances.

### 1.3 Long-range transport

For POPs, atmospheric transport should be seen as 'single-hop' pathways or 'multi-hop' pathways. When a compound is emitted to the atmosphere, transported and deposited to earth's surface and never returns to atmosphere, the process is called 'single-hop'. If a compound re-enters the atmosphere after initial deposition to the earth's surface, it can travel long distances via subsequent multiple atmospheric hops, (so-called 'grasshopper effect') (Fig. 1.1) [*Wania and Mackay, 1996*]. This can occur via volatilisation from the earth's surface under high temperatures driven out by soil moisture, or sudden exposure of ocean water to the atmosphere after being covered by ice, or by resuspension of dust or snow by winds. In principle it could happen following a diurnal temperature cycle with hopping during day-time and residing in condensed state during night-time. The transfer of chemicals from land surface to atmosphere comprises two steps: change from liquid or solid state to vapour and subsequent dispersion by turbulent mixing.

The general circulation of the atmosphere plays a key role in the global transport. During northern hemispheric winter, the continents are dominated by high pressure cells, and low pressure is dominating over northern Pacific and Atlantic oceans. Air is driven out from Eurasia into the Arctic in the case of intense Siberian high. On the other hand, the high pressure ridge over North America drives air out southward from the Arctic. This results in a mean flow of air out of Eurasia into the Arctic and out of the Arctic into southern North America. In summer the continental high-pressure cells disappear and the oceanic low pressure cells weaken, resulting in a decrease of the northward transport [*AMAP, 1997, 1998*].

In soil, transport follows the liquid water flux in the soil as dissolved constituents. Downward fluxes (leaching) will move the pesticides from the solid surface to deeper soil layers depending upon the water fluxes and partition in the multiphase system [*Plimmer, 2002*]. Upward fluxes are normally caused by evaporation at the soil surface or by water abstraction for plant transpiration [*Schafer et al., 2001*]. Diffusive transport occurs in both gas and liquid phase of the chemical. Diffusion and convection usually occur together [*Mackay, 2002*].

In the case of vegetation, penetration of substances into the wax layer of the leaves, mainly hydrocarbon, and further penetration into cuticle are related to the octanol-water partition coefficients [Trapp *et al.*, 1990; Trapp and Matthies, 1995; Boehme *et al.*, 1999; Franzaring and van der Eerden, 2000]. These processes are only understood for some compounds and some plant species [Mclachlan, 1996; Mclachlan and Horstmann, 1998; Kylin and Sjoedin, 2003]. Penetration into epicuticular waxes depends on the lipophilicity of the compound, and some empirical rules on this are: (1) non-polar compounds are better absorbed than polar, (2) solids with a low melting point better than those with a high melting point, and (3) liquids better than solids [Simonich and Hites, 1995].

Once deposited into the ocean surface, or received via river runoff, the substance is mixed with the bottom layers due to turbulent mixing, and transported to long distances via ocean currents. The air-sea gas exchange as influenced by many parameters, may be a very complex process [Tanabe *et al.*, 1982; Iwata *et al.*, 1993]. Temperature, wind and bubble breaking play key roles in this process. Studies show that non-polar persistent organics accumulate in ocean sediments or in biota (e.g. Baltic sea, coastal waters) [Hühnerfuss *et al.*, 1992; Breivik and Wania, 2002a, b].

## 1.4 Exposure and contamination

Exposure of invertebrates to harmful substances could occur directly or indirectly for soil dwelling organisms, by contamination of the soil by wet and dry deposition. For pesticides in air the predominant route of exposure is by inhalation. Pesticides may also be absorbed through skin, but this route of entry is limited largely to substantial direct contact between a liquid form of the pesticide and the skin. For land animals exposure could occur via the ingestion of contaminated plants, and contaminated aquatic species [Unsworth *et al.*, 1999]. Studies have shown that organic chemicals can be found on the surface and in leaves of non-target forest plants [Franzaring and van der Eerden, 2000; Barber *et al.*, 2003; Kylin and Sjoedin, 2003]. It is well established that forests are sinks for certain pesticides [Simonich and Hites, 1995]. There are no evidences so far on effects on trees. The uptake of pesticide vapour by plants has been examined in several studies [Boehme *et al.*, 1999; Franzaring and van der Eerden, 2000]. The results showed that local concentrations in air differed between upwind and downwind of a hedge due to the aerodynamic conditions around the hedge.

In the Arctic region, organochlorine insecticides are found at elevated levels in human milk compared to populations living outside this area which is a concern for breast fed babies. One of the reasons is possibly the deposition of the insecticides into the oligotrophic (low nutrient system) Arctic ocean. Thus the lipophilic molecules are taken up by the available plankton, bio-

magnification then occurs as the plankton are consumed by fish, the fish by seals and fish and seals by the indigenous population. Related effects have been recently assessed [WHO, 1985; Xhillari, 2000; AMAP, 2003b].

## 1.5 Effects on wildlife and humans

Effects resulting from chronic low level exposure are incompletely understood. There is plenty evidence that the long biological half-life in organisms causes accumulation of seemingly small unit concentration over extended periods of time. Accumulation of organochlorine pesticides in the body may lead to toxicologically relevant concentrations. There is epidemiological evidence of associations with chronic non-lethal effects including potential immunotoxicity, dermal effects, impairment of reproductive performance, cancer and others [AMAP, 2003a]. Immune dysfunction causes increased mortality among marine mammals [Jukes *et al.*, 1973]. Consumption of contaminated diets in seals may lead to vitamin and thyroid deficiencies and concomitant susceptibility to microbial infection and reproductive disorders [WHO, 1989; Ritter *et al.*, 1995; WHO, 2003; UNEP, 2003].

Exposure to persistent organochlorine pesticides has been correlated with population declines in a number of marine mammals including the common seal, the harbour porpoise, bottle-nosed dolphins and beluga whales from the St. Lawrence River [WWF, 1999a]. Studies demonstrated a direct cause-effect relationship in mink and ferrets between PCB exposure and immune dysfunction, reproductive failure, increased kid mortality, deformations and adult mortality [AMAP, 1998].

The risk is greatest in developing countries where the use of POPs in tropical agriculture has resulted in a large number of deaths and injuries. In addition, exposure during waste management is a significant source of occupational risk in many countries. Reports have suggested that children with high organochlorine dietary intake may experience rates of infection some 10-15 times higher than children with much lower intake levels [WHO, 2000]. Similar to wildlife species, also humans may encounter a broad range of environmental exposures to a mixture of chemicals at any one time. Evidences suggest a possible association between breast cancer and elevated concentrations of DDE (a metabolite of DDT) [WHO, 2003; WWF, 1999a; WHO, 1985]. Scientific evidences suggest that some POPs, e.g. PCBs, have the potential to cause significant adverse effects to human health, not only at the local but also at the regional and global levels following long-range transport [Sang *et al.*, 1999; UNEP, 2003].

### 1.5.1 Toxicological and ecotoxicological effects of DDT

Problems related to extensive use of DDT began to appear in the late 1940s. Many species of insects developed resistance to DDT, and DDT was discovered to have a high toxicity towards practically all species [Jukes *et al.*, 1973]. The chemical stability and its lipophilicity compounded the problem. In humans, blood cell cultures of men occupationally exposed to DDT showed an increase in chromosomal damage. Acute effects in humans due to low to moderate exposure may include nausea, diarrhea, increased liver enzyme activity, irritation of the eyes, nose or throat, malaise and excitability at higher doses, and tremors and convulsions [PAN, 1997]. Singh [1993] estimated that in some regions of India, average daily intake of DDT from mother's milk was between 13 and 24 times in excess of current WHO/FAO guidelines ( $0.005 \text{ mg kg}^{-1}$ ). A study in humans showed that women who had high amounts of DDE in breastmilk had an increased chance of having premature babies [ATSDR, 2002a]. Male reproductive abnormalities including malformed sexual organs, testicular cancer and related problems are reported [ATSDR, 2002a; Paasch *et al.*, 2003]. The Environmental Protection Agency (EPA) of the USA determined that DDT, DDE, and DDD are probable human carcinogens.

Lab experiments conducted with rats reveal that one-time administration of DDT to rats at doses of  $50 \text{ mg kg}^{-1}$  led to decreased thyroid function and single doses of  $50 - 160 \text{ mg kg}^{-1}$  produced tremors. A single dose of  $150 \text{ mg kg}^{-1}$  led to increased blood levels of liver-produced enzymes and changes in the cellular chemistry in the central nervous system of monkeys and hind leg paralysis in guinea pigs [EXTOXNET, 1996]. DDT has caused chronic effects on the nervous system, liver, kidneys, and immune systems in experimental animals. The main effect on liver seen in animal studies was localised liver damage due to long-term exposure to smaller amounts [ATSDR, 2002a]. Kidney effects observed include adrenal gland hemorrhage in dogs. Immunological effects observed in test animals include reduced antibody formation in mice and reduced levels of immune cells in rats. It has been shown to cause increased tumor production (mainly in the liver and lung) in test animals such as rats, mice and hamsters [Tomlin, 1997; WHO, 2000].

DDT is highly toxic to many aquatic invertebrate species and fish species. Fish uptake of DDT from the water will be size-dependent with smaller fish taking up relatively more than larger fish. In addition to acute toxic effects, DDT may bioaccumulate significantly in fish and other aquatic species, leading to long-term exposure. In birds, exposure to DDT occurs mainly through the food web through predation on aquatic and/or terrestrial species such as fish, earth worms and other birds [EXTOXNET, 1996].

### 1.5.2 Toxicological and ecotoxicological effects of $\gamma$ -HCH

$\gamma$ -HCH is generally considered to be the most acutely toxic of the HCH isomers (see chapter 2, section 2.2 for details of HCH isomers) following single uptake. The most important route of human exposure is oral, via contaminated food, and dermal when it is applied to the skin as a lotion or shampoo to control lice and scabies (a contagious skin disease caused by mites) [Willet *et al.*, 1998]. Infants are exposed through ingestion of mother's milk. Higher concentrations of lindane (> 99%  $\gamma$ -HCH, see section 2.2) and other HCH isomers have been found in human tissues and mother's milk in developing countries [Sang *et al.*, 1999]. In humans, the effects of breathing  $\gamma$ -HCH and or other isomers of HCH are, blood disorders, dizziness, headaches, and changes in the levels of sex hormones. These effects have occurred in workers exposed to HCH vapours during pesticide manufacturing. People who have swallowed large amounts have had seizures and some died. Cases were reported where the use of large amounts of  $\gamma$ -HCH or frequent application to skin led to blood disorders or seizures [ATSDR, 1994].

Effects of high acute exposure to lindane may include central nervous system stimulation (usually developing within 1 hour), mental/motor impairment, excitation, clonic (intermittent) and tonic (continuous) convulsions, increased respiratory rate and/or failure, pulmonary edema, and dermatitis [WWF, 1999b]. Other symptoms in humans are more behavioural in nature such as loss of balance, grinding of the teeth and hyper-irritability. Lotions applied for scabies have resulted in severe intoxication in some children and infants. It is reported that single application of 120 mg kg<sup>-1</sup> inhibited the ability of white blood cells to attack and kill foreign bacteria in the blood of rats, and 60 mg kg<sup>-1</sup> inhibited antibody formation to human serum albumin [Ulmann, 1973; Bennet, 2003].

Multiple studies have reported that lindane exposure (as measured by body tissue level of lindane) is associated with premature labor and spontaneous abortions [Selby *et al.*, 1969; Trifonova *et al.*, 1970]. Reproductive studies in male rats found decreased sperm counts at 50 mg kg<sup>-1</sup> d<sup>-1</sup> in a 50-d study, and seminiferous tubular degeneration at 6 mg kg<sup>-1</sup> d<sup>-1</sup> in a 180-d study [Palmer and Neuff, 1971]. A study conducted on female rats found uterine, cervical, and vaginal biochemical changes at 20 mg kg<sup>-1</sup> d<sup>-1</sup> in a 30-d study [Willet *et al.*, 1998]. Animals fed with  $\gamma$ -HCH during pregnancy may have an increased number of fetuses with extra ribs. Long-term oral administration to laboratory rodents has been reported to result in liver cancer [ATSDR, 1995]. Egg-shell thinning and reduced egg production has occurred in birds exposed to lindane [Walker, 2003]. Residues can be stored in the fat of birds, and egg yolks. Also it is highly to very highly toxic to fish and aquatic invertebrate species [WWF, 1999b; Tomlin, 1997].

## 1.6 Control measures

Much work remains to be done in order to understand the human health impact of exposure to POPs, particularly in view of the broad range of concomitant other exposures experienced by humans. Occupational, bystander and near-field exposure to toxic chemicals is often difficult to minimise in developing countries. Obstacles in managing workplace exposure are in part due to poor or non-existent training, lack of safety equipment, and substandard working conditions. As well, concerns resulting from near-field and bystander exposure are difficult to identify due to inadequacies in medical monitoring, diagnosis, reporting and treatment. These factors contribute to a lack of epidemiological data.

In 1985, the Pesticide Action Network (PAN) launched the Dirty Dozen Campaign to target a list of particularly hazardous pesticides for strict controls, bans, and ultimately elimination. The goals of the campaign were to stop the use of the most hazardous chemicals wherever safe use cannot be assured, ensuring that human and environmental health are considered foremost in all pesticide policy decisions, eliminating uneven terms in the international pesticide trade, and generating support for research and implementation of sustainable pest control methods [PAN, 1997; Weber, 2001]. PAN International participants selected the “Dirty Dozen” pesticides based on criteria that included: hazards to human or environmental health, evidence of widespread use and resulting harm, bans in exporting countries, and their value as examples of problems caused by pesticide dependence. The original “Dirty Dozen” list contained 18 pesticides, later grouped into a “bakers dozen” of 12.

More than a decade later, in 1997, the United Nations Environment Programme (UNEP), called for global action to reduce and eliminate releases of hazardous substances. The Intergovernmental Negotiating Committee (INC) for POPs control held its inaugural meeting in Montreal in June 1998 and agreed to target 12 chemicals, ‘Dirty Dozen’, for immediate action. This was followed by INC meetings in Nairobi, Geneva, Bonn and Johannesburg. Finally, a multinational, internationally legally binding treaty to ban POPs was signed on May 23, 2001, in Stockholm by 87 countries, and is in force since May 2004 (Stockholm or UNEP POP Convention). This “Dirty Dozen” includes 8 pesticides; aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene, mirex, toxaphene, 2 industrial biproducts, dioxins and furans, and one industrial chemical, PCBs. The list includes hundreds of substances on the congeners level and several isomers (of DDT) and dozens of isometric different substances (Toxaphene) [WWF, 2001; Weber, 2001].

The POP protocol to the UNEP Convention on long-range transport of air pollutants was

signed in 2001 and is in force since 2003. It lists 16 substances (including groups of substances), with DDT and HCH, besides others.

Now there are bans and severe restrictions on the Dirty Dozen pesticides in 122 countries. It also includes limited information of unregistered pesticides, e.g. pesticides that were withdrawn by the manufacturer, never registered, or whose registration has expired. The effectiveness of pesticides bans and restrictions differs greatly among countries, due to widely varying levels of enforcement. While such actions are sometimes quite effective, illegal use of banned or restricted pesticides occurs in all countries.



# Properties of DDT and $\gamma$ -HCH, their Global Usage and Compilation of Application Inventories

Halogenated hydrocarbons are a major group of POPs and, of these, the organochlorines are by far the most important group. The carbon-chlorine bond is very stable against hydrolysis and the greater the number of chlorine substitutions and/or functional groups, the greater the resistance to biological and photolytic degradation. Chlorinated POPs are typically ring structures with a chain or branched chain framework. By virtue of their high degree of halogenation, POPs have very low water solubility and high lipid solubility leading to their propensity to pass readily through the phospholipid structure of biological membranes and accumulate in fat deposits. These properties could be estimated with different methods, and the estimated values lie within a wide margin [*Boethling and Mackay, 2000*].

Chlorinated pesticides often share physico-chemical characteristics and include some of the earliest organochlorine pesticides such as DDT, chlordane, HCH, heptachlor, dieldrin, aldrin, toxaphene, mirex and chlordane. They are typically semi-volatile, a characteristic that favours the long-range transport of these chemicals. In the environment they can be transformed by a variety of microbial, chemical and photochemical processes (e.g., metabolic conversion of DDT to DDE and DDD). The vapour pressures of these substances are sufficiently high to cause appreciable evaporation over a period of weeks to years, enabling the compounds to cycle between gaseous and condensed phases in the environment.

## 2.1 DDT (dichlorodiphenyltrichloroethane)

DDT or 2,2-bis(chlorophenyl)-1,1,1-trichloroethane, the first of the chlorinated organic insecticides, was first synthesised by Othmar Zeidler in 1874. But the chemical remained in obscurity until 1939, when Dr. Paul Mueller discovered its insecticidal qualities while working with Geigy Pharmaceutical in Switzerland. He was awarded the Nobel Prize in medicine and physiology in 1948 for this discovery. As soon as the remarkable efficacy of the chemical was noted, DDT was adopted by malaria control programmes around the world, primarily because of its effectiveness against the mosquito that spreads malaria and lice that carry typhus. The World Health Organization estimates that during the period of its use approximately 25 million lives were saved. After World War II, this extraordinary insecticide eradicated malaria from southern Europe and the United States and proved to be the most effective weapon against malaria at that time [ESEF, 2002]. DDT seemed to be the ideal insecticide, due to its low cost and relatively low acute toxicity to mammals (oral LD50 is 300 to 500 mg kg<sup>-1</sup>). It was not until decades later that the true impact of DDT on wildlife became known. DDT is a mixture of several active ingredients (2,2-bis(chlorophenyl)-1,1,1-trichloroethane). Other isomers than *p,p'*-DDT, e.g. *o,p'*-DDT are also active [AMAP, 2003a] and were probably always part of the mixture applied.

Trade and other names are Anofex, Cesarex, Chlorophenothane, Dedelo, Dichlorodiphenyltrichloroethane, Dinocide, Didimac, Digmar, ENT 1506, Genitox, Guesapon, Guesarol, Gexarex, Gyron, Hildit, Ixodex, Kopsol, Neocid, OMS 16, Micro DDT 75, *p,p'*-DDT, Pentachlorin, Rukseam, R50 and Zerdane [EXTOXNET, 1996].

DDT is highly persistent in the environment, with a reported half-life of between 2-15 years over land, and is immobile in most soils [WHO, 1989; Reinhard and Drefahl, 1998]. The half-life over soil is reported as 10-15 years [OSU, 1997]. Routes of loss and degradation include runoff, volatilisation, photolysis and biodegradation (aerobic and anaerobic). In the environment DDT metabolites readily (in about two days of exposure to sunlight) into 1,1-dichloro-2,2-bis(*p*-dichlorodiphenyl)ethylene (DDE) and 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane (DDD), which are also highly persistent and have similar chemical and physical properties. The transformation is very slow in animal organisms, and the metabolites readily store in fatty tissues. The biological half-life of DDT is about 8 - 15 years [Tomlin, 1997; Eliasson, 2004].

Due to its extremely low solubility in water, DDT will be retained to a greater degree by soils and soil fractions with high organic matter content [WHO, 1989; UNEP, 2003]. It usually accumulates in the top soil layer only. Generally DDT is tightly sorbed by soil organic matter, but it has been detected along with metabolites in soil and groundwater in mobile and bioavailable

forms. This is probably due to its high persistence: although it is immobile or only very slightly mobile, over very long periods of time it may be able to eventually leach into groundwater, especially in soils with little soil organic matter. Residues at the surface of the soil are much more likely to be broken down or otherwise dissipated than in lower soil (leach) horizons. Studies have shown that volatilisation losses may be significant and rapid in soils with very low organic matter content (desert soils) and high irradiance of sunlight [Jorgensen *et al.*, 1991]. Many POPs show an affinity towards organic matter in soil. This property together with physical processes like bioturbation, sequestration in forest soils, and physical occlusion will remove the POPs from soil surface to below 'skin' layer, thereby hindering the exchange with the atmosphere, leading to an accumulation in the soil compartment.

DDT may reach surface water primarily by runoff, atmospheric transport, drift, or by direct application (e.g. to control mosquito-borne malaria). DDT is almost insoluble in water. The water solubilities are reported as zero [Tomlin, 1997] to  $0.0077 \text{ mg L}^{-1}$  (at  $20^\circ\text{C}$ ) [Klöpffer *et al.*, 2000]. The reported half life of DDT in the aquatic environment is 150 years [HSDB, 1998]. The half life is reported between 26-28 days in river water and 52-56 days in lake water [USEPA, 1989; EXTOXNET, 1996]. The main pathways for loss are volatilisation, photodegradation, adsorption to water-borne particulates and subsequent sedimentation. Aquatic organisms also take up and store DDT and its metabolites. Lack of degradability in terrestrial compartments can enhance the fraction of a substance residing in the Arctic or Antarctic environment. Hence as long as there is continuous input into the environment, accumulation will result in the cold polar regions.

### 2.1.1 Global usage

The total estimated usage of DDT in agriculture from 1950 to 1993 is  $\sim 2.6 \text{ Mt}$  [Voldner and Li, 1995]. The total cumulative production in the U. S. alone between 1945 and 1972 was  $1.34 \text{ Mt}$  with domestic usage of  $645 \text{ kt}$  [AMAP, 2004]. Li and Bidleman [2000] compiled the data and restriction status of DDT. The details for the top ten countries with highest usage of their study are given in Table 2.1. DDT is totally banned for agricultural usages in 26 countries. Limited usage is allowed in vector control in lack of effective and cheap substitutes [UNEP, 1995]. Even though the use of DDT was banned in the USA in 1972, it was still manufactured for export. In 1985, there were two producers of DDT in the USA, and in that year,  $303 \text{ kt}$  of DDT were exported [ATSDR, 2002b]. Mexico stopped the production recently, when its malaria control programme shifted to alternative approaches [IPEN, 2002]. Mexico signed the Stockholm Convention treaty with the DDT elimination target of reduction of 80% by 2001 and complete elimination by 2006

[Gary and Lucier, 1997; EHP, 1997]. Currently only two countries, India and China, produce DDT and export to other countries, even though the usage in agriculture is banned in China since 1983 and severely restricted in India since 1995 [Li and Bidleman, 2000; WWF, 2001]. The production capacity of India is approximately 0.007 kt per year and is not fully utilized. China's production capacity is unknown. For fighting malaria and other insect-borne diseases, DDT is still in use in over 25 countries [AMAP, 2004].

For this study, DDT production data have been compiled from various sources, and temporal and spatial interpolations performed, according to the requirements of the model (Section 2.4).

Table 2.1: Top 10 countries with highest DDT usage in agriculture during the period 1950-2000 [Li and Bidleman, 2000].

Country	Usage(kt)	Year of ban
United States	590	1972
Soviet Union	320	1971
China	260	1983
Mexico	180	2000
Brazil	106	1998
India	75	1995
Egypt	66	1972
Guatemala	60	1985
Italy	46	n/a
Hungary	43	n/a

## 2.2 $\gamma$ -Hexachlorocyclohexane( $\gamma$ -HCH)

$\gamma$ -hexachlorocyclohexane ( $\gamma$ -HCH) is one of the eight isomers of technical 1,2,3,4,5,6-hexachlorocyclohexane (HCH). HCH, is sometimes called benzenehexachloride (BHC). The different isomers are named according to the orientation of the C-H and C-Cl bonds.  $\gamma$ -HCH is the 1- $\alpha$ , 2- $\alpha$ , 3- $\beta$ , 4- $\alpha$ , 5- $\alpha$ , 6- $\beta$ -hexachlorocyclohexane. HCH was first prepared by Michael Faraday in 1825 by adding chlorine to benzene in sunlight [IARC, 1979]. During first world war it was used as a smoke bomb. The insecticidal properties of HCH were discovered in 1940 by French and British entomologists. In its technical grade formulations only the  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -, and  $\epsilon$ -isomers

are stable and commonly identified. Generally technical HCH contains the isomers in the following percentages: 55-80%  $\alpha$ , 5-14%  $\beta$ , 8-15%  $\gamma$ , 2-16%  $\delta$ , and 3-5%  $\epsilon$ . However, the information about relative contribution of different isomers in technical HCH differs in different publications (Table 2.2). Even though only  $\gamma$ -HCH exhibits any significant insecticidal activity, all isomers are acutely and chronically toxic for mammals as well as humans. Consequently, the  $\gamma$  isomer was isolated in manufacture and sold as the odourless insecticide 'lindane'. The effects of HCH superficially resemble those of DDT, but occur much more rapidly, and result in a much higher rate of respiration in insects. Because of its very low cost, HCH is still used in many developing countries.

Table 2.2: Relative contribution of different isomers in technical HCH (%) (According to various sources)

$\alpha$	$\beta$	$\gamma$	$\delta$	$\epsilon$	References
55-80	-	-	-	1-2	UNEP [1995]
55-80	5-14	8-15	2-16	1-5	Wayland [1982]
60-70	5-12	10-15	6-10	3-4	Kutz <i>et al.</i> [1991]
55-80	5-14	8-15	2-16	3-5	Metcalf [1955]
53-70	3-14	11-18	6-10	3-5	Gunther <i>et al.</i> [1968]
64	10	13	9	1	Li <i>et al.</i> [1998]
70	5	10-12	7	-	Slade [1945a]
65-70	5-6	13	6	-	Ramsey and Patterson [1946]
55	14	12	8	-	Kauer <i>et al.</i> [1947]
55-80	5-14	8-15	2-16	-	Riemschneider [1955]
64	10	13	9	-	Lehman [1965]

Other registered trade names of  $\gamma$ -HCH are Etan 3G, Forlin, Gamaphex, Isotox, Germate Plus, Gamma-Mean 400 and Gamma Mean L., Hammer, Lindagam, Novigam, Silvanol, Kwell [ATSDR, 2002b].

The insecticide lindane consists of almost 99%  $\gamma$ -HCH and it has been used on a wide range of soil-dwelling and plant-eating (phytophagous) insects. It is commonly used on fruits, vegetable, a wide variety of crops, in forestry, in warehouses, in public health to control insect-borne diseases, and (with fungicides) as a seed treatment. It is also presently used in lotions, creams and shampoos for the control of lice and mites (scabies) in humans. Lindane is also marketed in formulations together with other fungicides and insecticides. It is available as a suspension,

emulsifiable concentrate, fumigant, seed treatment, wettable and dustable powder, and ultra low volume (ULV) liquid. Lindane is still in use in many countries for insect control.

$\gamma$ -HCH is found in all environmental compartments, human and wildlife tissues as well as food products, including fruits, vegetables, meat, milk products, fish and other seafood.  $\gamma$ -HCH is slightly soluble in water, which is more than common for non-polar organics, and has a tendency to stick to water bodies. The water solubilities are reported to vary between the range of 35 to 45 mg L<sup>-1</sup> (25°C) [Klöpffer *et al.*, 2000]. Contamination of surface water may occur as a result of surface runoff from agricultural land or via rain, snow and dry deposition. In the water column, it may be adsorbed or desorbed to sediment or other suspended materials, and the half-life in sediment has been estimated as 90 days, and that in rivers and lakes ranges from 3 to 300 days [AMAP, 2004]. The major sources for  $\gamma$ -HCH in the atmosphere are considered to be fugitive dust particles from wind erosion of contaminated soil, volatilisation from treated agricultural soil and volatilisation from plant foliage sprayed [Poissant and Koprionjak, 1996].

Lindane is highly persistent in most soils, with a field half-life of 13 days to 15 months [LERS; WWF, 1999b; Bennet, 2003; CEC, 2002] based on hydrolysis rate. In soil, it is either adsorbed to the soil particles, volatilised to the atmosphere or leached into groundwater. The half-life in soil is temperature dependent; as degradation is faster at higher temperature. The mean half-life in treated soil is estimated as 120 days. The major removal mechanism is volatilisation. In soils and sediments, degradation is primarily by biotransformation.

Plants may take up  $\gamma$ -HCH from direct application, and upon atmospheric deposition, through water, particulate and vapor phases. Plants with high lipid content have a higher concentration than others, and crops like cauliflower and spinach will accumulate  $\gamma$ -HCH less than crops like carrots [WWF, 1999b; Bennet, 2003]. The metabolism in plants is not well understood, but carrots are estimated to metabolize lindane with a half-life of just over 10 weeks (based on plant uptake) whereas it may have a half-life in lettuce of only 3 to 4 days [WHO, 1997]. Lindane is very stable in both fresh and salt water, and is resistant to photodegradation. It is removed from aquatic environment by deposition and adsorption to sediment, biodegradation by microflora and fauna, and adsorption by fish through gills, skin and food [ATSDR, 1994; Sang *et al.*, 1999].

### 2.2.1 Global usage

The usage of technical HCH began in 1943 and it is the most widely used pesticide in the world due to its effectiveness and low price. Li [1999] estimated the global usage from 1948 to 1997 as 10 Mt. The usage of lindane and technical HCH are banned in a number of countries

Table 2.3: Top 10 countries with highest technical HCH usage during 1950-1993 [Li, 1999]

Country	Usage(kt)	Year of ban
China	4464	1983
India	1057	1990
Former Soviet Union	693	1990
France	520	1988
Egypt	479	1981
Japan	400	1972
United States	343	1976
Germany(East)	142	1982
Spain	133	1992
Mexico	132	1993

and restricted in others. Lindane replaced technical HCH in Canada, United States and western European countries in the late 1970's and early 1980's. Global usage of lindane between 1948 and 1993 was estimated as 720 kt [Voldner and Li, 1995]. Europe used 81 kt lindane between 1970 and 1996 [Breivik et al., 1999]. China stopped the usage of technical HCH in 1983 and lindane has been produced and used from 1991 at the rate of 0.5 kt a<sup>-1</sup>. There are no reported data about the usage in between 1983 and 1991. The major usage is to kill locusts, wheat mole crickets, midges and wood moths in forestry. In Europe France was the major user of lindane and globally too, during 1992-1997, with an annual average consumption of 1.6 kt. France terminated lindane usage in July 1998 [Saladin and Dyke, 1999]. Next to China, India was the second major user in Asia. India stopped the usage of technical HCH in agricultural crops, fruits and vegetables in 1990, but continued to use it for public health purposes. A complete ban on production and usage of technical HCH came into effect in India in April 1997, and the Government of India is encouraging its replacement by lindane [PAN, 1997]. Lindane replaced technical HCH in many countries during the 80's. Current worldwide manufacturers of lindane are Austria, India, Germany, Spain, Japan and China [Sang et al., 1999].

For the compilation of  $\gamma$ -HCH usage, both technical HCH and lindane data are important, since technical HCH contains  $\sim 14\%$  of  $\gamma$ -HCH, and lindane,  $> 99\%$ . The top 10 countries with technical HCH usage and the restriction status are given in Table 2.3 adapted from Li [1999]. Lindane usage and restrictions are given in Table 2.4 as adapted from Li and Bidleman [2000].

Table 2.4: Lindane usage for some countries during different periods [Li and Bidleman, 2000]

Country	Usage(kt)	Time period
Canada	9100	1970-2000
USA	1600	1980-1995
Europe	81000	1970-1996
France	9600	1992-1997
China	3200	1991-2000
Brazil	19.7	1990-1992

### 2.3 Physico-chemical properties of DDT and $\gamma$ -HCH

The key properties of the organochlorine pesticides, that determine their persistence, volatility and phase partitioning are: vapour pressure,  $p$ , octanol-air partition coefficient,  $K_{oa}$ , octanol-water partition coefficient,  $K_{ow}$ , the Henry's law constant,  $H$  (air-water partition coefficient), degradation rates in soil, water and air  $K_{soil/water/air}$  and their temperature dependencies, and the water solubility (details and parameterisations in chapter 3).  $H$  is defined as the ratio of the vapour pressure of a substance to its solubility in water and describes the equilibrium air-water partitioning.  $K_{ow}$  is used to describe the equilibrium distribution of organic contaminants between lipid phase and water phase.  $K_{oa}$  is a measure of the distribution of organic contaminants between air and lipid phase (plant waxes) and organic films on aerosols [Howard, 1991; Mackay *et al.*, 1992a, b]. Many properties cannot be measured and hence are estimated based on different analytical methods [Boethling and Mackay, 2000]. This leads to a range of values for each property, based on the environmental conditions considered for this estimation [Schwarzenbach *et al.*, 1993; Harner and Bidleman, 1998; Klecka *et al.*, 2000]. A wide range of data are reported for the same property of a single substance [Pontolillo and Eganhouse, 2001]. The main physico-chemical properties of DDT and  $\gamma$ -HCH used for this study are given in detail in Chapter 5 and 6 (Table 5.1, Table 6.2).

### 2.4 Compilation of pesticide application inventory

The global usage of DDT,  $\alpha$ -HCH, and  $\gamma$ -HCH in agriculture from 1950 to 1990 were compiled based on the data availability. *alpha*-HCH data is not used in the current study. The data were collected or estimated for each country and for selected years from 1947 to 1990 based on:

- Statistical data on insecticide consumption in agriculture from FAO, EUROSTAT and UNEP,
- Reported data on usage from national reported data,
- information on national and other measures against usage of lindane and technical HCH.

All data were reported on a country basis. For the purpose of distributing this data on a model grid, each country was divided into model grids of T42 horizontal resolution ( $2.8125^\circ \times 2.8125^\circ$  interval) and is represented by allocated grid cell. One grid cell was added manually for Taiwan since the emissions from this country are important, which is absent in the T42 grid. Then the country-wise consumption data was distributed over the required model grid scaled with the intensity of cropland distribution within the country, i.e., higher consumption is assumed in areas of high cropland density and vice versa. The intensity of the cropland distribution was taken from Canadian Global Emissions Interpretation Centre (CGEIC), in  $1^\circ \times 1^\circ$  resolution [Li, 1999], and had been extrapolated into T42 model resolution. While doing this extrapolation one can expect loss of data, because some grid cells which were present in the  $1^\circ \times 1^\circ$  distribution are no more present in the T42 distribution. In such cases those grid cells are added manually, e.g. one grid cell in Saudi Arabia, one in Oman and a few in North African countries.

Due to the coverage of grid cells (T42) of more than one country, the data of those countries were added and put as that of the one with the largest area. (e.g. data of Gambia and Guinea Bissau were added to Senegal, Trinidad and Tobago were added to Venezuela, Luxemburg to Germany and Malta to Italy). Furthermore, the data for Austria were distributed equally among Switzerland, Slovenia, Italy and Czechoslovakia because no grid cell is allocated to Austria. Zero values are given to those countries for which no data are available. In most cases this causes negligible error, exemptions however, are Brazil, United Arab Emirates, Iran, and Ethiopia.

The data set scaled with crop distribution within countries has T42 horizontal resolution and is used for ECHAM5 simulations. Extrapolation into T30 resolution was done for ECHAM4 simulations. In these steps, again some countries lose their grid cell allocation, e.g. Malaysia, Philippines, and some Central American Islands. A linear interpolation with time is done to fill the gap in case of countries with missing data during certain years. Fig. 2.1 and Fig. 2.2 show the global application of DDT and  $\gamma$ -HCH for the year 1980, in T42 resolution. See chapter 4 for the distribution of data in T30 resolution ( $3.75^\circ \times 3.75^\circ$ ).

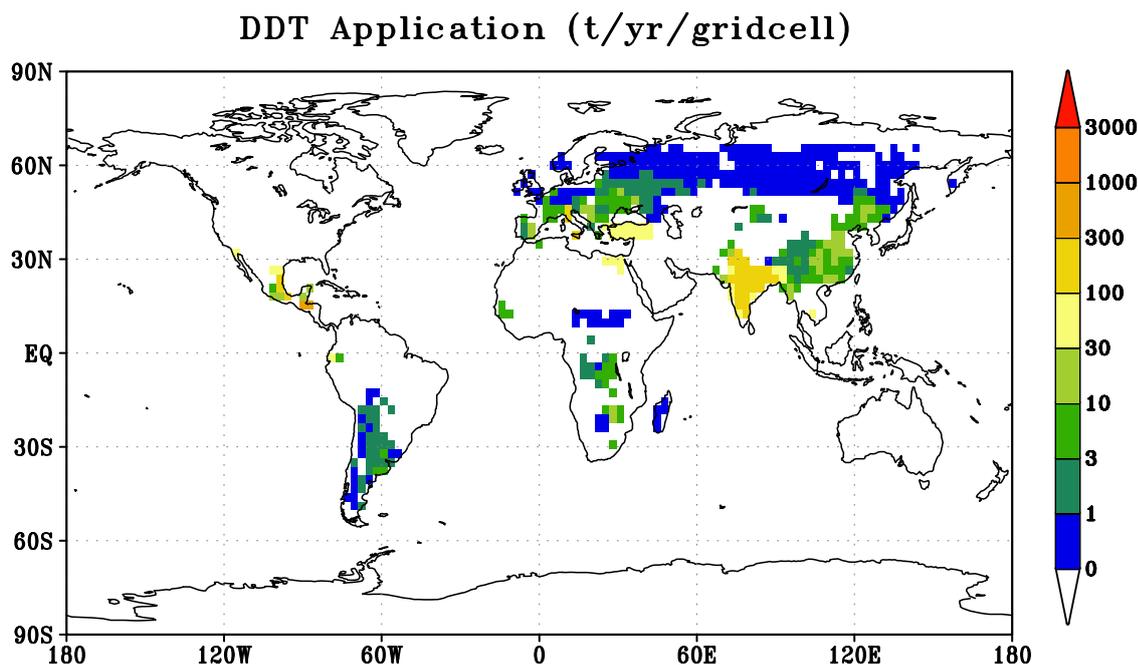


Figure 2.1: Global Usage of DDT in 1980 in T42 model resolution

### 2.4.1 DDT

Data were taken from statistical data on insecticide consumption from FAO (1947-1989) [FAO, 1988, 1989]. This data set includes for North and Central America, the amounts used in households and the quantities sold for all uses during the period 1947-1965. For the period 1966-1971, the data comprise the quantities used in or sold to agriculture, while for the rest of the period include also imports. For Europe, most of the reported data are referring to production only, but for the period 1947-1951 include quantities imported by private business [FAO, 1988]. For the years 1970, 1975, 1980, 1985, 1990 and 1995 data for almost all European countries were taken from Pacyna *et al.* [1999]. For South America, the data include imports also for 1947-1988. Data from Asia, Africa, Pacific, and Indian ocean islands contain quantities used in or sold to agriculture for the period 1947-1970, and 1971-1988 contain the consumption. This is compared with the informations from different articles (e.g. Pacyna *et al.* [1999]). These authors have prepared the data on the basis of information on national insecticide usage available from international statistics (FAO/UNEP, OECD (1991,97), Eurostat). In addition, there is some information on national DDT usage available in these statistics and in the open literature [WHO, 1989; Heinisch, 1992] especially for the early 1970s. The data set was prepared as five year averages starting from 1947 until 1989.

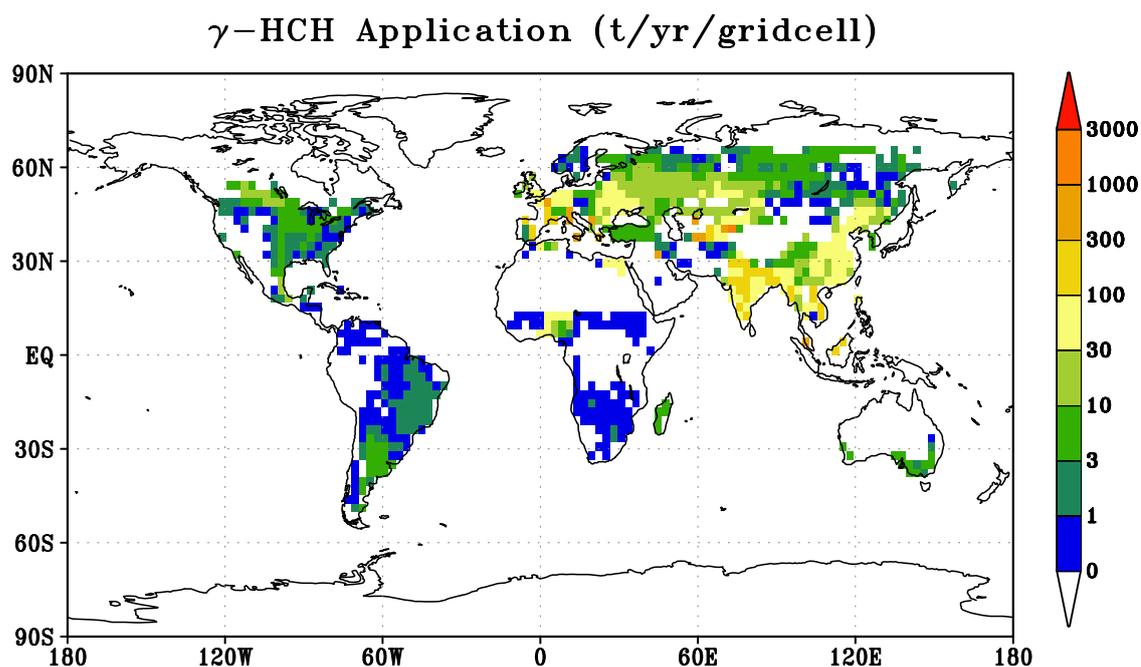


Figure 2.2: Global Usage of  $\gamma$ -HCH in 1980 in T42 model resolution

#### 2.4.2 $\gamma$ -HCH

For the selected years 1950, 1955, 1960, 1965, 1970, 1975, 1980, 1985 and 1990 data were taken from [FAO, 1989]. Data for Europe and Russia were taken from *Pacyna et al.* [1999] for the period 1970-90. The FAO data for the years 1954-56 in some cases include the quantities imported by private business (Greece), or production only (Hungary) (foot notes from the FAO 1959, 1961). For 1957, the data include quantities sold for all uses (United States), quantities used by Bureau of Plant Industry (Philippines) (FAO notes 1961). Data for the countries India, France, Italy, Nigeria, Canada, United States, China and Spain for the year 1990 were obtained from [AMAP, 1997]. The data for lindane and technical HCH were compared with other data sets available from different articles [Li *et al.*, 1996, 1998, 1-29, 1999b; Sang *et al.*, 1999; Voldner and Li, 1995]. For this study, it was assumed that 14% of the technical HCH used was the  $\gamma$  isomer.

### 2.5 Uncertainties of inventory

The compilation of application inventories are not perfect as the data are based on reported numbers. Non-reported data certainly lead to uncertainties in the global inventory, in addition to uncertainties in reported data [Li *et al.*, 1998]. Further, in case of DDT, the reported usage is for total DDT, assumed to be 100% *p,p'*-DDT. Moreover, this study neglects the usage in forestry and health programmes - the distribution in the model was according to agricultural area only.



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## Model Configuration

### 3.1 ECHAM4

ECHAM4 [Roeckner *et al.*, 1991] is the 4th generation of the three dimensional Atmospheric General Circulation Model of the Max Planck Institute for Meteorology, Hamburg, which basically evolved from the numerical weather prediction model developed at the European Centre for Medium Range Weather Forecasts (ECMWF).

The general circulation model is formulated in spherical harmonics with 19 vertical layers in a  $\sigma$ -p coordinate system. This enables the model to use either the usual terrain-following  $\sigma$  coordinate [Phillips, 1957], or a hybrid coordinate for which upper-level model surfaces “flatten” over steep terrain, becoming surfaces of constant pressure in the stratosphere [Simmons and Burridge, 1981; Simmons and Struening, 1981].

Prognostic variables are vorticity, divergence, temperature, surface pressure, humidity and cloud water. Surface boundary conditions are SST and sea-ice, orography, roughness length, vegetation and albedo. Physical parameterisations include radiation [Hense *et al.*, 1982; Eickerling, 1988; Rockel *et al.*, 1991], clouds [Sundquist, 1978; Roeckner and Schlese, 1984; Roeckner *et al.*, 1991], convection [Tiedke, 1989], planetary boundary layer [Louis, 1979], land-surface processes [Sellers *et al.*, 1986; Blondin, 1989; Dümenil and Todini, 1992], horizontal diffusion [Laursen and Eliassen, 1989], and gravity wave drag [Palmer *et al.*, 1986; Miller *et al.*, 1989].

The model comprises atmosphere, soil, vegetation and ocean compartments. Land surface processes are described by a 5-layer heat conductivity soil model and by a hydrological model to determine evaporation and runoff. Over land, each grid square is subdivided into 4 fractions to distinguish between snow coverage, bare soil, water in the skin reservoir (water stored within

the canopy and on bare soil) and vegetation. Permanent ice cover over land is prescribed by a glacier mask. Surface flux of momentum, heat, moisture and cloud water are calculated from Monin-Obukhov similarity theory, with transfer coefficients depending on roughness length and Richardson number. Above the surface layer, eddy diffusivity approach with coefficients depending on wind shear, thermal stability and mixing length is included. Above the planetary boundary layer, vertical diffusion is accounted only for unstable stratification. Over land, the roughness length is geographically prescribed, while over ice-free sea it is calculated following *Charnock* [1955]. Transport of water vapour and trace gases is described by a semi-Lagrangian advection scheme. No sediments and other biota exist in the model.

## 3.2 Substance cycling parameterisations

For SOCs studies, vegetation and soil are distributed geo-referenced as single layer boxes. A mixed layer ocean, which is a well mixed surface layer with locally and seasonally varying depth, is included. The mixed layer depth is taken from a 3D ocean general circulation model and is based on a density-criteria (density increase of  $0.2 \text{ kg m}^{-3}$  from the surface density) [*Drijfhout et al.*, 1996]. The global annual mean mixed layer depth is 80.2 m. The chemistry model included describes the atmospheric gas-phase and cloud water chemistry of sulfate species and depositions of short-lived substances [*Feichter et al.*, 1996], which has been modified for the study of SOCs [*Lammel*, 2001; *Lammel et al.*, 2001]. A schematic diagram representing the processes involved in the model is shown in Figure 3.1.

### 3.2.1 Atmosphere

The atmosphere is a three phase system (gas, particles, cloud water), with the mass exchange between them being controlled by instantaneous equilibria (Henry equilibrium for air-cloud-water equilibrium).

#### 3.2.1.1 Gas-particle partitioning of organic substances:

For organic substances, gas-particle partitioning is due to both adsorption on the surface and absorption into organic matter. This can also be an organic film on the surface of bulk organic particulate material [*Pankow*, 1994a, b]. In this study, we are estimating the partitioning between gas phase and atmospheric particulate matter,  $\theta$ , by absorption into organic matter, empirically, based on the octanol-air partition coefficient,  $K_{oa}$  [*Finizio et al.*, 1997]. The  $K_{oa}$  absorption model

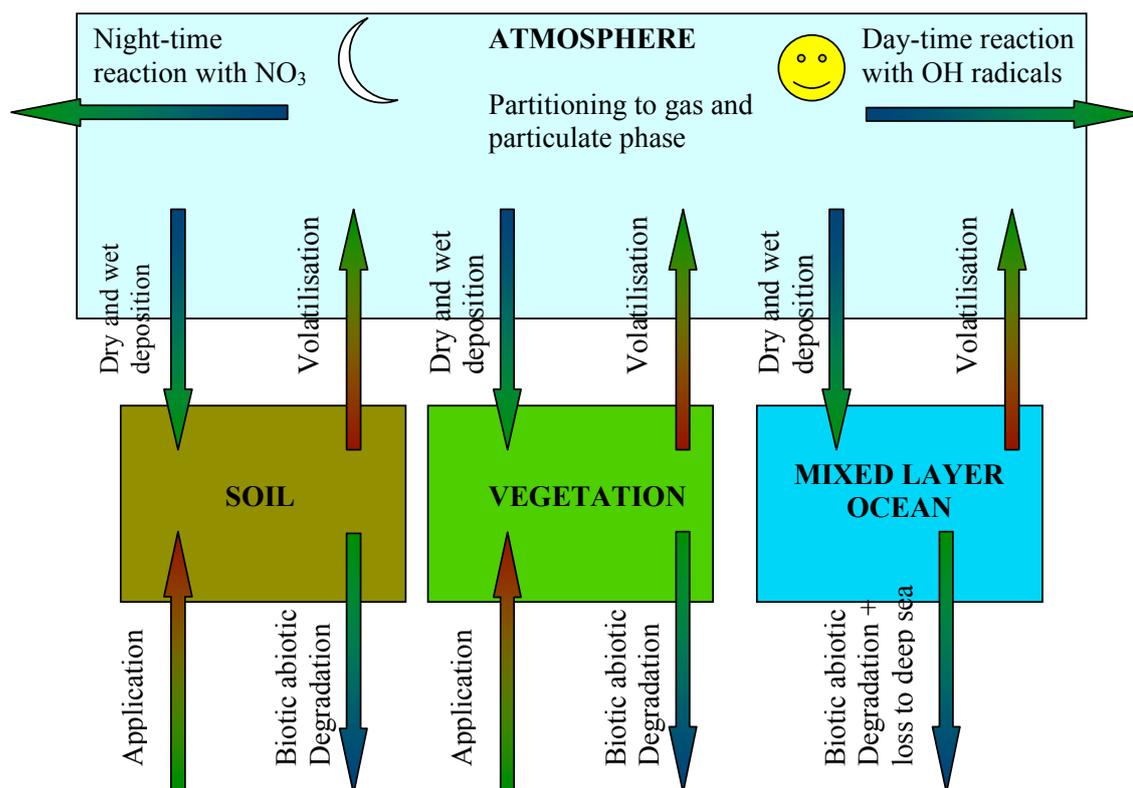


Figure 3.1: Multicompartimental approach, processes involved in substance cycling.

describes adequately the partitioning of a number of organochlorines (PCBs, DDT, besides others) [Finizio *et al.*, 1997; Harner and Bidleman, 1998]. Hence we use the relation for organochlorines including DDT and PCBs:

$$\log K_p = 0.55 \log K_{oa} - 8.23$$

$K_p$  is the particle-gas partition coefficient in  $\text{m}^3 \mu\text{g}^{-1}$  used for the determination of  $\theta$ .

$\theta$  is given as:

$$\theta = \frac{1}{\frac{1}{(K_p \times C_{tsp})} + 1}$$

where,  $C_{tsp}$  is the concentration of total suspended particulate matter in  $\mu\text{g m}^{-3}$ .

For  $C_{tsp}$ , we consider any material with the aim to account for the fact that even inorganic particulate matter through an organic film might provide a phase for types of partitioning, i.e. adsorption and absorption. For the substances under study, a value of  $K_{oa}$  is available for  $T = 298\text{K}$  but not as function of temperature (exceptions are cited in Harner and Bidleman [1998]). The ignorance of temperature dependence would be significantly misleading; however, e.g.  $\theta=0.0016$  would be predicted for DDT for all temperatures while  $\theta = 0.1-0.3$  was observed in the ambient

atmosphere [Kaupp and Umlauf, 1992]. In lack of measured data we assume that the temperature dependence of gas-particle partitioning,  $\theta(T)$ , behaves similar to the PAHs. For various PAHs,  $\theta$  doubles per 4.9 K temperature decrease (mean, individual species show similar behaviour: Pankow [1991]). The assumption of an analogy to PAHs may be justified to some extent, as these, similar to the organochlorines, partition due to both adsorption and absorption processes. Thus  $\theta$  is defined as:

$$\theta = \frac{1}{\left(\frac{1}{K_p \times C_{tsp}}\right) + 1} \times 2^{\frac{(298.-T)}{4.9}}$$

where  $T$  is the atmospheric temperature in K.

### 3.2.1.2 Degradation

For POPs that are not readily hydrolysed, photodegradation is the most important process for degradation in the atmosphere. POPs do not photolyze directly. They are, however subject to reaction with photochemical radicals such as the OH radical. During night, the  $NO_3$  radical provides another, in general less effective chemical sink.

Chemical degradation in the atmosphere is controlled by hydroxyl radical during day time and nitrate radical during night time as a function of latitude, longitude and time of day and month [Roelofs *et al.*, 1997]. SOC's day time atmospheric decay reaction rate is given as

$$\frac{\partial c}{\partial t} = k_{OH} \times c_{OH} \times c_{soc}$$

and the night time decay due to reaction with the nitrate radical is given as

$$\frac{\partial c}{\partial t} = k_{NO_3} \times c_{NO_3} \times c_{soc}$$

where the temperature dependent coefficients  $k_{OH}$  and  $k_{NO_3}$  are formulated following van't Hoff.

### 3.2.1.3 Dry and wet deposition

The deposition of chemicals is a complex process occurring through wet and dry deposition [Slinn, 1983; Cortes *et al.*, 1999]. Dry deposition as particulate matter, in general accounts for a relatively small part of the total deposition [Siebers *et al.*, 1994; Nations and Hallberg, 1992]. Sources at the ground create a vertical concentration gradient, spreading laterally and vertically from the source, which may be reflected in the concentrations in the local rainfall [Nations and Hallberg, 1992]. Removal by wet deposition is a combination of in-cloud and below-cloud scavenging.

In ECHAM4, we consider dry deposition to be driven by fixed deposition velocities,  $V_{dep}$ , for particulate-bound molecules [Slinn, 1982] and as temperature dependent function for gaseous molecules. The particulate dry deposition velocities are that of aerosols, while the gas phase has different deposition velocities over land and ocean based on the temperature. The model uses the following gas phase velocities:

Over land,

$$V_d = 1.30 \text{ cm s}^{-1}$$

for DDT, and

$$V_d = 2 \times 10^{-4}T^2 - 0.1116T + 16.882 \text{ m s}^{-1}$$

for  $\gamma$ -HCH.

Over the ocean they are

$$V_d = 6. \times 10^{-5}T^2 - 0.0357T + 5.389 \text{ m s}^{-1}$$

and

$$V_d = 2 \times 10^{-4}T^2 - 0.1116T + 16.882 \text{ m s}^{-1}$$

respectively for DDT and  $\gamma$ -HCH.

Wet deposition is parameterised as in-cloud and below-cloud scavenging from stratiform and convective clouds according to water solubility for gaseous molecules and a fixed wet-scavenging coefficient,  $\varepsilon$ , for particulate-bound molecules.

### 3.2.2 Soil

Once pesticides are applied to the soil, their behaviour will be controlled by this new environment. The important soil parameters are soil roughness, moisture content, organic matter content, bulk density and temperature. The surface roughness largely depends on the shape of the soil surface or vegetation. Both the thickness of the laminar layer just above the soil surface, and the eddy diffusion coefficient in the transition zone with turbulent mixing, are strongly influenced by the surface roughness. Adsorption and desorption is dependent on the organic matter content of the soil. The pore space for air and water is determined by the bulk density of the soil, and thus this parameter puts a limit on the space available to these media and reduces the rate of transport. Also, bulk density plays a role in the phase partitioning, i.e., the amount of pesticide sorbed to the organic matter per unit soil volume. Temperature directly affects the physico-chemical parameters of the pesticides. Vapour pressure of the pesticides tends to increase sharply with increasing

temperature. Also, mass transport can occur from locations with high temperatures to locations where lower temperatures prevail.

The moisture content of the upper soil layer is of crucial importance for the volatilisation process. Volatilisation of pesticides from bare soils involves complex processes and mechanisms. Once the substance is partitioned into gas and particle phase, the resulting vapour is dispersed into the atmosphere through molecular diffusion and turbulent mixing. Substances with high vapour pressure volatilise readily, and vapour pressure increases with temperature, resulting in a high volatilisation rate and hence a higher concentration in the atmosphere.

A more appropriate indicator for the volatilisation may be the Henry's Law Constant, which is a measure of the volatilisation tendency of a pesticide from dilute aqueous solution. Since water is ubiquitous in soils and plants, this gives a better prediction of volatility. Henry's Law Constants are temperature sensitive and the values change diurnally and seasonally. Volatilisation occurs from the top soil layer and the rates will be at a maximum around solar noon or early afternoon and are assumed to be small during night. Convective transport is influenced by spatial and temporal variations in temperature.

Since the physico-chemical parameters depend highly on temperature, corrections were made for the effect of temperature on the vapour pressure in the model using the Clausius-Clapeyron equation as:

$$p = e^{\frac{\Delta H}{R}((\frac{1}{T}) - (\frac{1}{T_0}))} + \ln p_0$$

where  $\Delta H$  is the heat of vaporisation in J/mol,  $T$  is the atmospheric temperature,  $T_0$  is the reference temperature and  $p_0$  is saturated vapour pressure (Pa) at  $T_0$ .

### 3.2.2.1 Gas liquid partitioning in soils

In the model, soil hydrology is represented by a bucket model [Roekner *et al.*, 1996]. Partitioning in soils is assumed on the basis of a temperature dependent phase equilibrium in the 3-phase soil system [Smit *et al.*, 1997]. The pore space in the soil is usually divided between an air fraction and an aqueous fraction. These fractions together with the liquid-gas partitioning coefficient determine which part of the pesticide will be in the gas phase and which part in the liquid phase. In the model world, phase partitioning is derived directly from the pesticide's physico-chemical properties and some of the most relevant atmospheric variables. The mathematical formulation of the phase partitioning is given as:

$$C_{liquid} = K_{\frac{l}{g}} \times C_{vapour}$$

where,  $C_{liquid}$  = concentration of pesticide in the liquid phase ( $\text{kg m}^{-3}$ ),  
 $C_{vapour}$  = concentration of the pesticide in the gas phase ( $\text{kg m}^{-3}$ ),  
 $K_{\frac{l}{g}}$  = liquid-gas partitioning coefficient (dimensionless).

When assuming a linear sorption isotherm, the partitioning between the solid and liquid phases can be written as :

$$X = K_{\frac{s}{l}} \times C_{liquid}$$

where,  $K_{\frac{s}{l}}$ , the solid-liquid partitioning coefficient can be calculated as:

$$K_{\frac{s}{l}} = K_{om} \times C_{om}$$

where  $K_{om}$  is the sorption coefficient and  $C_{om}$  is the organic matter content of the soil, and  $X$  = mass of pesticide adsorbed per mass of soil particles (dimensionless).

The concentration of the pesticide in the soil system is described by:

$$C_{soil} = \theta_{gas} \times C_{vapour} + \theta_{liquid} \times C_{liquid} + \rho_{soil} \times X$$

where,  $C_{soil}$  = concentration of pesticide in the soil matrix ( $\text{kg (m}^{-3}\text{)}$ ),  
 $\theta_{gas}$  = volume fraction of gas (dimensionless),  
 $\theta_{liquid}$  = volume fraction of moisture (dimensionless),  
 $\rho_{soil}$  = dry bulk density of the soil ( $\text{kg m}^{-3}$ ).

The above equation can also be written as:

$$C_{soil} = Q \times C_{vapour}$$

with the capacity factor  $Q$  as:

$$Q = \theta_{gas} + \theta_{liquid} \times K_{\frac{l}{g}} + \rho_{soil} \times K_{\frac{l}{g}} \times K_{\frac{s}{l}}$$

The dimensionless fraction of the pesticide in the gas phase is then calculated as

$$FP_{gas} = \frac{\theta_{gas}}{Q}$$

### 3.2.2.2 Volatilisation from soil

The process of volatilisation can be a significant contributor to the concentration of pesticides in the atmosphere away from the use area. Both soil parameters and the physico-chemical properties of the organic compound play important roles in the process of volatilisation. The physico-chemical properties of a pesticide relevant for volatilisation from the soil surface are molecular mass, vapour pressure, solubility in water, adsorption and half-life values. The most important factor which determines the volatilisation capacity is the vapour pressure ( $VP$ ) of the active substance.

We adopt an empirical relation for cumulative volatilisation ( $CV$ , of applied dosage) in the model. For normal to moist field conditions the  $CV$  is given by *Smit et al.* [1997] as:

$$CV_{normal-moist} = 71.9 + 11.6 \times \log[100FP_{gas}]; 6.33 \times 10^{-9} < FP_{gas} \leq 1$$

For dry field conditions at 21 days after application, the following relation is considered:

$$CV_{dry} = 42.3 + 9.0 \times \log[100FP_{gas}]; 1.9955 \times 10^{-7} \leq FP_{gas}$$

### 3.2.2.3 Degradation in soil

In the soil, substances undergo different degradation processes, like biological [*Karthikeyan and Bhandari, 2001*], chemical, or photochemical transformation into different metabolites. The type of process and transformation depend on the properties of the substance, application technique, climatic conditions and various soil parameters such as soil moisture content, organic matter content, bulk density and temperature [*Smit et al., 1997*].

An overall first order biological and chemical degradation in soil is considered and assumed to double per 10 K temperature increase to account for observations and according to recommendations [*TGD, 1996*]. The decay coefficient for soil is calculated as:

$$k_{soil(T)} = k_{soil} \times 2^{\frac{(T-298)}{10}}$$

### 3.2.3 Vegetation

In reality, the cumulative volatilisation depends on the pesticide residue on the leaves. Volatilisation from the plant surface is strongly related to its physico-chemical properties, leaf properties and environmental conditions.

In the model, vegetation is represented as a surface only. Application, deposition and volatilisation take place, but no mass exchange occurs into the vegetation compartment. The same  $k_{soil}$  is

assumed as degradation rate for vegetation also in lack of better knowledge. For a large number of compounds it was found however, that the vapour pressure alone can describe the cumulative volatilisation with sufficient accuracy. The empirical relation between cumulative volatilisation ( $CV$ ) and vapour pressure ( $VP$ ) can be written as  $\log CV = a + b \log VP$ , with  $a = 1.528$  and  $b = 0.466$ . Thus, the equation assumes the form [Smit *et al.*, 1998]:

$$CV = 10^{1.528 + 0.466 \log VP}; 5.2655 \times 10^{-7} \leq VP$$

### 3.2.4 Ocean

In the model, the mixed layer ocean, being non-advective, does not contribute to oceanic transport, but serves as a compartment for deposition with volatilisation and degradation.

Diffusive air-water exchange is calculated based on the standard two-film theory [Liss and Slater, 1974; Mackay and Leinonen, 1975] invoking two mass transfer coefficients in series,  $U_1$  ( $\text{m s}^{-1}$ ) for the stagnant atmospheric boundary layer and  $U_2$  ( $\text{m s}^{-1}$ ) for the stagnant water layer close to the air-water interface. These mass transfer coefficients are calculated as a function of wind speed using relationships by Mackay and Yuen [1983] as quoted in Schwarzenbach *et al.* [1993]:

$$U_1 = 0.065 \times \sqrt{(6.1 + 0.63 \times u)} \times .01$$

$$U_2 = 0.000175 \times \sqrt{(6.1 + 0.63 \times u)} \times .01$$

where  $u$  is the wind speed at 10m in  $\text{m s}^{-1}$ .

The D-values ( $\text{mol Pa}^{-1} \text{m}^{-2} \text{s}^{-1}$ ) for volatilisation from water are then calculated using the following equation:

$$D_{wa} = \frac{1}{\frac{R \times T_W}{U_1} + \frac{H}{U_2}} \quad (3.1)$$

where  $R$  is the universal gas constant ( $8.3143 \text{ Joule mole}^{-1} \text{K}^{-1}$ ),  $T_W$  is the sea surface temperature (K), and  $H$  is the Henry coefficient ( $\text{Pa mol}^{-1} \text{m}^3$ ).

#### 3.2.4.1 Degradation

Biological and chemical degradation in the ocean is also based on overall first order rates, and assumed to double per 10 K temperature increase. The mathematical formulation has the form:

$$K_o = K_{ocean} \times 2^{\frac{(T-273)}{10}} + K_{hydr} \times e^{\frac{-7818}{T}}$$

Concentration change due to the change in mixed layer depth of the ocean according to the season is considered as a permanent loss to deep sea.



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## Effects of Various Scenarios of Entry of DDT and $\gamma$ -HCH on the Global Environmental Fate as Predicted by a Multicompartment Chemistry-transport Model

### Summary

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

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

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

Keywords: Multicompartment modeling, environmental fate, long-range transport potential, mode of entry, persistent organic pollutants, air pollution

## 4.1 Introduction

Research on multicompartamental xenobiotics in the environment is motivated by fundamental interest and by transboundary regulatory needs. Much less than chemical transformations and mass exchange processes between phases of the same compartment e.g. atmospheric and aquatic chemistries, we understand the mass exchange processes between compartments and how substance properties interfere. As a consequence of adverse effects on the organism level in aquatic and terrestrial ecosystems, and furthermore, stimulated by risks for human health mediated through the food chain risks, from persistent xenobiotics need to be managed [Vallack *et al.*, 1998; Steinhäuser, 2001]. This in turn demands in first place for criteria to classify substances according to the environmental exposure they cause. Exposure in time and space is in principle predictable as being the result of the substance physico-chemical properties, its usage pattern and the geospheric transport patterns, both in time and space [GSF-Projektgruppe Gesellschaft für Strahlen-und Umweltforschung München, 1986; Klecka *et al.*, 2000; Lammel, 2002]. Models which are georeferenced and capable to reproduce the transports on the global scale have hardly been used so far [Koziol and Pudykiewicz, 2001; Lammel *et al.*, 2001].

With simulations of the environmental fate upon various scenarios of pesticide application we address and aim to quantify the sensitivity of long-range transport and compartmental distribution (hence, total environmental persistence) towards time, location and mode of entry. We selected two persistent organic pollutants which undergo long-range transport [Iwata *et al.*, 1993; Bailey *et al.*, 2000], the insecticides DDT (1,1,1-trichloro-2,2-di-(p-chlorophenyl)-ethane) and  $\gamma$ -HCH ( $\gamma$ -hexachlorocyclohexane), which both are subject to regulation under international chemicals legislation (UNEP Stockholm POPs convention, POPs protocol of the UN-ECE LRTAP convention, besides other). These two chemical substances differ considerably in their properties, however, DDT is merely volatile, merely water soluble and lipophilic, while  $\gamma$ -HCH is considerably volatile and water soluble and only moderately lipophilic. This is the first effort to study the environmental fate of these compounds on the global scale with a transport model.

## 4.2 Methods

### 4.2.1 Model structure

We use a four-compartment (air, soil, vegetation, ocean) global dynamic model which is based on a general circulation model of the atmosphere (19 vertical levels; ECHAM4; Roeckner *et al.* [1996, 1999]). Transports are only in the atmosphere. 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 georeferenced. The vegetation is represented as surface only - no uptake but application and deposition and (re)-volatilisation. The depth of the ocean mixed layer is spatially resolved and seasonally varying and was based on the results of a run of a general circulation model of the ocean [Drijfhout *et al.*, 1996]. Cloud processing, dry and wet deposition and tropospheric chemistry of gaseous and particulate trace substances including simple cloudwater chemistry and cloudwater acidity are represented [Feichter *et al.*, 1996]. Parameterisations used to describe the intra- and intercompartmental processes of mass exchange and conversion are listed in Table 4.1. These have been recently described in detail [Lammel *et al.*, 2001]. The substance physico-chemical and degradation data have been taken from Klöpffer and Schmidt [2001] and Moltmann *et al.* [1999].

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. E.g., no hydroxyl reaction rate coefficient of DDT has been ever measured. Only one value for DDT degradation in the ocean was reported (halftime of 56 days) which, given the many findings of DDT in ocean water in remote areas, may rather reflect an upper estimate than a best guess.

#### 4.2.2 Emission data

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

The DDT and  $\gamma$ -HCH application distributions used were taken from a data set of global agricultural usage of DDT and  $\gamma$ -HCH which we compiled for the years from 1947 to 1990.  $\gamma$ -HCH is entered with the usage of technical HCH (15%) or lindane (99%). These data were based on statistical data on insecticide consumption in agriculture, which were reported country-wise to FAO 1947-1989, and on other published data [FAO, 1988, 1989; WHO, 1989; Li *et al.*, 1996; Breivik *et al.*, 1999]. The country-wise consumption data were scaled with the intensity of the cropland distribution within the country and distributed over the global grid space.  $1^\circ \times 1^\circ$  cropland distribution data [Li *et al.*, 1996; Li, 1999] had been used for this purpose. The extrapolation would systematically suppress small-scale, isolated cropland areas which are represented in the  $1^\circ \times 1^\circ$  distribution but are too small to be represented in the grid. In such cases, grid cells were added manually into the field (e.g. one grid cell is added in Saudi Arabia, one in Oman and a few in North African countries). Due to the overlapping of grid cells over more than one country, the

Table 4.1: Features of intra- and intercompartmental mass exchange and conversion processes.

Process	Process description	Parameter representation
Partitioning between gas-phase and atmospheric particulate matter, $\theta$	Assumed to be determined by absorption into organic matter, empirically based on the octanol-air partition coefficient, $K_{oa}$ <sup>(1)</sup> (Finizio et al., 1997) prescribed spatially and temporally variable aerosol concentrations	Diagnostic
Chemical degradation in the atmosphere	Reaction with hydroxyl radical, similar in the gaseous and particulate-bound state; prescribed spatially and temporally variable oxidant concentration (Roelofs et al., 1997)	Prognostic
Degradation in soil, vegetation and in ocean	Overall first-order rates, assumed to double per 10 K temperature increase <sup>(2)</sup>	Prognostic
Partitioning in soils	Phase equilibrium in 3-phase soil system (Smit et al., 1997), temperature dependent, soil hydrology represented by bucket model (Roeckner et al., 1996)	Diagnostic
Volatilisation from soils	Loss of gaseous substance from the soil pore space using an empirically derived rate from pesticide application studies (Smit et al., 1997)	Prognostics
Volatilisation 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 et al., 2000), temperature dependent	Prognostic
Atmospheric dry deposition	Fixed deposition velocities 'vdep' for gaseous molecules <sup>(3)</sup> (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, $\epsilon$ <sup>(4)</sup> (particulate-bound molecule)	Prognostic

<sup>1)</sup> $C_{gas}/(C_{gas}+C_{particulate})=\theta=[1/(K_p C_{TSP})+1]^{-1}$ ;  $\log K_p=0.55 * \log K_{oa} - 8.23$ ; particulate matter concentration  $C_{TSP}(\text{cm}^{-3})$ , gas-particle equilibrium constant  $K_p$ , Temperature dependence of  $\theta$  assumed to be similar to polycyclic aromatic hydrocarbons (Pankow, 1991)

<sup>2)</sup>according to the recommendations<sup>[25]</sup> besides others;  $k_{soil}=k_{vegetation}$ ; in the case of  $\gamma$ -HCH the contribution of the hydration reaction to the degradation in ocean water is accounted for, too (Ngabe et al., 1993)

<sup>3)</sup>dry deposition velocities are 1.4 and 1.38  $\text{cm s}^{-1}$  over land and 0.08 and 1.38  $\text{cm s}^{-1}$  over sea for DDT and  $\gamma$ -HCH, respectively (Tucker, 1983 and Tucker et al., 1990)

<sup>4)</sup> $\epsilon=1.0$  and  $0.1$  for in-cloud and below-cloud scavenging, respectively

data of those countries are added together and allocated to the country which occupies the largest portion of the grid cell. For example, the data of Gambia and Guinea Bissau were added together to Senegal, Trinidad and Tobago to Venezuela, Luxembourg to Germany, Malta to Italy. Data of Austria were distributed equally among Switzerland, Slovenia, Italy and Czechoslovakia. Zero values were given to those countries with no data available. Besides small countries these were

Table 4.2: Scenarios of DDT and  $\gamma$ -HCH entry into the environment.

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

(1)cf. Fig. 2

Brazil in the case of DDT and Japan and Mexico in the case of  $\gamma$ -HCH. Linearly interpolated data were used to fill gaps in case of countries missing data in between the years.

For this simulation we have used data of the years 1966-1970 and 1976-1980, to produce 5-year mean data for DDT experiments (DG7020, DG8020; cf. Table 4.2). Data of the year 1990 is used for the other DDT experiment, DG9020, and the  $\gamma$ -HCH data from 1980 is used for the experiments LN8020, LT8020 (cf. Table 4.2). For DG9020 application is only in India, whereas the amounts applied in other countries are assumed to be negligible.

### 4.2.3 Model run initialization

The model was run with a 30-min time step and ca.  $3.75^\circ \times 3.75^\circ$  (T30) horizontal resolution in all compartments. Model runs were performed with 15 years of physical spin-up, i.e., simulation of atmospheric dynamics prior to the entry of the substances. Then, February-October of the 16<sup>th</sup> year, the substances were introduced into receptor compartments assuming seasonally variable applications (cf. Table 4.2, Fig. 4.1, 4.2). The application pattern remained the same in consecutive years of the model runs and we report on results of the second year of application (Section 4.3). The second year upon entry is the first one with the substances being in the environment throughout the entire year i.e., January - December. The various scenarios were exposed to the identical climate.

The scenarios were selected such as to address questions on the environmental fate of substances for the same substance but changing over time (DG scenarios), changing as a function of geographic regions of entry (LN8020 vs. LT8020) or function of mode of entry (LN8020 vs. LT8060) and for two substances under the same application scenario (at least time and mode of

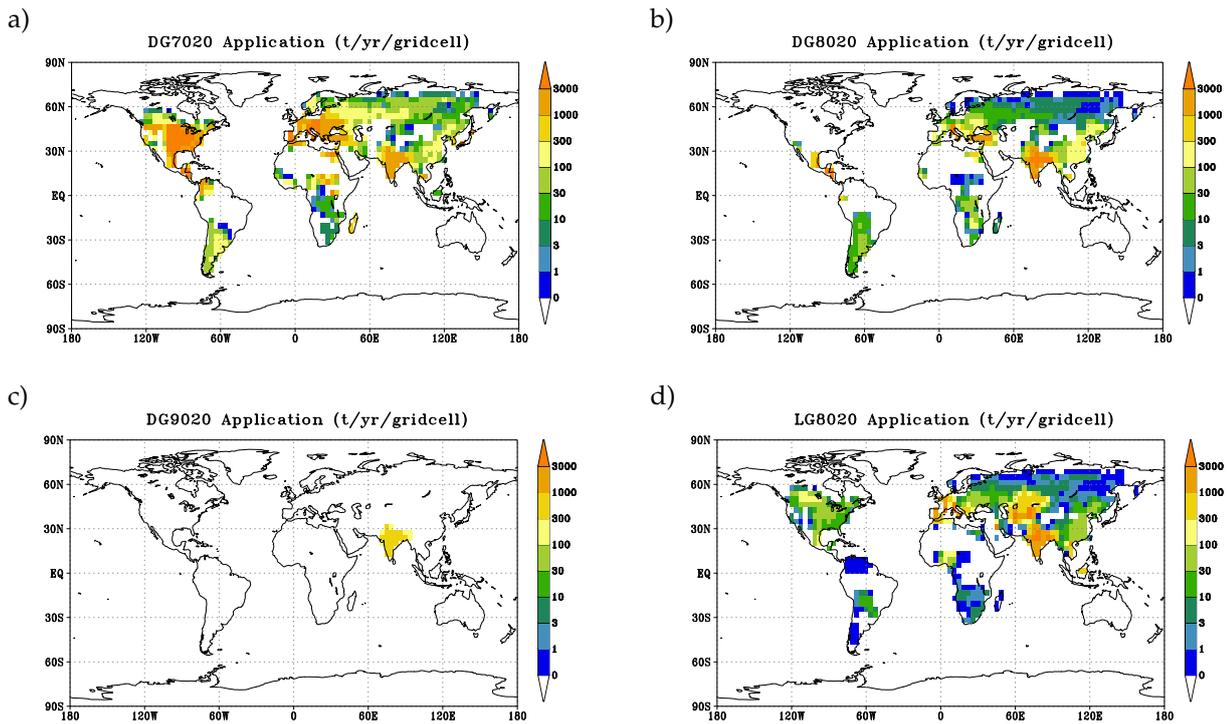


Figure 4.1: Geographic distributions of applications ( $\text{t a}^{-1} \text{ gridcell}^{-1}$ ) of DDT scenarios: (a) DG7020, (b) DG8020, (c) DG9020 and (d)  $\gamma$ -HCH (LG8020).

entry; DG8020 vs. the sum of the scenarios LN8020 and LT8020; G, N and T stands for global, northern and tropic latitudes, respectively). The amount and distribution of  $\gamma$ -HCH applied globally is given by the sum of the scenarios split at  $30^\circ \text{ N}$ :  $\text{LN8020} + \text{LT8020} = \text{LG8020}$ . The temporal application pattern in the simulations is not uniform, but limited to the daylight hours with no rain in order to come closer to agricultural reality. Furthermore, a seasonality was included with maximum in April to July: each 20% of the amount to be applied in one year are distributed over the daylight hours of April to July and each 5% over the daylight hours of February, March, August and September. Non-zero precipitation during a day-light time step (30 min) in each grid cell causes a delayed application during the next 'dry' day-light time step in the same grid cell. Due to this rule, application in the model world was February - October (Fig. 4.2).

## 4.3 Results

### 4.3.1 Compartmental distributions and residence times

The compartmental burdens and intercompartmental mass fluxes of DDT upon 1980 emissions are shown in Fig. 4.3a. According to the entry scenario, in total  $7665 \text{ t a}^{-1}$  of DDT enter the environment through application to the vegetation (spraying on crop plants) and to the soil, as

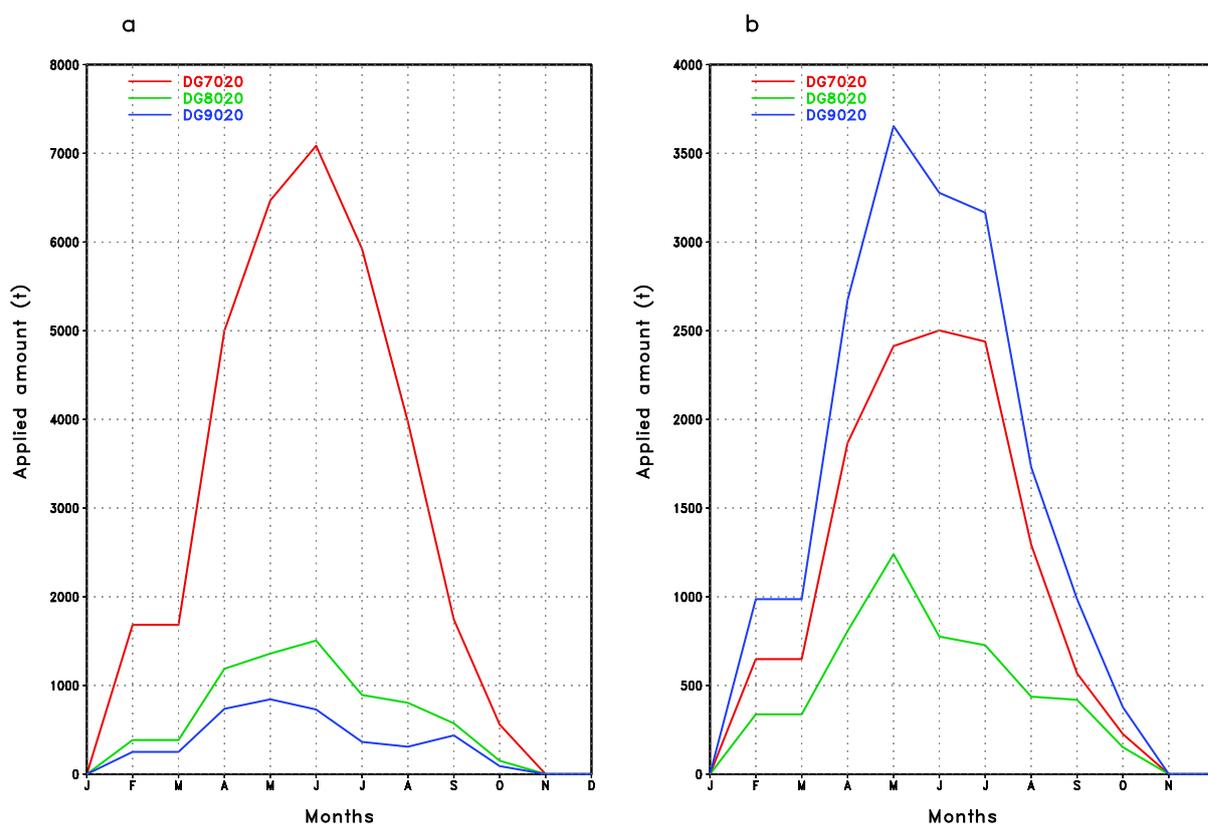


Figure 4.2: Temporal application patterns (t) of (a) DDT and (b)  $\gamma$ -HCH scenarios to the global vegetation and soil.

80:20. Upon volatilisation from vegetation and soil, the atmosphere and, upon subsequent deposition processes, the ocean also experience uptake in the period of study (second year upon entry). The atmosphere experiences the largest turnover:  $17311 \text{ t a}^{-1}$  of received substance (volatilisations, sum of arrows to the the atmosphere) correspond to an annual average burden of  $246 \text{ t}$ , i.e. annual mean atmospheric residence time would be  $\tau_{atmosphere} = 0.0142 \text{ a}$  (ca. 5 days) in steady state. Steady state is not fulfilled however, but there is a compartmental net uptake of  $81 \text{ t a}^{-1}$  between January and December. The residence time limited by all compartmental first-order loss processes under non-steady state condition can be derived from the mass conservation equation:

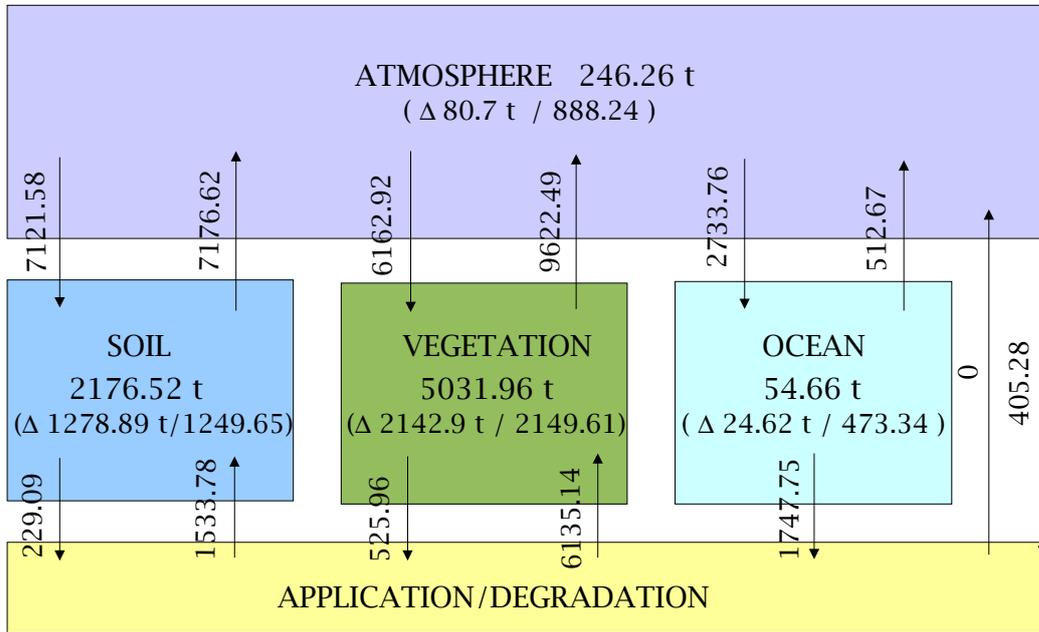
$$\Delta c / \Delta t = E - c / \tau$$

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

where  $c$  is the compartmental burden,  $E$  the sum of import fluxes to the compartment and  $\Delta c / \Delta t$  the net uptake ( $81 \text{ t a}^{-1}$ ), and then  $\tau_{atmosphere}$  is  $0.0143 \text{ a}$ . Most of it leaves the atmosphere through the deposition processes while the chemical degradation accounts for only ca. 2.5% of the losses ( $405 \text{ t a}^{-1}$ ). The atmospheric turnover exceeds the input into the environment by 109%.

a)

DG8020



b)

LN8020+LT8020

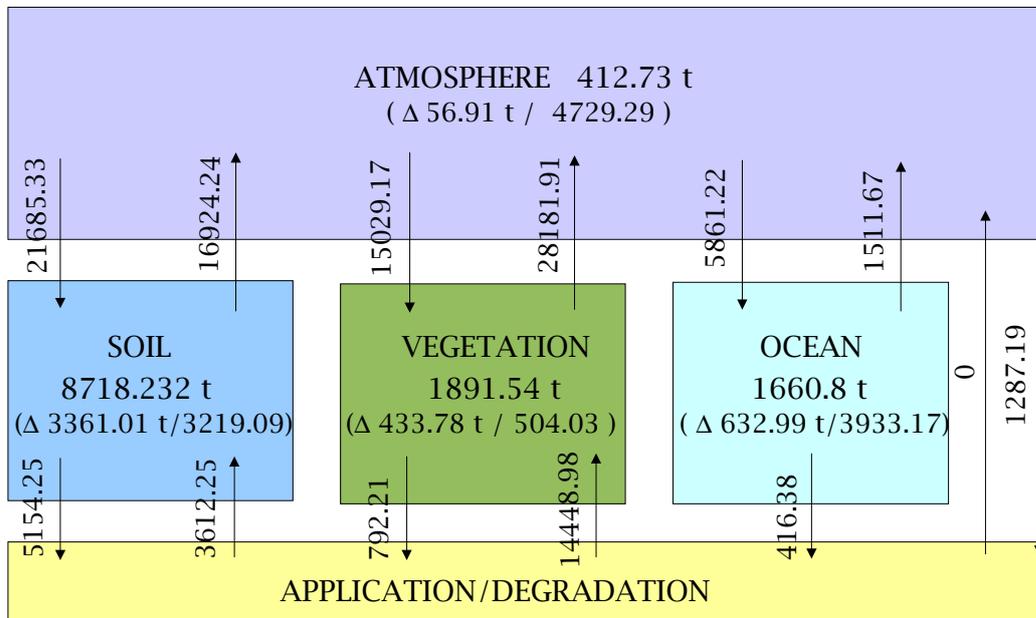


Figure 4.3: Global environmental fate of (a) DDT and (b)  $\gamma$ -HCH upon 1980 applications (scenarios DG8020 and LG8020): mass exchange fluxes between compartments (arrows), and compartmental budgets in the form 'burden ( $\Delta$  change)'. All values are given in t or t a<sup>-1</sup> and are annual means except values of change ( $\Delta$ ), which are defined as December mean - January mean.

That means, that the average DDT molecule undergoes 2.09 cycles of emission into and deposition from the atmosphere (number of completed hops). The turnover rates in other compartments are lower and the corresponding mean residence times are 0.30 a, 0.50 a and 0.020 a (ca. 7 days) in the soil, vegetation and in the ocean surface mixed layer, respectively (see also Table 4.5). The compartmental residence times are influenced by the corresponding halftimes towards degradation, ca. 6 a in soil and vegetation (assumed to be equal; *Hornsby et al.* [1996]) and 56 d in the ocean (values for 273 K). A significant fraction, 39%, of the entered substance is depleted (sum of arrows to degradation, 2908 t a<sup>-1</sup>) and it is predicted that this happens mainly in the ocean (1748 t a<sup>-1</sup>). Another significant fraction, in total 62% (sum of compartmental uptakes, 4761 t a<sup>-1</sup>) are added to the compartmental burdens. The residence time with respect to the sum of all sinks i.e., the overall environmental residence time limited by the sum of all first-order final sinks during a period  $\Delta t$ ,  $\tau_{overall}$ , can be derived accordingly from the mass conservation equation with  $c$  now representing the sum of the burdens in air, soil, vegetation and ocean surface layer (7510 t for DDT under DG8020),  $E$  the flux of entry into the multicompartmental system (i.e., application, 7665 t a<sup>-1</sup>) and  $\Delta c/\Delta t$  the change of burden of the multicompartmental system during  $\Delta t$  (from December - January, 3527 t a<sup>-1</sup>). Only first-order final sinks are given in the system. This calculation delivers  $\tau_{overall} = 1.8$  a as the annual mean value in the second year upon entry. Various but similar definitions have been used by modelling approaches for  $\tau_{overall}$  [*Pennington*, 2001].

The accumulation of DDT in the total environment is predicted to be concentrated to the soils and the vegetation: these compartments take up 1250 and 2150 t a<sup>-1</sup>, respectively, while the atmosphere and the ocean take up only 888 and 473 t a<sup>-1</sup>. A net uptake of 62% of the entered amount, far from zero, reminds us that DDT in its second year upon entry is of course still far from compartmental equilibrium. Another substance fate simulated is loss to the deep sea: in the model this loss is given by the seasonal narrowing of the ocean surface mixed layer and means a final removal from the mass exchanging compartments. This process is the fate for 16% of the substance (1234 t a<sup>-1</sup>).

In the case of  $\gamma$ -HCH environmental fate upon 1980 emissions (Fig. 4.3b) the atmosphere experiences the largest turnover, too: 47292 t a<sup>-1</sup> of received substance correspond to an annual average burden of 413 t i.e., annual mean atmospheric residence time ( $t_{air}$ ) of 0.009 a (ca. 3 days). This shorter lifetime compared to the ca. 5 d of DDT reflects the differences in hydroxyl reaction rate coefficients,  $1.0 \times 10^{-13}$  cm<sup>3</sup> molec<sup>-1</sup> s<sup>-1</sup> for DDT (estimated) and  $1.9 \times 10^{-13}$  cm<sup>3</sup> molec<sup>-1</sup> s<sup>-1</sup> for  $\gamma$ -HCH [*Brubaker and Hites*, 1998], and in susceptibility to wet deposition, which is larger for the more water soluble  $\gamma$ -HCH. The effect of the latter difference is more significant: despite

Table 4.3: Compartmental distributions: annual mean burdens in the second year upon entry. (Cf. Table 4.2 for amounts entering into the environment).

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

an assumed more rapid chemical degradation, an even higher fraction of atmospheric  $\gamma$ -HCH is lost through the deposition processes than in the case of DDT with the chemical degradation accounting for only  $\approx 2.9\%$  of the  $\gamma$ -HCH atmospheric sinks ( $43863 \text{ t a}^{-1}$ ).

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

For  $\gamma$ -HCH as well as for DDT it is found that the burdens are subject to a significant seasonality in all compartments: in the global oceans surface mixed layer only 633 t  $\gamma$ -HCH and 25 t of DDT are more stored at the end of the year compared to the beginning of the year (numbers marked with  $\Delta$ , Fig. 4.3) despite an annual mean uptake of 3933 t and 473 t, respectively. This is not surprising regarding the temporal application pattern and the compartmental residence times. It indicates that the seasonal amplitude must be very significant. The seasonalities of the soils and vegetation burdens are less pronounced. These differences are caused by the geographic distributions and seasonalities of DDT emissions, depositions and temperature in these compartments.

Most of the substances are stored in soils and vegetation, 69 - 82% of DDT and 38 - 70% of  $\gamma$ -HCH under the various scenarios (Table 4.3). Only for LT8020 the ocean is more important

Table 4.4: Compartmental residence times (d) and mean number of completed atmospheric cycles<sup>a</sup> (numbers in brackets) in the second year upon entry.

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

<sup>a</sup> Derived as: atmospheric total deposition flux divided by total application flux

reflecting the smaller land area fraction south of 30°N. The soils are more prominent for  $\gamma$ -HCH and the vegetation are more prominent for DDT. The difference in vapour pressures (0.034 and 2.9 mPa at 25°C, respectively) causes  $\gamma$ -HCH to volatilise more rapidly from the vegetation surfaces than DDT such that the residence time of DDT upon application and, later, atmospheric deposition into this compartment is longer. The large fraction stored in soils is somewhat contra-intuitive, because the lipophilic tendencies of DDT and  $\gamma$ -HCH ( $K_{ow} = 1.55 \times 10^6$  and  $3.98 \times 10^3$ , respectively) would suggest DDT to be more sticky to soils. However, it is not only the lipophilicity which prevents volatilisation from soil but also solubility in soil water.  $\gamma$ -HCH is water soluble to a significant extent while DDT is practically insoluble ( $s = 7.4$  and  $0.034 \text{ mg l}^{-1}$  at 25°C, respectively). The change in mode of entry from vegetation:soil = 80:20 to vegetation:soil = 40:60 reduces the fraction of  $\gamma$ -HCH stored in vegetation upon the 1980 applications from 11.6 to 8.4% and enhances the fraction stored in soil from 52.4 to 61.6%. In total, 52 t  $\gamma$ -HCH or 0.4% more are in the system. The corresponding change in total environmental residence time is an increase by 10%, 1.2 instead of 1.1 a (Table 4.4).

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

A change in mode of entry of  $\gamma$ -HCH i.e., shift of application split to vegetation and soils from 80:20 to 60:40, affects the substance mobility as volatilisation from vegetation occurs more fre-

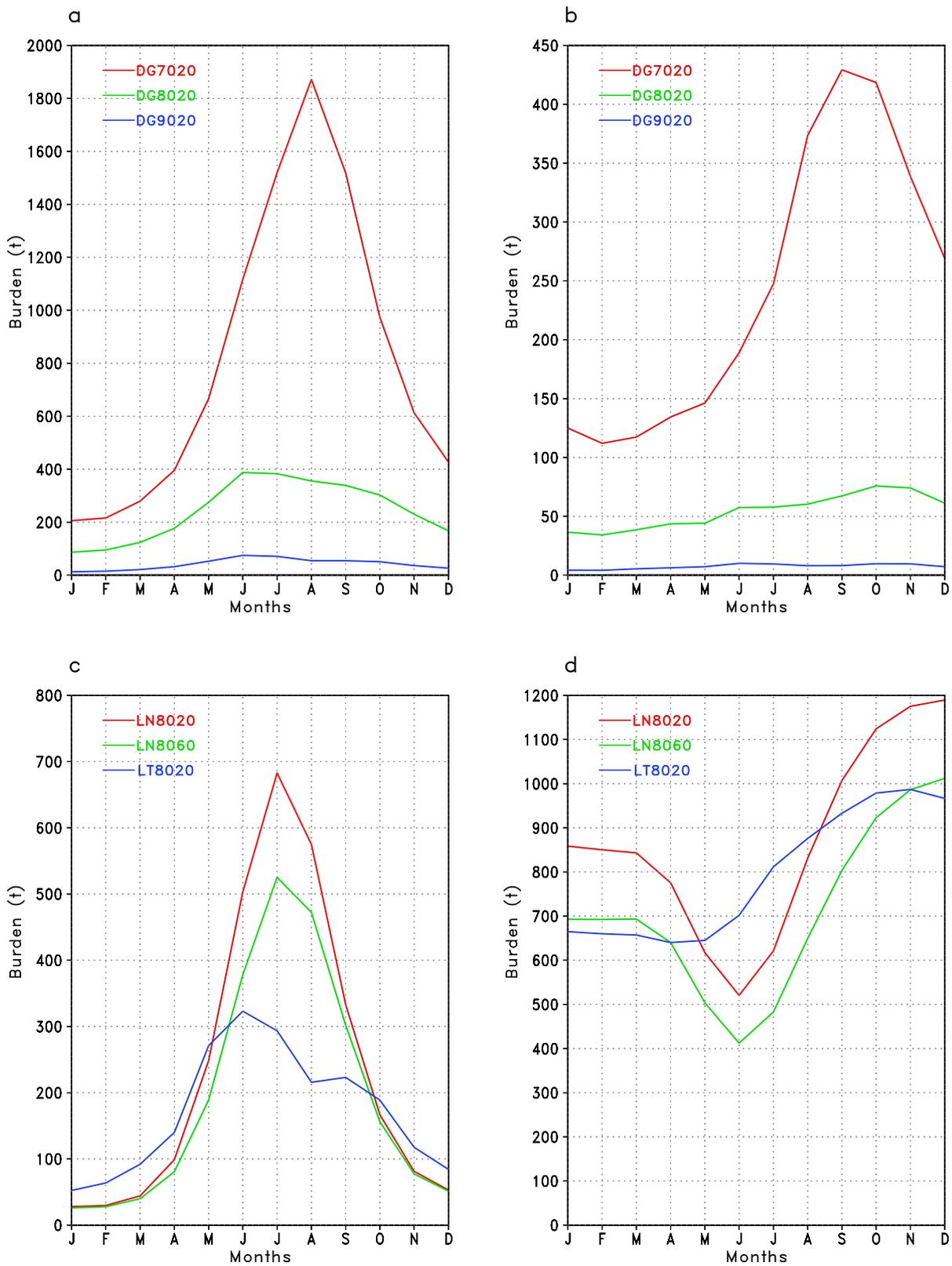


Figure 4.4: Seasonal variation of compartmental distributions: monthly mean values of the burdens (t) in (a, c) the atmosphere and (b, d) the ocean surface mixed layer of (a, b) DDT and (c, d)  $\gamma$ -HCH under the various application scenarios.

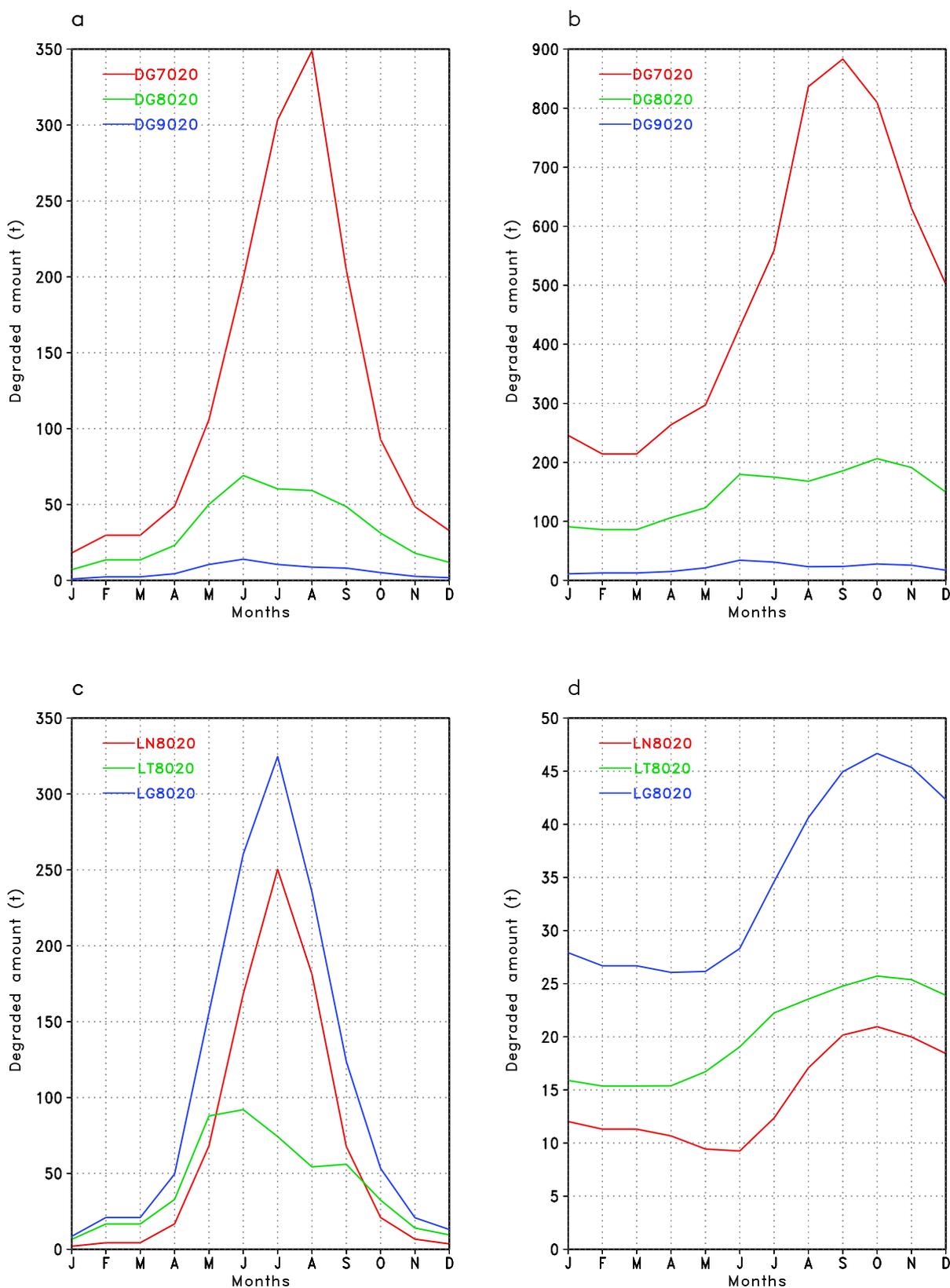


Figure 4.5: Seasonal variation of compartmental losses (t): monthly mean values of (a, c) atmospheric and (b, d) oceanic degradation of (a, b) DDT and (c, d)  $\gamma$ -HCH under the various application scenarios.

quently than from (moist) soils: the combined volatilisation from soils and vegetation is reduced by 14% and less substance is transferred into the atmosphere (burden is 1.4 instead of 1.8%) and into the ocean (burden is 28.6 instead of 34.2%, cf. also Fig. 4.4b). The mean number of atmospheric cycles completed is reduced from 2.2 to 1.9 (Table 4.4). The predicted overall effect is a by 10% increased environmental residence time. This result is not influenced by the compartmental degradation rate, as we assumed that substance degradation in soil and vegetation obey the same time law.

Persistence of  $\gamma$ -HCH is strongly influenced by the location of entry, northern mid latitudes (LN8020) vs. tropics (LT8020): the warmer tropics push more of the substance into the atmosphere (Table 4.3). Therefore, substance mobility is enhanced and persistence is suppressed, because the atmosphere is the compartment with the most rapid degradation. The residence times in the ground compartments are reduced, because we assumed enhanced degradation resulting from higher temperatures. The effective residence time in air is, however, longer in the tropics, because of a larger number of completed atmospheric cycles, 2.7 instead of 2.2 (Table 4.4). Obviously, the higher tendency to volatilise in the warmer climate overcompensates for the more effective atmospheric sink processes in the tropics (precipitation frequency).

The seasonal patterns of the atmospheric burdens (Fig. 4.4a, 4.4c) reflect the superposition of the seasonalities of the application (maximum around June, Fig. 4.2) and of the air temperature which drives volatilisation from the ground surfaces and obviously causes a delay of about one month. As a consequence of the short residence time, degradation in the atmosphere (Fig. 4.5a, 4.5c) is in phase with the burden. The same applies for the DDT burden in the ocean mixed layer which as a consequence of the time needed for atmospheric transport and deposition and the slower degradation there is, however, delayed to the application pattern by one more month ( $k_{air}^{(0)} = 5.2 \times 10^{-8} \text{ s}^{-1}$ ,  $k_{ocean}^{(0)} = 5.9 \times 10^{-7} \text{ s}^{-1}$  for average conditions, i.e.  $c_{OH} = 0.52 \times 10^6 \text{ cm}^{-3}$  and  $T_{ocean} = 15^\circ\text{C}$ ; Fig. 4.4b, 4.5b). Together with the absolute amounts also the annual amplitudes of the atmospheric and oceanic DDT burdens are expected to shrink from DG7020 to DG8020 and DG9020 (Fig. 4.4a). This is because the sink terms do balance the smaller sources (emission upon application and deposition for atmosphere and ocean, respectively) more rapidly. There is also a shift of the annual maximum in air from August for 1970 emissions to June for 1980-1990 emissions. This is caused by the shift of the center of gravity of the applications from northern mid-latitudes in 1970 ( $44^\circ\text{N}$ , cf. Table 4.5) to the subtropics in 1980-1990 ( $29^\circ$ - $27^\circ\text{N}$ ): the atmospheric degradation is more efficient in the tropics than in the mid latitudes (24-h and annual mean hydroxyl radical, OH, concentrations are  $0.70 \times 10^6 \text{ cm}^{-3}$  and  $0.46 \times 10^6 \text{ cm}^{-3}$ , respec-

Substance	Scenario	lat05	lat50	Lat95
DDT	DG7020	11.6°N (12.4°N)	43.5°N (40.9°N)	56.3°N (52.4°N)
	DG8020	4.6°N (13.9°N)	28.9°N (26.9°N)	53.3°N (48.0°N)
	DG9020	12.8°N (14.8°N)	27.1°N (25.7°N)	37.4°N (33.0°N)
$\gamma$ -HCH	LG8020	27.4°S (2.1°N)	27.7°N (31.0°N)	61.0°N (50.1°N)

Table 4.5: Characteristics of the latitudinal distributions of the total environmental burden of DDT (application scenarios DG7020, DG8020, DG9020) and  $\gamma$ -HCH (LG8020): 5, 50 and 95%iles (lat05, lat50 and lat95 respectively) of the cumulative zonal distribution of the geographical 2D projection, running from 90°S to 90°N during the second year (annual mean) and at the time of entry into the environment (in brackets).

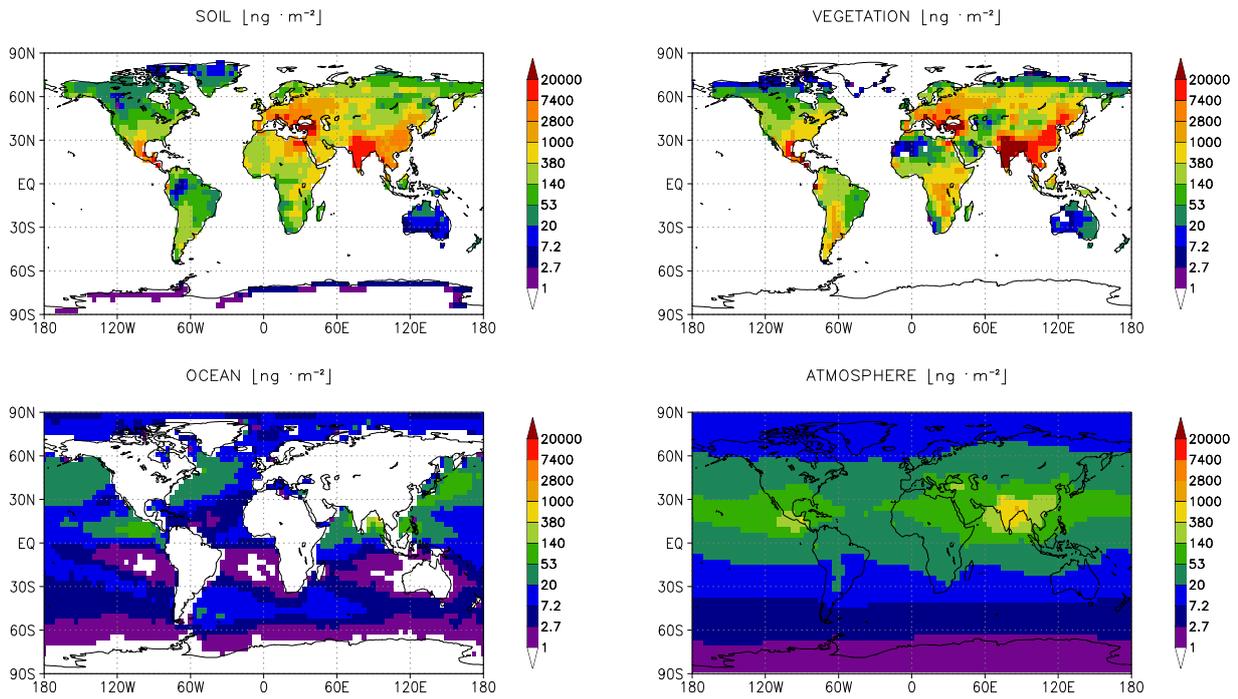
tively).

The same is seen for the atmospheric  $\gamma$ -HCH burden upon emissions in the mid latitudes and in the tropics (Fig. 4.4c): northern and tropical scenario are out of phase because of the difference (both level and seasonal variation) in OH supply. A second, smaller seasonal maximum in September under LT8020 indicates the impact of a southern winter (mid latitudes) and a precipitation minimum in the area of the most dense  $\gamma$ -HCH application in the tropics i.e., India. The oceanic burden of  $\gamma$ -HCH is dominated by the superposition of atmospheric deposition, volatilisation loss and loss to the deep sea: degradation accounts for only a small fraction (Fig. 4.2b, 4.5d). The more volatile  $\gamma$ -HCH is lost significantly to the air in the warm season. In the LT8020 scenario the seasonal warming of the tropical and southern hemispheric waters is by average less pronounced and is out of phase with the application pattern. This results in a steady uptake throughout the year with a cease in the southern summer months (Fig. 4.4d). In phase with the temperature variation is the depth variation of the surface mixed layer: The thinning of the mixed layer occurs in spring (depth halves in the northern hemisphere between February and July) and is most pronounced in mid to high latitudes (maxima at 50 - 70°).

### 4.3.2 Geographic distributions

The geographic distributions demonstrate the long-range transport potential of the substances studied. The distribution in soil (Fig. 4.6) resembles most closely the applications (Fig. 4.1b, d). But, also soil far from the areas of application are affected: North America including the Arctic archipelago and Greenland, desert regions of North Africa, Central Asia and Australia and northern parts of South America (in the case of DDT which was not applied there; Fig. 4.1b).

a)



b)

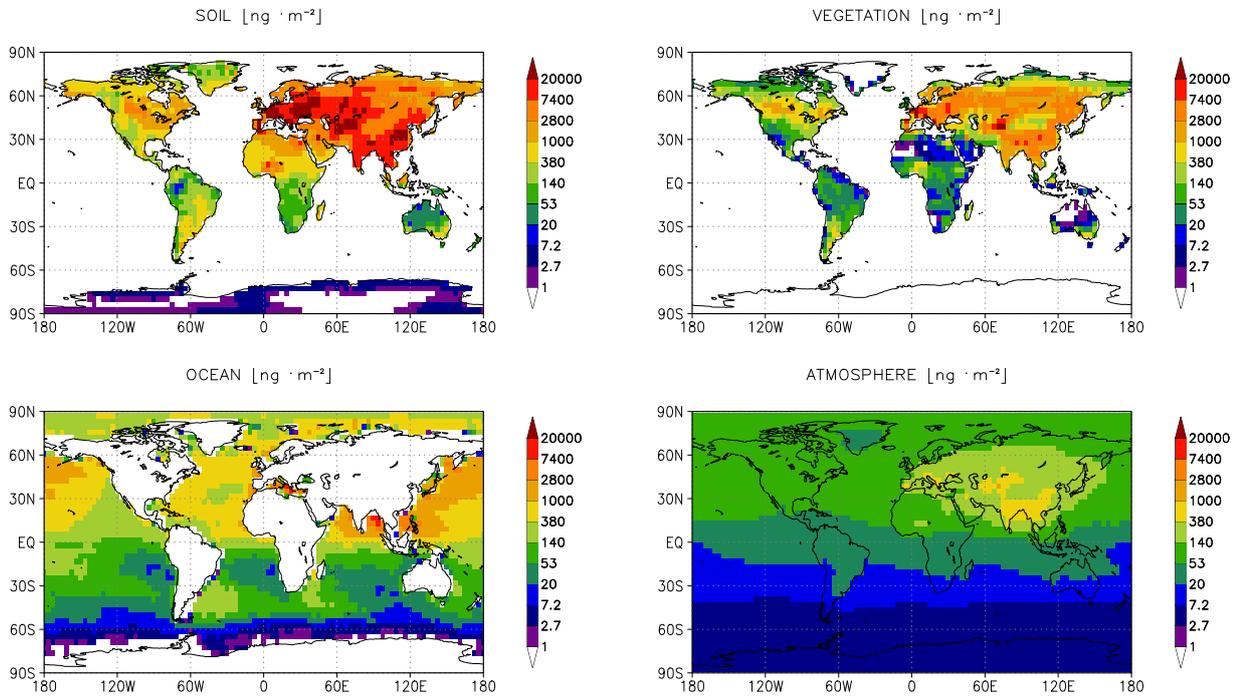


Figure 4.6: Geographic distributions in the individual compartments for (a) DDT (DG8020) and (b)  $\gamma$ -HCH upon 1980 applications (LG8020). Annual mean values ( $\text{ng} \cdot \text{m}^{-2}$ ).

As to DDT, the distribution in vegetation is distorted in the direction of the prevailing winds in some regions: Southeast and East Asia are obviously largely impacted by substance application in India and applications in Europe affect most parts of European Russia. The patterns of the two substances' distribution in the oceans are similar with high concentrations in oceanic downwind regions of North America (western parts of the North Atlantic), of East Asia (western and central areas of the North Pacific), of southern parts of South America and Africa, as well as in the seas adjacent to the Indian subcontinent and Southeast Asia. As DDT was not applied in the USA and Canada according to DG8020 the oceanic DDT concentration maximum in the western North Atlantic is remarkable. A DDT plume stretching out from Central America into the eastern Pacific and a  $\gamma$ -HCH plume in the Atlantic ocean west of the West African coast are obviously explained by transport in trade wind systems from upwind source areas. The atmospheric distributions (Fig. 4.6) reveal that the substances are globally distributed reaching also the Arctic, but not the Antarctic. The total environmental distribution of DDT is shown in Fig. 4.7. Fig. 4.8 represents the zonal distributions of DDT and  $\gamma$ -HCH. Sequential distributions upon 1970, 1980 and 1990 DDT applications indicate that significantly less must have been contributed to the total environmental burden of DDT during the more recent years. The more recently introduced substance is, however, despite the limited region of application still globally distributed, adding e.g. to contamination of East Africa, the Mediterranean and as far as northern parts of South America, the eastern USA and even the Arctic (Fig. 4.7c). As a general conclusion, it is expected that the DDT load which enters areas adjacent to application areas (e.g. Scandinavia in 1980, Myanmar and Thailand in 1990) is expected to be almost as high or even higher (Ethiopia and Somalia in 1980) as in the source areas of the region (central Europe, India and central Africa, respectively; Figures 4.1 and 4.5).

### 4.3.3 Meridional distributions

We were in particular interested in migrations of the distributions in north-south direction (Fig. 4.8, Table 4.5), because the observations of xenobiotics in the Arctic and Antarctic are the most striking evidence for persistence and long-range transport.

Of course, the burdens of the substances after some time elapsed since entry are zonally wider distributed than upon application. For the second year upon entry we find that the distances between the 5%ile and 95%ile of the cumulative zonal distributions increased by 43% (from 34.1° to 48.7°) in the case of DDT (DG8020) and by 82% (from 48.0° to 88.4°) in the case of  $\gamma$ -HCH (Table 4.5). 5% of the total environmental burden of this insecticide is expected in latitudes north of

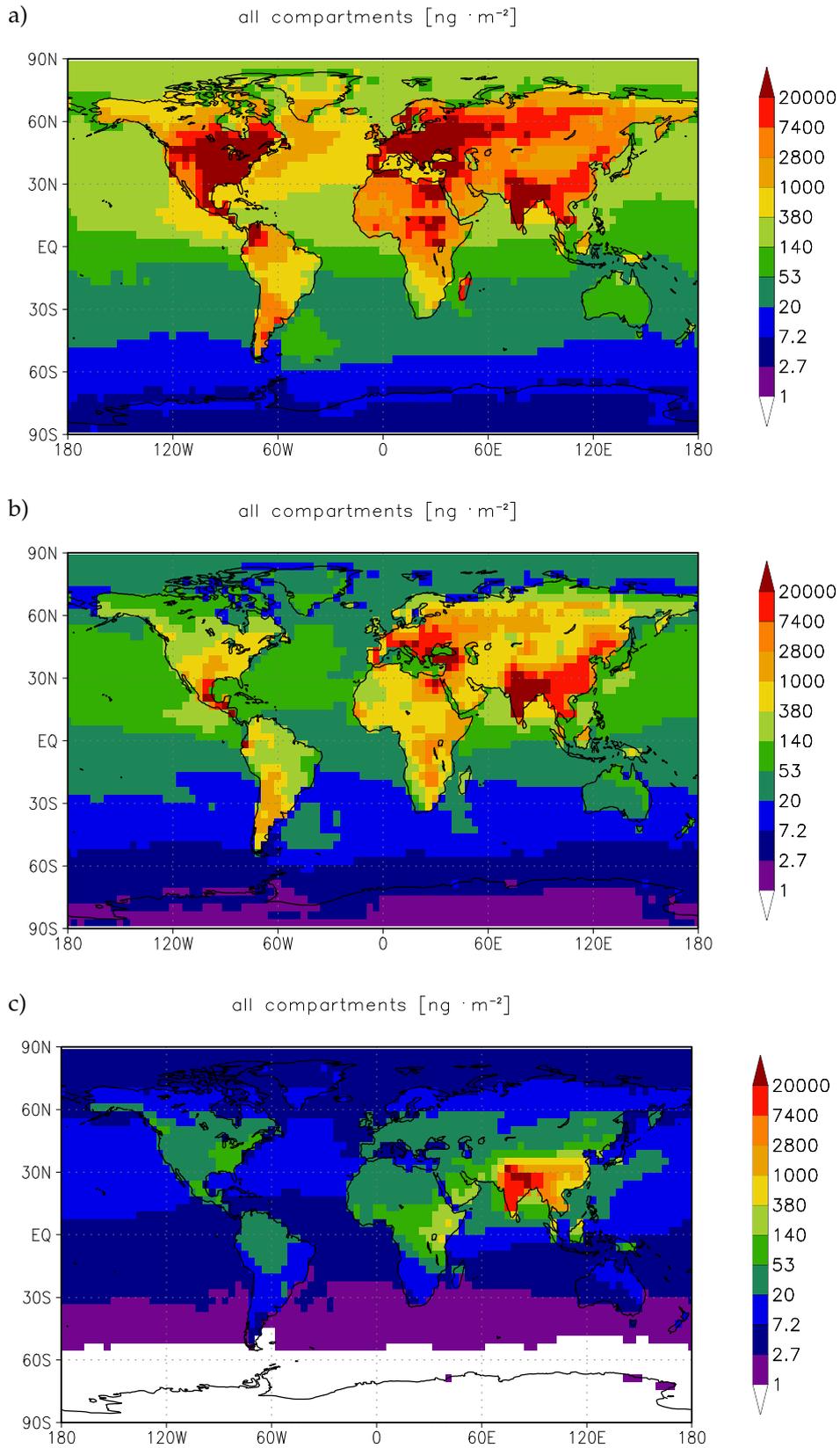


Figure 4.7: Geographic distribution of DDT in the total environment for (a) 1970, (b) 1980 and (c) 1990: annual mean values ( $\text{ng} \cdot \text{m}^{-2}$ ), application scenarios DG7020, DG8020 and DG9020 respectively.

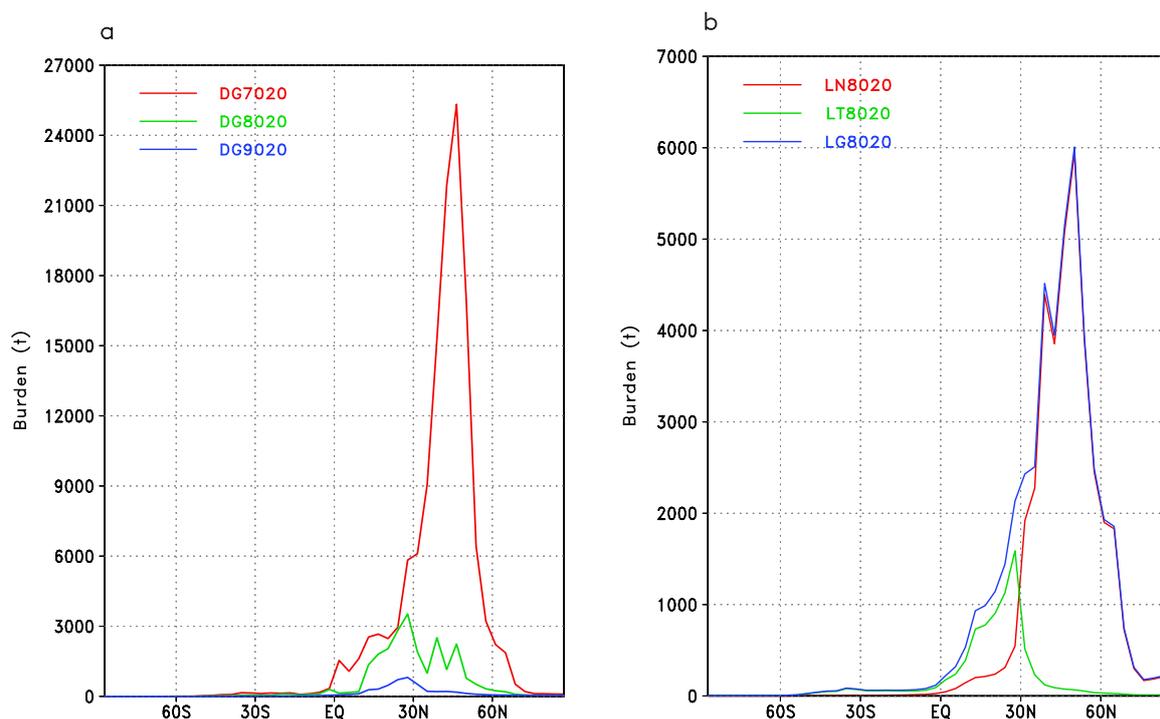


Figure 4.8: Meridional distributions of the total environmental burden of (a) DDT (application scenarios DG7020, DG8020 and DG9020) and (b)  $\gamma$ -HCH (application scenarios LN8020, LT8020 and LG8020): zonally averaged and annual mean values ( $\text{ng m}^{-2}$ ).

61°N while 5% only were applied north of 50°N. The transports made the center of gravity even to shift somewhat towards south ( $\approx 3^\circ$ ). This comparison reveals  $\gamma$ -HCH to be the more mobile substance on the global scale.  $\gamma$ -HCH applied  $> 30^\circ\text{N}$  contributes significantly to the burden of this substance as far south as  $\approx 10^\circ\text{N}$  and, in opposite direction,  $\gamma$ -HCH applied south of  $30^\circ\text{N}$  is expected to reach even  $> 60^\circ\text{N}$  (Fig. 4.8b). 3.4% of  $\gamma$ -HCH found in the Arctic (total environment,  $> 66^\circ\text{N}$ ) originates south of  $30^\circ\text{N}$ . The widening of the zonal distribution was less pronounced for DDT upon the 1970 emissions (from  $40.0^\circ$  to  $44.7^\circ$  i.e., by 12%) which were centered significantly more north ( $40.9^\circ$  under DG7020, but  $26.9^\circ$  under DG8020). The zonal distributions are very different, not only in level but also in shape and number of maxima (Fig. 4.8a). The northern tailing of the DG8020 zonal distribution is reaching also beyond  $60^\circ\text{N}$  (Fig. 4.8a). The dispersion of the DDT plume originating in India (DG9020) is still quite significant in absolute numbers ( $24.6^\circ$ ), as well as relative to its application upon entry: spread of the zonal distribution by 40%. The model predicts DDT also to reach the Arctic. The annual mean near-ground atmospheric concentrations of DDT in the Arctic ( $> 66^\circ\text{N}$ ) are predicted to have dropped from 7.3 upon DG7020 to 0.52 and 0.03  $\text{pg m}^{-3}$  upon DG8020 and DG9020. These values compare with observations of 0.14-0.16  $\text{pg m}^{-3}$  in the Canadian Arctic in 1993-94 (Macdonald et al., 2000) and 0.11- 1.6 in the

European Arctic (Spitzbergen) in 1998 (Berg et al., 2000). Much of the burden in recent years will be due to emissions before 1990 which were not simulated. The seasonality predicted for DG9020 compares well with what has been observed in 1993-94 (May-Sep / Oct-Apr = 1.0-1.1) and 1998 (1.1, predicted: 1.3).

#### 4.3.4 Environmental fate of DDT changing historically

As a consequence of the historic change of the geographic application pattern of DDT, increasingly more of this substance was stored in the atmosphere: from 1.5 in 1970 to 2.8 and 3.7% in 1980 and 1990 (Table 4.3). The fraction stored by the ocean was the highest (28.9%) upon emissions in 1970 and lower upon emissions in 1980 and 1990 (14.7 and 18.4%, respectively). The cycling of DDT molecules through the atmosphere increased from 1.8, to 2.1 and 2.6 completed hops for the average molecule. This tendency corresponds with an increase in atmospheric residence time from 4.4 to 5.2 and 5.4 d. Consequently, the residence times in the ground compartments decreased over time: mean residence times in the soil were 0.40, 0.30 and 0.18 a, in the vegetation 0.51, 0.50 and 0.41 a and in the ocean mixed surface layer 0.026, 0.020 and 0.018 a for molecules emitted under the 1970, 1980 and 1990 scenarios, respectively. The overall environmental residence time (disregarding the storage in deep sea) changed in parallel from 1.5, to 1.8 a and back to 1.5 a. Such trends are the consequences of the globally prevailing precipitation and large-scale circulation patterns, but above all in the regions of application and during the application period. The most significant changes from the 1970 to the 1980 geographical application pattern (Fig. 4.1a, 4.1b) is the cease of application in the USA (mostly eastern parts) and in Europe. Much of what had been applied in the USA will have ended up in the Atlantic ocean. In 1990 DDT was applied in India only (according to DG9020; Fig. 4.1c) which experiences precipitation only in the southwestern part from June-September while the rest of the country and of the application period is without precipitation. Precipitation most effectively limits the atmospheric residence time and, hence, reduces the fraction of the substance stored in air. The same process may explain the reduced atmospheric fraction when stepping from 1970 to 1980 emissions: application in relatively dry subtropic areas became more prominent while application in humid temperate climate became less prominent (Fig. 4.1, Table 4.5).

## 4.4 Conclusions

We studied the environmental fate of DDT and  $\gamma$ -HCH during the first two years upon entry into the environment with the focus on the effect of various scenarios of pesticide application. As

the amounts entered were the same in consecutive years of the model run and the time periods spanned by the historic usage of the substances studied (starting in the 1940s) was not covered, the scenarios are significantly artificial and do not aim to simulate historic processes. Validation through comparison with observational data is not possible. We neglected ocean transports which are expected to be significant for long-range transport of persistent substances on the time scale of 5-10 years and beyond. The conclusions drawn from the results are limited to the relative effects as forced by the selected scenarios. As being influenced by the climate, multicompartamental fate is also subject to interannual variability, an aspect also not covered by this study. As a more general conclusion, we found that long-range transport and compartmental distribution (hence, total environmental persistence) are significantly sensitive towards mode and location of entry. The influence of the latter could only be appropriately addressed using a complex transport model. We did not study the influence of time of entry explicitly but expect also sensitivity to season and even day-time of application, because of the seasonal and diurnal variabilities of the atmospheric loss processes due to oxidant availability and precipitation in most regions of the world. In our simulations  $\gamma$ -HCH is predicted to be the more mobile but less persistent substance. The difference in a factor of 2 of the total environmental residence time is, however, not significant considering the large uncertainties in the physico-chemical substance data. Mobility is obviously determined by the substances' physico-chemical properties, but also by the geographic application pattern: in the warmer tropics substance mobility is enhanced and persistence is suppressed. We assumed faster degradation in the ground compartments at higher temperatures. The high sensitivity of the multicompartamental fate to the temperature dependence emphasizes the need to improve the respective knowledge. We also found that the zonal dispersion of DDT would be more efficient upon applications to the subtropics than upon the earlier applications which had been centered in the mid latitudes. Substance mobility and persistence are also a matter of mode of entry with application to vegetation rather than soil favouring mobility and decreasing persistence. The so-called long-range transport of substances in the environment is a notion of the changes geographic substance distributions undergo from the time of entry under the influence of the geospheric transports. Diffuse sources, together representing areas of entry will be most common, but point emissions may occur as well. The change of these distributions and plumes over time is complex and influenced by location, time (season, time of day/weather) and mode of entry. These features have also been addressed using more generic models [e.g. Scheringer *et al.*, 2000]. Also persistence of a substance is determined by these features. To characterise environmental exposure in space and time as a contribution to risk assessment, scenario-specific ranges

of values of indicators for long-range transport and persistence have to be allocated to substances. Such indicators should be low- dimensional (ideally numbers) but still be able to cover the complexity of the geo- and time-referenced system.

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## The Significance of the Grasshopper-effect on the Atmospheric Distribution of Persistent Organic Substances

### Summary

Slowly degradable, semivolatile organic compounds (SOCs) may undergo more than one volatilisation-transport-deposition cycle through the atmosphere (multi-hopping). The significance of this process for the potential for long-range transport (LRT) is addressed for the first time. We use a multicompartment model which in turn is based on a general circulation model. The results suggest that both transport by single-hopping and multi-hopping contribute significantly to LRT of DDT and  $\gamma$ -HCH (lindane) and to accumulation in high latitudes. Multi-hopping is more efficient for LRT but the difference is small. A larger fraction of those molecules transported by multi-hopping is deposited to the world's oceans. Multi-hopping prevails in the boundary layer far from the source regions. However, single-hopping contributes an equal amount to the deposition of DDT and  $\gamma$ -HCH in the Arctic.

### 5.1 Introduction

Semivolatile organic compounds (SOCs) may undergo more than one cycle through the atmosphere (multi-hopping or 'grasshopper effect'), because their vapor pressure is such that ambient temperatures allow for atmospheric condensed as well as gaseous states and low degradability prevents them from rapid breakdown at the ground (land or ocean) upon atmospheric deposition.

The potential for several volatilisation-transport-deposition cycles makes the global environmental exposure particularly difficult to assess. Unlike in the case of single-hopping pollutants, such as the classical air pollutants (e.g. sulfur dioxide), it is not only the spatial and temporal emission patterns, the atmospheric oxidants distribution and the actual weather which determine the distribution and fate, but, additionally, the ground conditions and their spatial and temporal variabilities, i.e., the retaining capacity influenced by temperature, water availability and organic matter content come into play. Furthermore, also the spatial substance usage patterns may contribute to the horizontal and vertical gradients of the substances' dispersion. The role of these various influences on distribution and fate remains to be elucidated.

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

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

## 5.2 Methodology

### 5.2.1 Model description and substance properties

We used for the first time a multicompartment model which comprises an atmosphere general circulation model (AGCM), to study the large-scale transport and distributions of SOCs. The processes in the model have been described previously [Lammel *et al.*, 2001; Semeena and Lammel, 2003]. Ground compartments (soil top layer and vegetation surfaces) and the ocean surface mixed layer are coupled as single-layer compartments to the AGCM. Inter- and intra-compartmental mass exchange processes of SOCs comprise volatilisation, transport, atmospheric wet and dry

Table 5.1: Physico-chemical properties of the compounds used<sup>a</sup>

Physico-chemical properties	$\gamma$ -HCH	DDT
Water solubility (298 K) [mg l <sup>-1</sup> ]	7.4	$3.4 \times 10^{-3}$
Enthalpy of Solution $\Delta H_{sol}$ [kJ mol <sup>-1</sup> ]	2.7	2.7
Saturation vapour pressure p [Pa] (298 K)	$2.9 \times 10^{-3}$	$3.4 \times 10^{-5}$
Enthalpy of Vapourization $\Delta H_{vap}$ [kJ mol <sup>-1</sup> ]	115	118
Octanol-water partitioning coefficient $K_{ow}$ [-]	$3.98 \times 10^{-3}$	$1.55 \times 10^6$
OH reaction rate constant $k_{oh}$ [cm <sup>3</sup> molecules <sup>-1</sup> s <sup>-1</sup> ]	$1.9 \times 10^{-13}$	$1.0 \times 10^{-13}$
$\Delta E/R$ of OH reaction [K <sup>-1</sup> ]	-1710	-1300
Degradation rate in ocean water $k_{ocean}$ [s <sup>-1</sup> ] (298 K)	$2.3 \times 10^{-8}$	0
Degradation rate in soil $k_{soil}$ [s <sup>-1</sup> ] (298 K)	$2.0 \times 10^{-8}$	$4.1 \times 10^{-9}$

<sup>a</sup>Data sources are available through the authors

deposition, transfer to the deep sea, dissolution in cloudwater, and partitioning to aerosol particles (adsorption only, following [Junge, 1977]). Air-sea exchange is parameterised following the two-film model. The depth of the ocean mixed layer is spatially resolved and seasonally varying. SOC transfer to the deep sea is represented as consequence of the seasonal variation of the mixed layer depth: the substances dissolved in the lower part of the mixed layer are considered to be lost to the deep sea when the mixing depth decreases in spring [cf. Lammel *et al.*, 2001]. For the simulations reported here, the model was used with the AGCM ECHAM, version 5 [Roeckner *et al.*, 2003] and with modifications regarding dry deposition of gaseous molecules (now resistance scheme) and the aerosol module (now dynamic sources, microphysics and size-dependent sinks using a preliminary version of the aerosol sub-model HAM; [Stier *et al.*, 2004]).

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

The physico-chemical properties and environmental degradation rates for DDT and  $\gamma$ -HCH for this study (Table 5.1) are taken from literature [cf. Rippen, 2000; Klöpffer and Schmidt, 2001]. DDT has a higher affinity to soils and a lower vapor pressure and water solubility than  $\gamma$ -HCH.

As some substance properties are not known, assumptions had to be made on the temperature dependencies (degradation in ocean, soils and on vegetation assumed to double per 10 K temperature increase) and degradation rate coefficients for DDT (0 in ocean, and  $1 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$  for  $k_{\text{OH}}$ ). No degradation of the aerosol particle-bound molecules was assumed. The degradation rates in soils were also adopted for the vegetation compartment.

### 5.2.2 Model experiments and substance entry

Ten year simulations of a test run and a control run were performed. In the test run, the SOC is precluded from re-volatilisation upon atmospheric deposition to land surfaces or the ocean by setting the re-volatilisation rate to zero (single-hopping transport mode). The mass balance is still closed. In the control experiment, the SOC is allowed to undergo re-volatilisation (multi-hopping transport mode) according to substance properties and local conditions (or degradation in the ground compartment). The fraction transported by multi-hopping (FMH) of the SOC is accessible by subtraction of the test run output fields from the control run output fields. The temporal, vertical and horizontal resolutions of the runs were 30 min, 19 levels (within 1000-10 hPa) and ca.  $2.8^\circ \times 2.8^\circ$  (i.e., T42), respectively. The scenarios describe 1980 usage of the chemicals. The geographic distributions of the application of the two insecticides in the world's agriculture are based on country-level FAO data scaled with the crop density distribution ( $1^\circ \times 1^\circ$ ) [Semeena and Lammel, 2003]. In 1980,  $\gamma$ -HCH and DDT were applied in all major agricultural economies, except for several European countries, Australia, Brazil, Canada and the US, which had phased out DDT by that time. The latitudinal center of gravity (COG, as derived from a zonal distribution) [Leip and Lammel, 2004] of DDT application was at  $25^\circ\text{N}$ . The global usage patterns of  $\gamma$ -HCH in 1980 can be considered as representative for most globally used pesticides and will not deviate tremendously from the emission pattern of industrial chemicals (latitudinal COG at  $39^\circ\text{N}$ ). Without a geographic differentiation, we assume application to take place continuously, Jan-Dec over ten years, day and night. The applied amounts are assumed to be distributed 20% to soil and 80% to vegetation surfaces. The SOCs enter the air by later volatilisation from vegetation surfaces and soils.

The spatial pattern of volatilisation of the substance transported by single-hopping is determined by the usage pattern only, while the spatial pattern of volatilisation in the control run reflects the superposition of usage, deposition and degradation patterns. The model experiment is artificial as it neglects some temporary SOC reservoirs (land and sea ice, vegetation, except its surfaces) and does not represent any historic situation. Model-predicted air concentrations were

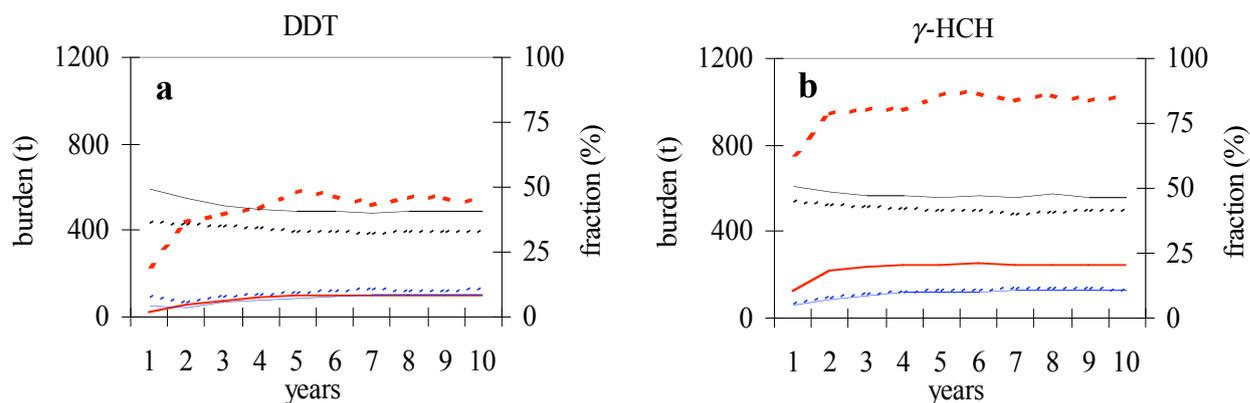


Figure 5.1: Temporal trends of global atmospheric burdens (red lines, left y-axis) transported by multi-hopping (full line) and single-hopping (dotted line) (t) and fractions of these burdens (%) in the boundary layer (750-1000 hPa, black lines, right y-axis) and in the stratosphere (10-100 hPa, blue lines, right y-axis). Annual means.

compared to observations at remote sites in the 1980s and discrepancies mostly within a factor of three and up to one order of magnitude were found.

### 5.3 Results

Due to the fast turnover in the atmosphere and vegetation surfaces compartments, quasi-steady-state is reached in these compartments within 3-6 years, while the soil and ocean compartments are still filling, because of the large capacities and relatively slow turnover. In the 10th year of the control run, 5, 83, and 12% of the global burden of DDT and 7, 51, and 42% of  $\gamma$ -HCH are stored in air, on terrestrial surfaces (vegetation plus soils) and in the ocean surface layer, respectively. The vertical distributions in the atmosphere stabilize after 5 years from the initialization of the simulation (Fig. 5.1). The burden of  $\gamma$ -HCH residing in the stratosphere reaches quasi-steady-state 1-2 years later than in the atmosphere as a whole (Fig. 5.1b). This is in accordance with the understanding that the age of air is 1-5 years at 100-10 hPa and mostly < 1 year below (maxima in high latitudes) [Manzini and Feichter, 1999]: 8 and 10% of  $\gamma$ -HCH and DDT, respectively are found in heights corresponding to < 110 hPa and 41% of  $\gamma$ -HCH and 32% of DDT in heights < 300 hPa. There are no photochemical sinks as partitioning to aerosols is almost complete there and we do assume zero reactivity for molecules in the particulate phase. The global mean atmospheric lifetimes are 20 days for DDT and 18 days for  $\gamma$ -HCH. The mean number of completed volatilisation-transport-deposition cycles is 0.93 for DDT and 1.1 for  $\gamma$ -HCH. These numbers are low, because a significant fraction does not enter the atmosphere but remains and is degraded at the ground. The reason for the higher hopping frequency of  $\gamma$ -HCH is its higher susceptibility to wash-out in combination with its higher tendency to re-enter the atmosphere

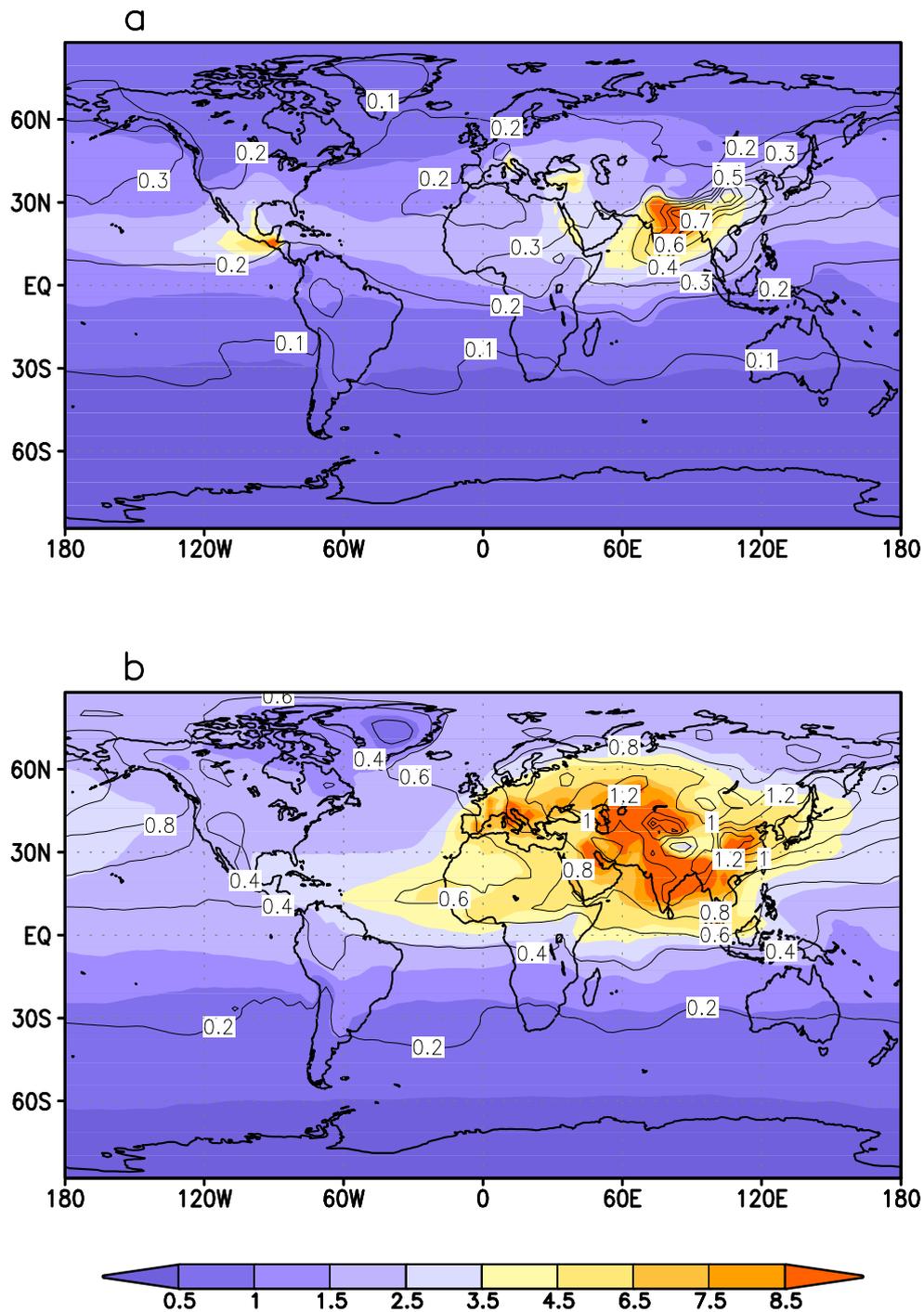


Figure 5.2: Atmospheric burdens ( $\mu\text{g m}^{-2}$ ) of the substances transported by multi-hopping or single-hopping (shades) and multi-hopping only (isolines). Mean of the 10<sup>th</sup> simulated year.

(higher vapor pressure and less efficiently sorbed to organic matter in soils than DDT).

Re-volatilisation originates mostly from soil surfaces (50-60%). Allowing for multi-hopping increases air concentrations in particular within and downwind of the source regions (Fig. 5.2). Concentrations more than double (FMH > 0.5) in the boundary layer of the mid and high lati-

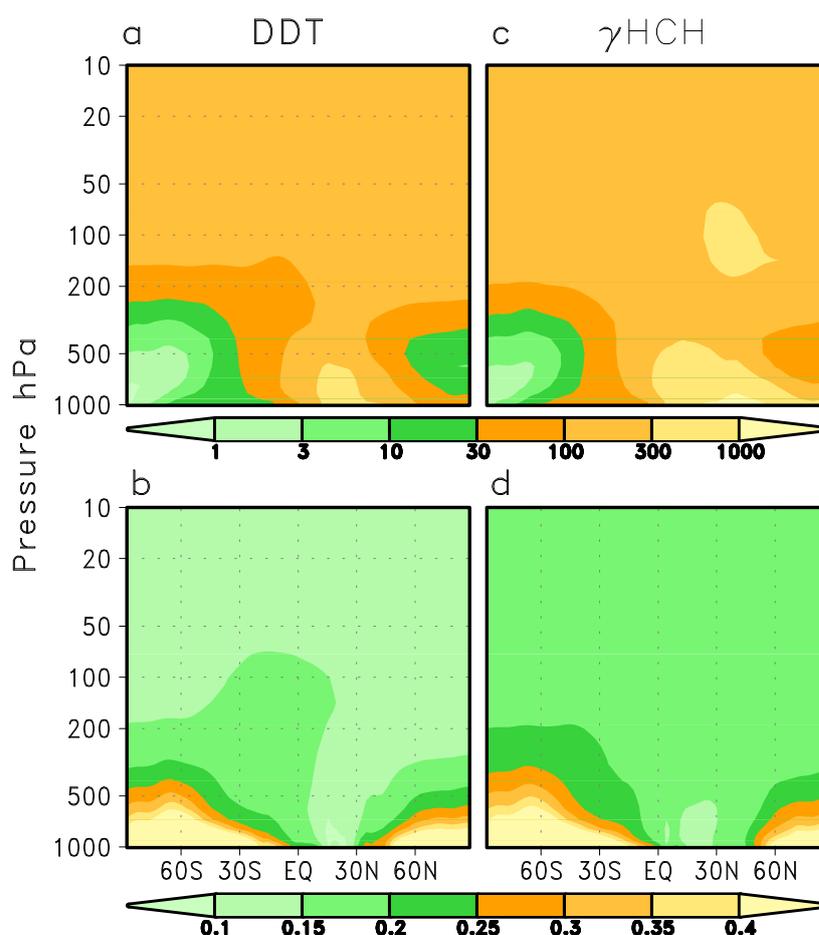


Figure 5.3: Zonally averaged global atmospheric distributions of (a, b) DDT and (c, d)  $\gamma$ -HCH, (a, c) transported by multi-hopping or single-hopping and (b, d) multi-hopping fraction (FMH). Mean mass ratios ( $\text{pg kg}^{-1}$ ) in the 10<sup>th</sup> year.

tudes ( $> 50^\circ\text{N}$  and  $> 30^\circ\text{S}$  for DDT and  $> 60^\circ\text{N}$  and  $> 20^\circ\text{S}$  for  $\gamma$ -HCH; Fig. 5.3b, d). This seems to confirm the common perception that SOCs in the Arctic and Antarctic boundary layer reached there mostly by multi-hopping. However, up to half of the boundary layer reservoirs in high latitudes and for DDT even more of the stratospheric reservoir is fed from single-hops. A quantification of the tendencies of the substance distributions to spread from the areas of application (indicators not detailed here) [Leip and Lammel, 2004] shows that under quasi-steady-state conditions transport by single-hopping contributes more than multi-hopping to this spreading. For the shares of the global atmospheric burdens found in the Arctic or Antarctic it is found that 49% of DDT and 57% of  $\gamma$ -HCH deposited in the Arctic and 13% of DDT and 12% of  $\gamma$ -HCH deposited in the Antarctic are transported by single-hopping (Table 5.2; for the global depositions, the single-hopping fractions are 76% for DDT and 72% for  $\gamma$ -HCH). Obviously, the polar regions can be reached via single-hops from mid latitudes and equatorial regions. The ratio of the fraction of the

depositions to the Arctic and Antarctic and the corresponding area fractions of these regions is  $> 1$  - except for DDT transported by single-hopping (Table 5.2). These values imply that  $\gamma$ -HCH's global distributions are predicted to follow cold condensation when transported by both single- and multi-hopping while DDT's predicted to follow only when transported by multi-hopping. The world oceans receive a higher share of the depositions of the substances being transported by multi-hopping than by single-hopping (Table 5.2). In consequence, multi-hopping significantly changes the multicompartamental distribution and tends to increase the total environmental residence time. As any long-lived tracer with sources exclusively at ground level, SOCs are lifted in tropical latitudes into the stratosphere (and higher). 11 and 15% of  $\gamma$ -HCH and DDT, respectively, are found in 10-100 hPa. In the height of the tropopause and stratosphere of the mid to high latitudes the FMH is preserved during transport due to lack of mixing from below. Sinking occurs in the polar regions, and in sub-tropical tropopause breaks [e.g. *Manzini and Feichter, 1999*]. A larger fraction of  $\gamma$ -HCH (19% of the substance residing above the 500 hPa level) than DDT (14%) is introduced into the free troposphere due to multi-hopping and then distributed into higher altitudes and poleward. Every precipitation event which an air parcel undergoes, causes some fraction of the SOC, maybe tiny but non-zero, to be washed out and later re-volatilised into then advected air and, hence, contributes to multi-hopping transport of the substance. Over the continents, this effect is more pronounced for the more water soluble and more readily volatilising  $\gamma$ -HCH. In addition, the region where multi-hopping dominates  $\gamma$ -HCH transport, unlike in the case of DDT, encompasses large semi-arid areas of central Asia (longer atmospheric lifetime).

## 5.4 Discussion and conclusions

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

Table 5.2: Values characterising the distributions of DDT and  $\gamma$ -HCH in the Global Atmosphere<sup>a</sup>

	DDT		$\gamma$ -HCH	
	Multi-hopping	Single-hopping	Multi-hopping	Single-hopping
Total burden(t)	95	520	240	1000
Burden in the Arctic/Antarctic(t)	7/2	22/9.9	32/4	53/14
Burden in the boundary layer/stratosphere (t)	39/12	172/78	112/26	418/111
Total depositions (t)	2112	6540	6169	16010
Deposition to sea (%)	56	37	40	33
Deposition in the Arctic/Antarctic (t)	353/46	347/7.2	2038/85	2720/11
Ratio of depositions in the Arctic and Antarctic over their area share	2.1	0.7	4.1	2.1

<sup>a</sup>Annual sums or mean values for the 10<sup>th</sup> year. Boundary layer: 750 - 1000 hPa, stratosphere: 10 - 100 hPa. Arctic and Antarctic: 66.5°N - 90°N, 66.5°S - 90°S.

<sup>b</sup>8% of the globe's area is located > 66.5° N or > 66.5° S.

therein]. Above, the FMH is expected to be higher in the case of substances which are more water soluble and more volatile (high vapor pressure) (such as  $\gamma$ -HCH) and low for opposite properties (such as DDT).

In a quantitative sense, the results are limited to the two SOCs and the very usage patterns studied, because SOC's fate on large spatial scales (including its tendency to undergo more than one volatilisation-transport-deposition cycle) depends strongly on both the substance properties [Beyer *et al.*, 2003] and the location and time of entry [Leip and Lammel, 2004]. Furthermore, the LRT potential may be overestimated as the atmospheric lifetime in general and in the free troposphere is not well known for SOCs, because gas-particle partitioning is not well understood and we assumed gas-particle partitioning to be explained by adsorption only and zero degradability of particle-bound molecules. Any other parameterisation of the gas-particle partitioning (e.g. accounting for absorption into the organic matter matrix) or non-zero photochemical degradability of the particle-bound molecules would lead to enhanced degradability and, in turn, reduce the spatial range.



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## Significance of Global and Regional Climate and of Substance Properties on the Fate and Long-range Transport of Persistent Organic Pollutants - DDT and $\gamma$ -HCH

### 6.1 Introduction

The presence of pesticides in the atmosphere was first reported in the 1960s, when there was significant usage of chlorinated products on a global scale. Obviously some persistent pesticides like DDT and  $\gamma$ -HCH, besides others, undergo long-range transport and were found in the polar regions at remarkably high concentration levels [Bidleman *et al.*, 1990; Egan *et al.*, 1995; Harner *et al.*, 1999; Macdonald *et al.*, 2000; Pacyna, 1995]. Since then, techniques for collection and analysis of atmospheric samples of organic contaminants have been developed and improved and more evidence was accumulated and preliminarily assessed [UNEP, 2003; AMAP, 2004]. The atmosphere provides both carrier and sink medium for many organic compounds. The cycling of the semivolatile organic compounds (SOCs) in the environment is the result of the combined action of many processes the molecules undergo: mode, temporal and spatial patterns of application in agriculture, uptake by leaves through stomata or cuticula, partitioning in the soil multi-phase system, washout to ground water, degradation or volatilisation from leaves and soil, transport by winds, partitioning to atmospheric particles and cloud droplets, chemical degradation by radicals, dry and wet deposition of the gaseous molecules or of the particulate or droplet carrier, again partitioning in the soil or, aquatic multi-phase system, vertical transport to ocean or freshwater sediments and horizontal transport by ocean currents and rivers, biotic or abiotic chemical degradation, uptake by organisms of the lowest trophic level or grazers, eventually re-volatilisation from ground to air. The substance properties are important for all of these processes with the

exception of transport with winds or water currents [AMAP, 2004]. It is difficult to decide upon the right physico-chemical properties of the substance, where a wide variety of data are reported for a single property [Pontolillo and Eganhouse, 2001].

Mathematical models could play a key role, if they were to simulate atmospheric loading and transport of pesticides. Several box models and regional models have been in use to understand the behaviour of these substances in the multi-media environment [Klöpffer, 1994; Wania *et al.*, 2000]. Box models have been combined to zonally averaged 1-2D models also [Wania and Mackay, 1995, 1999]. Limitations exist in predicting long-range transport with these models, because the environment is not geo-referenced in the model world, geographic transports (winds, ocean currents) are represented by mean large-scale eddy coefficients and the temporal variability of climatic conditions are not reflected. To study the interplay of release, phase partitioning, degradation and long-range transport, atmospheric general circulation models should be used. With this modelling study we make an effort to shed some light on the various significances of these processes for the cycling of two substances with different characteristics, *p,p'*-DDT and  $\gamma$ -HCH. These are subject to regulation under international conventions for the protection of human health and the environment (so-called POPs conventions, UN-ECE, DDT also under UNEP) and conventions for the protection of the seas. Not all the aforementioned processes are captured by our model: sediments, ocean transport and the inner volume of biota are not represented in the model. The model is based on an atmosphere general circulation model (AGCM) which had been shown to be well suited to represent the large scale atmospheric dynamics and, in particular, the monsoon system [Gates *et al.*, 1999].

## 6.2 Model description

The AGCM used in this study, ECHAM5, is the most recent version of the atmospheric general circulation model, ECHAM (European Centre Hamburg Model; [Roeckner *et al.*, 2003]). A chemistry scheme [Feichter *et al.*, 1996] and a dynamic aerosol model (HAM, [Stier *et al.*, 2004]) are included. In HAM, aerosols are represented as being composed of 7 components, four soluble and three insoluble. The particles are represented in four size modes in which each mode follows the mass and number in log-normal distribution. As the mass fraction of SOCs in total suspended particulate matter (TSP) is negligible, we neglect interaction with the aerosols, but use them as a carrier of the mass. As soon as the substance is released into the model atmosphere, partitioning between gas and particulate matter phase takes place and both phases are transported independently. By addition of 2D ground compartments, a multicompartment model is complemented

(first described in [Lammel *et al.*, 2001]). Vegetation and soil are distributed geo-referenced as single layer boxes. A well mixed surface layer ocean with locally and seasonally varying depth, taken from a 3D ocean general circulation model, [Drijfhout *et al.*, 1996] is included. The substances are treated similarly upon deposition from gas or particulate phase.

## 6.3 Parameterisations of substance cycling processes

### 6.3.1 Atmosphere

The atmosphere is a three phase system (gas, particles, cloudwater), with the mass exchange between them being controlled by instantaneous equilibria (Henry equilibrium for air-water equilibrium).

#### 6.3.1.1 Gas-particle partitioning of organic substances

In this study, we estimate the ratio between gas-phase and atmospheric particulate matter,  $\theta$ , by either absorption into organic matter empirically based on the octanol-air partition coefficient,  $K_{oa}$  [Finizio *et al.*, 1997], or adsorption onto aerosol surfaces empirically based on relationship between vapour pressure and aerosol surface, which Junge [1977] first suggested and Pankow [1987] reviewed.

The Junge-Pankow equation has the form:

$$\theta = \frac{c \times \phi}{c \times \phi + p}$$

where,  $\phi$  is the surface area of particles per unit volume of air ( $\text{cm}^{-1}$ ),  $p$  is the vapour pressure (Pa) and the parameter  $c$  (Pa cm) is related to the heat of desorption from the particle surface, the heat of vapourisation of the compound, and the moles of adsorption sites on the aerosol [Boethling and Mackay, 2000]. Junge [1977] proposed a value of 17.2 Pa cm for  $c$ .

The  $K_{oa}$  absorption model was found to describe adequately the partitioning of a number of organochlorines (PCBs, DDT, besides others [Finizio *et al.*, 1997; Harner and Bidleman, 1998]). Hence we use the relation for DDT and PCBs:

$$\log K_p = 0.55 \log K_{oa} - 8.23$$

where,  $K_p$  is the particle-gas partition coefficient in  $\text{m}^3 \mu\text{g}^{-1}$  for the determination of  $\theta$ .

$\theta$  is given as:

$$\theta = \frac{1}{\frac{1}{K_p \times c_{TSP}} + 1}$$

where,  $c_{TSP}$  is the concentration of total suspended particulate matter in  $\mu\text{g m}^{-3}$ .

For  $c_{TSP}$ , we consider any material with the aim to account for the fact that even inorganic particulate matter through an organic film might provide a phase for both types of partitioning, i.e. adsorption and absorption. For the substances under study, a value of  $K_{oa}$  is available for  $T = 298\text{K}$  but not as a function of temperature (exceptions are cited in *Harner and Bidleman* [1998]). Neglecting temperature dependence would be significantly misleading, however, e.g.  $\theta = 0.0016$  would be predicted for DDT for all temperatures while  $\theta = 0.1-0.3$  was observed in the ambient atmosphere [*Kaupp and Umlauf*, 1992]. In lack of measured data we assume that the temperature dependence of gas-particle partitioning,  $\theta(T)$ , behaves similar as the PAHs. For various polyaromatic hydrocarbons (PAHs),  $\theta$  doubles per 4.9 K decrease in temperature (mean, individual species show similar behaviour, *Pankow* [1991]). The assumption of an analogy to PAHs may be justified to some extent as these, similar to the organochlorines, partition due to both adsorption and absorption processes. Thus,  $\theta$  is defined as:

$$\theta = \frac{1}{\frac{1}{K_p \times c_{tsp}} + 1} \times 2^{\frac{(298-T)}{4.9}}$$

where  $T$  is the atmospheric temperature in K.

### 6.3.1.2 Degradation

Chemical degradation in the atmosphere is controlled by reaction with the hydroxyl radical during daytime and with the nitrate radical during night-time. These radicals are fed to the model prescribed as a function of latitude, longitude and time of day and month [*Roelofs et al.*, 1997]. SOC's day time atmospheric decay reaction rate is given as

$$\frac{\partial c}{\partial t} = k_{OH} \times c_{OH} \times c_{SOC}$$

and the night time decay due to reaction with the nitrate radical is given as

$$\frac{\partial c}{\partial t} = k_{NO_3} \times c_{NO_3} \times c_{SOC}$$

where temperature dependent rate constants,  $k_{OH}$  and  $k_{NO_3}$  are formulated following van't Hoff.

### 6.3.2 Soil

In the model, soil hydrology is represented by a bucket model [*Roeckner et al.*, 1996]. Volatilisation occurs from the top soil layer and the rates will be at a maximum around solar noon or

early afternoon and are assumed to be small during night. Since the physico-chemical parameters depend highly on temperature, corrections were made for the effect of temperature on the vapour pressure using the Clausius-Clapeyron equation as:

$$p = e^{\frac{\Delta H}{R}(\frac{1}{T} - \frac{1}{T_0}) + \ln p_0}$$

where,  $\Delta H$  is the heat of vapourisation ( $\text{J mol}^{-1}$ ),  $T$  is the atmospheric temperature at ground level,  $T_0$  is the reference temperature and  $p_0$  is saturated vapour pressure (Pa) at  $T_0$ .

### 6.3.2.1 Gas liquid partitioning in soils

Partitioning in soils is assumed on the basis of temperature dependent phase equilibrium in 3-phase soil system [Smit *et al.*, 1997]. In the model, phase partitioning is derived directly from the pesticide's physico-chemical properties and some of the most relevant atmospheric variables. The mathematical formulation of the phase partitioning is given as:

$$c_{i,liquid} = K_{\frac{l}{g}} \times c_{i,vapour}$$

with:  $c_{i,liquid}$  = concentration of pesticide in the liquid phase ( $\text{kg m}^{-3}$ ),  $c_{i,vapour}$  = concentration of the pesticide in the gas phase ( $\text{kg m}^{-3}$ ), and  $K_{\frac{l}{g}}$  = liquid-gas partitioning coefficient (dimensionless).

The concentration of the pesticide in the soil system ( $\text{kg m}^{-3}$ ) is described by:

$$c_{soil} = Q \times c_{vapour}$$

with the capacity factor  $Q$  as:

$$Q = \theta_{gas} + \theta_{liquid} K_{\frac{l}{g}} + \rho_{soil} K_{\frac{l}{g}} K_{\frac{s}{l}}$$

with:  $K_{\frac{s}{l}}$  = solid-liquid partitioning coefficient ( $\text{kg m}^{-3}$ ),  $\theta_{gas}$  = volume fraction of gas (dimensionless),  $\theta_{liquid}$  = volume fraction of moisture (dimensionless),  $\rho_{soil}$  = dry bulk density of the soil ( $\text{kg m}^{-3}$ ).

$K_{\frac{s}{l}}$  can be calculated as:

$$K_{\frac{s}{l}} = K_{om} \times c_{om}$$

where  $K_{om}$  is the sorption coefficient and  $c_{om}$  is the organic matter content of the soil.

The dimensionless fraction of the pesticide in the gas phase is then calculated as

$$F_g = \frac{\theta_{gas}}{Q}$$

### 6.3.2.2 Volatilisation from soil

The most important factor which determines the volatilisation capacity is the vapour pressure ( $P_v$ ) of the active substance. We adopt an empirical relation for cumulative volatilisation ( $CV$ , of applied dosage) in the model. For normal to moist field conditions,  $CV$  is given by *Smit et al.* [1997] as:

$$CV = 71.9 + 11.6 \log(100F_g)$$

with  $F_g \leq 16.33 \times 10^{-9}$

For dry field conditions, the following relation is considered:

$$CV_{dry} = 42.3 + 9.0 \log(100F_g)$$

with  $F_g \geq 1.9955 \times 10^{-7}$

### 6.3.2.3 Degradation in soil

An overall first order biological and chemical degradation in soil is considered and assumed to double per 10 K temperature increase to account for observations and according to recommendations, *TGD* [1996]. The decay coefficient for soil is calculated as:

$$k_{soil(T)} = k_{soil} \times 2^{\frac{(T-298)}{10}}$$

### 6.3.3 Vegetation

In the model, vegetation is represented as a surface only. Application, deposition and volatilisation take place, but no mass exchange into the vegetation compartment. We adopt the same  $k_{soil}$  as degradation rate for vegetation also in lack of better knowledge. For a large number of compounds it was found however that the vapour pressure alone can describe the cumulative volatilisation with sufficient accuracy. The empirical relation between cumulative volatilisation ( $CV$ ) and vapour pressure ( $VP$ ) can be written as

$$\log CV = a + b \log VP, \quad (6.1)$$

with  $a = 1.528$  and  $b = 0.466$ .

Thus the equation take the form [*Smit et al.*, 1998]:

$$CV = 10^{1.528 + 0.466 \log VP}$$

with  $VP \geq 5.2655 \times 10^{-7}$

### 6.3.4 Ocean

In the model, the ocean is non advective and therefore does not contribute to tracer transport. The ocean surface mixed layer receives deposition and loses substance through volatilisation, degradation and loss to the deep sea. In the model world, the latter process is caused by a seasonal change of the depth of the surface mixed layer.

#### 6.3.4.1 Air-water gas exchange

Diffusive air-water exchange is calculated based on the two-film model [Liss and Slater, 1974] and Mackay and Leinonen [1975] invoking two mass transfer coefficients in series,  $U_1$  ( $\text{m s}^{-1}$ ) for the stagnant atmospheric boundary layer and  $U_2$  ( $\text{m s}^{-1}$ ) for the stagnant water layer close to the air-water interface. These mass transfer coefficients are calculated as a function of wind speed using relationships by Mackay and Yuen [1983] as quoted in Schwarzenbach *et al.* [1993].

$$U_1 = 0.065 \times \sqrt{(6.1 + 0.63 \times u)} \times 0.01$$

$$U_2 = 0.000175 \times \sqrt{(6.1 + 0.63 \times u)} \times 0.01$$

where,  $u$  is the wind speed at 10m in  $\text{m s}^{-1}$ .

The D-values ( $\text{mol Pa}^{-1} \text{m}^{-2} \text{s}^{-1}$ ) for volatilisation from water are then calculated using the following equation:

$$D_{wa} = \frac{1}{\frac{R \times T_W}{U_1} + \frac{H}{U_2}}$$

where,  $R$  is the universal gas constant ( $8.3143 \text{ Joule mole}^{-1} \text{K}^{-1}$ ),  $T_W$  is the sea surface temperature and  $H$  is the Henry coefficient in units of  $\text{Pa mol}^{-1} \text{m}^3$ .

#### 6.3.4.2 Degradation

Biological and abiotic degradation in ocean is assumed to obey first order kinetics, and assumed to double per 10 K temperature increase. Then the mathematical formulation has the form:

$$k_{oc} = k_{ocean} \times 2^{\frac{(T-273)}{10}} + k_{hydr} \times e^{\frac{-7818}{T}}$$

### 6.3.5 Deposition

Dry deposition flux is calculated from the concentration in the lowest atmospheric layer and dry deposition velocity:

$$F_d = c \times \rho_{air} \times V_d,$$

where,  $c$  is the tracer concentration ( $\text{kg kg}^{-1}$ ) at the surface layer,  $\rho_{air}$  is the air density ( $\text{kg m}^{-3}$ ) and  $V_d$  is the dry deposition velocity ( $\text{m s}^{-1}$ ).

The dry deposition velocity for gas phase is calculated according to the 'big-leaf' approach by *Hicks et al.* [1987], where the turbulent transfer and vegetation activity is calculated by ECHAM, using the provided global uptake rates for soil, water, and snow/ice. Uptake resistance for the trace gases, for which the dry deposition velocities have not been observed or estimated, are calculated based on the Henry coefficient and a reactivity coefficient [*Ganzeveld and Lelieveld, 1995; Ganzeveld et al., 1998; Ganzeveld, 2001*], implying that water solubility controls the surface resistance. Scavenging of gaseous molecules is calculated based on the liquid fraction of the total substance derived from Henry's law [*Seinfeld and Pandis, 1998*]. Particle dry deposition is calculated using a dry deposition velocity model, which has been applied previously for sulfate aerosol dry deposition parameterisation [*Ganzeveld et al., 1998*]. The particulate phase wet deposition is calculated based on a composition-dependent scavenging coefficient, which is defined as the fraction of the tracer in the cloudy part of the grid box that is embedded in the cloud liquid/ice water.

## 6.4 Input data and model run initialisation

The physico-chemical properties DDT and  $\gamma$ -HCH are given in Table 6.1 [*Rippen, 2000; Klöpffer and Schmidt, 2001*]. Data for DDT and  $\gamma$ -HCH usage are compiled based on statistical data on insecticide consumption in agriculture reported by each country to FAO (1947-1990) and also on published data [*FAO, 1988, 1989*]. Data for most European countries for the study period are taken from *Pacyna et al.* [1999]. The country-wise consumption data are distributed over the corresponding model grid through allocation of grid cells to countries scaled by the intensity of cropland distribution ( $1^\circ \times 1^\circ$  resolution; CGEIC, [*Li, 1999*]) of the country, i.e., higher consumption is assumed in areas of high cropland density and vice versa.

## 6.5 Model experiments

The model is simulated for 10 years, after a physical spin up of 8 years. Substance input into the model environment is the same every year. Even though this is not a realistic scenario, these experiments can simulate the residence time of the substances in the total environment, the long-range transport potential, geographical distribution in atmosphere, soils, vegetation, and the ocean surface layer, and the vertical distribution in the atmosphere (10 hPa, i.e., until  $\approx 30$  km on a global average).

Table 6.1: Physico-chemical properties of DDT and  $\gamma$ -HCH used for the model simulations

Physical Chemical properties	Unit	DDT	$\gamma$ -HCH
Molecular mass	g mol <sup>-1</sup>	354.5	290.83
Sorption coefficient	m <sup>3</sup> kg <sup>-1</sup>	888	1.91
Saturated vapour pressure at 293 K	Pa	2.5 × 10 <sup>-5</sup>	3.0 × 10 <sup>-3</sup>
Heat of Vapourization	J mol <sup>-1</sup>	118.0 × 10 <sup>3</sup>	115.0 × 10 <sup>3</sup>
Heat of Solution	J mol <sup>-1</sup>	2.7 × 10 <sup>4</sup>	2.7 × 10 <sup>4</sup>
Water solubility at 296 K <sup>a</sup>	mg l <sup>-1</sup>	3.4 × 10 <sup>-3</sup>	7.4
Ocean water solubility	mg l <sup>-1</sup>	3.4 × 10 <sup>-3</sup>	7.4
Biotic and abiotic degradation rate in soil at 273 K	s <sup>-1</sup>	4.05 × 10 <sup>-9</sup>	2.0 × 10 <sup>-8</sup>
Biotic and abiotic degradation rate in ocean at 273 K	s <sup>-1</sup>	0	1.86 × 10 <sup>-8</sup>
OH radical rate constant of gaseous molecule	cm <sup>3</sup> molec <sup>-1</sup> s <sup>-1</sup>	<sup>b</sup> 4.5 × 10 <sup>-12</sup>	1.9 × 10 <sup>-13</sup>
		<sup>c</sup> 1.0 × 10 <sup>-13</sup>	
OH radical rate constant on particle sorbed molecule	cm <sup>3</sup> molec <sup>-1</sup> s <sup>-1</sup>	<sup>b</sup> 4.5 × 10 <sup>-12</sup>	0

<sup>a</sup> land and ocean water <sup>b</sup> low mobility scenario <sup>c</sup> all other DDT scenarios (cf. Table 6.2)

Five scenarios, four for DDT and one for  $\gamma$ -HCH were tested (Table 6.2). The latter is based on 1980 usage, while for DDT the scenarios reflect 1980 and 1990 usage. Non-agricultural usage is not captured by the data. DDT is represented as the *p,p'*-DDT isomer. Even though DDT was still in use in many European, Asian and African countries in 1990, the usage in India alone consumed more than 75% of the total global consumption because usage had decreased substantially in many countries in the previous years. Hence, under the 1990 scenarios we neglect usage outside India. Application is during June, July, November and December, which are the main pre-harvesting months of the year in India.

Significant discrepancies between reported data of the physico-chemical properties of the substances exist [Klöpffer *et al.*, 2000; Pontolillo and Eganhouse, 2001] and some data are totally missing. With the pair of scenarios DG80LW/DG80HM, we make an effort to account for these uncertainties: DG80LW stands for an upper, and DG80HM for a lower estimate with respect to atmospheric degradability ( $k_{OH} = 4.5 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$  against  $1.0 \times 10^{-13} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$  on gas phase and  $4.5 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$  against zero on particulate phase, respectively). Furthermore, partitioning to the particulate phase is due to adsorption alone (DG80HM) [Junge, 1977] or absorption (DG80LM) [Finizio *et al.*, 1997].

Table 6.2: Scenarios of DDT and  $\gamma$ -HCH entry into the model world

Substance	Scenario	Year	Applied amount (t a <sup>-1</sup> )	Period of application	% applied to vegetation/soil/atmosphere
DDT	DG80LW <sup>a</sup>	1980	9299	Feb-Aug	80/20/0
	DG80HM <sup>b</sup>	1980	9299	Jan-Dec	80/20/0
	DG90HA <sup>b</sup>	1990	4498	Jun-Jul, Nov-Dec	80/10/10
	DG90HM <sup>b</sup>	1990	4498	Jun-Jul, Nov-Dec	80/20/0
$\gamma$ -HCH	LG80HM	1980	20365	Jan-Dec	80/20/0

<sup>a</sup> low mobility scenario and  $\theta$  based on [Finizio et al., 1997], <sup>b</sup> high mobility scenario and  $\theta$  based on [Junge, 1977].

## 6.6 Results and discussion

### 6.6.1 Global distributions and filling of compartments

Quasi steady state is expected once the substance sinks in a compartment balance the sources. The dynamics of compartmental filling is different for the compartment and for the substances (Fig. 6.1). E.g., biotic degradation, deposition to deep sea and volatilisation are the sinks in the ocean compartment to balance the only source, i.e., atmospheric deposition. The runoff from the continents are not included in the model. Application and deposition are the sources and volatilisation and chemical degradation are the sinks in the soil and vegetation compartments. Volatilisation from the ground compartments are the sources and depositions (wet and dry) and photolysis are the loss processes in the atmosphere (cf. Fig. 3.1).

The atmosphere and vegetation compartments reach quasi-steady state in 3-4 years in the case of DDT, while it takes only 1.5-2 years in the case of  $\gamma$ -HCH (Fig. 6.1). In soil, DDT shows a tendency to reach equilibrium nearly after 10 years and the  $\gamma$ -HCH approaches equilibrium in 10 years. The substances behave significantly different in oceanic compartment where the accumulation of hydrophobic DDT is very slow and the simulated time to achieve equilibrium is nearly 10 years, while the higher water solubility and low volatility of  $\gamma$ -HCH than that of DDT, cause a faster accumulation in oceanic compartment especially when the biotic degradation is slow. In the 10th year, half of the DDT in the total environment is found in the soils (Table 6.3). Under the high mobility scenarios 12% is found in the ocean surface layer and ca. 5% in air, while under the low mobility scenario these burdens amount to only 2 and 1%, respectively.

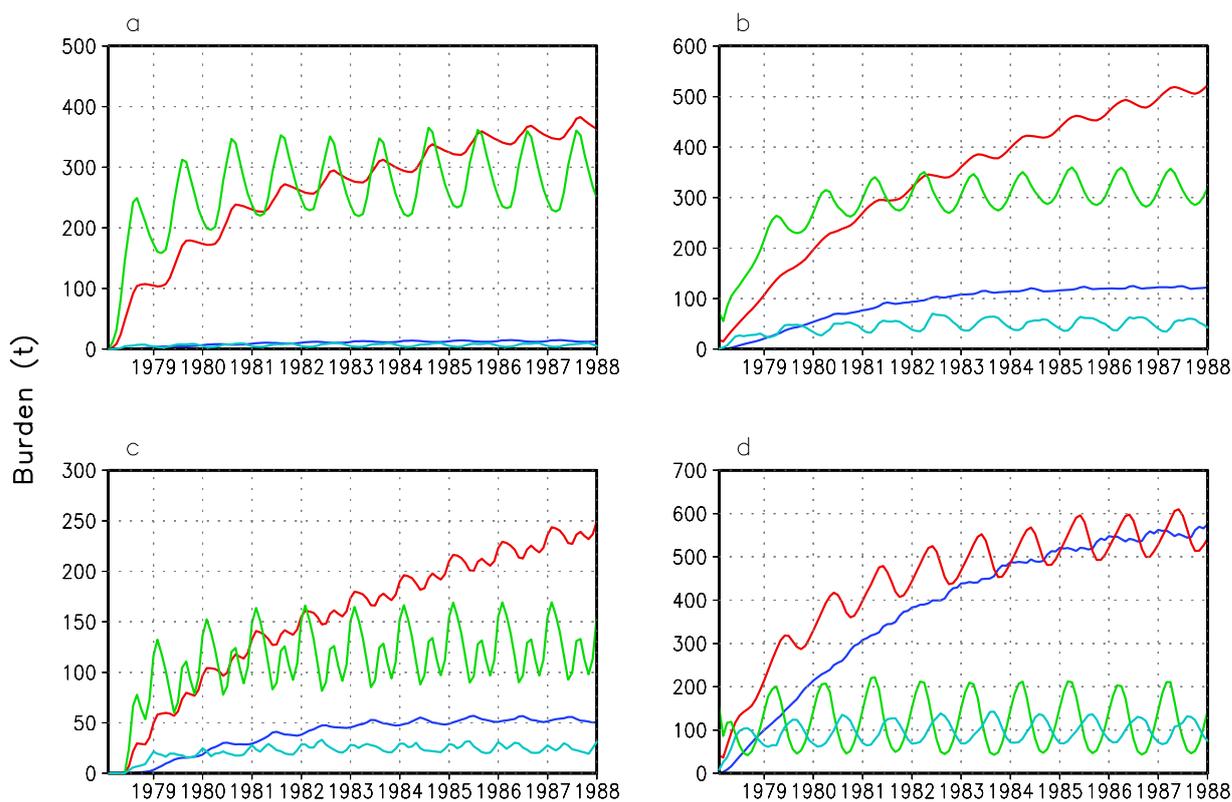


Figure 6.1: Global burdens of DDT and  $\gamma$ -HCH (t) over time (ten years) in soils (red), vegetation (green), ocean surface mixed layer (blue) and the atmosphere (cyan), under the scenarios (a) DG80LW, (b) DG80HM, (c) DG90HA and (d) LG80HM.

As a consequence of differences in volatility and water solubility between the substances, a much smaller fraction of the total environmental burden of  $\gamma$ -HCH than for DDT is found on vegetation surfaces to the benefit of the ocean surface layer burden (Table 6.3). Until the 10th year, upon entry of the substances, large amounts comparable to total environmental burdens had been transferred to the deep sea.

The fast atmospheric degradation in the case of DG80LW destroys 7170 tonnes of DDT globally and annually (10<sup>th</sup> year) in contrast to only 16 tonnes in the case of DG80HM. This discrepancy is explained by the difference in  $k_{OH}$ , that exceeds one order of magnitude for DG80LW than DG80HM. Obviously, the atmospheric decay dominates the total environmental fate even for a substance like DDT which is hardly volatile and hardly partitioning to the gas phase in the atmosphere.

The geographic distributions (Fig. 6.2) always show maxima in or near the application area in all compartments. The difference in compartmental distribution between the low and high mobility scenarios for DDT is noteworthy (DG80LW and DG80HM). This is due to the fact that the faster degradation in atmosphere removes the substance rapidly in DG80LW, compared to that

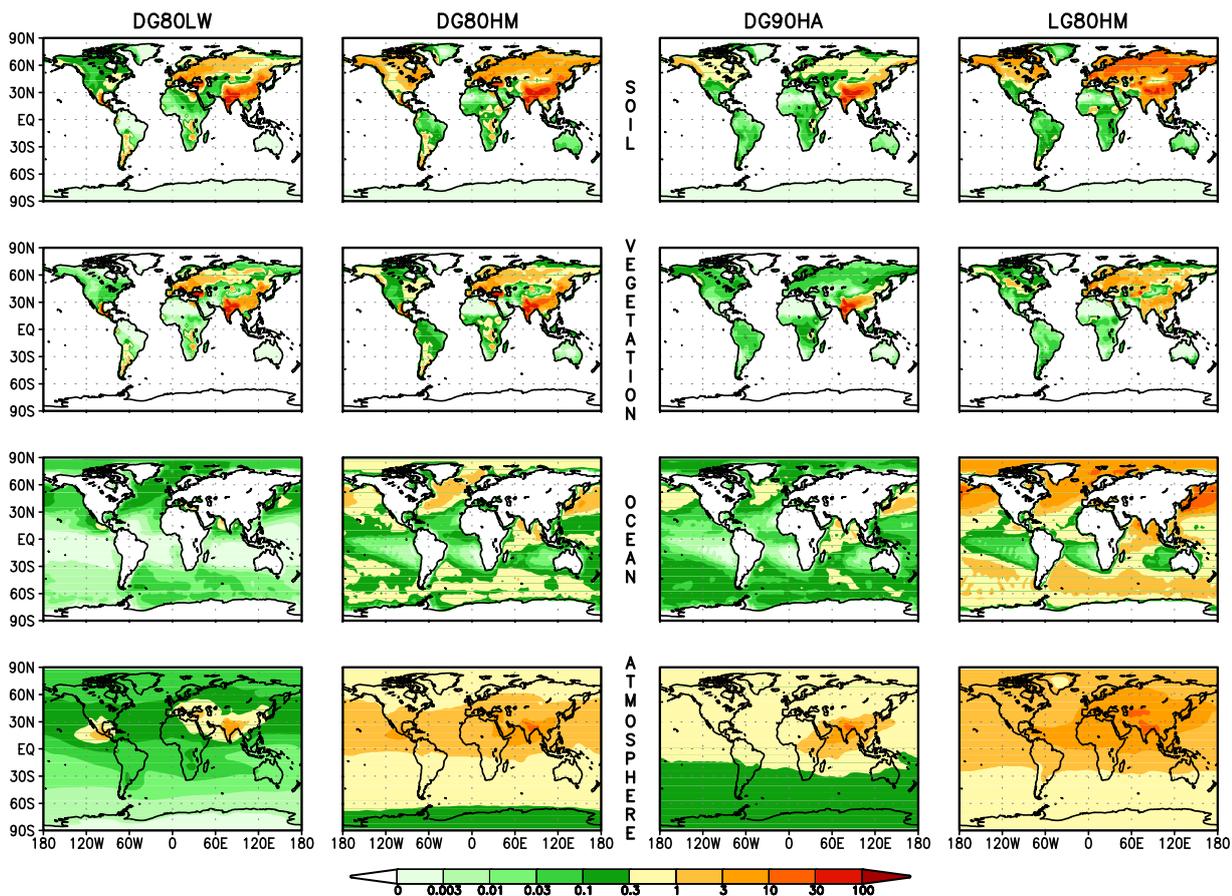


Figure 6.2: Geographical distribution of burdens ( $\text{ng m}^{-2}$ ) in soil, vegetation, ocean and atmosphere for the scenarios DG80LW, DG80HM, DG90HA and LG80HM, 10<sup>th</sup> year average.

of DG80HM. In the presence of ocean currents, these could transport over long distances, which is not the case with this study due to the absence of ocean currents in the model. Accumulation in all compartments is well simulated by the model even with the regional emission from India (Fig. 6.2, DG90HA). The geographical extension of plumes in all compartments in DG90HA scenario is much larger than that of the global emission scenario, DG80LW. This explains that a slow atmospheric degradation favours long-range transport and longer residence times in the multimedia environment, while the source region is less significant. Within ten years the entire northern hemisphere and part of the southern hemisphere is contaminated with DDT, while the whole global environment is filled with  $\gamma$ -HCH. A significant contamination of the Antarctic by  $\gamma$ -HCH is found, even though more than 50% of the  $\gamma$ -HCH usage took place north of  $37^\circ\text{N}$ . The results compare well with predictions by unit type multimedia box models [Mackay and Wania, 1995]. In the atmosphere,  $\gamma$ -HCH seems to be more mobile than DDT.

The difference in the entry scenarios of DG90HA and DG90HM do not propagate into signifi-

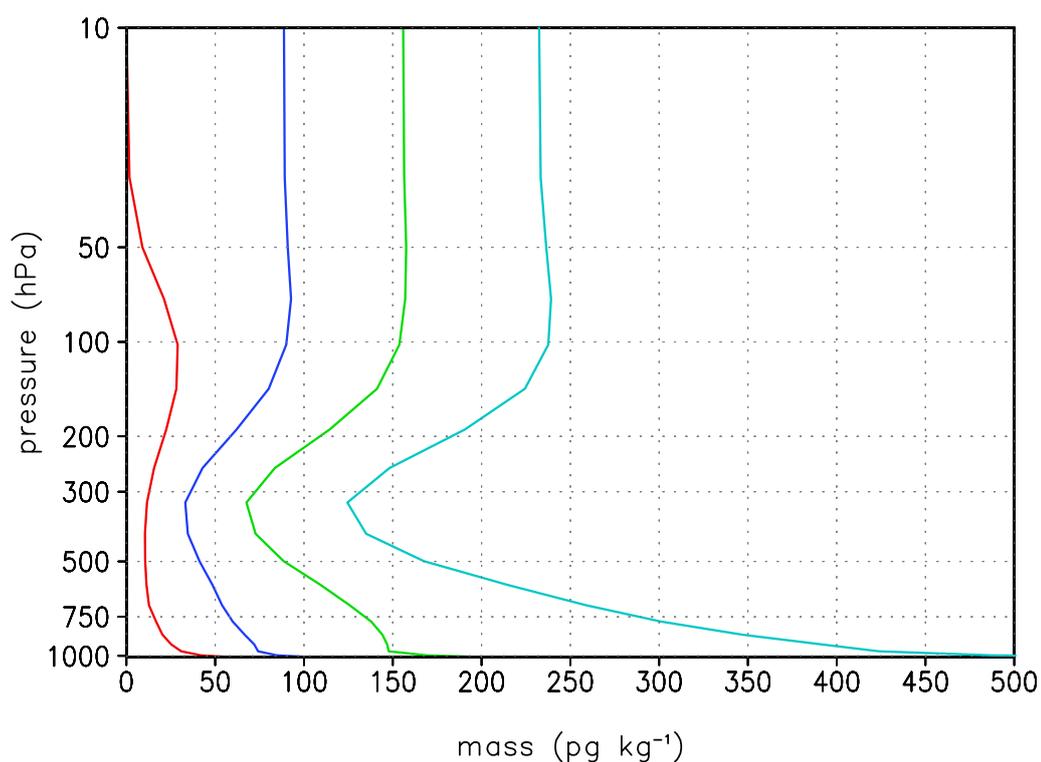


Figure 6.3: Globally averaged vertical distribution in  $\text{pg kg}^{-1}$  for DG80LW (red), DG80HM (green), DG90HA (dark blue), and LG80HM (cyan), 10<sup>th</sup> year mean.

cant geographic distributions. Moreover, the differences in the global compartmental distribution between these scenarios are negligible. Therefore, for much of the following discussion we refrain from covering DG90HM as differentiated from DG90HA. However, transport differentiating between DDT regional cycling under the two scenarios will be discussed later (section 6.5.3.2). The monsoon winds carry the substance towards southwest during the northeast monsoon season, while the plume spread is more uniform in longitudinal direction in the case of southwest monsoon (Fig. 6.2).

Most of the atmospheric burdens reside in the planetary boundary layer (PBL). The concentration decreases with increasing height in the troposphere up to the polar tropopause (300 hPa, 9 km) and then slowly increases up to the tropical tropopause (100 hPa, 16 km) on a global average [Wallace and Hobbs, 1977] for all scenarios of DDT and for  $\gamma$ -HCH (Fig. 6.3). Washout limits atmospheric residence time in PBL, while reaction with the OH radical limits residence time aloft. As different assumptions on degradation in the gaseous and particulate phases and partitioning to particulate matter had been made for the scenario DG80LM in contrast to the high mobility scenarios (Table 6.1), and there most of the substance is predicted to be particulate bound, the mixing ratio is decreasing with height in the stratosphere in the case of the low-mobility scenario

but not under the high mobility scenarios (Fig. 6.3).

2-9% of the atmospheric burden of DDT resides in the stratosphere under DG80LW and 9-12% under DG80HM. The fractions residing in the stratosphere are higher for DG90HA, 12-31%. 7-19% of LG80HM resides in the stratosphere.

### 6.6.2 Global multicompartimental cycling

The terrestrial compartments always show maxima of substance burden during the application months (Fig. 6.1) coinciding with a minimum in the atmospheric concentration. A secondary peak in the atmospheric burden during the non-application months of spring in the case of DG90HA corresponds to the peak volatilisation from soil and vegetation compartments (Fig. 6.4a). During the post monsoon seasons the wet soil releases less substance back into the atmosphere, while a second maximum of volatilisation is found for the vegetation surfaces which coincides with a minimum in the vegetation compartmental burden. The convective loss from ocean is prominent during the northern hemispheric summer (Fig. 6.3a), where most of the application takes place in all tested scenarios. Volatilisation from ocean is increasing over years for both the DDT and  $\gamma$ -HCH.

The maximum storage in soil and vegetation compartments preceded by 2-3 months of that of ocean, corresponds well with the minimum in atmospheric concentration in the case of  $\gamma$ -HCH (Fig. 6.1d). This is due to the efficient washout of more water soluble  $\gamma$ -HCH, and also due to the faster atmospheric degradation due to the higher reactivity with OH radicals ( $1.9 \times 10^{-13} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ ) compared to that of DDT ( $1.0 \times 10^{-13} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ ). On a quantitative base, wet deposition dominates over dry deposition and hence the global average deposition patterns (Fig. 6.4b) resemble by and large the distribution of the globally averaged model precipitation (not shown).

The global mean residence times in the compartments are listed in Table 6.3. These are defined as:

$$\tau_i \approx m_i / (E - \Delta m_i / \Delta t) \quad (6.2)$$

with  $m_i$  being the burden of the compound in compartment  $i$ ,  $E_i$  the total compartmental source and  $\Delta m_i / \Delta t$  the net uptake ( $\text{t a}^{-1}$ ). As being the result of substance specific compartmental sinks and sources,  $\tau_i$  is not predictable on the basis of degradation rates (cf. Table 6.1) alone. E.g., while two of the sinks for the  $\gamma$ -HCH's reservoir in the ocean surface layer are more effective than for DDT, namely faster degradation (Table 6.1) and loss to deep sea (28.5 kt against 6.9-8.6 kt for the various DDT scenarios, not shown),  $\gamma$ -HCH takes a middle position among the DDT

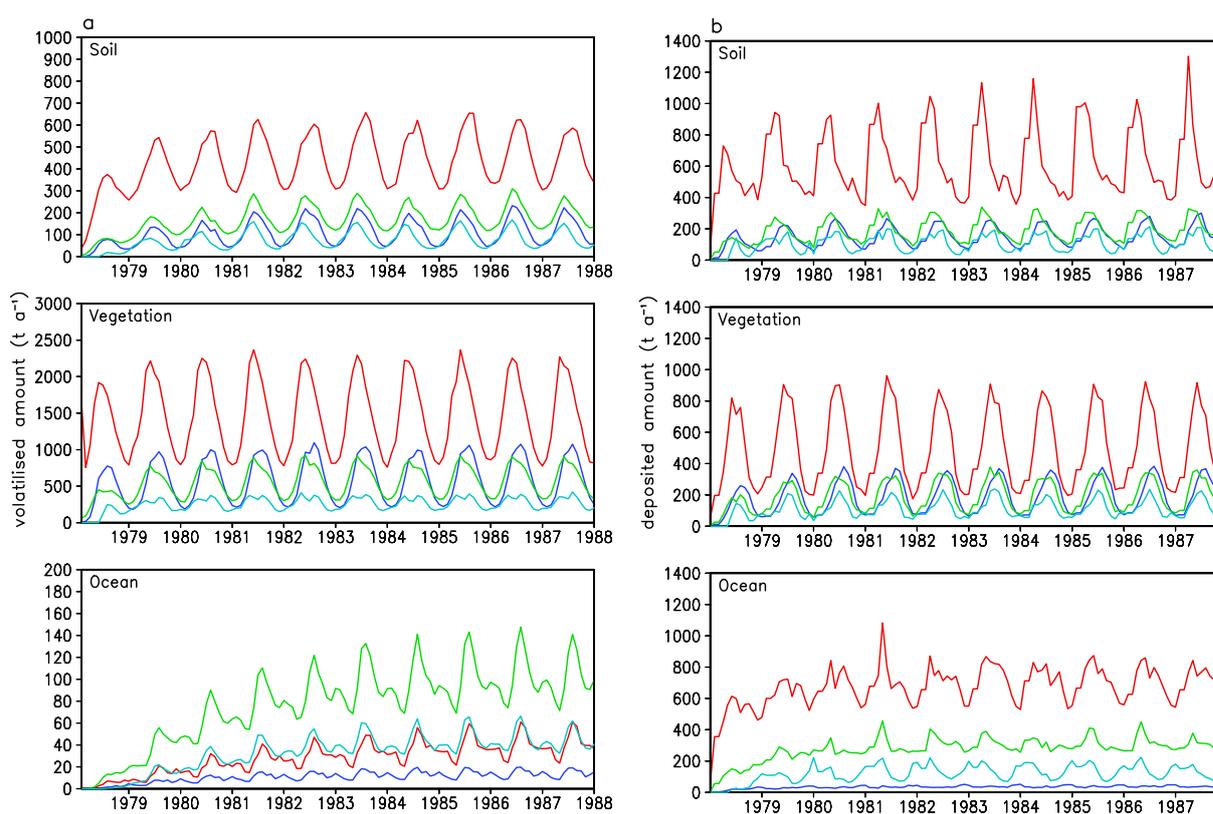


Figure 6.4: Volatilised (a) from, and deposited (b) amounts,  $t$ , to soil, vegetation and ocean for the scenarios DG80LW (blue), DG80HM (green), LG80HM (red) and DG90HA (cyan).

scenarios in the case of the third compartmental sink, volatilisation from sea to air (Fig. 6.4a). The residence time of  $\gamma$ -HCH in ocean is still predicted to double the residence time of DDT. The difference in residence times in ocean is due to the stronger compartmental source, i.e. atmospheric deposition (Fig. 6.4b) which, in turn, is due to the more efficient wash-out of  $\gamma$ -HCH. One potentially significant process with respect to ocean residence time is neglected here, i.e. partitioning to ocean suspended particulate matter. Its recognition would further differentiate between the two substances, as a higher affinity of DDT (predicted based on the sorption coefficient to organic matter, cf. Table 6.1) would add more to the effectiveness of loss to the deep sea of DDT than of  $\gamma$ -HCH. Therefore, it is suggested that the residence times of the substances in ocean surface layer are somewhat overestimated by the present model configuration and more so for DDT.

In contrast to the ocean surface layer, the model predicts longer residence times for DDT than for  $\gamma$ -HCH in the soil and vegetation compartments (Table 6.4). These result from stronger compartmental sinks for  $\gamma$ -HCH, volatilisation (Fig. 6.4a) and degradation (Table 6.1), which are obviously only partly compensated by stronger sources, i.e., agricultural application (Table 6.2) and atmospheric deposition (Fig. 6.4b). Together with the compartmental distribution (Table 6.3)

these differences in compartmental residence times translate into a difference in total environmental residence time,  $\tau_{overall}$ , of the two substances: DDT's partitioning to the global soils and vegetation (82-87% of the total reservoir) drives its total environmental residence time to higher values (354-485 d) than  $\gamma$ -HCH (287 d). This is because  $\gamma$ -HCH's partitioning to the compartment (ocean) with its longest residence time is not that pronounced (42% in the world oceans' surface layer).  $\tau_{overall}$  is given as the sum of the compartmental residence times,  $\tau_i$ , weighted by the compartmental mass fractions or can be approximated similar to  $\tau_i$  based on the total environmental burden,  $m$ , the total source to the system,  $E$ , and the total environmental net uptake,  $\Delta m/\Delta t$ .

Table 6.3: Global compartmental and total environmental residence times (d) and compartmental distribution (% , in brackets). Mean of the 10<sup>th</sup> year

Substance	Soil	Vegetation	Ocean	Atmosphere	Total Environment
DG80LW	429(54)	134(43)	126(2)	3(1)	354(100)
DG80HM	523(51)	143(32)	147(12)	20(5)	485(100)
DG90HA	564(54)	111(28)	147(12)	22(5.6)	430(100)
LG80HM	212(42)	24(9)	288(42)	18(7.5)	287(100)

The interpretation of the compartmental residence times of the various DDT scenarios shed light on the significance of mode of entry of substances and the role of the atmosphere in multi-compartmental cycling of organic compounds: DDT cycling under the scenarios DG80HM and DG90HA differs by the geographic and temporal application patterns and the modal split upon entry, while DG80HM and DG80LW differ in the atmospheric degradation rate (Table 6.2). All these influence the compartmental distribution. The total environmental residence times,  $\tau_{overall}$ , of DG80HM and DG80LW differ by 35% (longest for DG80HM). Tests show that this is due to the difference in atmospheric degradation rate ( $k_{OH} = 0.1 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$  for gaseous molecules only for DG80HM vs.  $4.5 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$  for all molecules, gas-phase and particulate matter phase, respectively for DG80LW) alone. It reduces  $\tau_{atmosphere}$  of DG80LW by 85%. In contrast, the change of geographic and temporal application patterns (corresponding to 1980 and 1990 scenarios) is predicted to reduce persistence by decreasing the residence time in soil and vegetation only by 10-20%. Under a scenario of 10% substance loss to air upon entry the model predicts an increase of the global and annual mean atmospheric burden by 2%, while the residence time in air,  $\tau_{atmosphere}$ , and the atmospheric share of the total environmental burden are reduced by 6 and 2%, respectively (cf. Table 6.3, data partly not shown).

Most of the aforementioned results were presented geographically aggregated as the global mean compartmental sources, sinks and distributions. Cycling between compartments, however, will of course be influenced by regional climate, expectedly leading to significant differences between climate zones and characteristics, e.g., alpine and coastal climates. In the following subchapter we focus on long-range transport (LRT) towards the poles, the role of the monsoon and substance cycling in three regions exhibiting very different climates.

### 6.6.3 Long-range transport and influence of regional climate

#### 6.6.3.1 Long-range transport to polar regions

We quantify the long-range transport potential (LRTP) using indicators for substance migration [Leip and Lammel, 2004]. The zonal spreading,  $ZS$ , which quantifies the tendency of a distribution to spread in meridional direction, shows the highest value for the scenario with release into air (DG90HA). But the Spatial Scale 'S' is maximum for  $\gamma$ -HCH in 10 years, showing its high mobility than that of DDT (Table 6.4).

Long-range transport in meridional direction is significant for all scenarios tested. Even under the low mobility scenario a substantial fraction of DDT is transferred to the southern hemisphere. 0.13% and 0.01 % of the total environmental burden are found in the Arctic (i.e.  $> 66.5^\circ\text{N}$ ) and Antarctic ( $> 66.5^\circ\text{S}$ , mean of 10<sup>th</sup> year), respectively, under the low mobility scenario in contrast to 0.68% and 0.07 %, respectively, under the high mobility scenario DG80HM. The northeast (NE) monsoon winds over India carry more substance into the south, resulting into a 0.05% of total burden residing in the Antarctic polar circle for DG90HA. Even though this fraction appears to be less than that of DG80HM scenario, comparing with the temporal input scenario (only four months of the year for DG90HA, and all 12 months of DG80HM) this is much higher than what has been transported to the south by DG80HM. This difference is contributed by the fraction which is emitted directly in to the atmosphere (Table 6.2). 1.85% and 0.06% are reaching and residing over Arctic and Antarctic in the case of  $\gamma$ -HCH. These fractions of  $\gamma$ -HCH again emphasize the substance's large mobility. Despite a more northwardly application of  $\gamma$ -HCH than DDT (the centres of gravity of the application patterns are at 37 and 22 °N, respectively) larger fractions are found in the high latitudes of the southern hemisphere. The centre of gravity (COG) of a compartmental or total environmental substance distribution is defined as the geographic location where 50% of the mass is lying to the south of  $lat_{COG}$ , and 50% of the mass is lying east of  $lon_{COG}$ . Obviously, the larger mobility is important in this regard (which is driven by a higher saturation pressure and a smaller affinity to organic phases of  $K_{OW}$ , Table 6.1). But the two sub-

Table 6.4: Indicators for large-scale substance migration in the total environment. Mean of the 10th year.

Substance	$lat_{COG}$ Application (°N)	$lat_{COG}$ Total bur- den (°N)	Zonal spreading (ZS) (km)	Spatial scale (S) (km)	Spatial spreading (SS) (km)
DG80LW	23	27	1124	5064	749
DG80HM	23	26	6945	8633	4336
DG90HA	22	24	7993	7927	7023
LG80HM	37	32	6672	9024	5236

stances also differ with respect to atmospheric deposition:  $\gamma$ -HCH is more efficiently washed out than DDT. 2 and 0.1% of the global deposition of DG80LW is received by the Arctic and Antarctic respectively, while these fractions are 8 and 0.6% respectively under the DG80HM scenario and 3 and 0.4%, respectively, under the DG90HA scenario. The respective fractions for  $\gamma$ -HCH are 21 and 0.4%. The discrepancies in these fractions are explained by the atmospheric degradation rates assumed (for the comparison between DG80LW and DG80HM), more northward application of  $\gamma$ -HCH (comparison between DG80HM and LG80HM) leading to higher/lower fractions reaching over the Arctic/Antarctic, and the low frequency of temporal application (comparison between DG80HM and DG90HA), thereby the fast removal of DG90HA from atmosphere due to wash out (cf. section 1.5.3.2).

The maximum amplitude of  $lat_{COG}$  of the total environmental burden (difference between the maximum shift to south and north) is 4.5 and 7.6 degrees for DG80LW and DG80HM and 6.2 degrees for DG90HA scenarios in 10 years, and that for  $\gamma$ -HCH is 13 degree. The  $lat_{COG}$  of total environmental burden of  $\gamma$ -HCH has moved 5 degrees towards south (32°N) from that of application (37°N). With a slower atmospheric degradation of DG80HM scenario, we expected a larger shift in COG of DG80HM scenario compared to DG80LW. But it is found that even though the plume spread is more wide in DG80HM (90% of mass lies between the latitudinal belts of 37.2°S and 60.7°), than DG80LW (90% mass is between 10.2 and 54.1°N latitudes), the shift in  $lat_{COG}$  of total environmental burden is more in DG80LW scenario (2° towards north from that of  $lat_{COG}$  of application). This shows that a slow degradability in the atmosphere gives more room to spread widely. Though DDT is emitted only from India, and also during only 4 months of the year, under the DG90HA scenario, the spreading is equally efficient as under DG80HM, where, by the end of tenth year, 90% of the mass is found between 29.1°S and 52.1°N latitudes. At the

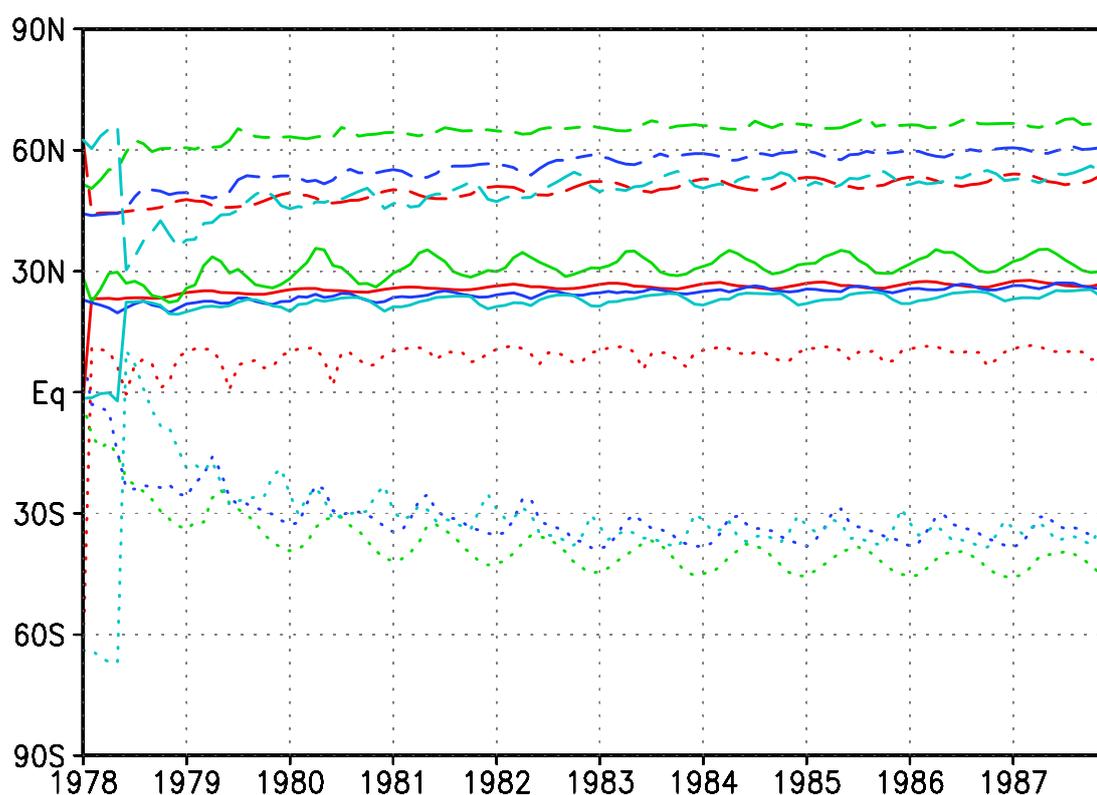


Figure 6.5: Distribution of mass between latitudes. Migration of lat05 (dotted lines), lat50 (solid lines) and lat95 (broken lines) percentiles, for DG80LW (red), DG80HM (blue), LG80HM (green) and DG90HA (cyan).

end of 10 years, 90% of  $\gamma$ -HCH is distributed between 45.7°S and 66.7°N latitudes (Fig. 6.5). In all cases the migration of the mass towards north is clearly evident from the Figure 6.5. Under the high mobility scenario a spatial spreading of ca. 4336 km is found for DDT and 5236 km for  $\gamma$ -HCH. Even a local application of DDT with high mobility scenario spreads more efficiently (5561 km) than a global application with low mobility (857 km).  $\gamma$ -HCH is supposed to be more mobile than DDT under local conditions.

### 6.6.3.2 Influence of the monsoon

The global atmospheric burden and the zonally averaged distribution of DDT in the atmosphere during summer (Jun-Jul) and winter (Nov-Dec) are shown in figure 5. June - August are the summer monsoon months or southwest (SW) monsoon period, and October - December are the northeast (NE) monsoon period for India [Blandford, 1886; Webster *et al.*, 1998; Gadgil, 2003]. The summer monsoon rains suppress the DDT potential to spread meridionally in the atmosphere for both the DG90HA and DG90HM scenarios where a more northeast shift of mass is contributed by the low level easterly jets (Fig. 6.6a). At the same time mass is shifted more towards equator

and towards west during the NE monsoon season due to the northeasterly winds (Fig. 6.6b). In the vertical not much substances escape into stratosphere due to the efficient washout during SW monsoon period, while more substance reaches stratosphere during NE monsoon period and spreads both vertically and horizontally (Fig. 6.6a, b). At the same time, in other DDT scenarios with global and year around emission, the fraction reaching stratosphere is much higher because of the higher fraction of geographical and temporal source. Only the higher atmospheric degradation restricts the horizontal and vertical spread in DG80LW compared to that of DG80HM scenario. The plume spread over the major source regions, is towards north east over Asia (due to SW monsoon winds), more meridionally over Europe (due to midlatitude westerlies) and eastward over central America (due to trade winds). Test runs with a modified, namely continuous year-around temporal application pattern show that  $\tau_{atmosphere}$  should be considerably longer, ca. 34 d, under the DG90HA scenarios. Here we assumed (Table 6.2) the substance to enter the model world during the peak monsoon months and to be washed out efficiently. Even though substance is entered again during Nov and Dec, the retrieval monsoon causes again washout during November, leading only the substance released in December to remain (Fig. 6.1).

### 6.6.3.3 Influence of regional climate

To study the combined action of climate, i.e. seasonal and inter-annual variability of climate parameters, and substance properties on substance fate, we focus on two tropical regions, 6-29°N / 67-93°E and 9°S-0° / 98-161°E, and one high-latitude region, 50-64°N / 159-226°E. Henceforth these are referred to as the Indian, Indonesian and Alaskan regions respectively. The size of these regions is comparable ( $\sim 6.5 \times 10^6$  km<sup>2</sup>) and each of these encompasses land and sea areas of about equal size. The climates are characterised by significant (Indian, Alaskan) or very little (Indonesian) seasonal temperature (Fig. 6.7a) and by very significant (Indian, Indonesian) [Nanjundiah *et al.*, 1992; Hendon, 2002; Goswami, 2005] or little (Alaskan) seasonal precipitation fluctuations [Christopher, 2002] (Fig. 6.7b), respectively. The model simulates significant interannual climate variability for precipitation in the Indonesian region. The land in the Indian region encompasses most of India south of the Himalayas and Bangla Desh and is a region with DDT and  $\gamma$ -HCH application under the studied scenarios in contrast to the other two regions. (The Indonesian region excludes application areas of  $\gamma$ -HCH in the northern parts of the archipelago.) The Alaskan region encompasses parts of eastern Siberia and Kamchatka and excludes the permafrost regions.

The deposition of DDT in the Indian region is obviously determined, and in the Indonesian region, at least influenced by the precipitation patterns: maxima of the time series coincide tem-

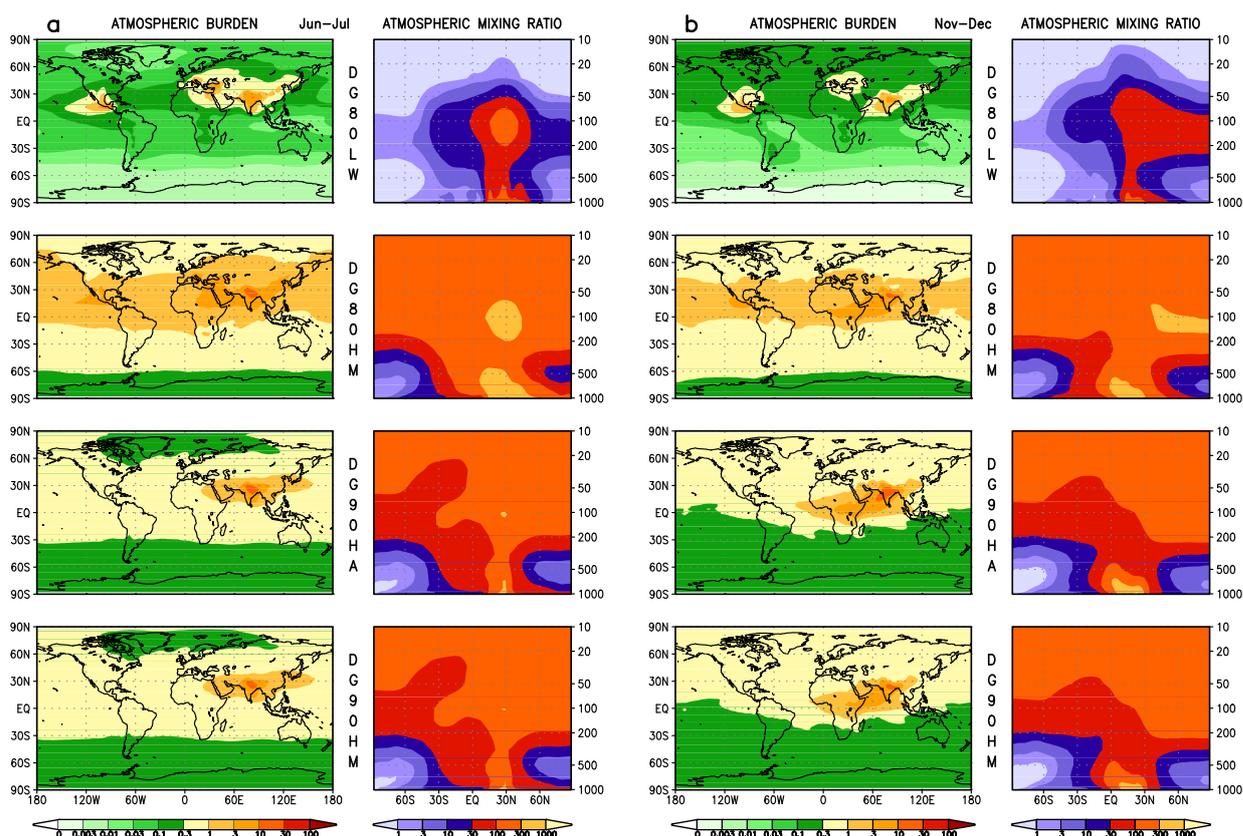


Figure 6.6: Jun-Jul (a) and Nov-Dec (b) average geographic distribution of the total atmospheric burden ( $\text{ng m}^{-2}$ ) and zonally averaged vertical mixing ratio profiles ( $\text{pg kg}^{-1}$ ) in the atmosphere, 10<sup>th</sup> year.

porally as well as with respect to extent. E.g., the weak precipitation high in Indonesia in year 8 translates into a corresponding annual low in the DDT deposition flux (cf. Fig. 6.7c). Dry deposition must be determining total deposition in the extra-tropical region, though. The deposition maximum occurs up to 3 months in advance of the precipitation maximum over Alaskan region (Fig. 6.7) and is related to seasonal winds (strong winds in the Bering Sea in late spring). The volatilisation flux of DDT and  $\gamma$ -HCH in the Indian and Alaskan regions is obviously controlled by temperature, over land (cf. Fig. 6.7e, f), and by winds over ocean (Fig. 6.7g, h). Hereby, a relatively short annual volatilisation maximum coincides with the seasonal warming (April-May) which is not sustained during the entire warm season. In contrast (and under conditions of little temperature fluctuations), it is the precipitation minimum (September-October) which triggers the volatilisation of DDT in the Indonesian region from land and ocean. Even though Indonesia is more near to source region than Alaska, the deposition and volatilisation from this region is much less than those of Alaska. This is explained by the low concentration of substance below the cloud level over Indonesian region, which is available for washout, compared to that of Alaska.

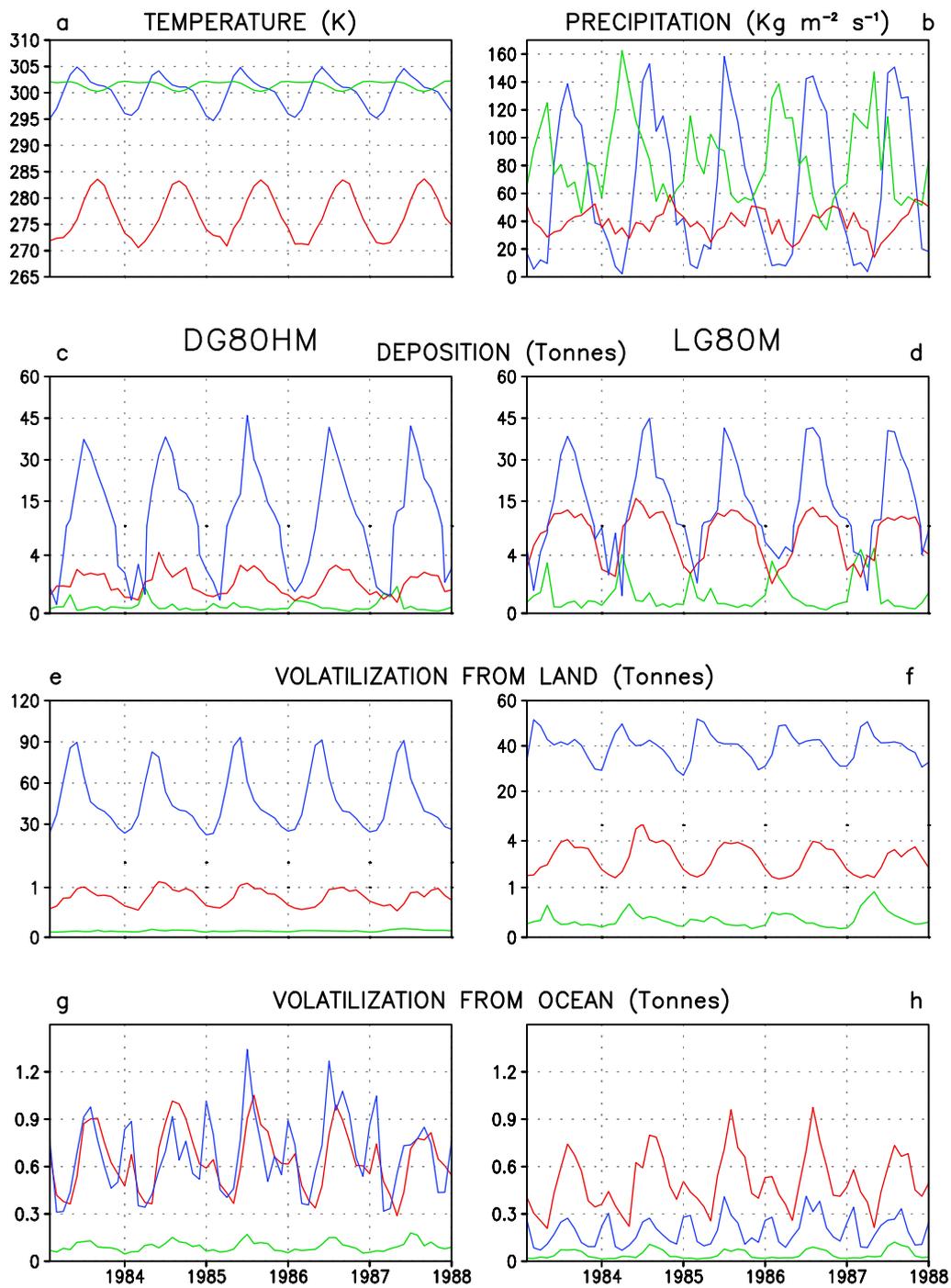


Figure 6.7: Seasonality of the temperature (a), precipitation (b), deposition (c, d), volatilisation from land (e, f) and ocean (g, h) for DDT (c, e, g) and  $\gamma$ -HCH (d, f, h), in the Indian (blue), Indonesian (green) and Alaskan (red) regions.

Also the general circulation in general transport the substance to the north than across the equator from the northern hemispheric source regions, which contributes the higher concentration over Alaska than Indonesia.

Even more clearly than DDT, the deposition of  $\gamma$ -HCH in the tropical regions is obviously determined by the precipitation patterns, while dry deposition is determining total deposition in the extra-tropical region. Similar to DDT, the deposition maximum of  $\gamma$ -HCH occurs up to 3 months in advance of the precipitation maximum and is related to seasonal winds. Out of 194 tonnes of  $\gamma$ -HCH deposited over Indian region during the 10th year of the simulation, the wet months (Jun-Nov) contribute 159 tonnes while only 35 tonnes is contributed by the dry months (Dec-May), while these are 166, 133 and 33 respectively for DDT. The Indonesian wet months (Dec-May, [Hendon, 2002]) contribute 6 tonnes out of 8 in total of the deposited DDT, while it is 17 tonnes out of 20 tonnes in the case of  $\gamma$ -HCH. In Alaska, the coastal regions experience relatively small variability, while the inland regions experience a continental climate with large daily and annual variability with respect to temperature and precipitation. Hence on we compare Jul-Dec as the months with more precipitation, with Jan-Jun as the ones with less precipitation. April is the driest month in all regions. Thus 14 out of 21 tonnes of DDT and 44 out of 75 tonnes of  $\gamma$ -HCH deposit during wet period. These numbers show that in all the three regions considered, washout is the main removal mechanism from the lower troposphere.

The volatilisation flux of  $\gamma$ -HCH in the tropical regions is controlled by precipitation (Indian region) or precipitation in combination with temperature (Indonesian region, cf. Fig. 6.7). The higher volatility of  $\gamma$ -HCH relative to DDT (vapour pressure) explains the additional influence of temperature besides precipitation. The seasonality of temperature alone seems to explain the seasonality of volatilisation in the Alaskan region. As the Indian region is a major entry region for the substances into the environment, it is a net exporting region ( $F_{vol} > F_{dep}$ ). In contrast, the non-application regions are net-importing regions ( $F_{vol} < F_{dep}$ ). Deposition exceeds volatilisation by 167% and 208% over Indonesian region for DDT and  $\gamma$ -HCH respectively, and these fractions are 27% and 102% respectively over Alaskan region. Hence, we find that the fraction of the substance cycling the receptor region, which accumulates in the region itself, is higher for the tropical region than for the high-latitude region. This is somewhat surprising as the cold condensation hypothesis [Wania and Mackay, 1993] would suggest the contrary.

#### 6.6.4 Comparison with observations

The scarcity of long term measurements of DDT and  $\gamma$ -HCH cause severe limitations to validate model results. Moreover, un-realistic usage scenarios (virgin environment, same amounts in sequential years), data uncertainties of physico-chemical data, degradation data and temporal usage patterns, that we cannot expect model results to match observational data.

Table 6.5: Model simulated and observed concentration over Arctic ( $\text{pg m}^{-3}$ )

Location	DDT				$\gamma$ -HCH	
	Simulated		Observed		Simulated	Observed
	DG80-LW	DG90-HA	DG80-HM		LG80-HM	
Ny-Ålesund (78.55°N, 11.56°E)	5.1	8.6	78.7	5.4	540	14
Alert (82.30°N, 62.20°W)	3.7	10.8	76.7	4.3	550	11
Tagish (60.20°N, 134.15°W)	3.0	38.0	134.6	1.4	460	11
Dunai Island (74.00°N, 125.00°E)	5.8	7.2	80.6	0.93	515	10
Heimaey Island (63.24°N, 21.17°W)	3.1	1.6	90.2	-nd-	800	15

-nd- Data not available or not determined

We compare model results with long-term measurements in the Arctic, which started in 1993 [AMAP, 1998]. We choose the atmospheric concentration data of the third simulated year under the 1990 DDT scenario and the 10<sup>th</sup> simulated year under the 1980 scenarios and  $\gamma$ -HCH. This is justified, since after a few years the modelled atmospheric concentration had reached quasi-steady state and does not change significantly thereafter (Fig. 1). The predicted values under the high mobility scenarios of both DDT and  $\gamma$ -HCH are much higher than what had been observed in the Canadian Arctic (Alert, Tagish, Dunay Island), and on Iceland (Heimay Island) and Spitzbergen (Ny-Ålesund) (Table 6.5). This could be caused by the assumption of continuously high applications in subsequent years in the model, while historically there was a steep decline in usage in the mid 1980s. The predicted concentrations are a factor of 0.6 (Ny-Ålesund) to 26 (Tagish) higher in the case of DG90HA, a factor of 14 (Ny) to 95 (Tagish) higher for DG80HM, and are a factor of 38 (Ny) to 53 (Dunai and Heimaey) more for  $\gamma$ -HCH, than that have been observed at different locations of the Arctic (Table 6.5). In contrast, the simulated concentration under the DG80LW scenario is in good agreement with the observation. The discrepancy lies between a factor of 0.05 to 5.2 between those of simulated and observed. This supports the assumption that the atmospheric decay kinetics of DDT lies between those assumed under the low and high mobility scenarios: an overestimated atmospheric source (emissions continuously on the high 1980

level) is compensated by an overestimated atmospheric sink (too fast degradation). Even though the absolute amounts reaching are overestimated in the model, the seasonality of the atmospheric concentration is reasonably captured by the model for the continental Arctic station (Tagish). The predicted yearly amplitude is 2.3, while the observed is 2. As local SOCs cycling at the coastal Arctic stations (Iceland and Spitzbergen) will be strongly influenced by sea ice and its seasonality and the substance cycling in the model is disregarding sea ice, we refrain from comparing with observations from these sites.

## 6.7 Conclusions and outlook

The behaviour of SOCs in the environment was studied using a multicompartment model which is based on an AGCM. The prime aim of this study was to investigate the combined influences of global and regional climate on one hand, and physico-chemical properties of SOCs on the other hand on the long-range transport potential and multicompartmental cycling. Under five scenarios five combinations of physico-chemical properties and emission patterns (temporal and spatial) were tested.

The ground compartment reservoirs are mostly controlled by the balance between atmospheric deposition and (re-)volatilisation fluxes. The model predicts the atmosphere and vegetation compartment to reach pseudo-steady state within 3-4 years, in the case of both DDT and  $\gamma$ -HCH and under all tested scenarios. DDT shows a tendency to reach equilibrium in slightly more than 10 years in soil, while  $\gamma$ -HCH almost achieved quasi-steady state in 10 years. Our study does not address the longer time scale ( $\gg 10$  years) nor does it account for transport with ocean currents. The deep ocean is considered as the final sink for many pollutants. The ocean surface mixed layer is predicted to approach quasi-steady state with respect to DDT cycling within ca. 5 years and with respect to  $\gamma$ -HCH cycling within ca. one decade. Once this state is reached the compartmental sources (atmospheric deposition) are balanced by the sinks (volatilisation, degradation, loss to deep sea). In reality, in particular DDT volatilisation from the world ocean might be more delayed, because the model is expected to underestimate SOCs' loss to the deep sea, and more so for DDT than  $\gamma$ -HCH, as it disregards the partitioning to sinking particulate matter. Due to the large gradients of the phytoplankton distributions [Yoder and Kennelly, 2003], this effect will be most significant close to continental margins and in shelf seas.

All environmental compartments are globally contaminated within two years. Expectedly, degradation in the atmosphere was found to be key for long-range transport. Even if the atmospheric burden accounts for only 1% of the total environmental burden, the total environmen-

tal persistence is strongly dependent on atmospheric degradation. The relative significances of various contributions to atmospheric degradation, OH reaction in the gaseous and particulate phases, and phase partitioning remain to be investigated. Contaminant accumulation spreads more rapidly towards north than towards south. On the time-scale of a decade and under scenarios of stable spatial emission patterns a northerly shift is predicted for the large-scale migration of DDT and more pronounced for  $\gamma$ -HCH.

The role of regional wind systems and atmospheric dynamics in general are relevant for the understanding of SOCs cycling on large spatial scales. This study shed some light on the role of the dynamics over and around Asia: a high latitude region (like the Alaskan region) seems to act as a better sink region for SOCs than a region close to the source areas (like the Indonesian region). The role of trade winds is evident in this context, because once SOC-loaded air flows out from Asia during the northern summer it is caught into the monsoon circulation. Further on, once it reaches over the mid-latitudes, the westerlies take over with a significant northerly component. On the other hand, during northern hemispheric winter, even though the trade winds change their location, the easterlies transport polluted air masses from the Asian source regions towards southwest. Low concentrations as well as elevated concentrations in the same latitudinal zone are predicted as a consequence of regions being located leeward (such as equatorial Africa) or far off (such as the Indonesian region) of source regions.

Multicompartment models on large spatial scales can hardly be validated due to knowledge gaps and severe uncertainties in substance properties and the description of processes. Modelling studies, transport as well as box models, should be used to explore sensitivities. Even in lack of sufficient model validation, AGCM-based models should be capable to simulate the long-range transport as well as the influence of regional climate. It is important to provide tools capable to study multicompartmental cycling, LRT potential and total environmental persistence, since the measurement of these characteristics are impossible. As mentioned above, the organochlorine pesticides have been in use from the late 1940s, while monitoring started only by the late 1980s. This calls for the combined cycling of increasing and fresh emissions and remnants from the earlier usage period. Therefore, a historic simulation with transient emission data is necessary to simulate the historic global cycling of these substances.

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## Conclusions and Outlook

### 7.1 Conclusions

The global multicompartamental fate and long-range transport of two persistent semivolatile organic pollutants, DDT and  $\gamma$ -HCH, were studied on the time scale of years (up to 10 years) using a multicompartement model which is based on an atmosphere general circulation model. This is to our knowledge, the first such study.

All the conducted model experiments point to the fact that these substances are accumulating in the environment on the time scale of years. Accumulation in high latitudes is also found. The study shows that the atmosphere plays a leading role among the probable pathways for POPs to reach remote regions. Even without 'multi-hopping' in the multicompartamental environment, the substances reach the Arctic or Antarctic regions ('single-hopping'), albeit to a lesser extent. Furthermore, the substances reach the stratosphere and may accumulate over years - if part of the substance is shielded from photochemical decay as assumed in the model experiments for the fraction sorbed to particulate matter. Quasi-steady state of substance cycling is achieved within 3-4 years in the atmosphere and vegetation compartments. A slow degradation rate and the lipophilicity tend to enhance the residence time in soil. Gas-particle partitioning, a consequence of semivolatility, is significant for the long-range transport potential in air, because the residence time of the compounds is limited by wash-out, dry deposition and photochemistry, each of these differentiating between the gaseous and particulate phases. One of the experiments conducted could predict a probable range of the gas-particle partitioning coefficient. Regional case studies have shed light on the significance of regional weather systems and large scale atmospheric dynamics for substance cycling in the multicompartement environment and the long-range transport

potential. For many pollutants, oceanic sediments are considered to act as the final sink. Due to the absence of vertical mixing and advection in the ocean, the results on substance behaviour in the ocean obtained in this study are not fully conclusive.

The model setup was artificial with regard to prior pollution (virgin environment in the model) and temporal emission pattern (unchanged in subsequent years). Uncertainties with regard to other input data, e.g. the physico-chemical substance properties, may add to discrepancies between model predicted and historic occurred global contamination. The aim of these model experiments was not to reproduce environmental concentrations, but rather to study the major processes of the cycling of persistent semivolatile organic compounds and the significance of substance properties, substance usage and regional and global climate for the cycling. Even so, the model atmospheric concentrations were compared with observations in the Arctic and the agreements add confidence to this type of modelling.

## 7.2 Outlook

It is important to improve the understanding and better physically base the description of exchange processes between and within the environmental compartments (air, sea water, terrestrial compartments, ice, sediment, biota, snowpack), because some of these are merely understood on a qualitative basis or parameterisations are insufficiently based.

Contaminants certainly reach the Arctic environment by long-range transport from mid-latitude or tropical regions. The atmosphere, ocean currents, rivers, ice packs, and even biota (migratory birds, sea mammals) are all transport routes for persistent contaminants to the Arctic. Among them, air currents are the most efficient transport media on the time scale of years. Under favourable conditions, an air parcel can even reach the Arctic within a few days or weeks from the mid latitudes and subtropics [Shaw and Khalil, 1989]. Water and ice are dominant compartments in high latitudes: sea ice acts as a cover on the ocean surface hindering ocean-atmosphere exchange of contaminants. For many compounds, ocean currents could be important transport media on a time scale of decades. Hence it is important to have a fully coupled atmosphere-ocean general circulation model to understand the behaviour of these substances in the marine environment.

Model experiments which promise to add complementary insights include:

(1) testing a single pulse emission into the soil/vegetation/atmosphere and to investigate the long-range transport time and persistence in the multimedia environment. This will help to estimate the half-life of the substances in the total environment, based on different geographical location of entry and degradation rates assumed in different compartments.

(2) studies with polyaromatic hydrocarbons (PAHs) which interact with ozone. It will be of great interest to see their behaviour in the stratosphere together with overall fate in the total environment.

(3) a long simulation with transient emissions starting from the beginning of usage of organochlorine pesticides with a changing climate is necessary to reflect on the fate of the persistent organics, as they have been in use since the 1940's, and any observation that started in the late 1980s will definitely include the residues from previous years. This will give an insight into the historical behaviour of POPs in a multi-compartmental environment. Another isomer of technical HCH,  $\alpha$ -HCH is also of great concern.

(4) studies with  $\alpha$ -HCH. There is knowledge about the outgassing of  $\alpha$ -HCH from the Arctic seas from the beginning of 1990's [Jantunen and Bidleman, 1995], following the ban of technical HCH usage in China (banned in 1983), and India (agricultural usage banned in 1990), the major consuming countries in Asia. Hence it would be of interest to see the behaviour of  $\alpha$ -HCH in a long term simulation.



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