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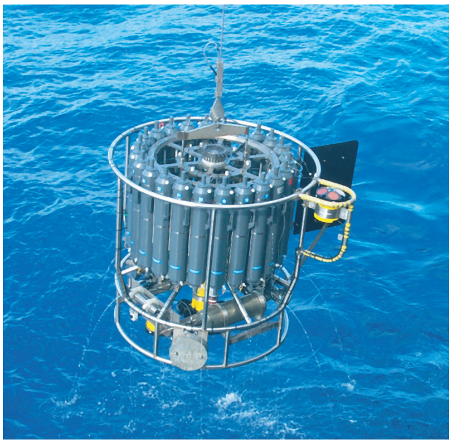
Global cycling of semivolatile organic compounds in the marine and total environment - A study using a comprehensive model

Francesca Guglielmo



Berichte zur Erdsystemforschung 54/2008

Reports on Earth System Science

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Layout:

Bettina Diallo, PR & Grafik

Titelfotos:
vorne:
Christian Klepp - Jochem Marotzke - Christian Klepp
hinten:
Clotilde Dubois - Christian Klepp - Katsumasa Tanaka

Berichte zur Erdsystemforschung 54/2008

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Dissertation zur Erlangung des Doktorgrades der Naturwissenschaften
im Departement Geowissenschaften der Universität Hamburg
vorgelegt von

Francesca Guglielmo

aus Neapel, Italien

Hamburg 2008

Reports on Earth System Science 54/2008

ISSN 1614-1199

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Als Dissertation angenommen
vom Departement Geowissenschaften der Universität Hamburg

auf Grund der Gutachten von
Prof. Dr. Hartmut Graßl
und
Prof. Dr. Gerhard Lammel

Hamburg, den 24. Juni 2008
Prof. Dr. Jürgen Oßenbrügge
Leiter des Departements für Geowissenschaften

ISSN 1614-1199

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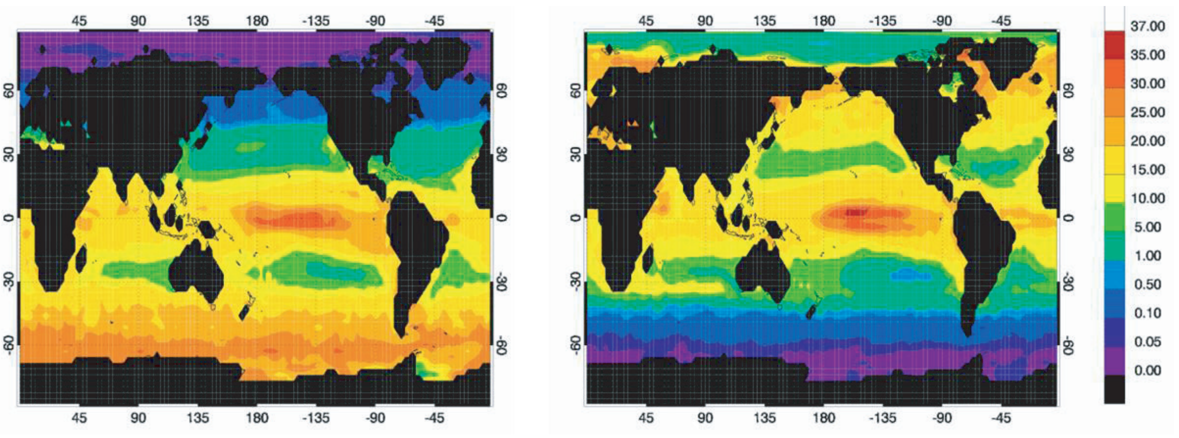

Dampening of DDT ocean volatilisation (%) by partitioning to organic phases (northern winter, northern summer)

Francesca Guglielmo

Hamburg 2008

Abstract

Organic compounds which are persistent and toxic constitute a major threat for human health and ecosystems.

Mainly agrochemicals and used or produced in the industry, many of these have been or continue to be employed in large amounts. Due to properties as vapour pressure and sorption coefficient, they partition between different environmental media (multicompartmental behaviour). As a consequence of persistence and semivolatility, these compounds are available for long-range transport in atmosphere and ocean; their geographical occurrence is therefore not limited to the emission areas, but can be ubiquitous. Being also lipophilic, i.e. showing affinity to organic phases in the environment, and slowly degrading, they accumulate in exposed organism tissues and, along the trophic chain, biomagnify. Exposure to semivolatile organic compounds (SOCs) can be associated with a wide range of detrimental effects on organisms; it is an international issue (e.g. Stockholm Convention on Persistent Organic Pollutants) to control the risk related to it.

Whilst the study of the relevance of the atmosphere in the multicompartmental global fate and distribution of the agrochemicals hexachlorocyclohexane (HCH) and DDT is already object of various modelling efforts, the role of the ocean in the global cycling, as a transport medium as well as as a compartment, and of the processes involved, is still to be investigated. For this purpose an environmental exposure model has been furthermore enhanced. The three-dimensional ocean version of the MTCM, Multicompartment Chemistry-Transport Model is based on the coupling of atmosphere and ocean General Circulation Models (ECHAM5 and MPI-OM). The system encompasses as well a representation of terrestrial compartments (soil and vegetation) and of the marine cryosphere (sea ice), a fully dynamic atmospheric aerosol (HAM) model and an ocean biogeochemistry model (HAMOCC5). The multi-year cycling of γ-HCH (lindane), α-HCH and DDT was studied in the global environment. As all compounds accumulate mostly in soil, the soluble lindane is also found in comparable amount in ocean and DDT has the highest residence time in almost all compartments. The sea-ice compartment (newly represented in the model) does not appear to bear a significant influence, in the simulated scenarios, on the distribution of DDT and γ-HCH on the global scale. Locally, the sea-ice cover inhibits ocean volatilisation by two-three orders of magnitude. This study addresses a fundamental process for SOCs in sea-water: partitioning to organic phases. As the distribution of organic phases is very inhomogeneous in the global ocean, equally spatially high resolved effects on other processes are observed. The volatilisation results inhibited, for DDT up to 35%, as the ocean retaining capacity increases. Sorption to organics has also implications on vertical export, especially on the local scale. The sinking is, however, a combination of biogeochemistry and dynamics (which proved to be more important than sinking associated with particulate matter), and is obviously favoured by persistence. DDT, the most persistent and lipophilic substance chosen, reaches the deep ocean in higher amounts everywhere. DDT and HCH are environmental contaminants of concern in Arctic because of the hazard they pose to the pristine environment. Results show that long-range global transport is determined by the fast atmospheric circulation. At low latitudes the transport in the ocean is however traceable, even after just a few months of

run. There, the substances result more uniformly distributed, by tropical currents, with respect to the depositional patterns. Net meridional transport taking place in the ocean is, as well, effective, mostly via western boundary currents, and for persistent compounds (DDT). On a global scale, the actual northward advection is barely appreciable.

According to the global temperature distribution, the intercompartmental cycling of SOCs (and therefore the net meridional transport) can occur as a sequence of volatilisation, transport in the atmosphere, deposition and transport in the ocean, the so called *grasshopping*. As the potential for several cycles makes the global environmental exposure particularly difficult to assess, a modeling study is especially significant. As shown also in previous studies, an atmospheric single hop travels higher and is already sufficient to reach the Arctic. The significance of the grasshopping is, however, different for the two chosen substances. For γ-HCH the burden originating from the the first cycle constitutes most of the total burden. For the persistent DDT the multiple cycles are responsible for the most part of the burden in all compartments. Conclusion, is, furthermore, that the occurrence of the multi-hopping behaviour might enhance the long-range transport potential for both DDT and γ-HCH.

Zusammenfassung

Toxische, schwer abbaubare, organische Chemikalien stellen ein großes Gefahrenpotential für Mensch und Ökosysteme dar. Viele von ihnen sind anthropogen und werden in Industrie und Landwirtschaft angewandt. Aufgrund ihrer physikalisch-chemikalische Eigenschaften, wie Sättigungsdampfdruck und Sorptionskoeffizient, verteilen sich die Stoffe über verschiedene Umweltmedien (Multikomapartimentverhalten). Viele der Substanzen sind mittelflüchtig. Deshalb können sie sich global ausbreiten und fernab ihres Eintragsortes Mensch und Umwelt belasten. Sie sind somit potentiell ubiquitär. Fettlösligkeit und Persistenz ermöglichen die Anreicherung in den Schadstoffen ausgesetzten Organismen (Bioakkumulation) und in der Nahrungskette (Biomagnifikation). Exposition durch schwerabbaubare, organische Chemikalien kann zu gesundheitlichen Störungen führen: deshalb wird das Risiko der Umwelbelastung durch sie auf der internationalen Ebene reguliert (Stockholmer Übereinkommen zu persistenten organischen Schadstoffen).
Die Bedeutung der Atmosphäre für die globalen Zyklierung der Pestizide DDT und Hexachlorcyclohexan wurde in der Vergangenheit mit Hilfe verschiedener Modelle untersucht. Die Rolle des Ozeans, sowohl als Kompartiment, als auch als Transportmittel, und der dazugehörigen Prozessen wurden noch nicht ausreichend betrachtet. Aus diesem Grund wurde ein Multikompartiment-Modell um ein 3-dimensionales Ozeankompartiment erweitert. Das Multikompartment-Chemie-Transport-Modell (MTCM) basiert auf einem gekoppelten 3-dimensionalen Erdsystemmodell, bestehend aus dem atmosphärischen allgemeinen Zirkulationsmodell ECHAM5 und dem Ozeanmodell MPI-OM. Im Modellsystem sind außerdem Böden und Vegetationsoberflächen und ein Meereiskompartiment, ein voll dynamisches Aerosolmodell (HAM) und ein Biogeochemiemodell (HAMOCC5) integriert. Die räumliche Auflösung beträgt 2.8° × 2.8° (T42). In dieser Arbeit wurde die Zyklierung von γ-HCH (Lindan), α-HCH und DDT untersucht. Alle Chemikalien reichern sich vorwiegend in Böden an. Lindan wurde, aufgrund seiner Wasserlöslichkeit, in vergleichbaren Mengen auch in Ozean im Modell gefunden. DDT hat eine längere Verweilzeit als Hexachlorcyclohexan. In den hier aufgestellten Szenarien scheint das Meereiskompartiment keine wichtige Rolle bei der Verteilung von DDT und Lindan zu spielen. Die Meereisoberfläche dämpft lokal die Ozeanvolatilisierung um maximal drei Größenordnungen.
In dieser Studie wird die Bedeutung der Anlagerung der Stoffen an marine organische Phasen im Wasser dargelegt. Dieser Prozess beeinflusst unter anderem die Volatilisierung von der Oberfläche. Für DDT beobachtet man eine lokale Dämpfung von bis zu 35%. Er beeinflusst den vertikalen Transport. Für den globalen Netto-Transport spielt die Ozeandynamik eine grössere Rolle. Aufgrund seiner Eigenschaften (Persistenz), ist DDT in großen Mengen überall in der Tiefsee present. DDT und HCH werden insbesondere auch in abgelegenen Regionen wie der Arktis gefunden. Die Modellergebnisse zeigen, dass der Transport überwiegend durch die im Vergleich zum Ozean schnelle Atmospäre stattfindet. In den Tropen sind Ozeanströmungen für die horizontale Verteilung der Pestiziden von Bedeutung. Effektiver meridionaler Netto-transport, durch z.B. die Golfstrom, lässt sich für DDT beobachten. Insgesamt sind auf globaler Skala diese Effekte weniger relevant.
Der Ferntransport persistenter organischer Schadstoffe kann durch mehrere Emissions-

Transport-Depositions-Zyklen, welche die globale Temperaturverteilung widerspiegeln, (sog. Grashüpfer-Effekt) bestimmt werden. Die daraus resultiende Umweltexposition lässt sich am besten mit Hilfe von Modellexperimenten abschätzen. Die Bedeutung des Grashüpfer-Effekts (multi-hop) für das Ferntransport-Potenzial von DDT und HCH im Gegensatz zu einmaligem Transport (single-hop), wurde durch Separation der beiden Transportmodi untersucht. Für Lindan ist die Umweltbelastung durch einmaligen Transport größer als durch multiple Zyklen. Im Fall von DDT beobachtet man das Gegenteil. Der Grashüpfer-Effekt erhöht das Ferntransportpotenzial mittelflüchtiger Stoffe.

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Chapter 1

Introduction

Semivolatile Organic Compounds (SOCs), which are slowly degrading and have adverse effects on living beings, represent a major threat for the Earth System.

Many among these substances are of anthropogenic origin, have been or continue being used in large amounts as agrochemicals (pesticides, herbicides) and in the industry (components of plasticisers, anti-fouling agents, flame retardants, among others).
SOCs are present in all environmental compartments (atmosphere, soil, vegetation, ocean, ice, biota) and show a unique cycling behaviour.
Their resistance to degradation and semi-volatility imply the possibility for these substances of undergoing long-range transport, far from the sources, in atmosphere, rivers and ocean. Their presence can be, as confirmed by measurements, ubiquitous on the globe.
Moreover, SOCs show affinity to organic phases and accumulate in the tissues of exposed organisms, biomagnifying along the trophic chain.
Exposure to these substances can be associated with a wide range of detrimental effects on living beings. Particular concern raises the contamination of remote environments like the Arctic, due to the hazard SOCs pose to the pristine ecosystems. It is an international issue (Stockholm Convention on Persistent Organic Pollutants [138], UNECE on Long-Range Transboundary Air Pollution [1], Protection of the Seas, etc) to control the risk related to the exposure.

In order to study the multicompartmental fate of agrochemicals as hexachlorocyclohexane and DDT, a multicompartmental modelling approach, is necessary. For the first time a modelling tool based on the coupling of atmospheric and oceanic general circulation models (GCMs) has been designed and used here.

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[1] http://www.unece.org/env/lrtap/welcome.html, accessed September 2007.

Motivation

Whilst the study of the relevance of the atmosphere in the multicompartmental global fate and distribution of SOCs is already object of various modelling efforts, the role of the ocean in the global cycling, as a transport medium as well as as a reservoir, is still to be investigated. Several questions are open. The model was developed and used in order to:

- estimate of the impact of a three-dimensional ocean approach on the simulated fate and distribution of SOCs,
- investigate the relevance of partitioning to organics,
- investigate the global meridional transport, the role of the ocean in it and its mechanism,
- analyse the multicompartmental cycling and effects of sea-ice.

The tool designed and used for this purpose is, for the first time for HCH and DDT, based on the coupling of atmospheric and oceanic General Circulation Models and encompasses as well a description of the dynamics of SOCs in all other relevant environmental compartments as soil, vegetation and sea-ice.
In an effort to describe the dynamics of the organic phases influencing the fate of SOCs in the environment, an atmospheric aerosol and a marine biogeochemistry sub-models are also embedded in the modelling system.

Outline of the thesis

In Chapter 2 semivolatile organic compounds are introduced and the properties and environmental history of HCH and DDT presented.

Chapter 3 describes in detail the modelling approach followed in this study.

The results of the experiments aiming to a description of the cycling of HCH and DDT in the global ocean are presented and discussed in Chapter 4.
As a first step, the novel modelling approach has been evaluated by a comparison with model results obtained with a simplified setup representing the ocean as a bidimensional surface (similar to the one proposed and studied by Semeena and Lammel, 2006 [106]).
Furthermore, key aspects like retentive capacity of the ocean reservoir (and influence of different phases on it), influence of transport on spatial patterns of volatilization, vertical export (determined by sinking of particle-bound compounds and thermohaline circulation), when the complete 3d dynamics and the biogeochemistry are considered, are investigated.

Chapter 5 studies HCH and DDT in their multicompartmental fate, including the roles of the ocean reservoir and of the ocean currents in the cycling. The global meridional transport mechanism is furthermore investigated.

Chapter 6 summarizes the main findings of the study and Chapter 7 suggests further investigations.

Chapter 2

Semivolatile Organic Compounds

Compounds and properties

Highly stable chemicals which persist in the environment, accumulate in biota and have detrimental effects on humans and wildlife are known as Persistent, Bioaccumulative and Toxic (PBT) substances. They are used in large amounts in agriculture, forestry, households (pesticides, biocides in marine transport and households) and in the industry (components of plasticisers, flame retardants, among others). Another term widely used, especially in legislation and policy making, POPs, standing for Persistent Organic Pollutants, identifies organic persistent chemicals with harmful effects (therefore excluding [100], for instance, CFCs, chlorofluorocarbons).

The denomination used in this study, Semivolatile Organic Compounds (SOCs), refers to POPs with vapour pressure ranging between 10^{-5} and 10^{-2} Pa at ambient air temperature levels. This peculiar characteristic, the semivolatility, together with the lipophilicity (i.e. the solubility in other organics) allows them to reside in different phases (and therefore compartments) in the environment. This enables the compounds to be transported in both the gas and particle-bound phases in atmosphere and in water or suspended phases in ocean for long distances and, eventually, condense and accumulate in colder regions of the planet.

The partitioning between the phases affects all inter- and intracompartmental processes, such as the removal mechanisms (deposition, photolysis, chemical degradation) of SOCs from the atmosphere, the most significant of which is deposition (dry and wet in all phases) to aquatic and terrestrial ecosystems. One of this processes, the gas exchange, occurs in both directions; it is not only a removal process for the atmosphere, but a source, too. The compounds in fact undergo atmospheric transport and deposition to other environmental compartments, which may hold them in different extents according to substance properties and environmental conditions, but the compounds may also be re-emitted back into the atmosphere.

The chemical composition, in particular the presence of halogens (chlorine, in most cases) and/or of functional groups in their structure, may quantitatively hinder the action of enzymes determining degradation. This characteristic determines the persistence of SOCs in the environment, allowing them to be subject for a long time to atmosphere and ocean transport (and thus to actually reach the most remote regions worldwide) and/or to be (permanently) stored in compartments when ambient conditions do not favor revolatilisation. The above-mentioned lipophilicity is due to the weak tendency of halogens bound to aromatic carbon bounds to engage in hydrogen bonds with H-donors as water [104]. This leads SOCs to be bound not only to atmospheric aerosol, but to organics everywhere including, to different extents for different compounds, marine organisms and fatty tissues of animal and plants. This, joint with the slight water solubility (that hinders their excretion), makes them persist also in exposed organisms. This triggers a progressive increase in concentration in them with respect to the surrounding environment (bioaccumulation). Proceeding through the trophic levels, the concentration levels grow (biomagnification), so that big carnivorous (including humans) store a high share of SOCs in their bodies.

Semivolatile Organic Compounds have therefore a unique multicompartmental behaviour. As soon as they are first released into the environment (typically in vegetation and atmosphere, but not necessarily), they start cycling between the compartments which, in turn, become recipient, reservoirs, sinks, long-range transport vectors (atmosphere and ocean) and secondary sources for them (Fig.2.1).

The geographical distribution for SOCs is therefore not limited to areas adjacent to the release zones, but can be ubiquitous on the globe (in the Arctic, for instance, high concentration levels have been historically recorded in water and biota [11], [9]).

Many Semivolatile Organic Compounds (and all PBTs by definition), are toxic to many organisms.

Environmental and agricultural pollution determine food and forage contaminations. Particularly, marine edible fauna stores PBTs in high concentrations. Exposure to PBTs of living beings can be lethal or have severe long term harmful effects. The identification of chemical and non-chemical alternatives is an issue of high priority and non trivial solutions. Innovative technology implies consistent monetary and time investments for study, production, testing and, eventually, adequate technology transfer: a severe hindrance for developing countries or countries with an economy in transition.

Brief overview of international commitment on SOCs

Growing concern about the threats posed to the global environment and to human health by the release of synthesised chemicals has triggered action worldwide. The international community reacted at different levels, some control and prevention measures have been adopted on a national basis, but mostly agreements and directives have taken shape at international level (corresponding to the long-range distribution and transport).

In order to:

- protect human health and environment from potential harm,
- increase knowledge of the chemicals and raise public awareness of the related hazards,

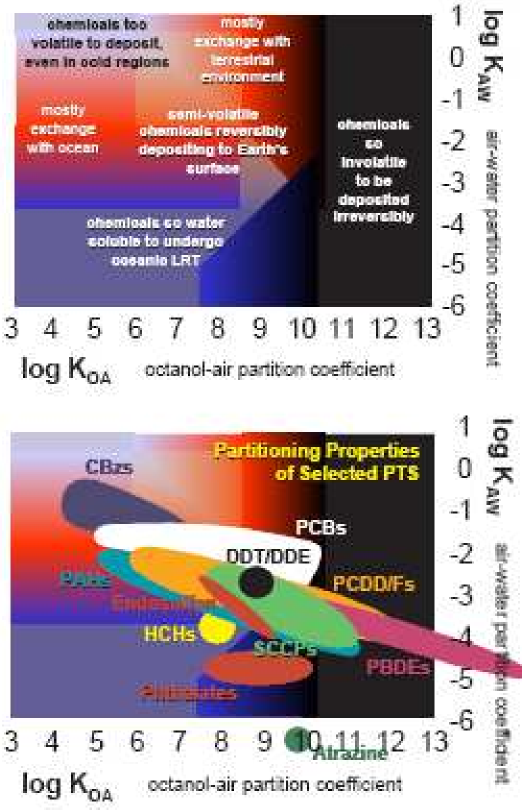

Figure 2.1: Partitioning and transport behaviour of organic compounds based on their properties. Adapted from UNEP Global Report, 2003[127].

- inform on the environmentally sound use of the hazardous chemicals, particularly at the decision-making level,
- promote exchange of informations,

several institutions and organizations have shown a cooperative effort in compiling joint programs, starting initiatives, producing guidelines, compiling inventories and databases (e.g. the PAN[5]), stipulating pacts and documenting ongoing activities.

The UN-ECE Convention on Long-range Transboundary Air Pollution[126] entered into force in 1983 and has *"substantially contributed to the development of international environmental law and has created the essential framework for controlling and reducing the damage to human health and the environment caused by transboundary air pollution"*. It meets annually to review ongoing work and plan future activities and to implement the Convention and its protocols across the entire UN-ECE region (with special focus on Eastern Europe, the Caucasus and Central Asia and South-East Europe) and sharing its knowledge and information with other regions of the world.

The Basel Convention and the Stockholm Convention are milestones of the international commitment aiming at the identification and management of persistent organics.

The Basel Convention[1] on the Control of Transboundary Movements of Hazardous Wastes and their Disposal, which came into force in 1992, is the most comprehensive (with 169 parties) global environmental agreement on wastes. It aims to protect human health and the environment against the adverse effects resulting from the generation, management, transboundary movements and disposal of hazardous and other wastes.

In December 2000, the Stockholm Convention[6] on Persistent Organic Pollutants banned or greatly limited the use and production of 12 chemicals (the so called "dirty dozen", all of them polychlorinated, 2 industrial chemicals, 2 byproducts of combustion and industrial processes, 8 pesticides, among them DDT) and regulated their storage and disposal, due to the known (at the time of first compilation of the list) higher risk posed by these compounds with respect to other POPs. The Stockholm Convention entered into force in 2004.

The Global Environmental Facility (GEF[3]) (in its second assembly, Oct. 2002) promotes the identification, test and implementation of innovative and sustainable technologies and of the technology transfer for the elimination of obsolete stockpiles of POPs, abundant in Africa, Central and Eastern Europe. It also explicitly contributes to the removal of the barriers impeding their successful implementation.

Other initiatives are the FAO Pesticide Management[2] and several programmes under the coordination of the World Health Organization (WHO).

The WHO Pesticide Evaluation Scheme (WHOPES[145]), established in 1960, promotes and coordinates the testing and evaluation of pesticides for public health and distributes information on the use of pesticides. The Intergovernmental Forum on Chemical Safety (IFCS[143]) and the International Programme on Chemical Safety (IPCS[144]) focus on prevention of the adverse effects to humans and the environment from production, storage, transportation, use and disposal of chemicals and publish guidelines of health criteria. The Inter-Organization Programme for the Sound Management of Chemicals (IOMC[4]) was established in 1995 to strengthen cooperation and increase coordination in the same field.

Most recently, the Rotterdam Convention[7] came into force in February 2004 to promote international responsibility sharing and cooperation in the trade of certain hazardous chemicals.

Two organochlorine agrochemicals

Semivolatile organic compounds, albeit all within similar ranges of peculiar characteristics described above, as semivolatility and persistence, and all displaying multicompartmental distribution, can have very marked different environmental behaviour and history. For this study, compatibly with data availability (agricultural application inventories), two differently behaving organochlorine agrochemicals have been chosen: DDT and hexachlorocyclohexane (HCH). DDT is in fact more lipophilic, less volatile and less water soluble than HCH. A brief description of the chemicals (of their history, properties and impacts) follows.

The substance properties used for this study (Tab.2.1) result from the compilations of Klöpffer and Schmidt, 2001[58], Moltmann et al., 1999[86] and Sander, 1999[96].

Properties	units	α-HCH	γ-HCH	DDT
Molecular mass	$gmol^{-1}$	290.83	290.83	354.50
Vapor pressure	Pa	3.8×10^{-3}	3.0×10^{-3}	2.5×10^{-5}
K_{ow}	m^3kg^{-1}	2.9	1.91	888
Water solubility	mgl^{-1}	1.4	7.4	3.4×10^{-3}
Heat of solution	$Jmol^{-1}$	2.7×10^{-4}	2.7×10^{-4}	2.7×10^{-4}
Heat of vaporisation	$Jmol^{-1}$	115.0×10^3	115.0×10^3	118.0×10^3
Degradation rate in soil	s^{-1}	2.0×10^{-8}	2.0×10^{-8}	4.05×10^{-9}
OH degradation rate	$cm^3mol^{-1}s^{-1}$	0.14×10^{-12}	1.9×10^{-13}	1.0×10^{-13}
Degradation rate in ocean	s^{-1}	see text	1.86×10^{-8}	0.0

Table 2.1: Compound properties and degradation rates adopted in this study.

DDT

The acronym DDT stands for *dichlorodiphenyltrichloroethane* or $1,1,1-trichloro-2,2-di(p-chlorophenyl)-ethane$. DDT, the first of the chlorinated organic insecticides, was initially synthesised in 1873, but employed only since the beginning of the 1940's, when its use increased enormously on a worldwide basis after World War II, primarily due to its effectiveness (a WHO estimate[1] reports it contributed to save, during the period of its use, approximately 25 million lives) against malaria and typhus spreading vectors. Problems related to extensive use of it first arose in the late 1940s as many species of insects developed resistance and it was found to be highly toxic for fish.

DDT is a stable, highly lipophilic chemical; in comparison to HCHs, it shows higher affinity to organics and lower water solubility and vapour pressure (Tab.2.1). The five chlorine atoms are arranged on the molecule (Fig.2.2) in such a way that they hinder the action of enzymes, found in microorganisms, plants or animals, that might otherwise degrade it. In

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[1] as reported in http://www.3dchem.com/molecules.asp?ID=90

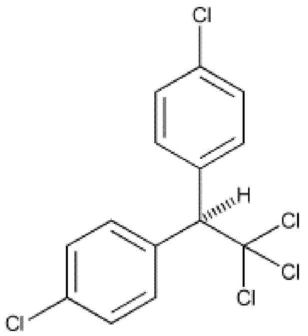

Figure 2.2: DDT molecular structure[a]

[a] from http://www.3dchem.com/molecules.asp?ID=90

living beings exposed to it through the food chain, DDT is not easily metabolised, with a biological half-life[2] of 8 years; it tends, on the contrary, to accumulate in fatty tissues. In soils, the half-life is 1.1 to 3.4 years. DDT is acutely toxic for mammals (oral LD_{50}[3] is 300 to 500 mg/kg) and shows xeno-hormonal activity and is suspect to carcinogenicity in humans. DDT is therefore of great concern in the Arctic due to the high concentrations of its toxic metabolites (DDD and DDE, mostly) found in top predators.

DDT is part of the "dirty dozen" under the Stockholm Convention, banned in most countries and only being allowed against malaria-bearing mosquitos. A study of the U.S. Environmental Protection Agency (EPA[8]) shows that measures like total ban of DDT in 1973 can revert the buildup of DDT in natural waters: a 90% reduction of DDT in fish of Lake Michigan was recorded by year 1978.

Hexachlorocyclohexanes

The hexachlorocyclohexanes have been widely used as pesticides since 1943, mainly in the Northern hemisphere. A chemical preparation known as *technical* HCH, also called benzene hexachloride (BHC), consists of a mixture containing five stable isomers of HCH (Fig.2.3), named according to the chlorines at axial and equatorial positions, in the following ranges of proportions: 60-70 % α, 10-12 % β, 6-10 % γ, 3-4 % δ, 3-4 % ϵ [146]. Although *technical* HCH was first prepared in the 19^{th} century, insecticidal properties of the γ isomer, were discovered only in the early 1940s. Lindane is a compound constituted for more than 90% by the γ- isomer. *Technical* HCH has been banned in the 1980s after evidence of its toxicity. HCH isomers may have in fact serious short and long term health effects. In spite of restrictive measures, α- β- and γ- HCHs are still widely distributed in the world oceans [15], [102], [60]. HCH is not among the compound selection for the Stockholm convention.

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[2] The half-life, $T_{1/2}$, a common persistence indicator, represents the time required, for a given amount of compound, to decay, or in case of biological half life to be metabolised, to half of its initial value

[3] The LD or lethal dose, a common metric in environmental toxicology, indicates the dose necessary to kill 50% of a given population exposed to a chemical.

HCH isomers are relatively persistent in water and soils with half lives above 1 year. Because of the relatively low lipophilicity, they are also much less bioaccumulative than other organochlorines of concern. As compared with DDT these species are less persistent. Their high volatility, (especially in case of the α- isomer), determine their long-range atmospheric transport. A large proportion of HCH isomers enters the ocean waters through flooding, run-off from treated areas and sewage systems, incorrect waste disposal. Atmospheric depositions represents also a significant source to the oceans.

In the environment the HCH isomers' proportion differs from the original technical HCH composition, due to the slightly different environmental behaviour of the different isomers. In order to study the multiyear fate of both α- and γ- isomers present in *technical* hexachlorocyclohexane, it may therefore help to compare their ratio to the gradients in observational data in the available literature (Iwata et al., 1993[50], Jantunen and Bidleman, 1998[51], Lakaschus et al., 2002[60]).

Although not officially a POP according to the UNEP list, HCH is object of the POPs Protocol of the UN-ECE LRTAP Convention.

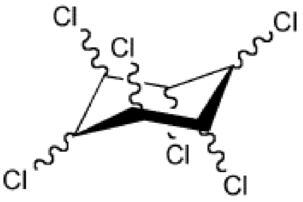

Figure 2.3: γ-HCH molecular structure: the arrangement of chlorine atoms in axial and equatorial position is different for different isomers.[a]

[a] from http://www.3dchem.com/molecules.asp?ID=140

γ-HCH

Highly water soluble, highly volatile, with relatively high water-air partitioning coefficient and low octanol-water partitioning coefficient, γ-HCH is the only HCH isomer with insecticidal properties in the mixture of *technical* HCH. The denomination *lindane* has been used to indicate preparations containing more than 90 % of γ-HCH (Willet et al., 1998[146]). γ-HCH is moderately toxic for fish and invertebrates, acutely toxic for mice and rats, with several studies reporting endocrine-disrupting activity in wildlife and humans.

Lindane is still relatively widely used in developed and developing countries as insecticide on crops and building preservative and as biocide to combat lice and scabies. It has been banned by the European Union countries for plant protection and California has banned lindane-based products used to treat lice and scabies. In Europe, lindane usage was reduced by two thirds between 1970 and 1996 (Breivik et al., 1999[20]), but is still extensively used as pesticide in the UK.

α-HCH

α-hexachlorocyclohexane presents properties (Tab.2.1) comparable to the ones of γ-HCH. It has a high vapour pressure, high water-air partitioning coefficient and low octanol-air partitioning coefficient. It partitions more readily into water than into solid particles. Due also to its low affinity to organic phases in previous modelling studies (Hansen et al., 2004[36]) it was described as a pure gas-phase chemical. A peculiar characteristic of α-HCH, its chirality[4], determines its presence with two different atom arrangements (enantiomers), with slightly different environmental stability, as enantiomers may show different behaviour in biotic (microbial, enzymatic) processes.

Release of α-HCH in the environment occurs mainly from the use of *technical* HCH as a pesticide, although exposure to sunlight may lead to isomerisation of the γ-HCH to α-HCH in small amounts (Hühnerfuss, 1997[47]). In water and soil (Vonk and Quirijns, 1979[130], Ludwig, 1991[74]) this process has also been observed. α-HCH has been banned two decades ago, whereas lindane is still in use in some countries.

Once in the atmosphere, it may, as for lindane, be subject to wash-out and dry deposition; in water environments, α-HCH is not expected to volatilise or hydrolyze extensively. It may slightly bioconcentrate in aquatic biota, for which it is highly toxic. Presence of α-HCH in soils will most likely result in groundwater pollution, although the compound can also be subject to slow volatilisation. As for many other SOCs, human exposure to α-HCH occurs mainly from food.

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[4] The chirality of a molecule implies that it cannot be superimposed on its mirror image.

Chapter 3

Modelling the Fate of Semivolatile Organic Compounds

Models are an indispensable tool to describe the dynamics and resolve the complexity of processes and budget mass cycling within the Earth System.

Models are able to integrate the necessary information inferred from measurements, with insights into the nature and character of single processes or provide an overall point of view on the system as a whole, in an objective, transparent and definitely reproducible way.
Measurements of semivolatile organics, on the other hand, are difficult to obtain and often more expensive and can be biased by local phenomena (but deliver information with known uncertainty).

The environmental fate of SOCs is strongly influenced by the the reversible exchange between the different media and by the processes occurring in the different compartments.

This chapter outlines the necessity of a multicompartmental modelling approach to address the fate of SOCs in the global environment, describes the distribution and processes of the chemicals in the different reservoirs and the tool developed and used for the study.

Multicompartmental approach

Modelling the fate of substance partitioning to different phases in the environment offers additional challenges in comparison to modelling compounds present only in gaseous phase and mainly in the atmosphere.
A representation of the system in its complexity, including the different environmental compartments, is necessary to predict the cycling of semivolatile organics.
Several multicompartmental model solutions have been suggested, so far. Depending on the different investigation foci, the tools used have different resolution in time, space and processes.

Multimedia mass balance[1] box models (van de Meent, 1992[128], Scheringer et al., 2002[98]) are representation of a unit world with the different compartments described. Within a single compartment further differentiation of, for instance, different vegetation types or ocean layers are also possible. Such tools are developed in order to understand processes, to evaluate and test experimentally derived parameters, to select substances for environmental monitoring, to estimate toxic pressure on the environment, to develop indicators. In their simplest setups, such box models are not georeferenced and due to the lack of or the limited spatial resolution (several thousands of square kilometres) and the simplifications adopted (with consequences on the degree of realism of such approaches), they do not generally require large computer resources. This, together with their user-friendliness (in the stages of understanding, testing and interpretation of results) makes them valuable instruments in chemical risk assessment.

Multimedia boxes can be joined together in different arrangements, nested (Brandes et al., 1996[19]) or chained in different resolutions (Scheringer, 1996[97], Held, 2003[41]). Some of these models furtherly subdivide the globe or a specific region into different latitudinal (Strand and Hov, 1996[115]) or climate zones (Scheringer, 2000[101], MacLeod et al., 2001[79], Wegmann et al., 2002[140], Prevedouros et al., 2004[90], Wania and Mackay, 1995[134] and 2000[136], Toose et al.,[123]) often in latitudinally averaging bands and are used to calculate exposure patterns or describe meridional transport of the compounds and address long-range transport potential (LRTP). In some of these models ([97], [101]), the transport in atmosphere and ocean is described as macroscopic eddy diffusion, with coefficient obtained by large-scale oceanic studies and tracer experiments.

On a higher degree of resolution, but also with higher demand of computing resources, other approaches, meant to address the large (or global scale) of semivolatile organic compounds. Such modelling frameworks are based on the incorporation of circulation models of the atmosphere in multimedia models at the hemispheric (Sofiev and Galperin, 2002[112], Malanichev at al., 2004[82], Hansen, 2004[36]) or global scale (Koziol and Pudykiewicz, 2001[59], Semeena and Lammel, 2003[107], 2005[108], 2006[106] and, most recently, Gong et al., 2007[32]) and enable to reproduce the circulation features and the transport of tracers associated with them.

In order to focus on the role of the ocean in the environmental cycling of semivolatile organic compounds, ocean circulation models have been used at regional (Ilyina et al., 2006[49]) hemispheric scale or embedded in global multicompartmental models (Strukov et al., 2006[116]).

The approach proposed in this study is multicompartmental, highly resolved in time, space and processes, based on the coupling of two general circulation models (GCMs) for atmosphere and ocean.

The use of general circulation models in the investigation of the global fate and distribution of semivolatile organic compounds enables to:

- reproduce realistic physical forcings on different spatial and temporal scales,

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[1] I.e. based on mass equations, considering the balance of input and output fluxes of compounds in each environmental medium and taking into account inter- and intra- compartmental processes.

- identify and evaluate key-processes for the fate of the compounds,
- detect and quantify how local conditions can influence the transport and distributions (both geographical and compartmental) of the compounds as in recent studies (Leip and Lammel, 2004[66], Semeena et al., 2006[106]),
- investigate the long term behavior of the compounds. Between the first introduction of toxic organics, in massive amounts on global scale, and legislative bans, often decades have passed.

A three-dimensional model of the ocean has been coupled to an atmospheric GCM, probably for the first time for SOCs studies[2]. The ocean is the compartment which tends to accumulate substances (Iwata et al., 1993[50], Strukov et al., 2006[116]), thus becomes a reservoir and eventually a source compartment.
The proposed approach provides a better representation of the role of the ocean as transport medium and storage compartment, and consequently of the processes involving it, in a modelling system already developed and tested ([62], [107], [66], [61], [108], [106], [63]).

The Model

The three-dimensional ocean version of the multicompatmental chemistry-transport model (MPI-MTCM) from the Max Planck Institute for Meteorology in Hamburg, Germany, is based on the dynamic coupling of two general circulation models:

- the atmospheric GCM ECHAM5
- the ocean GCM MPI-OM

both including submodels for atmospheric aerosols (HAM) and marine biogeochemistry (HAMOCC5), respectively.

The use of submodels provides information on the organic phases in atmosphere and ocean. These phases are of essential importance for the fate and distribution of compounds of medium to high lipophilicity.
The system further encompasses a description of soil and vegetation as two-dimensional environmental compartments for SOCs distribution.

The actual model setup has been developed based on earlier versions of the MPI-MTCM (Lammel et al., 2001[62], Leip and Lammel, 2004[66], Semeena and Lammel, 2003[107] and 2005[108], Semeena et al., 2006[106].). From the initial setup, describing the fate and distribution of SOCs in atmosphere (with the GCM ECHAM5-HAM), surface ocean (using modelled mixed layer depth data), soil and vegetation, the model has been furtherly developed by the coupling with the ocean general circulation model (MPI-OM-HAMOCC5).

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[2] Another modelling setup based on an atmospheric general circulation model (Gong et al., 2007[32]), used to investigate the global transport and budgets of PCBs (Huang et al., 2007[46]), encompasses an ocean tracer transport module based on a tracer model, getting as an input prescribed global currents.

Processes within and between the compartments, have been mostly described as in the earlier versions of the MPI-MTCM. New parameterisations have been implemented and applied for ocean and sea-ice and in the description of mass exchange processes of both compartments.

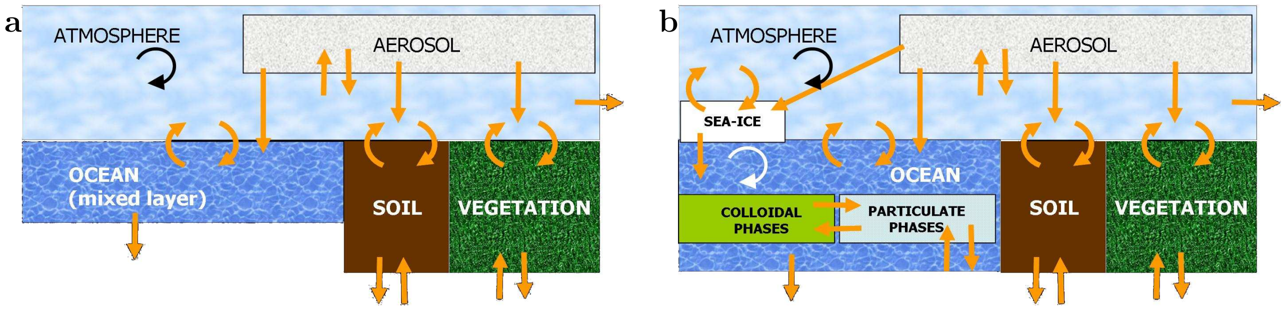

Figure 3.1: Model world: compartments, exchange, sources and sinks.
a: setup used in previous studies ([62],[66],[107],[108],[106]).
b: setup used in this study (note the three-dimensional representation of the ocean, with related biogeochemistry, and of the sea-ice compartment).

The transition from the initial to the new model is displayed in Fig.3.
In the following paragraphs a description of SOC dynamics in the different environmental compartments and their model representation is given.

Ocean

The total concentration change of the compound per unit of time and space in the multiphase (aqueous phase, available organic phases) ocean sub-system can be described as:

$$\frac{dc_{ocean}}{dt} = (\frac{\partial c}{\partial t})_D + (\frac{\partial c}{\partial t})_M \pm (\frac{\partial c}{\partial t})_A \pm (\frac{\partial c}{\partial t})_{Di} \pm (\frac{\partial c}{\partial t})_V - (\frac{\partial c}{\partial t})_{De} \qquad (3.1)$$

The compounds can reach the ocean reservoir, in gas-phase or bound to atmospheric particulate matter, via deposition (dry and wet, D) and, dissolved in water, via sea-ice melting (M). Once in the ocean, depending on the properties and local conditions, they are redistributed between the predominant aqueous phase and organic phases (the latter with different hydrodynamical behaviour). In seawater, SOCs can in fact sorb to suspended solids, which sink in the water column, and to other organic material, which is passively transported in water. This phase originates from organisms broken down into such a small size that they are dispersed in water (colloids). Some dissolved molecules are lipids, carbohydrates, proteins, humic or tannin substances. The aqueous phase is in turn in equilibrium with the compound in the atmospheric gas-phase at the air-water interface. This latter equilibrium is strongly influenced by local conditions, such as wind velocity and temperature, modulating the gaseous exchange between the two reservoirs. Advection (A) and turbulent diffusion (Di) of SOCs in the ocean, involve, at different

scales, the compounds in all the phases. Additionally, vertical export (V) to the deep ocean occurs for the fraction of the substance sorbed to particles which undergo gravitational settling (and finally could enter a sediment compartment, not yet explicitly described in the model). Chemical breakdown and microbial attack (De) in each phase are removal processes for SOCs.
The spatial displacement determined by the transport coupled with strong partitioning to sinking organic matter of species of high lipophilicity could act as downward pump of compounds from the atmosphere to the ocean. Sedimentation with particles, bringing the compounds below the mixed layer could prevent revolatilisation into the atmosphere and thus further recycling in the environment. Once in deep ocean the compounds are then only subject to degradation and transport. Only the most persistent can then be brought back to the surface.
As most of the processes in the ocean bearing an effect on SOCs distribution depend to different extent on various local conditions (temperature, radiation, nutrients availability, wind, etc.), the cycling of the compounds (not necessarily only in the ocean) is consequently affected by regional characteristics [64].

A description of the used tool and processes follows.

The Ocean General Circulation Model

The Max Planck Institute Ocean Model (Marsland et al., 2003[84]) (MPI-OM) is an ocean general circulation model (OGCM) based on primitive equations with a representation of thermodynamic processes. The model is able to simulate the ocean circulation from eddy up to gyre scales in response to atmospheric forcing. The transport is computed by means of a total variation diminishing (TVD) scheme (Sweby, 1984[118]). The horizontal discretisation is on a staggered Arakawa C-grid. The grid has a spatial resolution approximating spatial truncation T42 ($2.8° \times 2.8°$). The vertical dimension is discretised in 13 levels on z-coordinates, with 4 levels in the first 100 metres. At each horizontal grid point the deepest wet cell has uniform thickness interpolated from the discretised bathymetry, from the ETOPO-5 (NOAA, National Geophysical Data Center, Boulder, Colorado, 1988). The surface layer thickness is also adjusted to account for the sea surface elevation and the sea-ice drift where required. The model includes parameterisations of sub grid-scale mixing processes like eddy-induced tracer transport. The model contains a free surface and a sea-ice model (Hibler, 1977[42]), with viscous-plastic rheology.
There is no explicit mixed layer formulation: the wind stress input from the atmosphere is affecting only the uppermost model layer.
In view of the time scale of ocean overturning ($\approx$ 1000 ys [117]) the model was started with globally uniform tracer distribution with realistic mean values and spun-up for about 2000 years. After such long spin-up it is ensured that the resulting tracer distributions reflect the model dynamics and not the long time memory of any realistic initial values.
The model time step used in the present study is three hours. The MPI-OM has been online coupled with the atmospheric general circulation model (AGCM) ECHAM5 (introduced in the following). Both models exchange information every three hours.

The marine biogeochemistry module

In order to have a high spatially and temporally resolved estimate of the organic phases in the ocean compartment, a biogeochemistry model, online coupled to the ocean General Circulation Model MPI-OM, has been used. The two models share the same resolution and time steps [3].
The Hamburg Ocean Carbon Cycle Model HAMOCC5 (Wetzel et al., 2005[141]) simulates marine biology and biogeochemical tracers in the ocean water column. The carbon chemistry is described in the model as in Maier-Reimer 1993,[80]. The structure of the ecological model is based on HAMOCC3 (Six and Maier-Reimer, 1996[109]) and considers 4 component types (N, P, Z, D) i.e. nutrients, phytoplankton, zooplankton, detritus. Processes as photosynthesis and zooplankton grazing occur in the first 60 metres of the water column (euphotic zone). Detritus, in turn, can be differentiated into two classes, according to its origin and hydrodynamic behaviour. Particulate organic carbon consisting of dead phytoplankton and zooplankton and of fecal pellets, and originating in the first layers, sinks out of the euphotic zone through the whole water column. Phytoplankton exudation and zooplankton excretion (at a constant rate) are considered as dissolved organic carbon, generally assumed to be smaller than $1\mu m$, not affected by gravitational settling and therefore only subject to ocean advection and diffusion. Both organic carbon classes are subject to remineralisation following constant rates, depending on oxygen availability. This process makes them available to add to the pool of nutrients. Due to the lack of an explicit mixed layer formulation, the mixing depth for biogeochemistry is derived in MPI-OM based on pressure gradients and prescribed wind stirring. The coarse vertical resolution may lead to an overestimate of net primary production. Altogether, the model describes 18 tracers.

Equilibria in the multiphase system

The phases in the system are a bulk water phase and 4 organic phases. The fractions of chemicals sorbed to these organic phases are a function of the amount of organic matter associated with the phase and calculated from the organic carbon partitioning coefficient K_{oc}, in turn estimated from the octanol/water [3] partitioning coefficient K_{ow} [18], weighting the sorption coefficient K_d $[l\ kg^{-1}]$ with the organic content of the phases (Karickhoff, 1981[55]) as:

$$K_{oc} = 0.411 \times K_{ow} \tag{3.2}$$

The mass of the compound sorbed to organics is then calculated, assuming (at the considered temporal scales) instantaneous equilibrium, by:

$$c_{org} = K_{oc} \times c_{OC} \times c_w \tag{3.3}$$

where c_{OC} is the concentration of organic carbon and c_w the concentration of the compound in aqueous phase, in agreement with Scheringer et al., 2004[99].

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[3] Octanol, a fatty alcohol, is commonly used as surrogate for organic phases.

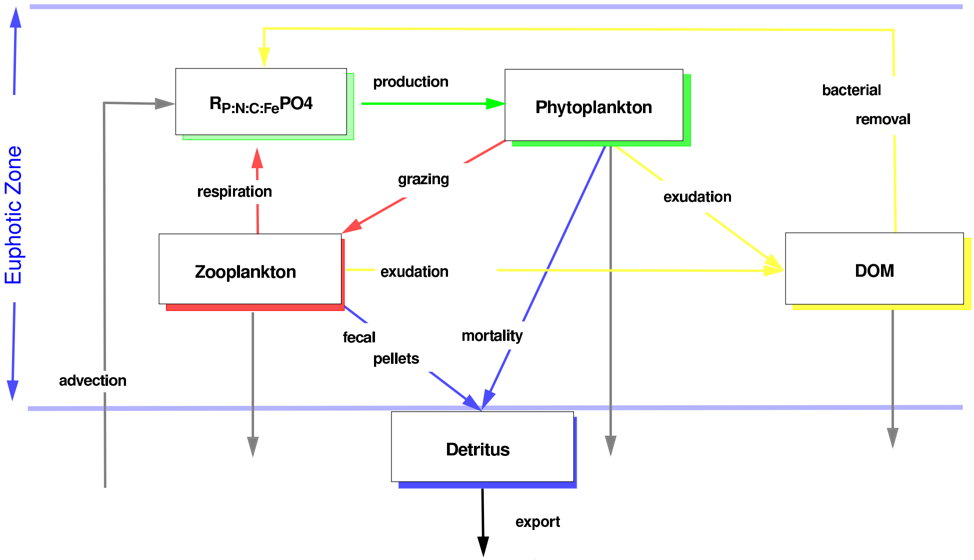

Figure 3.2: Carbon Cycle in HAMOCC5[1]. The hydrodynamic behaviour of the different phases is indicated by the downward arrows. Below the euphotic zone the plankton adds to the pool of detritus (particulate matter), which is the only phase subject to gravitational settling. All phases are subject to three dimensional advection.

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[a] from Maier-Reimer et al., 2005[81]

Mass exchange processes at the air-water interface

The transport of semivolatile organic compounds across the air-sea interface may occur by several processes. Dry deposition and wet scavenging of particles bearing adsorbed and absorbed particles and air-water gas exchange (deposition and volatilisation).

Atmospheric deposition The dry deposition of the compounds in gas phase is calculated according to a resistance scheme (Ganzeveld and Lelieveld, 1995[30]).
The particle deposition is calculated as a function of particle radius and density (Ganzeveld et al., 1998[31]). More details on atmospheric deposition follow in the chapter.

Volatilisation For the volatilisation, the diffusive air-water gas exchange is described based on the standard two-film model (Whitman, 1929[142], Liss and Slater, 1974[71]), following a fugacity-based[4] approach as in Mackay, 2002[77]. The scheme considers two resistances for the boundary layers of water and air at the ocean/atmosphere interface.

$$\frac{\partial c}{\partial t} = D_{wa} \times f \tag{3.4}$$

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[4] Fugacity $[Pa]$ is a way to express the chemical potential of a substance in a system of two or more phases. It can be defined as the tendency of a species to escape from one phase.

The term D_{wa} $[mol\ Pa^{-1}\ m^{-2}\ s^{-1}]$ (generally indicated as $D-value$[77]), for volatilisation from water, is calculated as:

$$D_{wa} = \frac{A}{\frac{1}{Z_a \times U_1} + \frac{1}{Z_w \times U_2}} \tag{3.5}$$

where A $[m^2]$ is the water/air interface.

Fugacity capacities Z are calculated for the boundary layers of air (Z_a $[mol\ Pa^{-1}\ m^{-3}\ ]$) and water (Z_w $[mol\ J^{-1}]$) as follows:

$$Z_a = \frac{1}{R \times T_w} \tag{3.6}$$

where H is the Henry's law coefficient $[mol^{-1}\ Pa\ m^3]$, and for water:

$$Z_w = \frac{1}{H} \tag{3.7}$$

The fugacity f $[Pa]$ in equation 3.4, representing the tendency of the compound dissolved in water to escape from the phase via volatilisation, is expressed as function of the water solubility c_w and of the fugacity capacity Z_w:

$$f = \frac{c_w}{Z_w} \tag{3.8}$$

where R is the universal gas constant $[J\ mol^{-1}\ K^{-1}]$, T_w $[K]$ the temperature at the sea surface.
The scheme considers, for the two stagnant boundary layers of the two media involved, two mass transfer coefficients $U1$ and $U2$ $[m\ s^{-1}]$ in equation 3.5, in series, as a function of the 10 metres wind speed u $[m\ s^{-1}]$ as in Mackay and Yuen, 1983[78] and Schwarzenbach et al., 1993[104]:

$$U1 = 6.50 \times 10^{-4} \times \sqrt{(6.1 + 0.63 \times u} \tag{3.9}$$

$$U2 = 1.75 \times 10^{-6} \times \sqrt{(6.1 + 0.63 \times u} \tag{3.10}$$

Degradation in the ocean

Chemical reactions and microbial attack are the sinks for semivolatile organic compounds in the ocean system. The degradation is a process strongly dependent on local environmental conditions: temperature influences (together with pH) hydrolysis (Ngabe et al., 1993[87]) and the activity of microorganisms able to metabolise a chemical in case of microbial reactions (Hühnerfuss, 1993[48], Macdonald et al., 2000[76], Harner, 2000[39]). In the model the processes are described as following a first order decay law:

$$\frac{\partial c}{\partial t} = k \times c \tag{3.11}$$

The exponential decay rate k $[s^{-1}]$ is the sum of two terms, to account for microbial attack and hydrolysis, respectively.

For the compound γ-HCH, both processes are represented as first order processes:

$$k = k_{md} \times 2^{\frac{T-T_{ref}}{10}} + k_{hydr} \times e^{\frac{-7818}{T}} \tag{3.12}$$

in agreement with recommendations [121].
For α-HCH the term accounting for the hydrolysis is a second order rate (Ngabe et al., 1993[87]) for basic, acid and neutral reactions. Considering the stability to acids of the compound and the slowness of neutral reactions (i.e. with water) only a term for basic reactions is considered.

$$k = k_{md} \times 2^{\frac{T-T_{ref}}{10}} + k_{bas} \times a_{OH^-} \tag{3.13}$$

with a_{OH^-} activity of the hydroxide ion in the solution. For the bacterial degradation the rate $[s^{-1}]$ is function of the microbial half-life which, following Li et al., 2004[69], is 9.5 $years$. The compound's racemic[5] ratio is assumed equal to 1, i.e. equal amount of each enantiomer. Assuming a diluted solution and considering the temperature dependency of dehydrochlorination for HCHs, the following regression equation for k_{bas} was estimated by Ngabe et al., 1993[87].

$$\log k_{bas} = \frac{14.151 - 4091}{T} \tag{3.14}$$

The compound DDT exhibits non significant biological-chemical decay.
Sediment dynamics is not explicitly described in the current model setup. Nevertheless, degradation in sediments has been described (for the compounds bound to organics at the ocean bottom) following a rate coefficient $[s^{-1}]$

$$k = 2 \times e^{-8} \tag{3.15}$$

selected from Hornsby et al., 1996[45].

Sea-ice

The sea-ice is a compartment which, due to its collocation, interacts with both the two major reservoirs and transport media it is in contact with. It is a substrate for atmospheric deposition and can host a fraction of the compounds present in the ocean as it forms and releases back the substances via volatilisation and melting processes. It may, therefore, delay the mass transfer between atmosphere and ocean in both directions, acting as an intermediate reservoir and hinder (Hargrave et al., 1997[37]) the volatilisation from sea water. A consequence of this are local deviations from air-sea exchange equilibrium and a virtual enhancement of the retention capacity of the ocean.

In the model the SOCs concentration change per unit of time and space in sea-ice is expressed as:

$$\frac{dc_{sea-ice}}{dt} = (\frac{\partial c}{\partial t})_D \pm (\frac{\partial c}{\partial t})_A - (\frac{\partial c}{\partial t})_V - (\frac{\partial c}{\partial t})_M \tag{3.16}$$

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[5] A racemic mixture is one that has equal amounts of left- and right-handed enantiomers of a chiral molecule.

Sea-ice is assumed to be covered by a snow pack of mature snow porosity and varying thickness and is described as including three sub-compartments: the air filling the snow pores, the interstitial liquid water and the snow-ice/air interface. Once at the air-snow interface (via atmospheric dry and wet deposition, D), SOCs can diffuse into the snow pore space air, dissolve in the interstitial liquid water or adsorb to the ice surface. Part of the snow-ice complex, the compounds are then subject to horizontal advection (A) of the compartment, i.e. sea-ice drifting. This is calculated by ice sub-model embedded in MPI-OM and based on Hibler, 1979[42]). The substance losses from the snow-ice compartment occur via volatilisation (V) and drainage with melt water (M). The amount of SOCs that can be possibly present in bulk ice, also in case of ice formation from freezing sea water is considered negligible (Weeks, 1994[139], Pfirman et al., 1995[89]). In addition, the storage in organic matter within the sea-ice reservoir is not considered in the current model set-up.

Volatilisation from sea-ice

The amount lost by volatilisation is calculated following, as for ocean volatilisation, a fugacity approach (Mackay, 2002[77], Wania, 1997[131]):

$$\frac{\partial c}{\partial t} = D_{sa} \times f \tag{3.17}$$

Where D_{sa} is the *D-value* [3] for the sea-ice-snow complex and f is the fugacity. The *D-value* is based on previous studies [131], [137], assuming the diffusive transport of a contaminant in interstitial air and water of snow comparable to the same process in another porous medium, the soil. A resistance is used for snow-air boundary layer and two parallel resistances for the diffusion within the snow pack.

$$D_{sa} = \frac{A_i}{\frac{1}{U_7 \times Z_a} + \frac{1}{U_5 \times Z_l + U_6 \times Z_a}} \tag{3.18}$$

Where A_i is the area $[m^2]$ of the ice-snow system and U_5, U_6 and U_7 are mass transfer coefficients $[m\ s^{-1}]$ for diffusion in snow-water, snow-air and for the snow-air boundary layer, respectively. A typical value for the latter, $1.38 \times 10^{-3}\ m\ s^{-1}$ is suggested by Wania, 1997[131]. For each of the three subcompartments a capacity term [44] is calculated, based on physico-chemical properties and partitioning coefficients. For pore air Z_a and liquid water Z_l, they are expressed in $mol\ m^{-3}\ Pa^{-1}$ as follows:

$$Z_a = \frac{1}{R \times T} \tag{3.19}$$

$$Z_l = \frac{K_{wa}}{R \times T} = K_{wa} \times Z_a \tag{3.20}$$

where R is the gas constant $[J\ mol^{-1}\ K^{-1}]$, T the absolute temperature, K_{wa} the water-air partitioning coefficient. The capacity for the ice-air interface, z_i $[mol\ m^{-2}\ Pa^{-1}]$, is:

$$z_i = \frac{k_{ia}}{R \times T} = k_{ia} \times Z_a \tag{3.21}$$

with k_{ia} ice surface-air partitioning coefficient, by definition $k_{iw} \times K_{wa}$, where k_{iw} is the ice-water partitioning $[m]$ coefficient. Hoff et al., 1995[44] suggest the following (at 20°C) expression:

$$\log(k_{iw}) = -0.769 \times \log(C_{ws}) - 8.58 \tag{3.22}$$

where C_w^s $[mol\ m^{-3}]$ is the solubility of the subcooled[6] liquid. The corresponding equation for k_{ia} is:

$$\log(k_{ia}) = -0.79 \times \log(C_w^s) - 5.97 + \log(K_{wa}) \tag{3.23}$$

furtherly extrapolated to -10°C:

$$\log(k_{ia}(T)) = \log(k_{ia}(20°C)) + DH_a/2.303 \times R \times (\frac{1}{263} - \frac{1}{293}) \tag{3.24}$$

The values for the enthalpy of adsorption DH_a at the interface are assumed [40] to be proportional to the ones of enthalpy of condensation of the subcooled liquid, DH_c, as in Hoff, 1995[44], and Wania, 1997[131], whose values are 92.9 and 83.0 $kJ\ moles^{-1}$, respectively for DDT and $\gamma-$HCH[7] as:

$$\frac{DH_a}{DH_c} = 0.878 \tag{3.25}$$

The mass transfer coefficients in 3.18 are calculated as:

$$U_5 = B_w \times (v_{sl}10/3/(v_{sa} + v_{sl})^2)/(\ln(2 \times d_s)) \tag{3.26}$$

$$U_6 = B_a \times (v_{sl}10/3/(v_{sa} + v_{sl})^2)/(\ln(2 \times d_s)) \tag{3.27}$$

Where B_w and B_a are the molecular diffusivities in water and air, whose values are, as in Jury et al., 1984[54], 1.8×10^{-6} and 1.8×10^{-2} $[m^2\ h^{-1}]$, respectively, taking into account the tortuosity[8] of the porous medium. V_{sl} and v_{sa} are the volume fractions of liquid water and air in the snow pack and d_s is the snow depth $[m]$. The equilibrium fugacity f can be calculated as follows:

$$f = \frac{M_{sp}}{(Z_a \times V_a + Z_l \times V_l + z_i \times A_i)} \tag{3.28}$$

where A_i is the area of the snow/air interface, V_a the volume of interstitial air, V_l the volume of liquid water.

The loss due to ice melting is dependent on the variation in surface of the ice cap only.

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[6] The subcooled liquid state is the state of a pure organic compound in which the most stable state, at standard conditions, is a solid. Compounds which are standard state solids behave in the environment according to liquid state properties because of the absence of crystalline lattice energies for the compounds dispersed in environmental media.

[7] The value of 83.0 $kJ\ moles^{-1}$, in absence of other sources, has been used for $\alpha-$HCH as well.

[8] The tortuosity refers to the ratio of the diffusivity in the free space to the diffusivity in the porous medium.

No differential release [9] [85], [131], based on different solubility and lipophilicity of the substance, is considered. Other phenomena driven by physico-chemical properties, like repartitioning between phases, phenomena linked with physical changes of the snow-pack as well as translocation within the snow-pack (with vapour diffusion and temperature), are not considered to be significant [131] at the spatial scales involved, and therefore, neglected.

Atmosphere

The atmosphere compartment is the reservoir in which, due to the high efficiency of sinks as degradation and deposition, the compounds exhibit the shortest residence time and where the transport is the fastest and most efficient.

With respect to the distribution of semivolatile organics, it is considered as a three phase system, encompassing a bulk gaseous phase, liquid water, and atmospheric organics.

The SOCs total concentration change per unit of time and space can be described as:

$$\frac{dc_{atm}}{dt} = (\frac{\partial c}{\partial t})_{App} + (\frac{\partial c}{\partial t})_{V} - (\frac{\partial c}{\partial t})_{De} - (\frac{\partial c}{\partial t})_{D} \pm (\frac{\partial c}{\partial t})_{A} \pm (\frac{\partial c}{\partial t})_{Di} \qquad (3.29)$$

Agrochemicals enter the atmosphere via releases as direct agricultural application (App) and volatilise (V) from terrestrial compartments, ocean and sea-ice. According to environmental conditions and to substances' properties, phase changes occur. In the atmosphere transport (A) and diffusion (Di) determine spatial relocation and ultimately regional to global long-range transport (Wania and Mackay, 1993[133], Klečka et al., 2000[57]). Sinks for the compartment are dry and wet deposition (De) of the compounds in each phase and degradation (D).

The AGCM ECHAM5

ECHAM5 (Roeckner et al., 2003[93]) is the most recent version of the atmospheric general circulation model (AGCM) ECHAM. The model version used here is formulated in spherical harmonics with a horizontal resolution T42 (2.8° × 2.8°) and 19 hybrid σ-pressure levels, up to 10 hPa in the vertical dimension. Prognostic variables are vorticity, divergence, surface pressure, temperature, water vapour, cloud water, cloud ice, cloud droplets and ice crystal number concentration. The advection of water vapour, cloud water and tracers (including the SOCs) is described by a semi-Lagrangian transport scheme (Lin and Rood, 1996[70]). Physical parameterisations include radiation, cloud convection and microphysics, planetary boundary layer dynamics, land surface processes, horizontal diffusion and gravity wave drag. In this setup, the AGCM encompasses as well a simple chemistry scheme (Feichter et al., 1996[28]) and the dynamical aerosol model HAM (Hamburg Aerosol Model, Stier et al., 2005[113]). This latter component describes the

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[9] When the snow melts, the more water soluble compounds like the HCHs are generally released with the first fraction: the *firstflush* effect. The remaining snow pack then becomes enriched in the less soluble ones, like DDT or PCBs, generally associated with the last melt fraction, containing organic phases (leading to a pulse-like spring release).

atmospheric aerosol dynamically by the superposition of seven log-normal size distributions. The seven modes are in turn divided into four geometrical size classes and consider 5 species, i.e. sulfate, black carbon, particulate organic matter, sea salt and mineral dust. The time step corresponding to the resolution employed in this study is 30 minutes.

Gas-particle partitioning

The gas-particle phase transition can occur via adsorption on aerosol surfaces and absorption into organic matrices, according to the substance properties. The ratio between the gas phase and the particle-bound compound is considered in this study as a result of absorption and described following an empirically derived regression (Finizio et al., 1997[29], Harner and Bidleman, 1998[38]).
The dependence on the octanol/air partitioning coefficient, K_{oa} is expressed as:

$$\log(K_p) = 0.55 \times \log(K_{oa}) - 8.23 \tag{3.30}$$

where K_p is the particle-gas partitioning coefficient $[m^3\ \mu g^{-1}]$ used to estimate the fraction of a compound bound to aerosol particles, θ, as follows:

$$\theta = \frac{1}{\frac{1}{k_p \times c_{tsm}} + 1} \tag{3.31}$$

where c_{tsm} in $[\mu g\ m^{-3}]$ is the concentration of total suspended matter, the sum of the 5 species described by HAM.

Degradation in air

Abiotic chemical transformation is another sink for SOCs in the atmosphere. The compounds in all phases react with atmospheric radicals as $OH^{\cdot}$ during daytime and $NO_3^{\cdot}$ during nighttime (Roelofs, 1997[95]). The degradation is described as:

$$\frac{\partial c_{SOC}}{\partial t} = k_{OH} \times c_{OH} \times c_{SOC} \tag{3.32}$$

for the hydroxyl induced decay and as

$$\frac{\partial c_{SOC}}{\partial t} = k_{NO_3} \times c_{NO_3} \times c_{SOC} \tag{3.33}$$

for the nitrate induced decay. The rates $[s^{-1}]$ are based on prescribed temporally and spatially resolved radical concentration. k_{OH} and k_{NO_3} are temperature dependent.

Deposition

The deposition of semivolatile organic compounds onto the surface occurs via dry and wet deposition of the substance as a gas or bound to particles.
The deposition velocities of the species in gas phase follow in the model the 'big leaf' approach (e.g. Hicks et al., 1987[43]) considering a series of resistances (Ganzeveld and Lelieveld, 1995[30]) for the turbulent transport to the Earth's surface, the molecular

diffusion through the quasi-laminar boundary layer and the surface absorption efficiency.

The particle deposition is calculated as a function of the simulated aerosol properties as particle radius and density (Ganzeveld et al., 1998[31]). The downward flux of the tracers is then subtracted from the emission flux and provides the lower boundary conditions for the vertical diffusion scheme of ECHAM5. The wet deposition is calculated differentiating between stratiform and convective clouds. For gases the fraction dissolved in cloud water is estimated based on Henry's law (e.g. Seinfeld and Pandis, 1998[105]).

Soil

Soil is a multiphase compartment containing solid matter (bulk phase) and air as well as water trapped in the porous soil matrix. Compounds diffuse in air and water and sorb to soil particles [92]. In this compartment, recipient of directly applied agrochemicals (*App*) and of deposition (*D*) from the atmosphere, the mass budget can be described as:

$$\frac{dc_{soil}}{dt} = (\frac{\partial c}{\partial t})_{App} + (\frac{\partial c}{\partial t})_{D} - (\frac{\partial c}{\partial t})_{V} - (\frac{\partial c}{\partial t})_{De} \tag{3.34}$$

Sinks are temperature dependent volatilisation (V) from the soil top layer, and degradation (De) within the soil. No runoff is considered. The soil hydrology is described in ECHAM5 as a bucket model (Roeckner et al., 1996[94]).

In the following paragraphs the processes affecting SOCs in the soil compartment are described.

Phase equilibria in the soil

In the soil compartment the behaviour of SOCs is described by temperature driven equilibria between the substances in organic matter, interstitial air and pore water. The total concentration $[kg\ m^{-3}]$ of chemical in the soil matrix can be expressed (Smit et al., 1997[111]) as a function of the concentration in gas-phase $[kg\ m^{-3}]$ as follows:

$$c_{soil} = Q \times c_{gas} \tag{3.35}$$

with Q, the capacity factor,a function of substance and soil properties and defined as:

$$Q = \theta_g + \theta_l \times K_{l/g} + \rho_{soil} \times K_{l/g} \times K_{s/l} \tag{3.36}$$

$K_{l/g} = \frac{c_l}{c_g}$ is the dimensionless water-gas partitioning coefficient, $K_{s/l} = \frac{c_s}{c_l}$ the soil-water partitioning coefficient $[m^3\ kg^{-1}]$ and describes adsorption following a linear isotherm. ρ_{soil} $[kg\ m^{-3}]$ is the soil dry bulk density and the θ terms express the volume fractions of gas θ_g and moisture θ_l in the compartment. $K_{s/l}$ is function of the organic matter sorption coefficient K_{om} $[kg\ l^{-1}]$ and of the organic matter content of the soil om as follows:

$$K_{s/l} = K_{om} \times c_{om} \tag{3.37}$$

The fraction of the total concentration of the compound in gas phase is then:

$$F_g = \frac{\theta_g}{Q} \tag{3.38}$$

Degradation in soil

Biological and chemical degradation in soils is described as a first order process. The degradation doubles per 10 K increase of temperature according to recommendations ([121]) following:

$$\frac{\partial c}{\partial t} = k_{soil} \times c_{soil} \tag{3.39}$$

where:

$$k_{soil(T)} = k_{soil} \times 2^{\frac{T-T_{ref}}{10}} \tag{3.40}$$

Volatilisation from soil

The volatilisation of applied pesticides from the soil is a key process in SOCs cycling. It makes the compounds available for long-range transport [57]. The process depends on the properties of the compound (vapour pressure, water solubility, sorption coefficient, Tab.2.1), on characteristics of the reservoir, namely density, roughness and water content and on conditions at the interface (soil surface), like the temperature (in turn affecting the vapour pressure).

Close to a solid surface there is insignificant vertical movement of air. Vaporised SOCs are transported away from the surface through this stagnant air boundary layer only by diffusion. The mass transfer rate is related to the diffusion coefficient and to the vapour pressure of the compound at the surface. Outside the surface-air boundary layer, the flow into the overlying atmosphere is turbulent, and dispersal of a vapour into the atmosphere can be described by eddy diffusion coefficients. The depth of the turbulent zone is several orders of magnitude larger than the stagnant layer, and the difference between the two diffusion coefficients is also very pronounced, so that the time scale of turbulent transfer is much smaller.

Volatilisation from soil is described empirically in the model in terms of CV, cumulative volatilisation, based on experiments on agrochemicals behaviour in the greenhouse and in the field (Smit et al., 1997[111]):

$$CV = 71.9 + 11.6 \times \log(100 \times F_g) \tag{3.41}$$

for normal to moist conditions. For dry field conditions,

$$CV_{dry} = 42.3 + 9.0 \times \log(100 \times F_g) \tag{3.42}$$

with F_g as the fraction of the total concentration of the compound in gas phase. For values of the gas fraction of the total amount in the soil reservoir:

$$F_g >= 1.9955 \times 10^{-7} \tag{3.43}$$

The parameterisation aims to capture all contributions to volatilisation. The effect of temperature on vapour pressure is calculated according to the Clausius-Clapeyron equation.

Vegetation

The vegetation is recipient of direct application (Appl) and atmospheric deposition (D). Once deposited, compounds can be taken up via the stomata, or sorbe to the cuticula [125], [124]. According to their properties, and on vegetation characteristics (as plant type, phenology) and local conditions, they will be stored, degraded (De), or released back to the atmosphere (V).

$$\frac{dc_{vegetation}}{dt} = (\frac{\partial c}{\partial t})_{App} + (\frac{\partial c}{\partial t})_D - (\frac{\partial c}{\partial t})_V - (\frac{\partial c}{\partial t})_{De} \tag{3.44}$$

The vegetation compartment is described in the model as a two-dimensional surface layer (expressed in terms of leaf area index), without an explicit compartmental volume. As in the case of soil, no intracompartmental mass exchange takes place in the vegetation compartment, unlike in the case of the sea-ice (Section 3).

Degradation in vegetation

Similar to previous studies [107] [108] [106], the degradation is described, as in assuming the same rate coefficient k_{soil} [3.39] [s^{-1}] as for the soil compartment.

$$\frac{\partial c}{\partial t} = k_{soil} \times c_{vegetation} \tag{3.45}$$

where:

$$k_{soil(T)} = k_{soil} \times 2^{\frac{T-T_{ref}}{10}} \tag{3.46}$$

Volatilisation from vegetation

As in the case of the soil compartment, volatilisation from vegetation is strongly related to the physico-chemical properties of the compound, to the type of substrate from which it occurs and to local conditions.
In the model it is described as CV, cumulative volatilisation, function of the vapour pressure of the compound P, following an empirical relationship derived from many studies of pesticide volatilisation (Smit et al.,1998[110]):

$$CV = 10^{1.528+0.466\times\log(P)} \tag{3.47}$$

for values of $P \geq 5.2655 \times 10^{-7}$.

Chapter 4

Cycling of HCH and DDT in the Global Ocean

The ocean is an important reservoir for many anthropogenic compounds.
Not only water contaminants fed through riverine sources reach the ocean: through atmospheric transport and deposition, also semivolatile substances accumulate in the ocean.
Due to its size and nature, it is also the compartment where final accumulation of water soluble and even insoluble persistent compounds occurs [104].
The oceanic transport obviously contributes to long-range transport. The extent of this contribution is, however, unknown.

In order to investigate the role of the compartment for semivolatile organic compounds, a three-dimensional modelling approach is appropriate.

In the following paragraphs the effects of the three-dimensional ocean on the dynamics of semivolatile organic compounds are presented. At first, a comparison with a pre-existing model approach is performed, then the partitioning to organics and its effects are investigated. Finally, the ocean transport is studied with a specific experiment.

Preliminary comparison with a two-dimensional ocean approach

In order to assess the influence of three-dimensional dynamics in the ocean on the fate of SOCs, and therewith to introduce the peculiarities of the novel approach introduced in this study, results obtained with the model setup described in Chapter 3 have been compared to the outcome of the nearest modelling approach (in terms of tool used, investigation focus and substances studied) documented in literature, i.e. of a model based on the same atmospheric GCM, but with a simplified two-dimensional ocean representation (Semeena and Lammel, 2006[106]).

Model setup and simulation scenario

The setups used for this experiment only differ in the description of the ocean compartment (cf. Tab.4.1). The common model core is based on the atmospheric GCM ECHAM5 including the aerosol submodel HAM, and encompasses as well a representation of soil and vegetation.

The model approach described in Chapter 3, in which the MPI-OM-HAMOCC5 model is used as a subsystem, is, from now onward, referred to as the 3DO model. For this comparison the sea-ice submodel is not considered.

features	2D ocean	3D ocean
horizontal transport	-	x
vertical resolution	-	x
vertical transport	-[a]	x
partitioning to organic matter	-	x
degradation in sediments	-	x[b]
sea-ice	-	-[c]

Table 4.1: Processes present (x) or absent (-) in the two approaches for ocean representation

[a] Although an explicit representation of vertical transport and sinking associated with suspended matter is not present in the 2D ocean approach used for the comparison, vertical export is parameterised as a function of a mixed layer depth obtained from an OGCM.

[b] Results show, however, that the contribution of this process to the ocean and total budget of compounds is extremely small.

[c] For the sake of comparison, not considered in this experiment.

The outcome of experiments performed with this 3DO model is compared to the results of a previous study (Semeena and Lammel, 2006[106]), for which the 3DO represents a natural evolution, when the aim is to study compounds either water soluble or persistent in ocean. In the study used for comparison, the ocean compartment is represented by a well mixed surface layer, varying in depth in space and time (with minima in February for the Northern Hemisphere and in September for the Southern Hemisphere). The information about the surface layer depth were, in turn, (offline) obtained from a 3D ocean general circulation model (Drijfhout et al., 1996[24]). Such ocean representation does not include horizontal advection, whereas the vertical export of compounds to the deep sea is represented only as a consequence of seasonal variation of the mixed layer depth. This sinking is considered to be a final loss for the compartment. Furthermore, no ocean biogeochemistry, hence no liquid-solid partitioning, is considered.

The described simpler setup is in this work referred to as the 2DO model. A schematic description of the two model setups is to be found in Chapter 3.

For this comparison experiment, the two model systems, 3DO and 2DO, sharing the same T42 resolution, have been run for 10 years with agricultural applications for the compounds[1] γ-hexachlorocyclohexane (lindane) and DDT[2].

Application data for agrochemicals

γ-HCH and DDT have been extensively used in the 1980's as agrochemicals and to control malaria vectors. The global application data (Semeena and Lammel, 2003[107]), shown in Fig. 4.1, used in this study consist of agricultural applications of the compounds, in different pesticide formulations, for the year 1980. The data are based on statistical estimates of FAO (1947-1990) and on publications and inventories (FAO, 1988[26], 1989[27], Pacyna et al., 1999[88], for some European countries). The data relative to each country's consumption are distributed over the model grid according to the relative cropland distribution (1° × 1° Li, 1999[67]).
The applications of DDT were mainly in Europe and Asia, due to restrictions in other countries (among them, USA, Canada, Brazil), whereas lindane was also applied in Africa and South America, adding up to about 19820 *tonnes* per year for γ-HCH and 9000 for DDT, globally.

In all model runs the application patterns and fluxes do not vary seasonally, nor interannually and the compounds are applied on vegetation (80%) and soil (20%). No direct emission to the atmosphere, i.e. no loss from the applications, is considered.

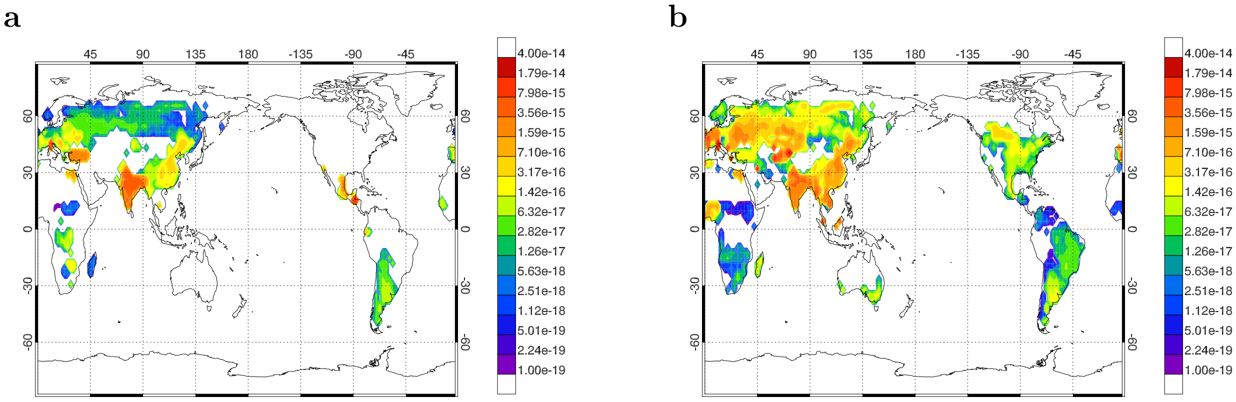

Figure 4.1: Global DDT (a) and γ-HCH (b) agricultural application $[kg\ m^{-2}\ s^{-1}]$.

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[1] Introduced in Chapter2.

[2] The acronym DDT stands for *dichlorodiphenyltrichloroethane* or $1,1,1-trichloro-2,2-di(p-chlorophenyl)-ethane$.

Results

Structural and dynamical differences in the two model formulations would project onto the results of their comparison, affecting the multicompartmental cycling. Therefore, spatial and temporal differences in the compartmental burdens and in the fluxes between them are to be expected in the 10 year runs.

Ocean representation

The way the ocean dynamics is described can crucially influence the cycling of SOCs in the environment. The assumption of well mixed surface waters, as recently underlined by Jurado et al., 2007[53], is not always fulfilled, with implications on fate and transport of SOCs. In Fig.4.2 the ocean burden gradients for 2DO and 3DO show the differences in mass distribution (average over 10 years). In the 2DO (4.2a), the mass in the ocean mirrors a typical depositional pattern. The absence of resolved ocean circulation generates a non-realistic representation of the equatorial and tropical concentration gradients, lacking latitudinal mixing and equatorial divergence features. As a consequence, also the spatial pattern of related processes (gaseous air-sea exchange) are affected when transport in the ocean is considered. In the bidimensional ocean, the amount of substance which may, in principle, volatilise is, in fact, the total burden within the (climatological) mixed layer, as the whole burden were stored at the water-air interface, even in the case of a mixed layer hundreds of metres deep. This may lead to an overestimate of the fluxes. In the 3DO the surface layer is about 20 metres thick, exchanging dynamically with the rest of the water via turbulent mixing. Furthermore, corrections the air-sea exchange parameterisation determine more realistic gradients, as observable within the tropics, where the wide minimum mirrors the ocean temperature distribution. Due to these differences, and taking into account further technical adjustments related to the evolution of the atmospheric model (from ECHAM5.2 to ECHAM5.3), only a comparison in terms of general multicompartmental cycling and residence times is possible.

Compartmental distribution and persistence

Applications distribute the compounds on soil and vegetation. Upon volatilisation to the atmosphere the compounds start their multicompartmental cycling. The distribution between different media is governed by the tendency to establish thermodynamic partitioning equilibria.

The compartmental distribution and related residence times, for the 10^{th} year of simulation, are presented in Tab. 4.
It should be anyway considered that the figures shown for the 2D ocean model setup do not take into account the amount of substance which might have sunk below the mixed layer (this sink can account, on spatial average, for up to 50% per month of the global ocean burden). A higher share of the total burden is therefore to be expected in the 3DO ocean.

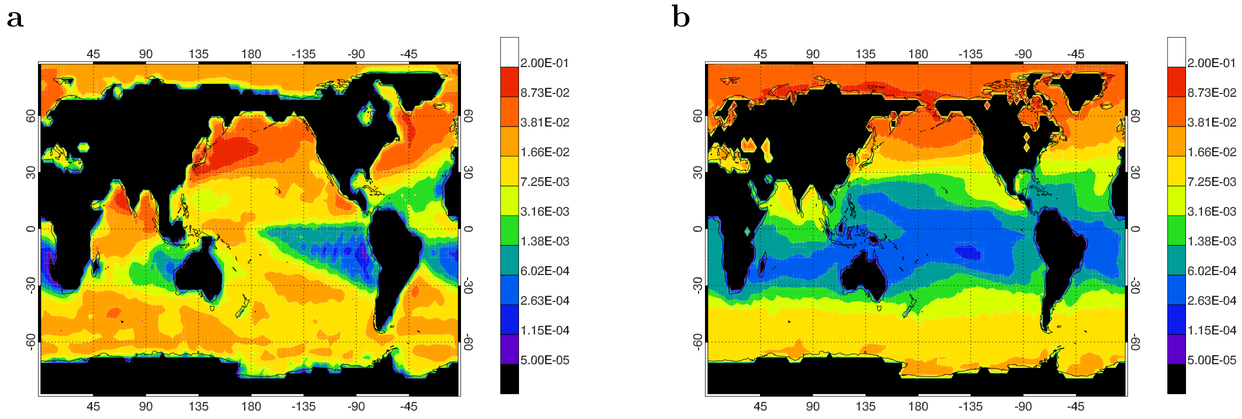

Figure 4.2: Concentration gradients in the surface layer as fraction [%] of the total burden. Average over 10 years. 2DO (a) and 3DO (b) approaches for DDT.

compound	compartment	2D ocean		3D ocean	
		m_i/m_{total}	$\tau(a)$	m_i/m_{total}	$\tau(a)$
DDT	ocean	12%	0.40	27%	1.48
	soil	51%	1.43	52%	3.09
	vegetation	32%	0.39	20%	0.63
	atmosphere	5%	0.05	1%	0.03
γ-HCH	ocean	42%	0.79	35%	1.60
	soil	42%	0.58	52%	1.07
	vegetation	9%	0.07	9%	0.10
	atmosphere	7.5%	0.05	4%	0.04

Table 4.2: Compartmental mass fractions, m_i/m_{total} [%] and residence times [a]. Averages of the 10th year of simulation)

A first glance at the table enables to notice some features common to both setups. For both compounds, the compartment holding the highest burden is the soil. Then, in case of γ-HCH, the ocean follows, storing different fractions for the two ocean representations. In the 2DO, after 10 years, ocean and soil bear each 42% of the total environmental burden. For the compound DDT in the 2DO, differently from the 3DO and from the correspond-

ing figures obtained for γ-HCH, the vegetation is holding the highest mass after the soil, i.e. in the ocean compartment only 12% of total mass is stored. In the three-dimensional approach, the figure for the storage in ocean are, in proportion, higher.
In terms of persistence, we observe, except for the atmosphere, higher residence time τ when the three-dimensional ocean is used. The overall residence time, τ_{ov}, has been estimated for DDT as 1.33 (2DO) and 2.13 (3DO) years, and for γ-HCH as 0.79 (2DO) and 1.13 (3DO) years.

Discussion

As the mass balance is closed (all sinks are budgeted) in the 3DO, it is expected (and observed) that the compounds stay longer in the system, having generally a higher residence time everywhere. The only exception, the higher τ calculated for the atmosphere in the two-dimensional approach for both compounds, is a technical consequence of the transition from the preexisting setup to the new one, which involved an optimisation of the scavenging processes, determining, in turn, more realistic and slightly shorter turnover times for this compartment.

As the numbers shown in Table 4 provide a picture of the state of the system after ten years, the notion of the absolute sources and sinks and of the exchanges between the compartments and, in particular, of the approach to steady state conditions of the burdens (not shown here[3]) can offer insight to the evolution of the cycling and thus to the past, present and future role of the reservoirs. Based on difference in the model setup, the most interesting compartment is undoubtedly the ocean. For DDT, at the end of the simulation, the 2DO ocean appears approaching steady state conditions (not budgeting the amount lost to the deep sea), whereas, when the complete three-dimensional dynamics is described, the compartment is still steeply accumulating mass. In this case, the fraction in the ocean is then meant to increase in time, determining an increase in the residence time, or characteristic time, of DDT in the reservoir and in the total environment.
For γ-HCH, in both 2DO and 3DO, and due to the degradation, which inhibits the persistence in water (in comparison with DDT), the ocean is close to have the sinks balance the sources at the end of the simulation. The higher values for the 3DO can be related to the fact that, in a fully dynamic ocean, transport towards colder latitudes causes a reduced volatilisation from sea-water and a slower degradation [127], thus enhancing the residence time in the compartment.
As studies based on downwards flux measurements (cf. Dachs et al., 1996[21] and Gustafsson et al., 1997[34]) stress the importance of sinking associated with particles for lipophilic compounds, and as this might determine an enhancement of the retention capacity of the ocean (cf. Dachs et al., 1999[22]), i.e. of the residence time of the compounds in the compartment, the results show a higher persistence estimate for DDT for the 3DO setup. The 3DO simulates dynamical processes as upwelling (for instance at the equator) and overturning. The latter, due to its long time scales [117] can be particularly significant

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[3] For the compartmental distributions obtained with the 2DO setup, cf. Semeena et al. 2006[106], for the 3DO setup, please refer to Chapter 5.

for very persistent compounds, as DDT. The compound can, therefore, never be considered 'lost' from the model system (unless degradation in sediments, accounting anyway only for $10^{-2}\%$ of the ocean budget, takes place). Once the SOCs are transported to the uppermost layers of the ocean, they would be again available for cycling. In the long scale (several decades, not considered in this study), the compartmental distribution is expected to be influenced by that.

Partitioning and vertical export

DDT and γ-HCH are, to a different extent, lipophilic, i.e. partitioning equilibria determine their distribution in the ocean between the bulk dissolved water phase and suspended and colloidal organic phases (cf. Chapter 2).
In the ocean, physical factors (wind induced mixing and light availability) bear an influence on biological factors (production) and, hence, on the abundance of organic phases, in turn affecting the fate of semivolatile organics.
When bound to suspended organic matter, the compounds are subject to gravitational settling in the water column (Dachs et al., 1996[21], 1999[22], 2002[23]). Therefore, a typical ocean vertical profile of a very lipophilic SOCs would exhibit a different vertical distribution from the one of the extensive investigated ocean passive tracers like CFCs[4] [91], due to the superposition of the particle-bound sinking and of the dynamics-induced vertical export. The difference will be proportional to the content in suspended organic matter. At least for large time scales and for sea regions with high suspended organic matter loads.

It is key for the understanding of substance cycling to investigate the efficiency of the partitioning and of the particle-bound sinking of SOCs.

The distribution of organic phases (zooplankton, phytoplankton, colloidal particles of humic substances or other detritus, fecal pellets), hence of partitioning substrates, is very inhomogeneous in the global ocean. The biological production exhibits differences between regions along the equator or close to coasts (where the waters are enriched in nutrients by local phenomena as upwelling and/or riverine inflow) and oligotrophic areas, for instance, in the middle of a subtropical gyre [83].
Therefore, a spatially heterogeneous influence on the geographical distribution of lipophilic compounds and their gravitational settling associated with suspended particulate matter (likely to be higher in high productivity areas) is expected.

Together with the transport associated with deep water formation areas [73], sinking of particles is responsible for vertical export of SOCs below the mixed layer.

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[4] Chlorofluorocarbons (CFCs) are compounds containing chlorine and fluorine, fairly water soluble and resistant to degradation, extensively studied because of their contribution to stratospheric ozone depletion and global warming. CFCs enter the surface ocean via gas exchange and, passively subject to transport by currents and mixing processes, are used as transient tracers in order to provide information on the ocean circulation and its variability.

The mixed layer depth (in the model function of pressure and stability) determines the supply of nutrients into the euphotic zone, where the availability of sunlight allows primary production. In temperate and polar waters convection of cooled surface waters and wind induced turbulence cause, in winter, a deepening of the mixed layer and a migration of nutrients into the euphotic zone and of phytoplankton cells out of it, hindering photosynthesis. In spring the surface warming triggers the opposite process, the mixed layer becomes shallower, leading to a great burst of phytoplankton activity (spring bloom). Phytoplankton is then grazed by zooplankton. In tropical and subtropical waters (covering more than a half of the world's ocean) the vertical structure is all year long similar to the late summer structure observed in temperate zones. The water column is clearly divided into a warmer less dense upper stirred layer and a cooler heavier lower layer, separated by a sharp pycnocline.A typical exception to this structure is the equatorial upwelling zone: major ocean currents cause upwelling and divergence of large volumes of water rich in nutrients from below the thermocline [83]. In any case, dead phytoplankton and zooplankton and fecal pellets are subject to gravitational settling below the mixed layer.

Once having left the mixed layer bound to sinking organic phases, the compounds are not anymore subject to revolatilisation to the atmosphere and, therefore, tend to accumulate (depending on persistence in ocean) in the deep ocean unless upwelling or overturning take place.
The vertical export, contributing also to the different transport efficiency of the ocean in comparison to the atmosphere, may not only limit the long-range transport, but can represent a major sink for very persistent SOCs at global scale, because, at least in the open ocean, sediments are considered to provide final sinks the total environmental system.

Several studies [23], [13], [132], [99] have been conducted, following different approaches, in order to determine the role of biogeochemical processes and related fluxes on the global dynamics of compounds such as PCBs[5], PCDDs and PCDFs[6]. Dachs and colleagues, 2002[23] estimated the highest downward fluxes at mid-high latitudes. Other studies of Axelman and Gustafsson, 2002[13], Wania and Daly, 2002[132], Scheringer et al., 2004[99] underlined the significance of the process. The efficiency of gravitational settling could determine the rate of concentration decline after the phasing-out of the use of lipophilic anthropogenic compounds [127]. No such studies have been conducted so far for DDT and HCHs.

Another important aspect in the ocean dynamics of semivolatile organic compounds is the

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[5] Polychlorinated biphenyls (PCBs) are a class of organic compounds of generally low water solubility and low vapour pressure. They are soluble in most organic solvents, oils, and fats. PCBs are very stable compounds and do not degrade easily. They are classified as persistent organic pollutants.

[6] Polychlorinated dibenzodioxins (PCDDs) and dibenzofuranes (PCDFs) are chlorinated compounds generally referred to as dioxins in literature. They are byproducts of production of chemicals or originate from combustion reactions and to be found in all environmental compartments, ubiquitous distributed [14]. They are lipophilic and toxic.

vertical export of the compounds as given by the deep water formation in the Greenland and Norwegian Seas, Labrador Sea, Weddell Sea, Ross Sea and other areas. In a study by Lohmann et al., 2006[73], estimates of surface water concentration of PCBs and deep water formation rates are combined. The resulting removal fluxes are found to be higher in Norwegian, Labrador, Weddell and Ross Sea (ca. 870 $kg\ a^{-1}$) than the vertical export associated with settling of particles (ca. 320 $kg\ a^{-1}$) for the same regions.

Model setup and simulation scenario

The model setup for this experiment has been previously described as the 3DO.
The emission scenario, with agricultural applications, is analogous to the one used in the comparison experiment. The applications sum up to about 9000 *tonnes* per year for DDT and 19820 for γ-HCH globally. For this experiment as well, the model, after a 2 year long physical spin up, has been run for 10 years.

Results

The input flux to the ocean is provided by the atmospheric dry and wet deposition (in Fig.4.3 the sum of all deposition processes over the ocean). The resulting spatial pattern is a combination of emission distribution, atmospheric transport and precipitation distribution. As expected, based on the continuous emission scenario, the maxima are in the northern hemisphere.
In Fig.4.4 the 10 years average of the ocean burden in the total water column is shown. It is the sum of the mass of the compounds in the bulk water phase and bound to the organic phases as well, passively transported by ocean currents and sinking with gravity. The picture shows clearly that processes taking place in the ocean redistribute the deposited compounds, smoothing the sharp gradients of the mid-latitudes. In the southern hemisphere (which they reach quickly via atmospheric transport), the compounds tend to accumulate. The minima at the equator and tropics reflect the temperature driven volatilisation and, in the case of γ-HCH, the degradation, high at high temperatures, too.

In the following paragraph the partitioning to organics and its effects on the SOCs dynamics are presented. A study on the vertical export follows in the chapter.

Partitioning

In Fig.4.5, the distribution of the phases contributing to the vertical export of SOCs is heterogeneous. The distribution of such biogeochemical tracers is governed not only by physical factors such as light availability, mixing and transport, but also by biological and chemical processes. The main mechanisms have been introduced in Section 4.
The Southern Ocean and the high northern latitudes of the Atlantic have a deeper mixed layer in winter and, thus, nutrients are mixed to the surface. The warm season triggers the biological bloom in temperate zones in both hemispheres. In subtropical gyres the surface convergence causes downward flow (Ekman pumping) and the mixed layer depth

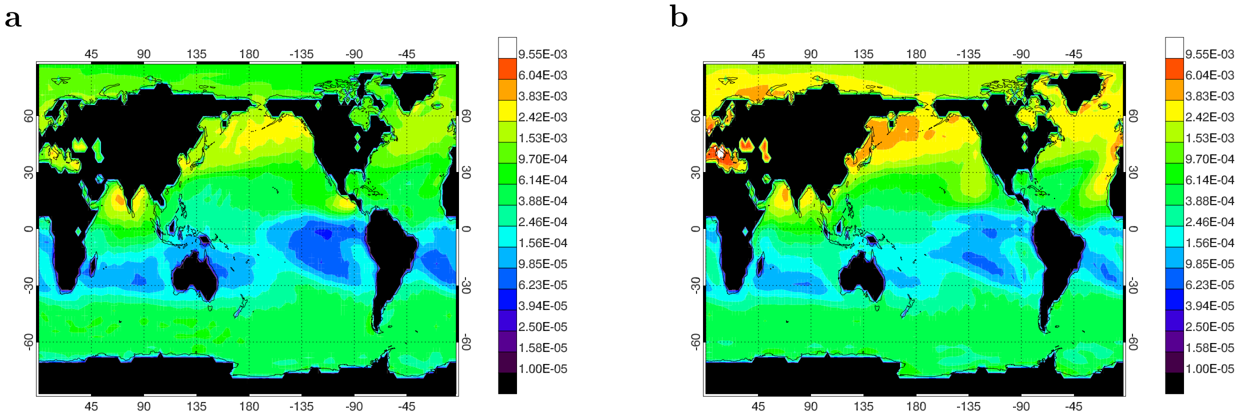

Figure 4.3: DDT (a) and γ-HCH (b) deposition [ngm^{-2}]. Average over 10 years.

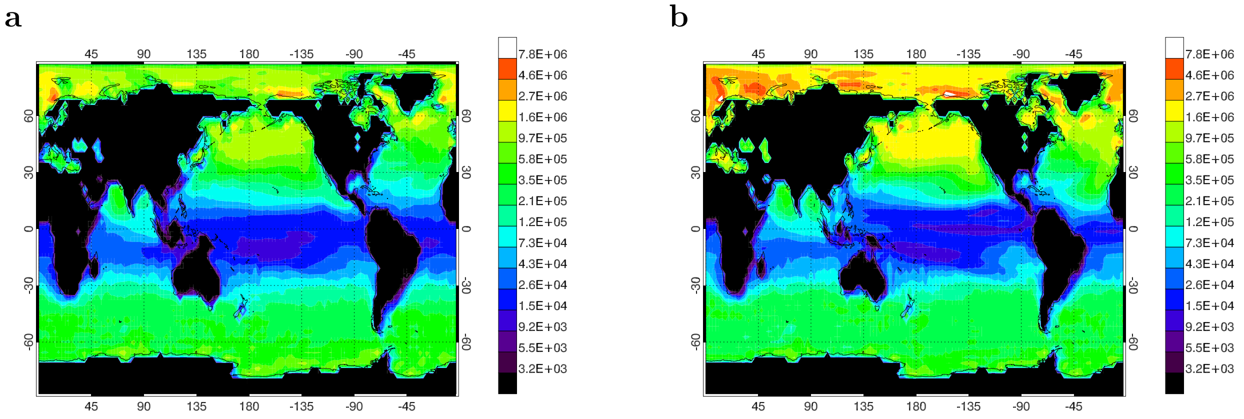

Figure 4.4: DDT (a) and γ-HCH (b) ocean burdens in the total column [$ng\ m^{-2}$]. Average over 10 years.

is low. Only a small amount of nutrients are mixed to the surface. This explains the minima in these regions. The flux of nutrients throughout the year provided by the wind driven upwelling explains the maxima in equatorial regions. As shelf processes are not captured and riverine input are not represented in this model setup, the high concentrations in coastal areas are not reproduced by the model[7].

The first three ocean model layers, 60 metres deep, can represent the processes occurring above the mixed layer (which, simulated, is in spatial and temporal average 60 metres deep), the euphotic zone, where the biological production occurs.
In Figures 4.6 and 4.7, the seasonal averages of vertically integrated concentration of DDT and γ-HCH [$ng\ m^{-2}$], over the uppermost 60 metres bound to the organic fraction (the

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[7] A study on vertical fluxes of particle-bound SOCs in the North Atlantic, Gustafsson et al., 1997[34] estimated that the area-integrated sinks for deep pelagic ocean are much more significant than the sinks in coastal and shelf waters.

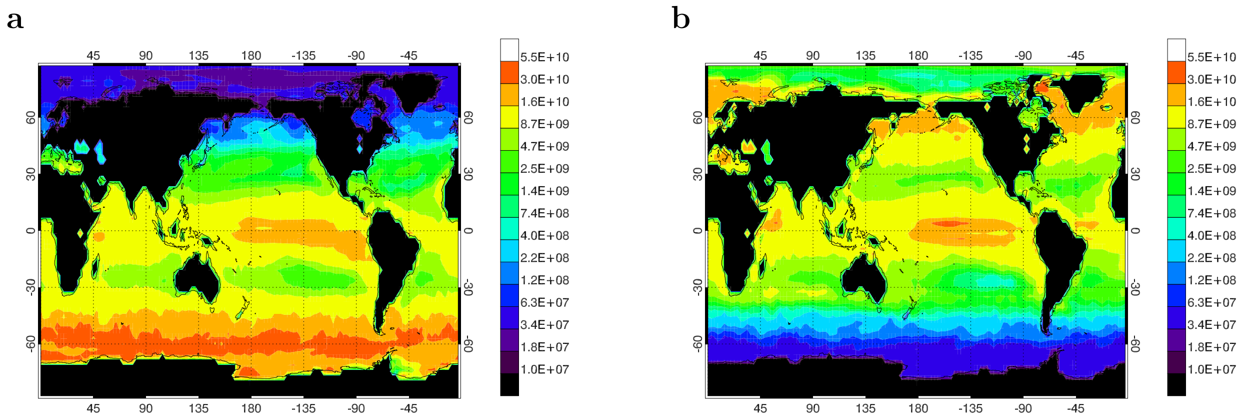

Figure 4.5: Simulated concentration of the organic phases in the ocean $[ng(C)\ m^{-2}]$, integrated over the uppermost $60m$: colloidal phases (phytoplankton, zooplankton), so-called dissolved organic carbon and particulate (sinking) matter (a: northern winter, b: northern summer)

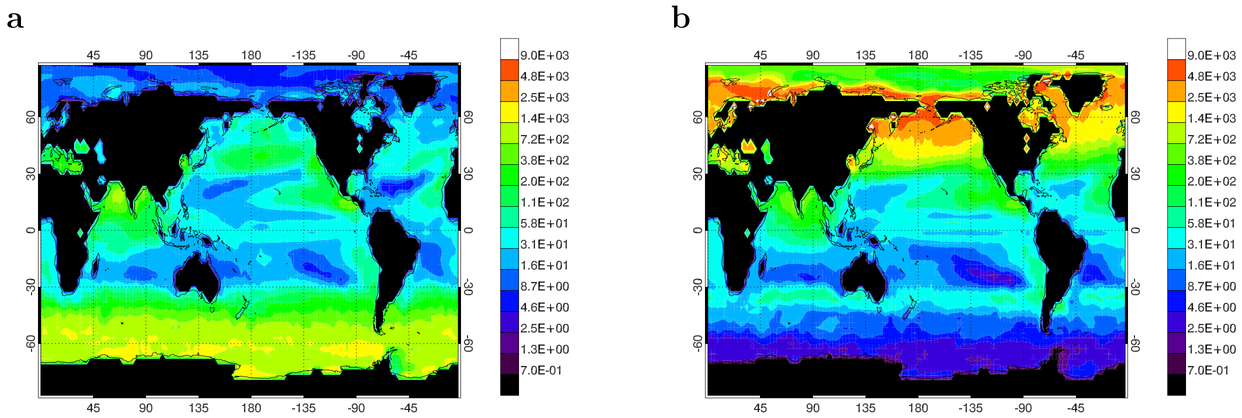

Figure 4.6: DDT in organic phases: seasonally averaged concentration integrated over the uppermost 60 metres $[ng\ m^{-2}]$ bound to the organic fraction in seawater (a: northern winter, b: northern summer). Average over 10 years.

sum of phytoplankton, zooplankton and dissolved and particulate carbon in seawater) is shown. The interpretation of the spatial distribution is not straightforward. All patterns shown result from the superposition of atmospheric deposition to the ocean (in Fig.4.3, continuously fueled by emissions in this scenario), ocean transport and distribution of the phases. The emissions are mostly located in the northern hemisphere. Temperature and wind (especially effectively in divergence areas) trigger massive volatilisation at the equator. As a consequence, the local maxima of the organic phases do not translate into high peaks of the pollutants distributed in organic phases as, on the other hand, occurs in the Southern ocean.

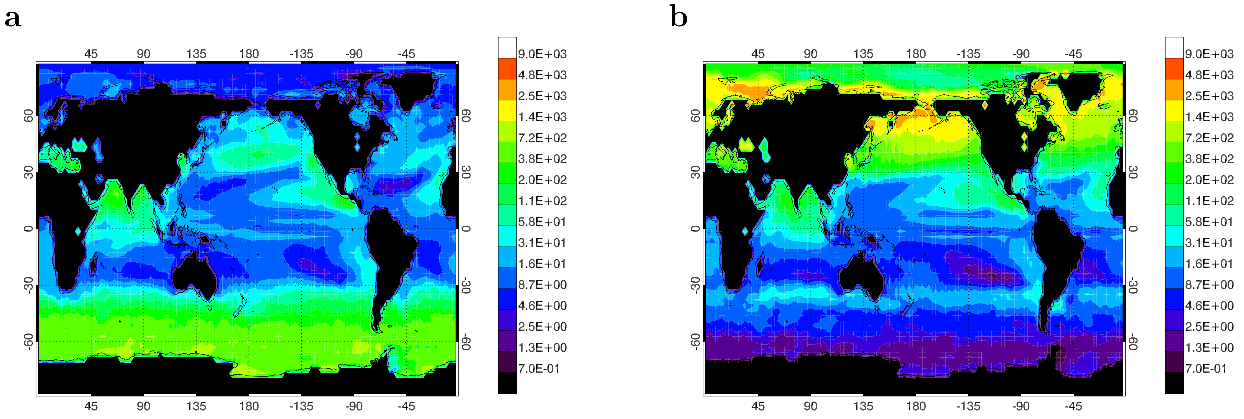

Figure 4.7: γ-HCH in organic phases: seasonally averaged concentration integrated over the uppermost 60 metres $[ng\ m^{-2}]$ bound to the organic fraction in seawater (a: northern winter, b: northern summer). Average over 10 years.

Due to the higher abundance of the colloids, i.e. species as phytoplankton, zooplankton and dissolved detritus, which are not sinking with gravity, among the partitioning substrates, the fraction of the compounds bound to organics is generally high where the colloids are abundant. The seasonality of the biological production determines the summer maxima in both hemispheres. The southern hemisphere holds a higher fraction in organic phases share, but a lower concentration, yet distributed over a wider area.

The spatial heterogeneity of the distribution of the phases translates into different degree of partitioning, as summarised in Table 4 for the first 20 metres in various sea regions. Within 20 metres the highest partitioning values are simulated, even in presence of maxima of organic phases below it.
The three-dimensional approach of this study allows to inspect differences in pattern along the longitude, generally not captured by other modelling approaches. The absolute maxima of partitioning are found at the equator and in the austral summer in the Southern ocean. Minima are found in the Arctic and in the subtropical gyres. Due to the higher abundance of organic substrates, higher fraction of compound bound to organic phases is generally predicted in the warm seasons.
The differences between the two compounds are striking. DDT bound to organics spans from 0.04% of the total amount in the Southern ocean in the production low season up to over 30% in the equatorial Pacific throughout the year. For γ-HCH, mostly in dissolved (aqueous) phase, the values are between 10^{-4} and 0.15%, again in the upwelling region. Fig.4.8 illustrates the time evolution of the global spatial average of the partitioning. For both compounds, as the highest contribution to the organic mass is provided by the non-sinking fraction (in Fig.4.5), the maxima are always reached within the first 20 metres and in northern spring, with only one secondary peak towards the end of the year.

	DDT	γ-HCH
Arctic ocean (85°N - 26°E)	3.6×10^{-2}-3.0	10^{-4}-8.0×10^{-3}
northern Atlantic (60°N - 329°E)	2.0×10^{-2}-19.4	4.0×10^{-4}-8.0×10^{-2}
temperate Atlantic (43.25°N - 326°E)	1.0-14.5	2.0×10^{-3}-4.0×10^{-2}
temperate Pacific (40.46°N - 197°E)	2.5-14.2	7.0×10^{-3}-4.0×10^{-2}
equatorial Pacific (0° - 202.5°E)	31-30	1.1×10^{-1}-1.5×10^{-3}
equatorial Atlantic (0° - 334.5°E)	18-19	8.0×10^{-2}-7.0×10^{-2}
Indian ocean (13°N - 64.5°E)	15-18	5.0×10^{-2}-6.0×10^{-2}
subtropical Pacific (29°S - 225°E)	5.7-1.2	1.5×10^{-2}-3.0×10^{-3}
Southern ocean (66°S - 180°E)	26-4.0×10^{-2}	1.3×10^{-1}-10^{-4}

Table 4.3: Fraction in organic phases [%] of the total pollutant concentration in seawater (northern winter, northern summer) in the uppermost 20 metres. Average over 10 years.

Effect of partitioning on volatilisation As shown in the previous paragraph, partitioning processes can be significant for the compounds in particular areas and seasons. The obvious consequence of the migration of the compounds from the bulk water phase into the organics is a reduction of the material ready to volatilise. The results of a comparison between the actual volatilisation and the amount evaporating in case of total absence of organic matter in the surface ocean, defined as potential volatilisation, are shown in in Fig.4.9. The dampening due to the partitioning is evident. Such an effect is clearly more pronounced for the more lipophilic compound, DDT, for which this reduction can reach up to 35%. It is most pronounced in southern latitudes between 30 and 60°S in winter, in the northern Pacific and Atlantic oceans in summer, the tropics (with maxima at the equator), the Pacific coast of Central America and the Indian ocean (Arabian sea, espe-

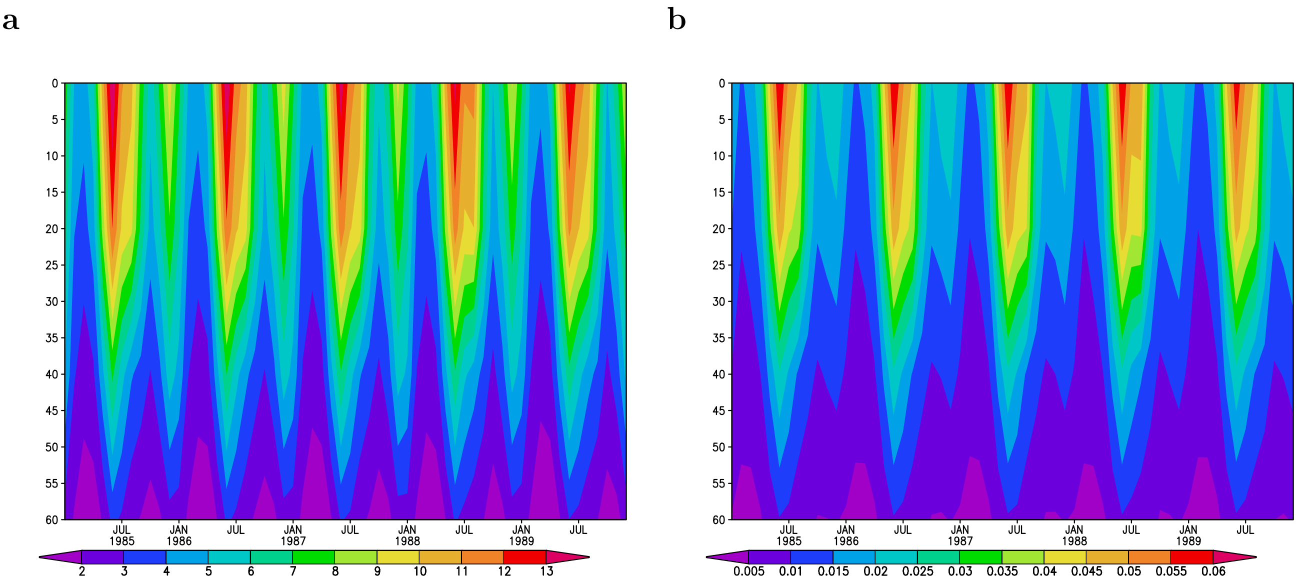

Figure 4.8: DDT and γ-HCH partitioning: partitioning to the total organic phases [%]. Time series (last five years of simulation) of the spatial average.

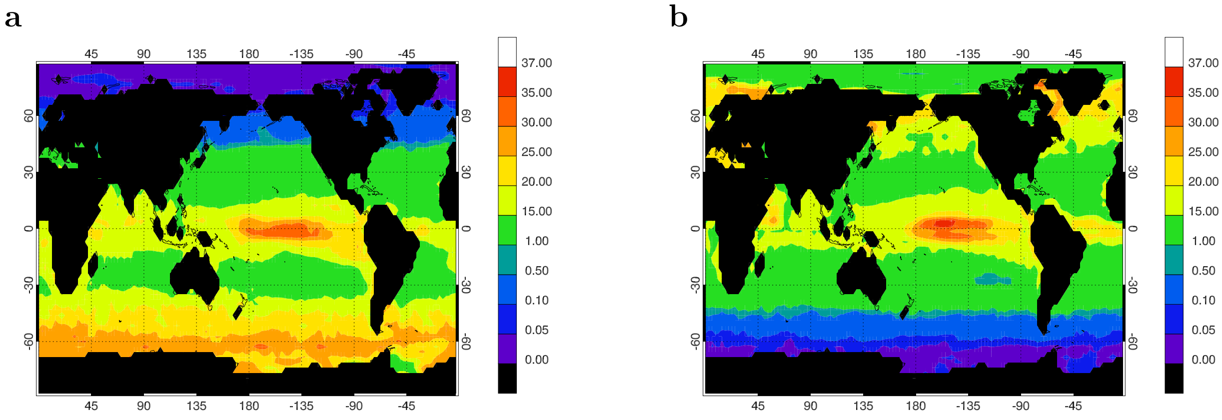

Figure 4.9: Effects of DDT phase partitioning on volatilisation [%] (a: northern winter, c: northern summer). Average over 10 years.

cially) throughout the year. In all these regions the actual volatilisation is reduced by at least 20% by the phase partitioning processes.In case of γ-HCH, less lipophilic compound, the dampening of volatilisation, not shown, is always less than 0.2%.

Vertical export

In order to study the sinking associated with particles, the concentration of particulate matter and of SOCs bound to phases subject to gravitational settling have to be considered.

The modelled geographical distribution of suspended detritus is shown in Fig.4.10. The organic mass subject to gravitational settling (with sinking velocity of $5m\ d^{-1}$) is a rela-

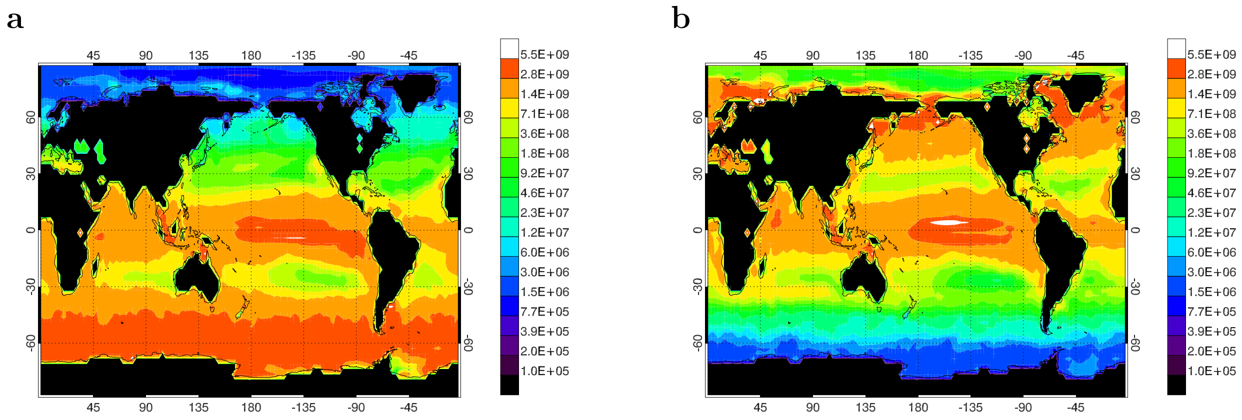

Figure 4.10: Simulated concentration of the organic phases in the ocean $[ng(C)\ m^{-2}]$, integrated over the uppermost $60m$: particulate (sinking) matter (a :northern winter, b: northern summer)

tively small fraction of the total organic mass in the ocean. It goes from approximately 3-5% (high latitudes in the cold season) to 16.5% at the equator. Thus, the fraction of compound partitioning to the sinking fraction is significantly, smaller than the total mass bound to organic phases. As the spatial distribution, shown in figures 4.11 and 4.12, part of the biological cycle of detritus, resembles the one of phytoplankton, zooplankton and colloidal detritus, the related migration to deep ocean is expected to occur where the maxima of particle sinking occur (not shown), where also, as stated previously, the volatilisation experienced the most significant dampening. Areas of most significant particle-bound sinking are then the northern high latitudes, the equatorial zone and tropics, the Southern ocean and the Indian ocean.

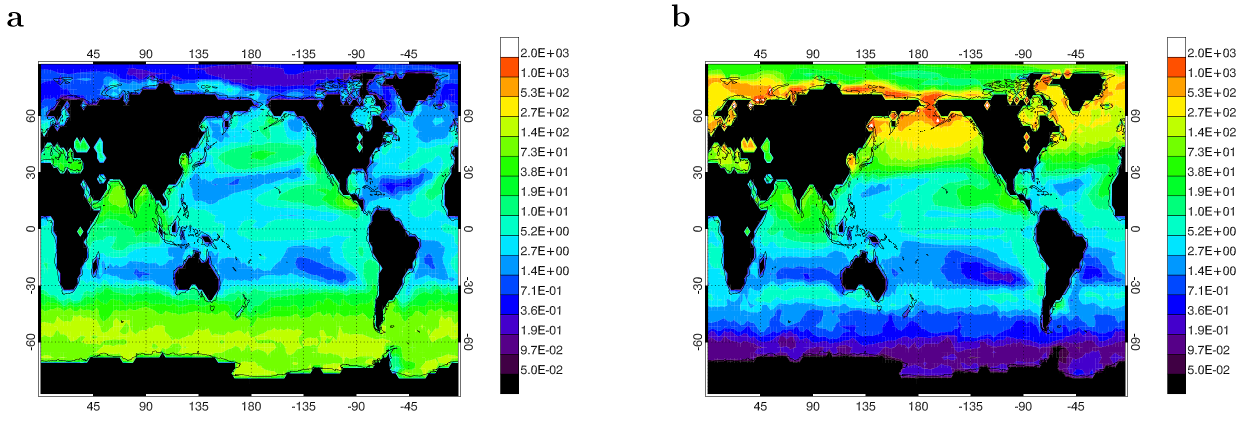

Figure 4.11: DDT partitioning: seasonally averaged concentration integrated over the uppermost 60 metres $[ng\ m^{-2}]$ bound to particulate (sinking) organic matter in seawater. (a: northern winter, b: northern summer)

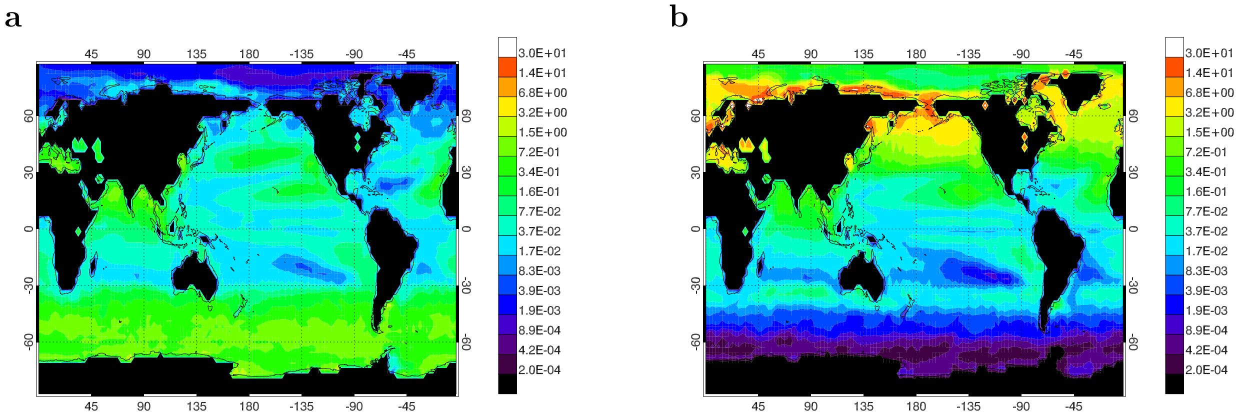

Figure 4.12: γ-HCH partitioning: seasonally averaged concentration integrated over the uppermost 60 metres [$ng\ m^{-2}$] bound to particulate (sinking) organic matter in seawater. (a: northern winter, b: northern summer)

In Fig.4.13, partitioning to organic matter is shown as a time series of monthly means, on a global spatial average. As in the case of the total organic matter in Fig.4.8, the DDT partitioned to sinking detritus is on global scale, dominated by the biogeochemistry of the northern hemisphere. Due to the very low values, 2% for DDT and only 0.008% for lindane, the maximum of the vertical distribution, beyond 20 metres, does not affect the vertical distribution of the total partitioning and, therefore, is not detectable in Fig.4.8.

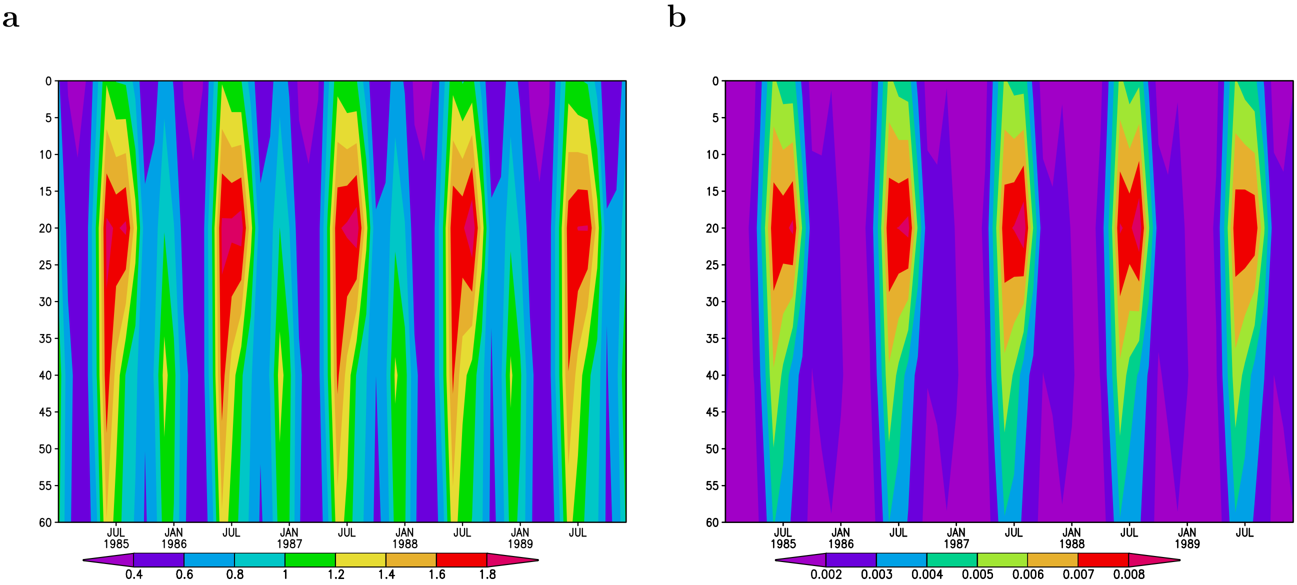

Figure 4.13: DDT and γ-HCH partitioning: partitioning to the sinking fraction [%]. Time series (last five years of simulation) of the spatial average.

This study focuses, in the following, on the influence of the ocean dynamics on vertical export. The fraction (Fig.4.15) below the simulated mixed layer, reaching 60 metres on

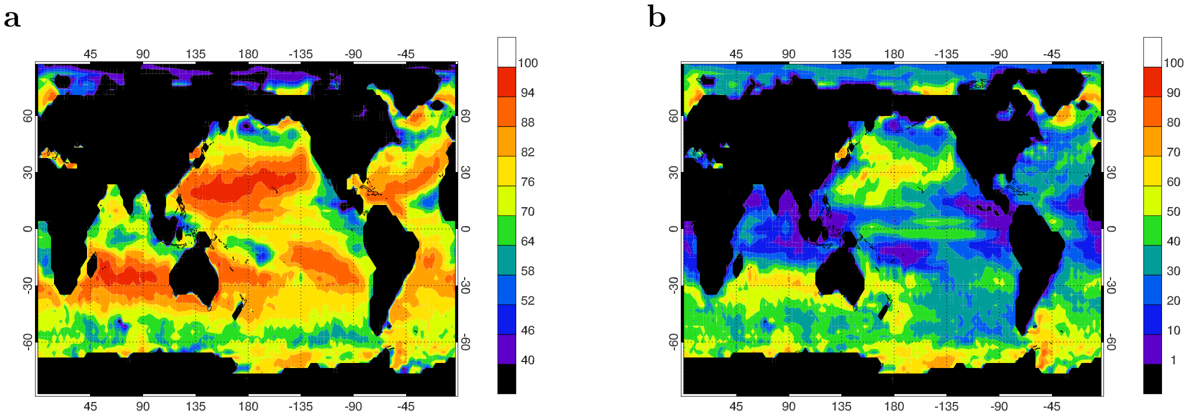

Figure 4.14: Fraction [%] of the total burden of DDT (a) and γ-HCH (b) reaching below 60 metres of depth after 10 years.

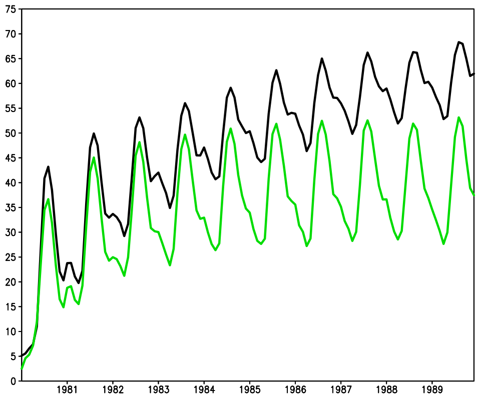

Figure 4.15: Fraction [%] of the total ocean burden of DDT (black) and γ-HCH (green) falling below the mixed layer. Time series of monthly global averages.

a global average, increases steadily for both compounds and reaches at the end of the simulation 50% for γ-HCH and 80% of the total ocean concentration in the case of DDT. Fig.4.14 shows the fraction [%] of the total burden sunk below the zone where (in the model) the biological production occurs (the first 60 metres). In case of both substances dynamical features are clearly bearing an effect on the vertical export. The figure shows that the ocean below 60 metres holds (afters 10 years of run) at least 40% of the total mass of DDT, with peaks of more than 80%. In case of γ-HCH, the spatial pattern and the figures show values on average around 25%. The compound, differently from DDT, is subject to degradation in seawater. The areas of most significant sinking are the subtropics and the mid latitudes due to the Ekman pumping. As this phenomenon translates into pushing water from the surface layers towards the deep ocean, it removes substance from the mixed layer and reduces volatilisation. Without a three-dimensional ocean approach, volatilisation would be overestimated. The geographical pattern of this process is strongly non uniform.

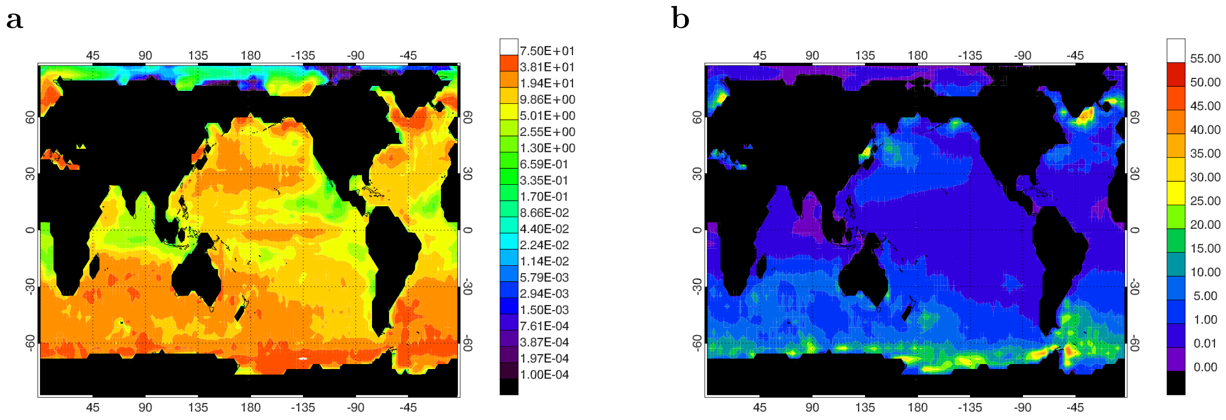

Figure 4.16: Fraction [%] of the total burden of DDT (a) and γ-HCH (b) reaching below 300 metres of depth after 10 years.

Fig.4.16 shows the fraction of the total column burden below 300 metres at the end of the simulation. Some of the dynamical features emerging from the previous picture are no longer propagating beyond this depth. Here deep water formation reflects onto the distribution of semivolatile organic compounds. Heavier water masses sink into deep ocean basins because of a density increase triggered by cold temperatures in high latitudes. The tracers are massively exported due to this process. Due to the temperature distribution, the degradation of γ-HCH is less effective and the compound is present in those areas in comparable amount to DDT. This phenomenon can be recognised in the Labrador, the Greenland and the Weddel Seas, where the values reach more than 50% of the total column burden.

Fig.4.17 shows vertical sections of the total ocean concentration [$ng\ l^{-1}$] (temporal averages of the tenth year of run) for both compounds. The export to the deep ocean is evident in both hemispheres at different latitudes. At the equator is recognisable the permanent thermocline, determining an extended minimum (the export associated with the downwelling areas at 4°N is not visible at this scale). Nevertheless the traceable sinking of the contaminants is determined by the local high values of partitioning (in 4.17a, b a global average, in 4.17e, f, the Pacific ocean at 180°E).

DDT, more persistent and lipophilic, reaches the deep ocean in higher amounts (in proportion) everywhere, especially within the tropics and in the southern hemisphere. On the other hand, the degradability of lindane accentuates its tropical minimum and makes its concentration comparable with the one of DDT, in spite of higher amounts entering the environment every year. The features of the thermohaline circulation north of 50 ° N (4.17c, d) and in the Southern Ocean (a, b, e, f), bring γ-HCH well below 2000 metres of depth. There the export is almost as efficient as for DDT.

Table 4.4 reports the fluxes of mass of DDT (the most persistent and lipophilic selected for this study) crossing the 300 metres depth surface in the four main ocean deep water formation areas, in the Northern Atlantic (Norwegian Sea: 68-80°N, 0-25°E, Labrador Sea: 50-60°N, 60-40°W) and in the Southern Ocean (Weddel Sea: 60-85°S, 70-20°W, Ross Sea: 60-80°S, 170°E-155°W). Value of different areas are in the same range, with the North Atlantic on the top end. As the compounds accumulate in the ocean (more information on the multicompartmental budget and residence time in the next chapter) the fluxes increase in time, less steeply toward the end of the simulation, without, however appearing to have reached steady state. The fluxes were estimated from model burdens under the assumption that at the depth in those areas and for that particular compound, concentration change is determined by vertical export, i.e. assuming horizontal advection of DDT negligible. Furthermore, the results are strictly scenario-dependent and, therefore, not immediately comparable with other studies quantifying the fluxes in the same areas, like Lohmann et al., 2006[73].

Discussion As the distribution of the phases contributing to the vertical export of SOCs is heterogeneous, also the effects of the partitioning, sinking and increase in retaining capacity of the surface ocean, are extremely related to local conditions. The inhibition of the volatilisation, to which all organic phases contribute, in an experiment in which the input/output ocean balance is almost purely depositional, reaches 35% in the equatorial Pacific, for the more lipophilic DDT. As volatilisation is a crucial process for the fate and distribution of SOCs, such partitioning-induced effect could affect, as suggested by Scheringer and colleagues, 2004[99], the long-range transport potential of the compounds. The extent of this influence is, however, strongly scenario dependent.

Only a fraction of the organic phases is contributing to vertical export. Moreover, most settling organic matter decomposes before reaching the ocean floor (Axelman and Broman, 2001[12][8]). This clearly weakens the reliability of the figures relative to the partitioning as they are not representative of the whole export associated with particles. This process does not anyway represent, at least for the compounds DDT and γ-HCH, the main source in deep waters, as some studies of the past might have suggested for PCBs [103][9].

The sinking of a substance is, in fact, a combination of biogeochemistry (sinking with particles), chemodynamics and physical dynamics (turbulent diffusion [53], vertical transport of water). In a study of the rates of loss in ocean of PCBs[10], Wania and Daly, 2002[132], concluding that burial in sediments is of very limited importance (on the global scale[11]), suggest the relevance of downwelling processes.

As the distribution of compounds below 300 metres is not explained by the sole sinking determined by the partitioning, even in case of a lipophilic persistent compound as DDT, the obvious conclusion is that dynamics plays a fundamental role in the multicompartmental fate of semivolatile organics. A similar outcome, namely that oceanic deep water formation could constitute relevant removal mechanism from surface waters for persistent organic compounds, results from a study by Lohmann et al.,2006 [73]. Other dynamical phenomena, which can be described by the three-dimensional model are upwelling and

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[8] Box-model study on PCBs.

[9] Based on point measurements of PCBs in a single region in North Atlantic.

[10] Based on theoretical and semi-empirical approaches, including zonally averaged global fate and transport modelling.

[11] On continental shelves (Jönsson et al. 2003[52]) and delta areas (Axelman and Broman[12]) sediments burial fluxes can, on the other hand, be important.

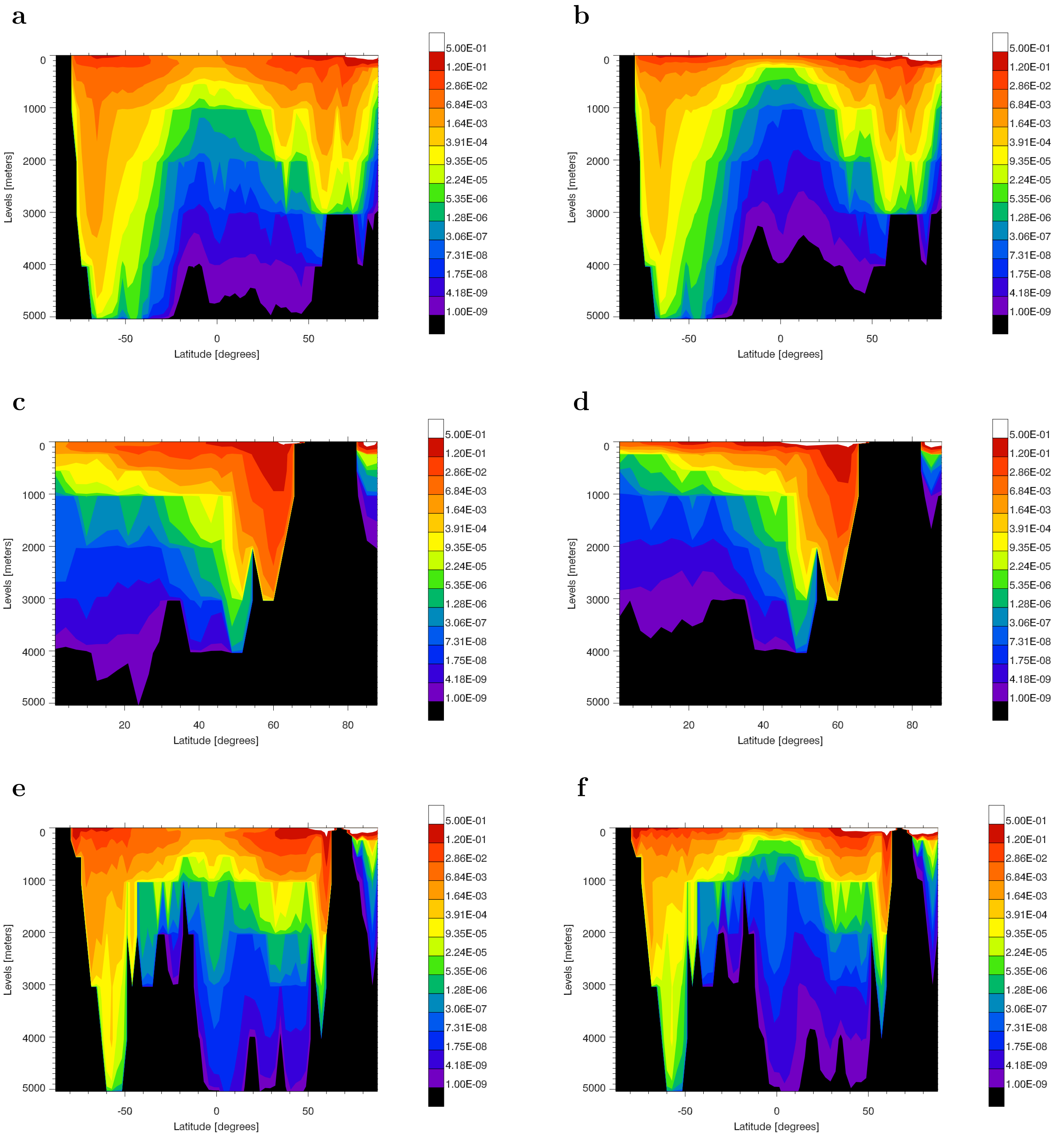

Figure 4.17: DDT (a, c, e) and γ-HCH (b, d, f) averaged vertical sections [$ng\ l$]: zonally averaged profile (a,b), cross sections at 323°E (hemispheric, c, d), and at 180°E (global, e, f). Averages of the 10^{th} year.

overturning. This processes determine, especially for persistent compounds, the enrichment of the surface ocean pool of compound, available for volatilisation. Vertical export does not therefore necessarily constitute a sink, at least for DDT.

year	Labrador Sea	Norwegian Sea	Weddel Sea	Ross Sea
1	7.10	1.80	9.54	3.13
2	168.73	76.34	139.49	49.75
3	370.91	358.32	355.45	166.29
4	641.16	660.16	467	545.45
5	1149.09	835.60	582.36	493.95
6	1258.94	1177.86	778.73	661.13
7	1311.59	1407.39	889.62	1000.03
8	1775.65	1630.22	846.74	1003
9	1790.45	1587.98	1112.62	1399.75
10	1493.71	1915.29	1206.19	1050.94

Table 4.4: Mass fluxes $[kg\ month^{-1}]$ of DDT crossing the 300 metres depth surface. The flux refers to the average yearly mass (December minus January). The estimates have been made under the assumption that concentration change is determined by vertical export in the regions.

Horizontal transport

Among the processes distributing SOCs throughout the global environment, transport by ocean currents is still under-investigated.
Whereas a persistence of only a few days is sufficient for a compound to be subject to long-range transport to remote latitudes in the atmosphere, several months or even years

are required [68] in the case of the slow-paced oceanic transport.
Therefore, the more soluble and long-lived compounds are in ocean waters, the higher the likelihood for them to reach remote regions carried by currents.

To a large extent, horizontal movement of ocean surface waters (Fig.4.18 shows the long-term average pattern of ocean surface currents) mirrors the long-term average atmospheric circulation. The westerly winds of middle latitudes and the trade winds of the tropics shape the most prominent features of ocean surface motion, large-scale current systems, developing circularly in gyres, typically clockwise in the northern hemisphere and counter-clockwise in the southern hemisphere.

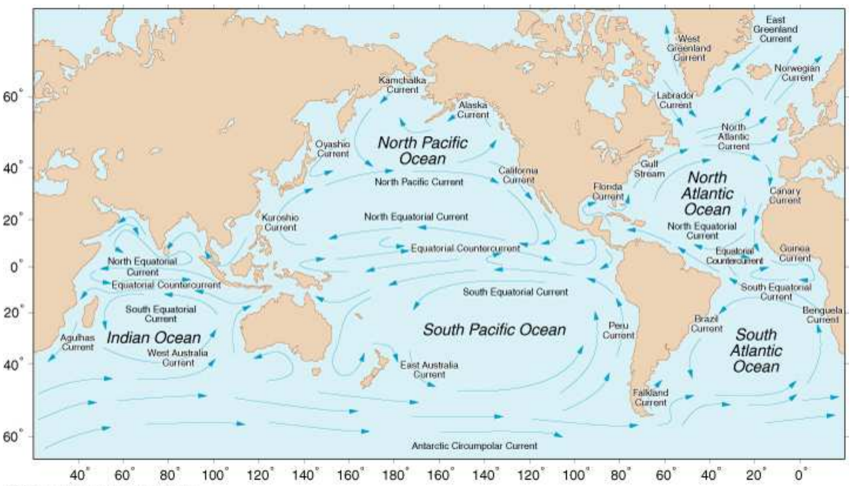

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Figure 4.18: Long-term average pattern of ocean surface currents.[a]

[a] American Meteorological Society

Deep ocean currents are driven by density and temperature gradients. The thermohaline circulation, the ocean's conveyor belt, a density- and gravity-driven system, transfers water masses between the oceans and between the surface and the deep ocean on a 1000 years time scale.

Particularly interesting for the environmental fate of SOCs is the long-range transport determined by wind-driven surface currents, which vary considerably in strength, width, and depth. The western boundary currents, warm, deep, narrow (usually measuring no more than 50 to 75 km across), and fast flowing (velocities averaging 3 to 4 km per hour) occurring on the west side of ocean basins. The Gulf Stream, the strongest western boundary current [122], in the northern Atlantic, or the Kuroshio Current, in the north-western Pacific, bring warm waters from the equator northward. The Southern ocean, with the Antarctic Circumpolar Current is, on the other hand, understood not to play a significant role in the oceanic long-range meridional transport [127].

With the aim to quantify the ocean's contribution to the large-scale transport of SOCs

to the Arctic, a sole-ocean fate scenario has been designed and tested.
As a second step, the transport in selected regions has been investigated.

Representation of ocean currents in the model Figure 4.19 shows the model simulated depth integrated transport. The large-scale roughly circular current systems is clearly defined, with the subpolar and subtropical gyres (bounded by zero stream function) and the typical equatorial structure of the Pacific with the countercurrent, flowing eastward between 5° and 15°N. In the Atlantic, the Gulf Stream reaches values around 20-30 Sv and extends, with the north Atlantic drift, clearly beyond 60°N.

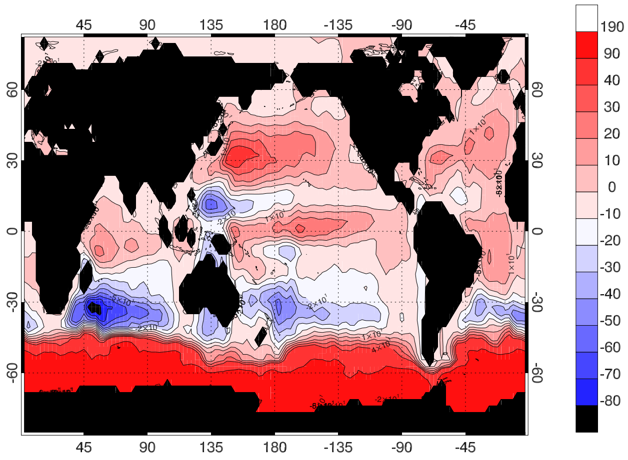

Figure 4.19: Depth integrated stream function [Sv; Sv=10^6 m^3 s^{-1}] for the world ocean calculated from the simulated horizontal velocities. Average over 10 years.

The transport associated with the other western boundary current in the northern hemisphere, the Kuroshio current, is of around 30 Sv. In reality such currents have a marked spatial variability, therefore the values of the transport can span within a wide range [122]. Clearly, the current version of the model, with T42 (2.8° × 2.8°) spatial resolution, underestimates such transport.

Model setup and simulation scenario

A scenario in which the compounds have been directly released to the uppermost ocean layer has been chosen to quantify the ocean's contribution to the large-scale transport of SOCs.
The area selected for the release, in Fig.4.20, 800000 km^2 centered at 30°N and spanning between 54°W and 66°W off the coast of Florida is particularly prone to transport by marine currents, namely by the Gulf Stream, towards the Arctic.

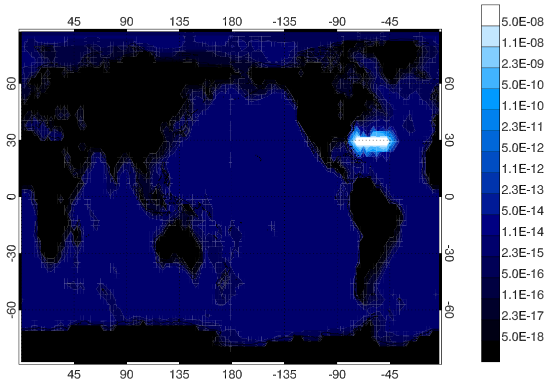

Figure 4.20: Transport to the Arctic: a line of pollutant has been released in a transport-prone area: t=0

The experiments focus on the fate of DDT and γ-HCH only in the ocean system. Once the compounds have volatilised, the are considered lost from the system and therefore they not enter cycles of atmospheric transport and deposition. As part of the 3DO model setup, the ocean model is part of a coupled system, interacting with the atmosphere in terms of (mutual) physical forcing. The experiment simulates 10 years.

Results

In the following paragraphs, estimates about the meridional migration of the compound after 10 years of simulations are presented.

Transport to the Arctic

The initial amount applied to the ocean (in Fig.4.20) sums up to approximately 170 t.
After release, the substances start being transported, mostly in north-east direction, by the Gulf Stream system. The Stream originates in the Gulf of Mexico, follows the coastlines of United States and Canada and crosses the Atlantic Ocean. At about 40° N/30°W, the Gulf Stream splits into two branches, with a northern stream, the North Atlantic drift, reaching northern Europe and further, with the Norwegian current, reaching the Arctic. In Fig.4.21 the status for both compounds after 5 years of simulation is shown. In the north, on both southern coasts of Greenland, the northward transport is clearly limited by the Labrador and the Eastern Greenland currents, cold currents heading south. At around 5-10°N the compounds, particularly evident in the case of DDT, are transported in west-to-east direction, by the Equatorial Countercurrent and reach the coasts of Africa. North of it, the southern branch of the subtropical gyre (North Equatorial Current) pushes water in the opposite direction, limiting the expansion of the contaminant plume toward east. Again, the substances behave differently because of differences in degradability.
In Fig.4.22, the transport of γ-HCH (a) and DDT associated with the main currents bearing an effect on the concentration in Arctic: the Norwegian Current, flowing northward in

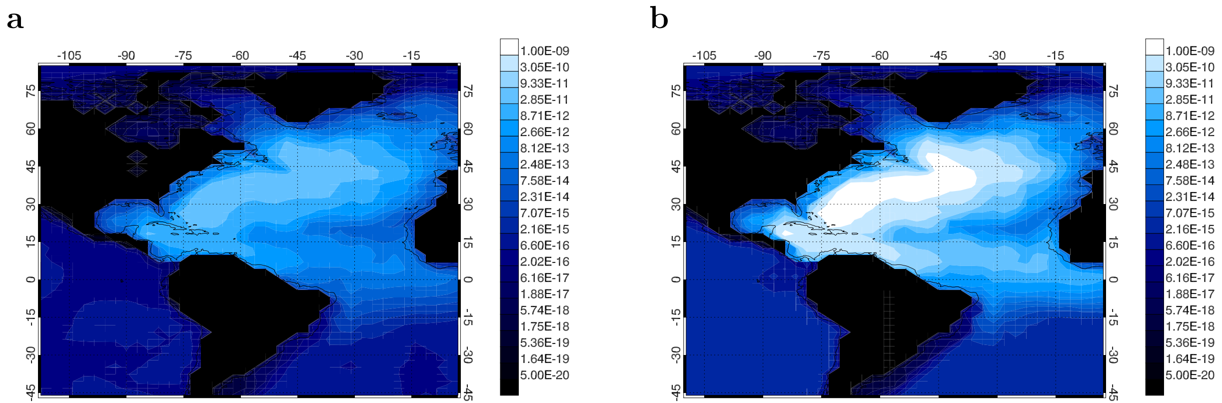

Figure 4.21: Transport to the Arctic: t= 5^{th} year. Vertically integrated ocean burden $[kg\ m^{-2}]$ of γ-HCH (a) and DDT (b).

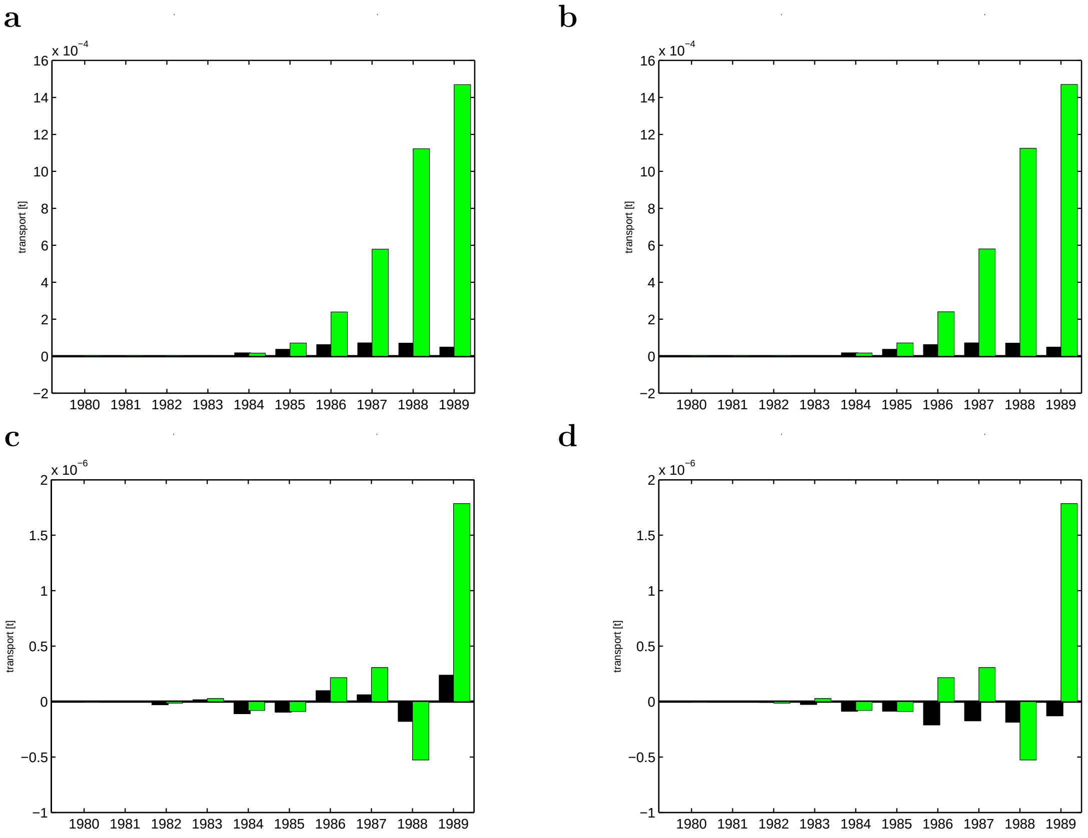

Figure 4.22: Transport of DDT (green) and γ-HCH (black) to the Arctic: net (a) and associated with water flowing (positive northward) through Norwegian Sea (b), Davis Strait (c) and Denmark Strait (d) [*tonnes*]. Monthly averages.

the Norwegian sea, the East Greenland current between Greenland and Iceland and the water circulation in the Davis Strait, resulting from the West Greenland current flowing in the Baffin Bay and the Baffin Island current, out of it. The net transport (4.22a), higher for DDT, which is present, as mentioned before, in always higher (than in case of lindane) amount, is clearly dominated by the circulation in the Norwegian Sea, northward.

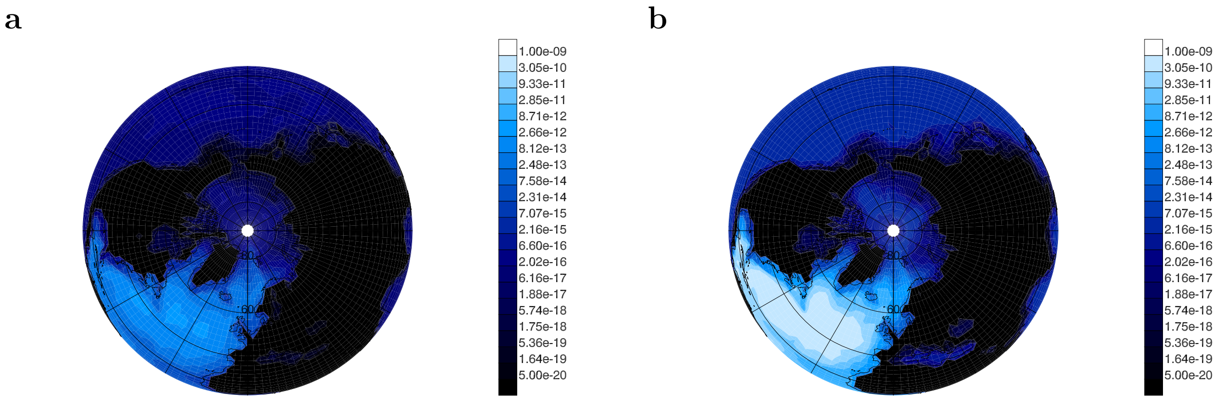

Figure 4.23: Transport to the Arctic: t= 10^{th} year. γ-HCH (a) and DDT (b) vertically integrated ocean burden $[kg\ m^{-2}]$

After 10 years of simulation, DDT is present in concentrations higher than in case of the other compound in the global ocean. Only a very small fraction is present in Arctic waters (in Fig.4.23) only by means of ocean currents. In Table 4 the amount of compound in the Arctic after 10 years with respect to the initial release and to the amount present in the system at the end of the simulation is given. In case of DDT, the amount present at mid latitudes is higher. In spite of a higher volatilisation rate, the compound is present in higher amount in the system, as a consequence of its persistence.

In Fig.4.24 the latitudinal migration of the of the centre of gravity (COG), a long-range transport indicator introduced by Leip and Lammel, 2004[66] (see glossary), of the distribution of the two substances is shown.

It is evident how the centre of the plumes moves, in both cases, only a few degrees north in 10 years. For γ-HCH, it is reaches beyond 40°N, over 2000 km away from the release area, whereas in case of DDT it does not overcome 35°N.
The zonal spreading, ZS (Leip and Lammel, 2004[66]), expressing the tendency of a distribution to spread in meridional direction, increases sharply for both compounds until the fifth year and reaches values around 4000 km (slightly overcoming them after 10 years of run).

compound	North of 45°N		North of 66°N	
	$m_{t=10}/m_{total,t=1}$	$m_{t=10}/m_{total,t=10}$	$m_{t=10}/m_{total,t=1}$	$m_{t=10}/m_{total,t=10}$
γ-HCH	2.1×10^{-4}	1.2	7×10^{-3}	41.4
DDT	4.5×10^{-3}	8×10^{-2}	1.5	26

Table 4.5: Meridional transport: fractions [%] of DDT and γ-HCH present beyond the latitudes 45°N and 66°N after 10 years with respect to the initial release and to the amount present in the system at the end of the simulation.

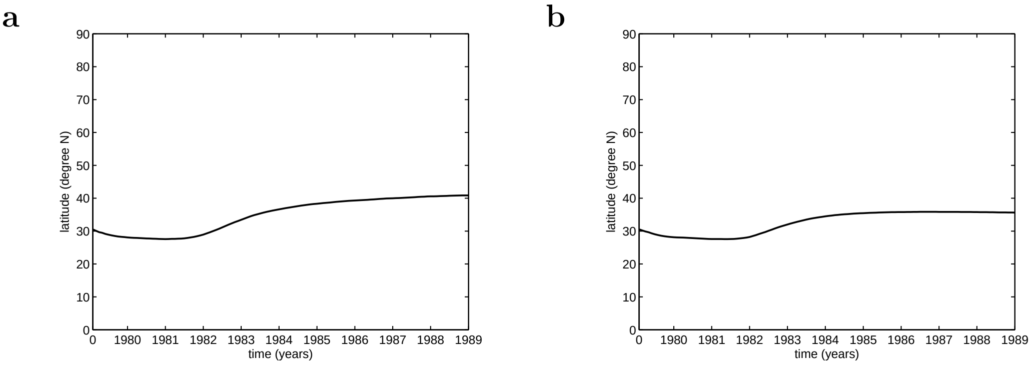

Figure 4.24: Meridional spreading over time: 50^{th} percentile of the cumulative zonal distribution for γ-HCH (a) and DDT (b).

Discussion An artificial entry scenario was designed in order to focus on the ocean fate of lindane and DDT upon first introduction into the environment. The location of application has been chosen based on local dynamics related to the transport to the pristine Arctic region. The resulting differences in the distribution of the two compounds are entirely determined by their properties as vapour pressure, solubility and partitioning coefficient. The choice of the simulation scenario, permitting to track the first-hand contaminant plumes, i.e. not considering deposition upon volatilisation, in a wide range of latitudes, allowed to assess and rank the relevance of temperature dependent processes as degradation in water (for γ-HCH; no degradation for DDT, cf. Tab.2.1) and volatilisation. The results show, after 10 years, a more efficient transport northward for DDT. The comparison of the fate of the two substances demonstrates that the persistence of DDT compensates for its solubility, lower than in case of lindane, which, degrading significantly, is present in smaller amounts in the system at the end of the simulation. The study of the meridional migration of the centre of gravity does not reflect, however, a higher northward transport for DDT. The fact that the compound does not degrade at the lower latitudes, actually keeps its plume centered further south than for lindane. Due to the model resolution, the transport associated to the Gulf Stream is still slightly underestimated.

Summary

The cycling of γ-HCH and DDT was studied in the global ocean, for the first time, with a model based on the coupling of an atmospheric and an oceanic general circulation model. As a preliminary step, the results of the model setup based on the coupling of two general circulation models for the atmosphere and the ocean has been compared to a two-dimensional ocean approach. The outcome of the comparison shows that a model setup with a higher degree of resolution in ocean processes affects the compartmental distribution and the environmental cycling of both substances. The residence times in the ocean and in the whole system are significantly higher when the three-dimensional approach is used.

A fundamental process for SOCs in sea-water is the partitioning to organics. This bears effects, in turn, on other processes, as the volatilisation, which results inhibited by it, as the ocean retaining capacity increases. For DDT this effect reaches up to 35%.

To a certain extent, the migration of the compounds to the deep ocean is also influenced by the sorption to organics. DDT, the most persistent and lipophilic substance chosen for the study, reaches the deep ocean in higher amounts everywhere. The sinking is, however, a combination of biogeochemistry (gravitational settling with particles) and dynamics (vertical transport of water), and is obviously favoured by persistence. Ocean dynamics proved to be, in fact, more important than sinking associated with particulate matter. In case of subduction of ocean waters, volatilisation (identified even more as a very sensitive and therefore fundamental process) is clearly inhibited.

In order to study the meridional transport in the ocean, a fictive entry scenario was designed and tested. The compound, applied to ocean in a sensitive region, subject to the Gulf Stream, was tracked only in their first ocean cycle. After 10 years, the most persistent and more volatile compound, DDT, is present in higher absolute amount in the Arctic.

Chapter 5

Multicompartmental Cycling of HCH and DDT

The role of the ocean as reservoir and transport vector in the multicompartmental environmental cycling of semivolatile organic compounds needs to be assessed.

For the first time for the compounds object of this study, the ocean is represented in the modelling approach as a three-dimensional sub-system.
At first, the global cycling of semivolatile organic compounds has been simulated and the resulting multicompartmental distribution analysed. As SOCs tend to have an ubiquitous distribution, i.e. to spread far from the application areas, mostly located at mid-latitudes, to remote (and pristine) areas, their transport, in particular its meridional component, has been studied. The compounds are transported via atmosphere, ocean currents, rivers or biota. Taking into consideration the hypotheses formulated so far in literature (*grasshopper effect* [133]) and employing a specifically designed scenario setup, the transport mechanisms have been furthermore investigated.
Finally, the role of sea-ice in hindering the substance volatilisation from the ocean has been estimated.

SOCs cycling in a fully dynamic three-dimensional system

When the aim is to study compounds either water soluble or persistent in ocean, the use of a modelling tool with a high resolution in the ocean allows to consider the full multicompartmental cycling and the role of the different reservoirs and transport vectors in the fate and distribution of the compounds as well as to estimate their persistence in both the whole system and in its components. In order to study DDT, γ-HCH and α-HCH in all environmental compartments, numerical experiments with global agricultural applications have been performed. The consideration of a third compound, α-HCH, albeit with an application scenario which is different from the ones employed in this study for the other two organochlorines, is meant to furthermore test the model setup with a compound sharing most of its properties (Tab.2.1) with the isomer γ-HCH.

Persistent bioaccumulative contaminants are of great concern due to the hazard they pose to pristine ecosystems, in remote regions like the Arctic. The general circulation of the atmosphere plays a fundamental role in transporting the substances from mid-latitudes to the Arctic. During northern hemispheric winter, high pressure over the continents, and low pressure systems over northern Pacific and Atlantic oceans form. Air flows out of Eurasia into the Arctic forced northward by the intense high pressure cell over Siberia and out of the Arctic driven, southward, by the high pressure ridge over North America. In northern summer, the dissolution of the continental high-pressure cells and the weakening of the oceanic low pressure result in a reduction of the northward transport (Macdonald et al., 2000[76], AMAP, 1998[10]). Ocean waters flow into the Arctic via the Fram Strait and the Barents Sea in the North Atlantic and via the Bering Strait in the North Pacific. Surface currents are the most important for contaminant transport (Macdonald et al., 2000[76]). The global atmospheric input to the ocean of organics as, among others, HCHs and DDT completely dominates their input via rivers (Duce et al., 1991[25]). At least for semivolatile organic compounds on global to medium scales, long-range transport is most efficient in the atmosphere. In the arctic ocean, the relatively small incidence of radiation, the low temperature and the limited biological activity may enhance the persistence of the compounds (Wania and Mackay, 1993[133]).

Model setup and simulation scenarios

The model setup used in these experiments is analogous to the one introduced in Chapter 3. The compartments atmosphere, (three-dimensional) ocean, soil, vegetation and sea-ice are represented.

An agricultural application scenario was employed for DDT and γ-HCH as described in Chapter 4. The entry scenario for α-HCH is introduced in the following paragraph.

For all the compounds and scenarios, the duration of the simulations is 10 years.

α-HCH agricultural data

Another hexachlorocyclohexane isomer, α-HCH, (for characteristics and properties refer to Chapter 2) has also been taken into consideration in a scenario, presented in Fig.5.1, with agricultural applications for the year 1980. The compound usage is distributed over Europe, Asia, Africa, South and Central America and Australia. Differently from other scenarios, with applications taking place all over the year, α-HCH follows a more realistic seasonal pattern, from February to September. The total applications sum up to 112139 *tonnes* each year.

The soil to vegetation release ratio, 20:80, is the same as for the other compounds and scenarios.

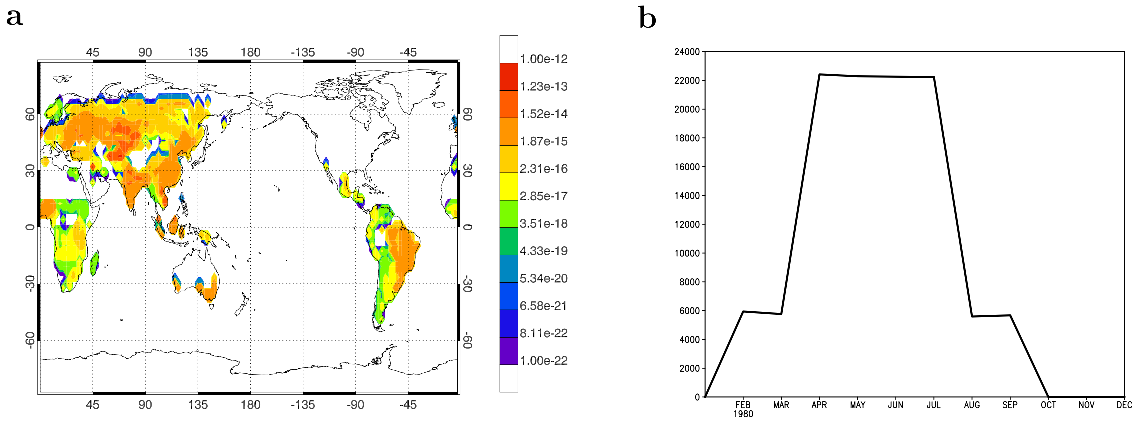

Figure 5.1: Global α-HCH agricultural applications $[kg\ m^{-2}\ s^{-1}]$: spatial (yearly average, a) and temporal (spatial sum, b) distribution $[tonnes]$.

Results

In the following paragraphs results of the experiments are presented and discussed.
At first the compartmental distribution in time and space and the residence times in the various environmental compartments are shown and analysed.
The analyses performed concern furthermore the long-range transport and a comparison of atmosphere and ocean as transport vectors for semivolatile organics.

Compartmental distribution and long-range transport

Upon volatilisation from the terrestrial compartments, where they are released into the environment, SOCs enter the atmosphere, are transported and deposit onto soils, vegetation and into the ocean. Once having accessed these compartments, the compounds can be permanently stored, being transported in the ocean and/or revolatilise to the atmosphere, cycling between the compartments as determined by their properties and the environmental conditions.
Fig.5.2 shows the time series of the compartmental burdens for γ-HCH, DDT and α-HCH. The soil burden of all three substances holds the highest share of compound, dominating, for DDT and α-HCH, the total environmental burden (as also evident in Tab.5.1, showing the state of the system at the end of the run). For all three compounds, the compartment is still accumulating at the end of the simulation, although following different regimes of growth. The burden follows a defined seasonal cycle, more pronounced in case of both the HCH isomers.
As for DDT and γ-HCH the applications are constant in time (cf. application scenario, Chapter 4), the cycling in soil is entirely determined by deposition, degradation and volatilisation. Due to the geographical distribution of the compounds and their emissions, the processes taking place in the northern hemisphere (where in the warm season both degradation and volatilisation are higher) clearly dominate the global figures. Depo-

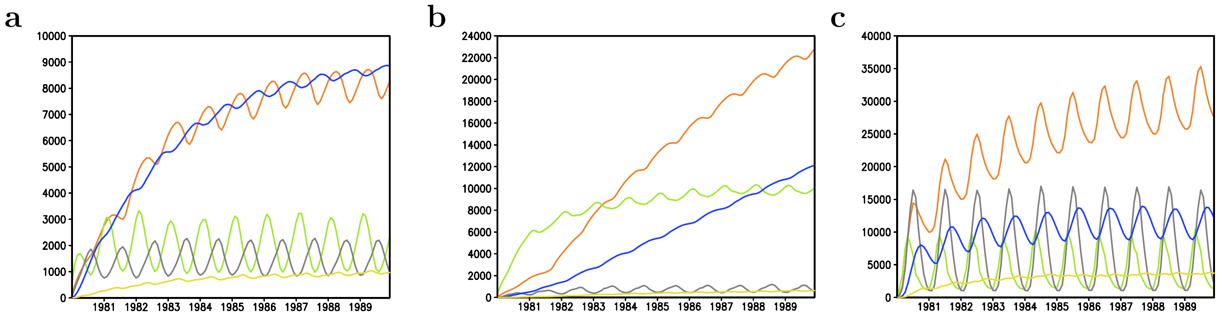

Figure 5.2: γ-HCH (a), DDT (b) and α-HCH (c): distribution [*tonnes*] in atmosphere (gray), vegetation (green), soil (orange), ocean (blue). Monthly means of a global sum. Monthly means of a global sum.

sition and volatilisation, considered on a global scale, peak in late spring-early summer, determining a corresponding drop in early autumn in the soil burden.
In case of α-HCH, the substance is applied from February to September, with maximum between April and July (in figure 5.1). For the compartments soil and vegetation, the seasonal variations of deposition, volatilisation and degradation are superimposed to the ones of the applications. Volatilisation and degradation peak in northern summer and have minima in winter, the deposition reaches the global maximum in April and has minimum in August for soil and towards the end of the year for vegetation. The seasonal variability of the atmospheric burden, similar for all compounds, with maxima in northern summer, is a consequence of the higher volatilisation in the warm season and of the deposition rate.

The atmospheric burden of γ-HCH shows maxima in August and minima in January, clearly in tune with the the seasonality of volatilisation. The deposition has, on the other hand, an inverted cycle, with repercussions on the burdens of the terrestrial compounds. For DDT, the seasonality of the atmosphere is similar to the one shown by γ-HCH, albeit the latter compound is faster degraded by reaction with $OH^{\cdot}$ radicals.
For α-HCH, the maxima in the atmospheric burden are achieved in July-August. The volatilisation has its minimum in January and maximum in June-July (global sum). The process is dominated by the contribution of vegetation, whose volatilisational loss is in phase with the global figures. From the other ground compartments, soil and ocean, the maximum in volatilisation is experienced later in the year and in significantly smaller amount (20% and 1.5% respectively of the total volatilisation). The atmospheric degradation, for α-HCH more efficient than in case of the other compounds selected for this study, has peaks also in northern hemisphere summer and is spatially concentrated within the tropics, obviously related to the availability of hydroxyl radicals. The deposition has its maximum in April and minima in winter.

The ocean burden of γ-HCH, the highest for this contaminant (40.5% of the total burden at the end of the run), shows a cycling much less pronounced in comparison with other compartments. The input flux of deposition, which exhibits minima in January and maxima in June is counterbalanced by volatilisation, which has peaks in October and minima

compound	compartment	m_i/m_{glob}	$m_{i_{arc}}/m_{glob}$	$\tau(a)$
γ-HCH	soil	38.5%	5.2%	0.86
	vegetation	9.5%	0.4%	0.09
	atmosphere	7%	0.4%	0.04
	ocean	40.5%	10.7%	1.40
	sea-ice	4.5%	4.3%	3.12
DDT	soil	49%	5.10%	3.10
	vegetation	22%	0.72%	0.70
	atmosphere	2%	0.04%	0.03
	ocean	26%	5.40%	1.22
	sea-ice	1%	0.98%	2.72
α-HCH	soil	53%	12%	0.83
	vegetation	8%	0.5%	0.05
	atmosphere	12.5%	0.6%	0.04
	ocean	20%	5.4%	0.45
	sea-ice	6.4%	5.5%	3.24

Table 5.1: Compartmental mass fractions, m_i/m_{glob} for the total global environment and $m_{i_{arc}}/m_{glob}$ for the Arctic [%] and global residence times [a]. Average of the 10^{th} year.).

in April. Degradation has maxima in September and minima in February.
α-HCH distributes in the ocean less the other isomer (20% vs 40.5%).The highest amount in ocean is found in October, the smallest in April. The atmospheric deposition and the sinks, degradation and volatilisation, peak respectively three, two and one months before the burden.
For DDT, the ocean burden peaks in February and maxima in late summer almost in tune

with deposition, with one-two months lag. The highest amount of DDT volatilises from the ocean in October, the smallest in May. The degradation in ocean, only described in sediments, does not play any significant role in the cycling of DDT.

The study of the evolution of the compartmental burdens and of their approach to steady state can provide information on the role of the reservoirs for the present state and for further developments.

In case of all three compound, the first compartment approaching a pseudo-steady state is the atmosphere. At the latest after two years in case of DDT, the sinks (wet and dry deposition and degradation) balance the sources (volatilisation and revolatilisation from ground compartments).

In vegetation, the compounds' burdens also stabilise within the first year for the HCH isomers and after the second for DDT.

The ocean compartment is still accumulating after 10 years for DDT, underway to steady state in case of the most water soluble compound, lindane, and, from the second year onwards, stable for α-HCH.

The sea-ice burden is accumulating for DDT, and tending to steady state for the HCHs from the fourth year onwards.

For the soil compartment, there is a clear tendency to reach a pseudo-steady state towards the ninth-tenth year in case of both HCH isomers.

The soil burden of the compound DDT is steeply increasing for the whole simulation. The slope of the curve appears to slightly reduce during the last two years.

A picture of the system at the end of the runs is presented in Tab.5.1, with the compartmental distribution and related residence times.

As seen before, a feature common to all compounds, and related to the properties of the compartment (as content in organic matter and porosity) is the high retaining capacity of the soil. The share for γ-HCH, DDT and α-HCH is respectively 38.5%, 49% and 53% of the total burden at the end of the simulation. The residence time associated to the soil is also the highest for DDT and α-HCH. As γ-HCH is moderately water soluble, the compound has, after 10 years, a burden in ocean (40.5%, with 1.4 $years$ of residence time) comparable to the one in soil. As both compartments are close to have the sinks balance the sources, their share would not change relevantly in the future.

DDT, the most lipophilic (and persistent) compound selected for this study, is mostly distributed to soil, with an ocean share which is 26% of the total burden. The residence time in the two compartments, are 3.1 and 1.22 $years$ respectively. As seen in the previous chapter, the contribution of the ocean organic phases to the retaining capacity reaches, at its maximum (in areas as the equatorial Pacific throughout the year), 30% of the compartmental burden of DDT. As the compartments soil, ocean and sea-ice (this latter with a residence time of 0.77 $years$) are still far from achieving steady-state conditions, they could host in the future an even higher share of the total environmental burden of DDT.

α-HCH, being more lipophilic and less soluble and more readily degradable in water than the other HCH, shows a marked gap in concentration between the two compartments,

with 53% and 20%, respectively. In spite of its comparatively higher share, the soil has, for this compound, due to a faster turnover, a residence time comparable to the one of the γ isomer.
The overall residence time τ_{ov}[1] sums up to 2.0, 1.05 and 0.75 *years* for DDT, γ- and α-HCH, respectively.

In figures 5.3, 5.4 and 5.5 the geographic distribution of γ-HCH, DDT and α-HCH, in soil (a), vegetation (b), atmosphere (c), ocean (d) and sea-ice (e) for the tenth year (average) of simulation are shown.
From a general point of view, in comparison to the application patterns (in Fig.4.1 for DDT and γ-HCH and 5.1 for α-HCH), the spatial patterns in the terrestrial compartments show the efficiency of the global transport in redistributing the compounds. Just a few days are necessary for the plumes in the atmosphere to spread zonally over the oceans and meridionally up to the Arctic. The westerly winds of the northern hemisphere spread the compounds, mostly applied in Europe and Asia, towards east, bringing DDT and α-HCH to north America, where they are not applied.
In case of γ-HCH, the emissions are centered in central Asia (see Table 5.2). The massive plume over India extends along the northeast/southwest diagonal, also seasonally influenced by monsoons (cf. Semeena et al., 2006[106]). Monsoon winds also affect the African emissions of both HCH isomers from the Gulf of Guinea. In turn, trade winds extend the plumes zonally to the south-American continent.
In case of DDT, due to the application maxima in central America and India, and clearly to the continuous emission scenario, the atmospheric burden has its maxima steadily around 20° North, with a plume experiencing seasonal variations and extending in the cold season between 50°N and 40°S and shifting northwards of around 15 degrees in summer.
For γ-HCH, the higher emissions over Eurasia shift the northernmost limit of an atmospheric burden, which is otherwise similar to the one of DDT, further north, up to 70°N. The plume reaches over the Arctic with a concentration comparable to the ones of mid-latitudes of the Northern Hemisphere.
α-HCH, applied in considerable amounts also in Brazil, has in the atmosphere the southernmost extended plume, reaching the mid-latitudes of the Southern Hemisphere.

The amount of substances stored in the soil and vegetation compartments originates from direct application and atmospheric deposition. As previously mentioned, the soil has higher retaining capacity. Deposition (or direct application) on vegetation ensures, on the other hand, a higher degree of mobility to the compound, prone to (re)volatilise and be transported further. Thus, the concentration per unit of surface of all three compounds stored in soil and vegetation results comparable, although the applications distribute 80% of the pesticides on vegetation. The compounds are also and more uniformly spread in

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[1] τ_{ov} has been derived as sum of single compartmental residence times, weighted by the respective mass fraction.

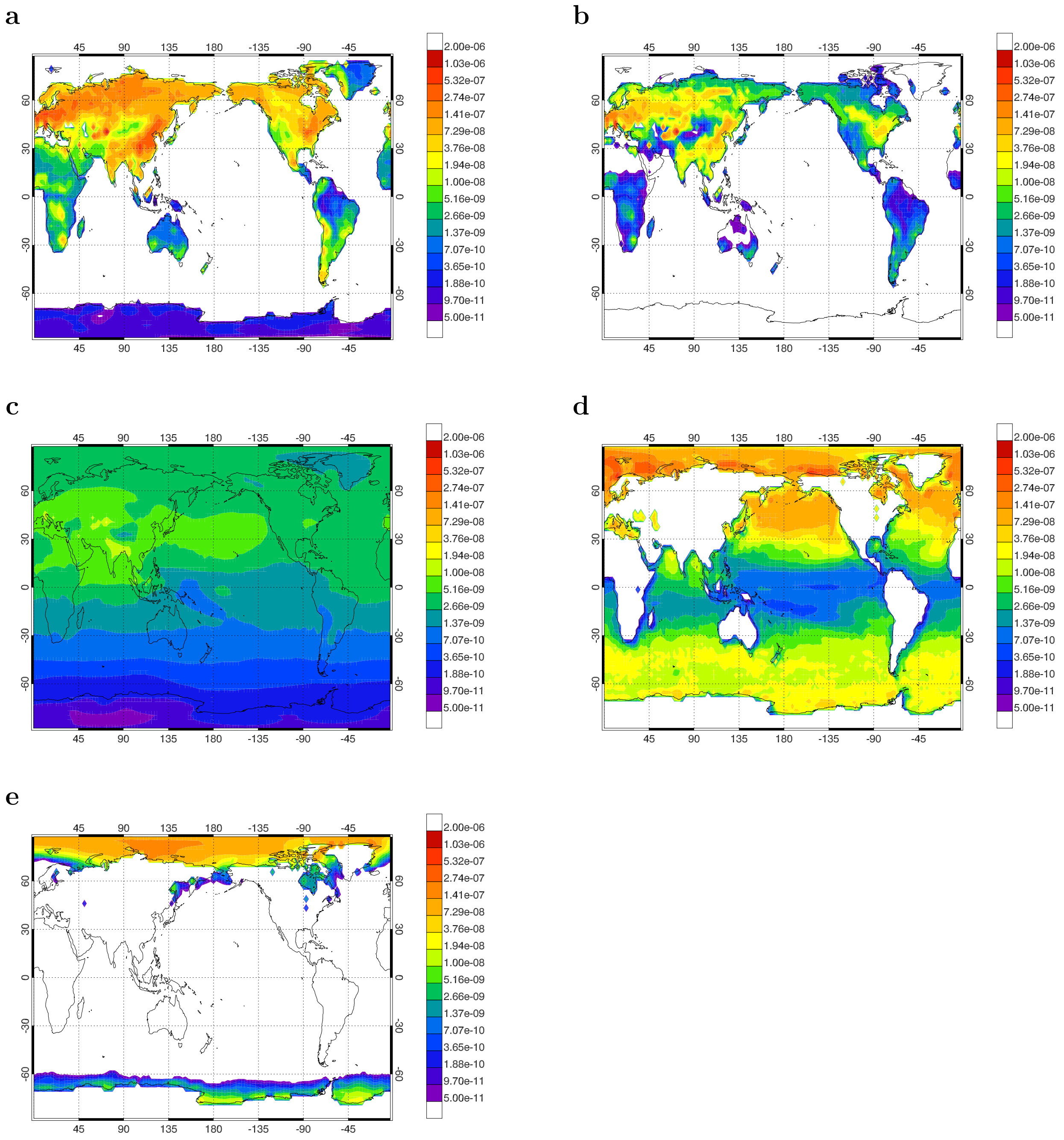

Figure 5.3: γ-HCH environmental burdens $[kg\ m^{-2}]$ (a: soil, b: vegetation, c: atmosphere, d: ocean, e: sea-ice. Average of the 10^{th} year.).

the northern hemisphere.

In the ocean, the distribution of the three compounds shows noticeable minima within the tropics, of different spatial extension for different compounds. This general pattern is due

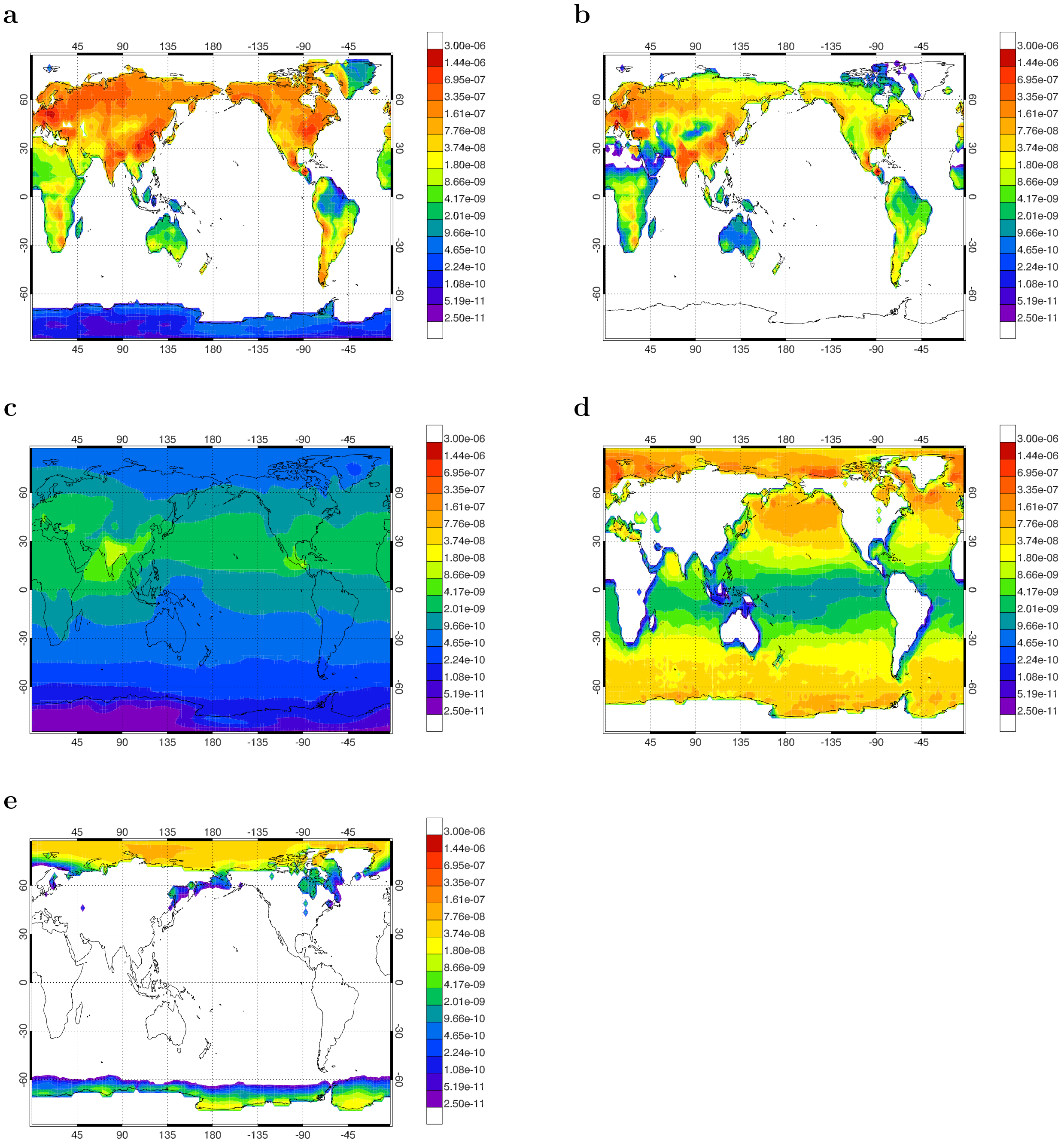

Figure 5.4: DDT environmental burdens $[kg\ m^{-2}]$ (a: soil, b: vegetation, c: atmosphere, d: ocean, e: sea-ice. Average of the 10^{th} year.).

to the combination of ocean transport and of temperature-driven degradation and volatilisation. The transport is traceable, even after just a few months of run. The equatorial northern and southern current and countercurrent redistribute the deposition (as shown and discussed in 4), which typically brings smaller amounts of substance at low latitudes.

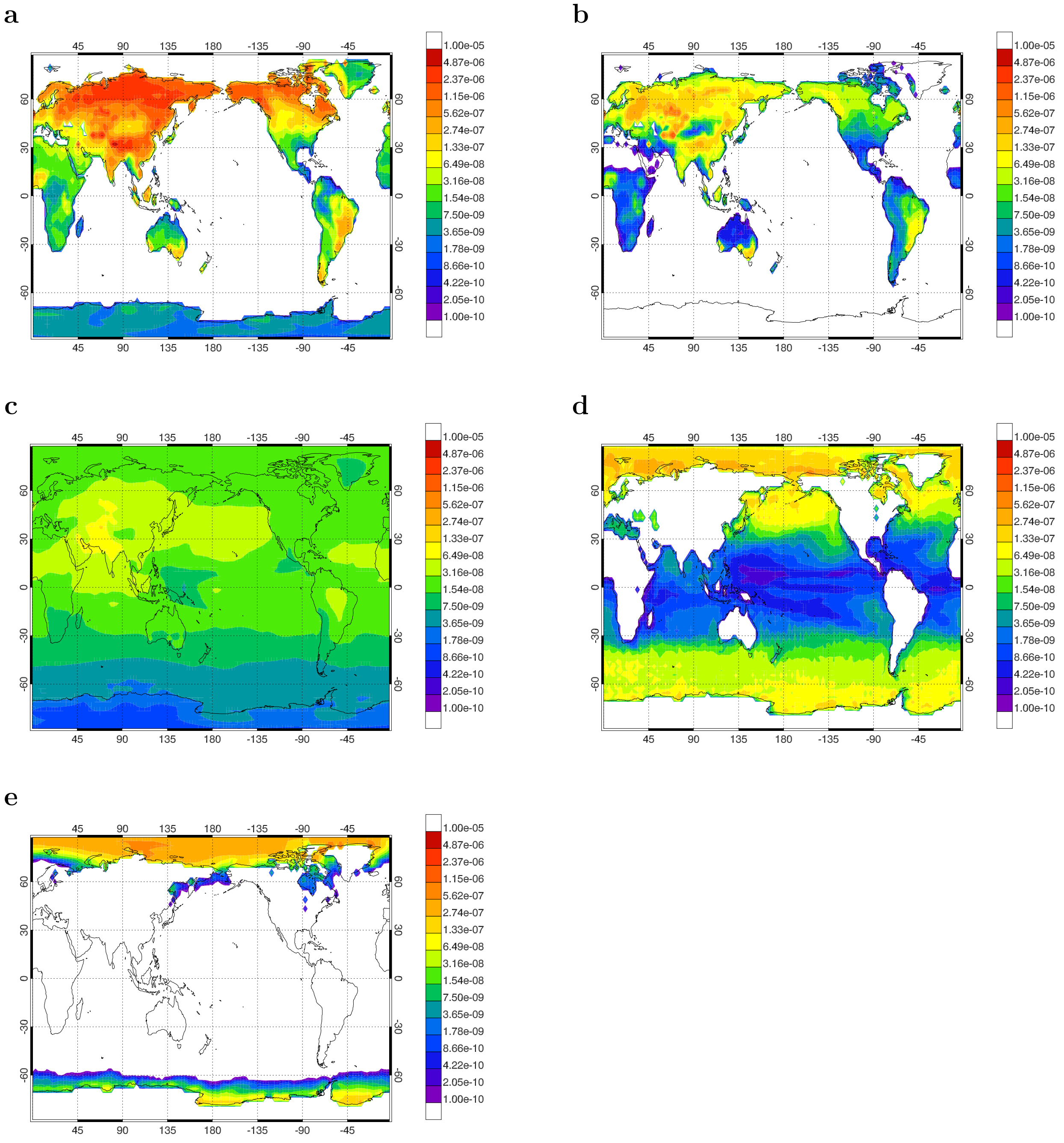

Figure 5.5: α-HCH environmental burdens $[kg\ m^{-2}]$ (a: soil, b: vegetation, c: atmosphere, d: ocean, e: sea-ice. Average of the 10^{th} year.).

The loss processes furthermore exacerbate the low concentrations in a region comprised between 30°N and 30°S. At these latitudes the volatilisation is also notably affected by wind. The resulting pattern exhibits a marked seasonality in its zonal and meridional features. In northern winter, the minimum is at its wider extension; toward the warm season, gradually it shrinks. The strongest variability occurs in correspondence of the equatorward branches of the subtropical gyres, where waters richer in contaminants move northward along the coasts of southern Africa, western Australia ans Peru and southward along California and Northern Africa. Permanent minima are simulated at the equator and at 5°N.

In case of the HCHs, the faster degradation of the α isomer in seawater and its lower solubility determine lower concentrations in the tropics, until mid latitudes (possible implications of the difference in application scenarios on the spatial distribution are discussed later in the chapter). For these compound, due also to the seasonal emission scenario, the strongest seasonality is simulated.

As DDT does not degrade significantly in seawater, its only loss from the compartment is volatilisation. The tropical minimum for this compound is narrower (horizontally as well as vertically) than in case of the HCHs.

The relatively high concentrations of all three substances in the southern hemisphere testify the efficiency of atmospheric transport, fueled not only by continuous emissions (in case of DDT and γ-HCH), but also by the high burden of the high latitudes where the compartments store and re-emit increasing amounts.

The long-range transport potential of the three compounds studied has been described using long-range transport potential indicators introduced by Leip and Lammel, 2004[66]. The indicators provide information on the geographical spreading of contaminant plumes. They are based on characteristic percentile values of the cumulative distribution functions of the concentration, in zonal and meridional directions (information on all indicators used in this study is provided in glossary).

The indicators have been used to study the long-range transport of DDT, α-HCH and γ-HCH by considering the total environmental burden, i.e. the sum of the single compartmental burdens, towards the end of simulation. The results are presented in Table 5.2.

compound	latitude COG applications	latitude COG total burden 10^{th} year	ZS	S	SS
γ-HCH	39°N	48°N	8965	7871	4204
DDT	26°N	43°N	10403	7992	4070
α-HCH	37°N	42°N	8235	9187	3773

Table 5.2: Long-range transport indicators: centre of gravity (COG), zonal spreading (ZS), spatial scale (S), spatial spreading (SS) in km after 10 years of simulation.

For all three compounds the net northward migration of the total environmental burden is expressed by the movement of the centre of gravity COG, with the coordinates of the 50^{th} percentile in both zonal and meridional direction.
In all three cases, a northward shift of the COG is observed. In case of DDT, from northern India the total burden experiences the most relevant meridional migration, from 26°N to 43°N.
For γ-HCH, the COG moves 9°N. The other isomer (applied only from February to September) show the smallest step northward, from 37°N to 42°N.
In general, the burden experiences a north-eastward displacement of plumes carried by westerlies, from central Asia to northern China.
Under the selected scenarios, DDT shows the highest tendency to spread along the north-south axis (confirming the results relative to the meridional migration of its COG), as quantified by the zonal spreading, ZS, although the values for the HCHs are in the same order of magnitude.
The values of the spatial scale S indicate a distributions of DDT and γ-HCH comparably extended in all directions, and slightly less than for the third compound (whose tendency to migrate also in zonal direction can be seen as it, not applied in northern America, spreads all over the world).
The evolution in time of the spatial scale, the spatial spreading, SS, show that, respect to the initial burden (mirroring the application patterns), the long range transport of the two substances applied continuously is also comparable. In case of the third compound, the applications have a wider north south pattern than for DDT and γ-HCH.

Transport to the Arctic The latitudinal migration of the compounds can be furthermore quantified taking a look to the compartmental burdens in the Arctic, as several studies (among others, AMAP, 2004[9], Macdonald et al., 2000[76], Barrie et al., 1992[16]) list DDT and the HCHs under the environmental contaminants of concern in Arctic. North of 66°N, the compartments recipient of the highest fraction of the total environmental burden, at the end of the runs, (Table 5.1) are ocean (with 5.4%) and soil (5.1%) for DDT, ocean (over 10%), soil (5.2%) and sea-ice (4.3%) in case of γ-HCH and again soil (12%), ocean (5.4%) and sea-ice (5.5%) for α-HCH. The HCHs are the compounds which most accumulate in the Arctic, with around 22% and 21% (vs 12% of DDT) for α- and γ-, respectively, of the total mass.

The fraction of the individual compartmental burdens that reaches north of 66°N, and its evolution, indicate, moreover, which compartments show the most pronounced meridional variability. The arctic fraction of soil, vegetation, atmosphere and ocean burdens is shown in Fig.5.6.
At first glance, all three compounds have the highest northward gradient in soil and ocean (the latter hosts a comparatively higher fraction due to the more favourable surface share in the Arctic). The HCH isomers have the most efficient accumulation in ocean. They are more soluble than DDT, although not particularly persistent in ocean. After 10 years, the arctic ocean burden of both is more than 27% of the global ocean burden. Whereas

in case of the γ isomer this burden appears to be increasing for the whole duration of the run, for α-HCH it stabilises from the eighth year onwards. The global ocean burden of this contaminant has already reached pseudo-steady state during the third year (cf. Fig.5.2). A northward shift in time is clear.

The arctic soil is accumulating with similar pace for DDT and lindane (12% and 8% at the end of the run, respectively). For α-HCH the accumulation is faster, and reaches 20% of the total soil burden.

The vegetation arctic share, visibly still increasing at the end of the simulation only in the DDT case, is otherwise generally stable after the first year, as the global share.

The atmosphere, the compartment subject to the fastest cycling, reaches, in the Arctic as well, stability in the very first years of simulation. Either under continuous (case of DDT and γ-HCH) or intra-annually variable (case of α-HCH) entry scenarios, the fraction of the compounds, due to the early established stability condition, is not increasing in time. As the atmospheric transport towards the high latitudes is extremely efficient, and together with the volatilisation (other source for the Arctic), soon in balance with deposition and degradation in the Arctic, also for the Arctic subsystem, the burden stabilises within the first year and does not appreciably change its trend.

For what concerns the sea-ice burden, not shown in picture, for the three substances in the Arctic it is (obviously) always over 80% of the total sea-ice burden. As the compounds do not directly enter the snow-sea-ice complex from the ocean waters (the process is considered negligible [139], [89]), the only source of SOCs for the sea-ice compartment is the atmospheric deposition. The burden (cf. Fig.5.2) reaches a pseudo-steady state (i.e. has also relevant volatilisation and release with melt water) for α-HCH (for which it is 6.4% of the total mass) and tends towards it for the other two substances at the end of the run.

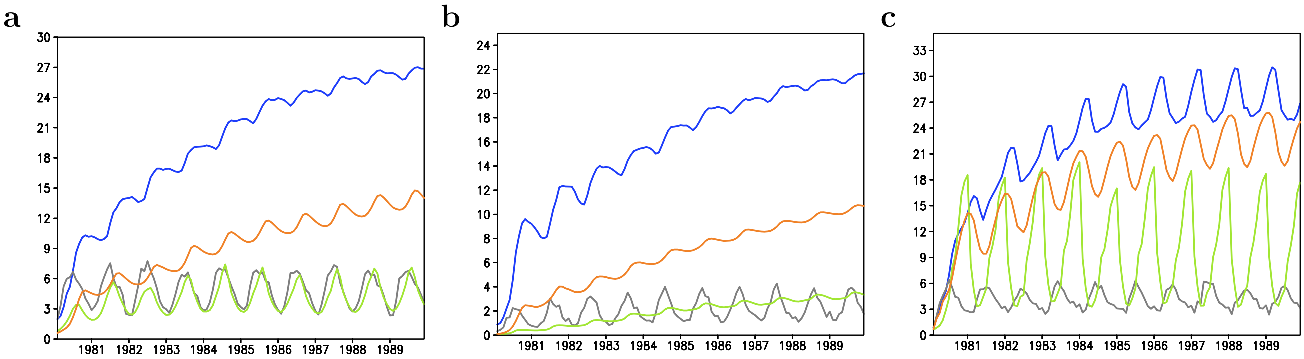

Figure 5.6: γ-HCH (a), DDT (b) and α-HCH (c): migration towards the Arctic. Burden in Arctic as fraction of the compartmental burden in time [%] in atmosphere (gray), vegetation (green), soil (orange), ocean (blue). Monthly means of a global sum.

Model vs observations Several factors limit the possibility to evaluate the current model results with observations. The compounds' application scenarios used for the model experiments are non realistic. The absence of interannual (or even intra-annual) variability in the amounts applied, furthermore, in a pristine environment, without any pre-contamination, severely impacts the possibility of a direct, quantitative comparison of concentrations with experimental data[2]

Several sets of observations are available for the organochlorines of concern, mostly point measurements of atmospheric concentrations from land based stations or sparse ocean data (among others, AMAP 2004[9] and 1998[10], Macdonald et al., 2000[76], Jantunen and Bidleman 1998[51], Bidleman, 1990[17], Tanabe et al., 1982[120] and 1983[119]). The selection of the appropriate dataset suiting the evaluation purposes and requirements is non trivial.

As the concentrations of some organochlorines were determined in air and surface water from various oceans in 1989-90, during five survey cruises, by Iwata et al., 1993[50], a comparison with model results has been performed. This particular dataset has been chosen since it provides atmosphere and seawater concentrations at the same location. Furthermore, the distribution of the contaminant had to be consistent with the extensive application in developing countries of the 1980s. The parameter chosen for the comparison is the air/seawater concentration ratio of γ-HCH, DDT and α-HCH. The simulation data used are averages of the 10^{th} year of run. At this stage, for all three compounds the atmosphere has reached pseudo-steady conditions, whereas the ocean is still accumulating (in spite of the continuous applications) for γ-HCH and, steeply, for DDT. Results are shown in Table 5.3.

In the Arctic the simulated values show good agreement with the measurements in case of the HCH isomers. However, due to the lack of precontamination in the application scenarios, makes it arguable to consider stations far from the application locations. Elsewhere the modelled values are, if not directly comparable with experimental data, within one order of magnitude. The model appears to generally underestimate the C_{air}/C_{wat} ratio in case of DDT. This could be a consequence of the continuous applications (for the massive volatilisation close to application peaks). Everywhere the ratio for DDT (and slightly for γ-HCH) is likely to decrease in further years, as its ocean burden continues to accumulate. Where the model exceeds the observations, there would be a better agreement, were the waters carrying more compound. Ocean transport is, in fact, still underestimated in the model.

Discussion

For the first time a three-dimensional modelling approach, based on the coupling of two GCMs has been used to describe the multicompartmental cycling of semivolatile organic compounds[3].

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[2] Generally speaking, uncertainties related to modelling in the physico-chemical properties and parameterisations (although all derived from experimental data) used and biases in the observational setup, also not immune to problems as contamination occurring on ships or in laboratory, may in principle as well prejudice the reliability of such evaluations.

[3] Most recently, another modelling setup based on an atmospheric general circulation model (Gong et al., 2007[32]), used to investigate the global transport and budgets of PCBs (Huang et al., 2007[46]), encompasses an ocean tracer transport module based on a tracer model, getting as an input prescribed

sampling location	DDT		γ-HCH		α-HCH	
	model	obs.	model	obs.	model	obs.
Chukchi Sea	0.0	19.3	0.0	0.1	0.1	0.2
Bering Sea	0.1	3.6	0.1	0.2	0.1	0.2
Gulf of Alaska	0.6	3.2	0.1	0.2	0.2	0.2
North Pacific	1	10	0.2	0.9	0.6	0.8
Caribbean Sea	5.7	3.3	1.5	0.7	7.6	0.5
Gulf of Mexico	5.2	21.8	1.7	1.1	5.2	1.4
North Atlantic	1.3	10.8	0.1	3.1	0.3	1.7
East China Sea	5.3	1.2	2	1.5	4.8	1.1
South China Sea	4.7	7.8	2.8	5.1	9.4	2.1
Bay of Bengal	15	25	5.7	10	2.0	14.1
Southern Ocean	0.4	2.3	0.0	0.9	0.2	0.4

Table 5.3: Transport towards the Arctic: observed and modelled air/seawater concentration ratio C_{air}/C_{wat} $[Lm^{-3}]$. Average of the 10^{th} year.

The results of ten years of simulation with agricultural applications scenarios show that the compartment holding the highest share of of DDT, γ- and α-HCH, still accumulating at the end of the run, is the soil. This highest retaining capacity is determined by its properties as porosity and content of organic matter. This effect is particularly pronounced for compounds of high lipophilicity (the highest among the substances selected for this study), as DDT. The substance has then its longer residence time (see Table 5.2) in the reservoir. After 10 years of run, DDT is mostly distributed to soil (49% of the total burden) and ocean (27%), this latter compartment also still steeply filling at the end of the run. DDT shows in ocean a residence time of 1.22 $years$ (only its τ in soil is higher). This is due to the lower water solubility and to the insignificant degradation in ocean. As seen in the previous chapter, the contribution of the ocean organic phases to the retaining capacity of the compounds reaches, at its maximum (in areas as the equatorial Pacific throughout the year), 30% of the compartmental burden. From these properties it descends that the tropical minimum for this compound is narrower (horizontally as well as vertically) than in case of the HCHs.

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global currents.

γ-HCH, moderately water soluble, is after 10 years mostly found in the ocean and soil. As the two compartments are close to have the sinks balance the sources, their share would not to change relevantly in the future. The amount of this compound in ocean is lower than in case of the other isomer, as its lower solubility suggests.

The distribution of the compound α-HCH is influenced, not only by its properties, but also, in comparison to the other two substances chosen for this study, by its application scenario, which follows a February-September entry pattern. The burden in atmosphere, vegetation and ocean reaches within two years a pseudo-steady state. In soil the slope of the curve decreases toward the 10^{th} year. This burden and the ocean burden (due to the limited water solubility relatively small) would be higher and probably accumulating, were the applications continuous in time. It is noteworthy that different emission scenarios (for α-HCH) only impact quantitatively the burden of the compounds in the compartments, and not the time length necessary for steady conditions to establish (when the case). Test runs show that, varying the pressure of sinks, as the degradation in the atmosphere, the trend reaches stability within the same time lag.

For DDT and γ-HCH, both applied with continuous application scenarios, the comparison between the results stresses the peculiar characteristics of the two compounds, making their environmental fate different. DDT is the last compound to reach steady state in atmosphere, the first compartment to reach stability. In soil, degradation is more effective for γ-HCH. As the atmosphere is the fastest transport vector, the study of the fluxes to and from this reservoir is particularly important. Volatilisation is a crucial process. The contribution to the atmospheric burden from volatilisation comes for DDT for the most part from vegetation at 58%, from ocean for 28% and then from soil, at the end of the simulation. For a water soluble compound like γ-HCH, the highest fraction volatilises from vegetation with 78%, then follow soil, with 18%, and ocean only with 4%.
The fact that the ocean burden of DDT, in comparison with γ-HCH, increases faster, despite higher fugacity of DDT from water, is obviously determined by its persistence in the compartment.

The cycling shows that the processes taking place in the Northern Hemisphere dominate the global figures. In the ocean, the combined effect of ocean transport and of temperature-driven degradation and volatilisation is clear.

The transport routes confirm the ones found by Huang et al., 2007[46] in a study on the global fate of PCBs. The inter-continental transport occurs mainly in the northern hemisphere in the eastward direction along the westerly winds. The inter-hemispheric migration, follows monsoons (with seasonality, also in Semeena et al., 2006[106]) or the easterly jet.
DDT has the most extended plume in the north south direction, as shown in other MPI-MTCM studies (Leip and Lammel, 2004[66]). In case of DDT and α-HCH, as the burden has spread to North America, where no applications take place, and the local concentra-

tion is comparable to the amount stored in regions where the compound was applied in first place. These areas can then become secondary sources.

Moreover, as volatilisation and degradation are more effective than for the other two compounds and thanks to the non-continuous application scenario, concentrated in the northern hemisphere in the warm season, when the degradation is more efficient, the long-range transport (and the multicompartmental cycling) of α-HCH may result limited.

As the centre of gravity of the atmospheric burden does not register a net migration towards north, the northward migration of the COG of the total environmental burden is determined partly by deposition patterns, but mostly by properties and conditions of the terrestrial compartments and ocean.

Under the selected scenarios, DDT shows the highest tendency to spread along the north-south axis (also with the most significant shift of the centre of gravity), as it resides longer than others in the environment. Nevertheless, the HCHs are the compounds which most accumulate in the Arctic, with around 22% and 21% (vs 12% of DDT, whose applications have the southernmost COG, at 26°N) for α- and γ-, respectively, of the total mass. They are more soluble, although not really persistent in ocean. For them the arctic ocean burden of both is more than 27% of the global ocean burden. Whereas in case of the γ isomer this burden appears to be increasing for the whole duration of the run, for α-HCH it stabilises from the eighth year onwards. The global ocean burden of this contaminant has already reached pseudo-steady state during the third year (cf. Fig.5.2). A northward shift in time is clear.

Based on results also from the previous chapter, if the ocean were the only transport vector, it would be at advantage of the most persistent compound in the reservoir, namely DDT. However, as the atmosphere is the fastest vector towards the Arctic, in the experiment with agricultural applications, γ-HCH, is transported in higher amount to the higher latitudes, in spite of its more efficient degradation in all compartments. Similar conclusions where also drawn in a previous study (Semeena et al., 2006[106]).

Striking are the large differences in the compartmental distribution between the two HCHs. These are slightly more pronounced in the Arctic than globally.

α-HCH being more lipophilic than the other HCH, mainly distributes to arctic soil. The burden even exceeds the area share of the Arctic (around 8%). Its limited water solubility causes its ocean fraction to be relatively small, whereas the γ-isomer has an arctic ocean burden comparable to its global vegetation burden.

The fair agreement with measurements presented in Table 5.3, does not prevent to stress the need of historical runs, to reproduce the fate of SOCs with chronological accuracy in order to more robustly and quantitatively compare model results with observations.

Effects of sea-ice on volatilisation

The sea-ice is an environmental compartment that, due to its collocation, interacts with both the two major reservoirs and transport media it is in contact with. It is a substrate for atmospheric deposition, can host a fraction of the compounds present in the ocean as it forms and release back the substances to the atmosphere or to the ocean via volatilisation and melting processes, respectively.

The distribution of SOCs in the sea-ice compartment is influenced by deposition, ice advection and ice melting.

The presence of an ice cover has been shown to prevent the air/water exchange in the case of rivers (Macdonald et al., 1991[75]). Also in the Arctic, ice cover generally inhibits ocean-atmosphere exchange (Pfirman et al., 1995[89]). However, the sea-ice cap rather than being a continuous interface is often fractured in many points, allowing volatilisation through the gaps. Such gaps have been found to be sources of organic compounds for the atmosphere (Leck and Bigg, 2005[65]). The exchange between ocean and atmosphere results, therefore, dampened by the presence of sea-ice (Hargrave et al., 1997[37]), rather than completely impeded. Since volatility increases with temperature, some chemicals, deposited onto the ice surface in cold seasons, are subject to be released back into the atmosphere once warmer conditions establish (Barrie et al., 1992[16]).

The semivolatility of DDT, γ-HCH and of other SOCs in general, their persistence and the cold condensation may have the effect of maintaining air concentrations in remote regions long after abatement policies and ban have taken effect in source countries (Halsall, 2004[35]).

Model setup and simulation scenario

Two versions of the model introduced in Chapter 3 have been used for this experiment. The only difference between the two setups is represented by the inclusion of a sea-ice compartment in one of them. (The model without sea-ice is the same used for the preliminary comparison of Chapter 4).

Also in this case, as in previous experiments, the duration of the runs is ten years.

The compounds selected, different in terms of volatility and water solubility, are DDT, γ-HCH and α-HCH and the entry scenarios, with agricultural applications, have been presented in Chapters 4 and 5.

Results

In Fig.5.7 the simulated sea-ice cover is shown. The compartment experiences considerable seasonal variation in width as well as in compactness (expressed in figure as fraction of the grid cell surface). Such variability influences both the release of the compounds from the ice-snow complex to ocean waters and the volatilisation.

The storage is shown in Fig.5.8. As mentioned previously, the ice burden for all compound in the Arctic accounts, at the end of the run, for at least 80% of the total ice burden. Also, the burden is reaching pseudo-steady state in case of α-HCH, applied with the non continuous scenario, and accumulates for most of the run for the other two compounds.

The volatilisation from ocean, in presence and absence of the sea-ice cover, is shown in Fig.5.9. The presence of sea-ice inhibits volatilisation, locally, by two-three orders of magnitude for all three compounds. This effect is less pronounced for lindane, the most soluble compound selected for this study. This dampening effect leads to a local increase

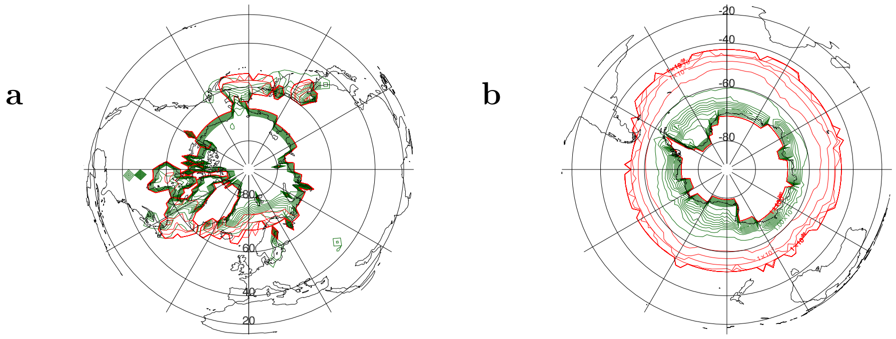

Figure 5.7: Simulated sea-ice cover in the northern (a) and southern (b) hemisphere [% of grid cell covered by ice, Δ=10%]. Green: northern winter, red: northern summer. Average over 10 years.

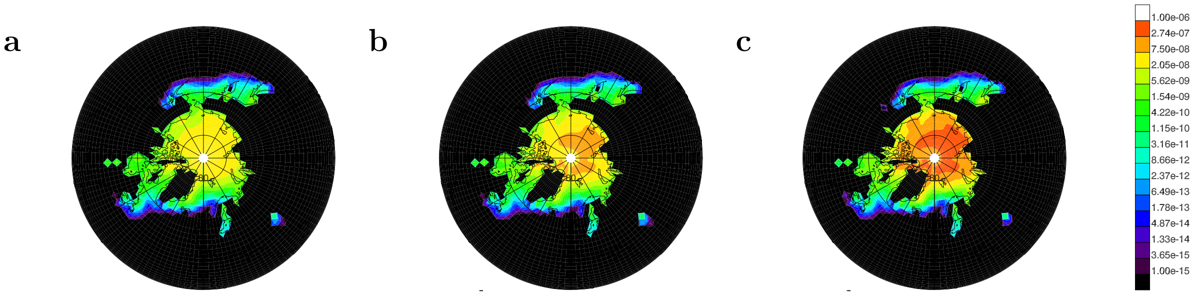

Figure 5.8: Sea-ice burden of DDT (a), γ-(b) and α-HCH (c) [$kg\ m^{-2}$]. Arctic ocean. Average over 10 years.

of the retaining capacity of the ocean underneath.
The spatial gradients in Fig.5.9 also show the transport of contaminants to the Arctic, from the north Atlantic, dominated, as seen before, by the Norwegian Current and, in the north Pacific, through the Bering Strait. The compounds partly end below the ice, but as the cover is inhomogeneous and seasonally varying in width, are as well subject to volatilisation.
The volatilisation from the sea-ice compartment does not, however, provide a significant contribution to the total volatilisation budget, being three orders of magnitude smaller than volatilisation from ocean through the ice. Whereas in the atmospheric column seasonal gradients are observed on a local scale, the distribution of compound on arctic soil and vegetation results, at least for the HCHs, barely affected.

Although geographically mostly limited to the areas interested by the presence of a cover,

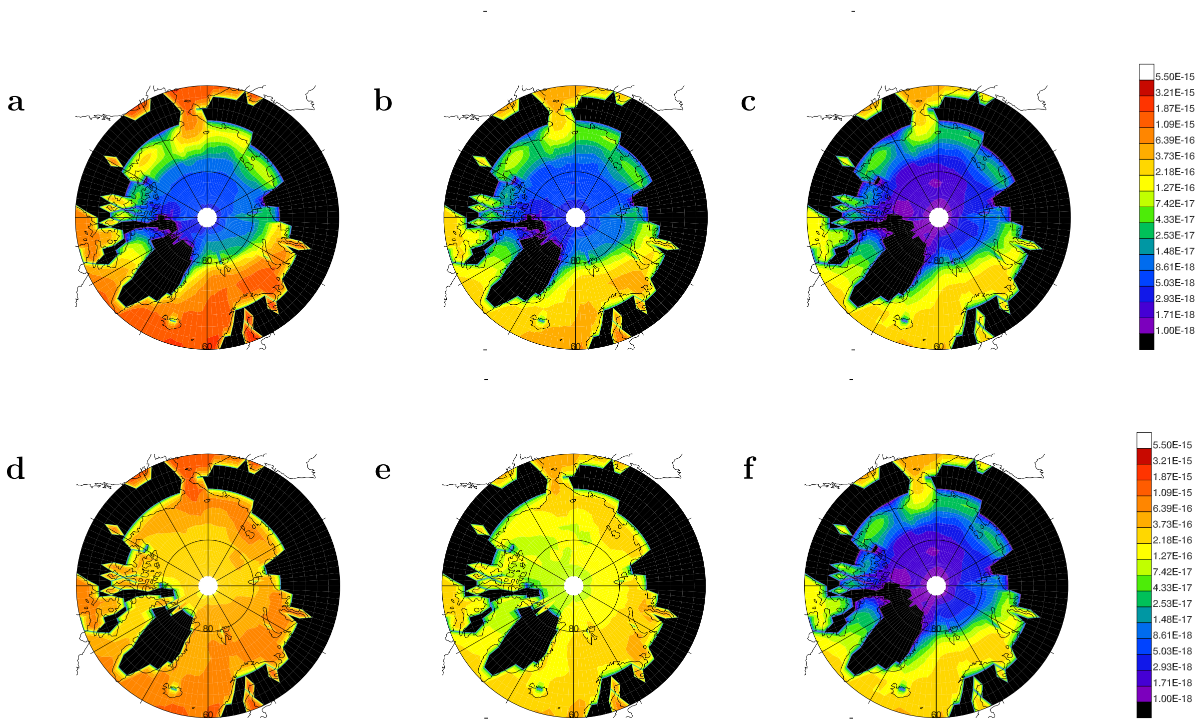

Figure 5.9: Ocean volatilisation $[kg\ m^{-2}\ s^{-1}]$ of DDT (a, d) γ- (b, e) and α-HCH (c, f) in presence (a, b, c) and absence (d, e, f) of the sea ice cover. Average over 10 years.

and on the surface layer (Fig.5.10), the effects of the sea-ice are visible, in the water column, on the concentration of the compounds, until a depth respectively of 70 metres for DDT and 100 metres for γ-HCH, the one with higher water solubility.

The effect of the presence of the sea-ice on the global compartmental distribution of DDT and γ-HCH, for the tenth year of run, is inferable from the comparison of Tables 4 and 5.1, reporting the compartmental fractions of the total burden for the setup without (3D ocean in table) and with sea-ice, respectively. In absence of the compartment and for both compounds, the amount that would be stored in the sea-ice is distributed to soil and ocean. The overall persistence of the compounds in the environment results slightly affected; for lindane τ_{ov} is 1.12 and 1.05 and for DDT 2.13 and 2.0 $years$, in absence and presence of the compartment, respectively.

Discussion

The results show that the presence of sea-ice inhibits volatilisation regionally by two-three orders of magnitude. The differences observable between the three compounds are driven by their solubility in seawater. Other modelling studies by Strukov et al., 2006[116] and Stocker et al., 2007[114] also underlined the dampening of volatilisation by sea-ice. This

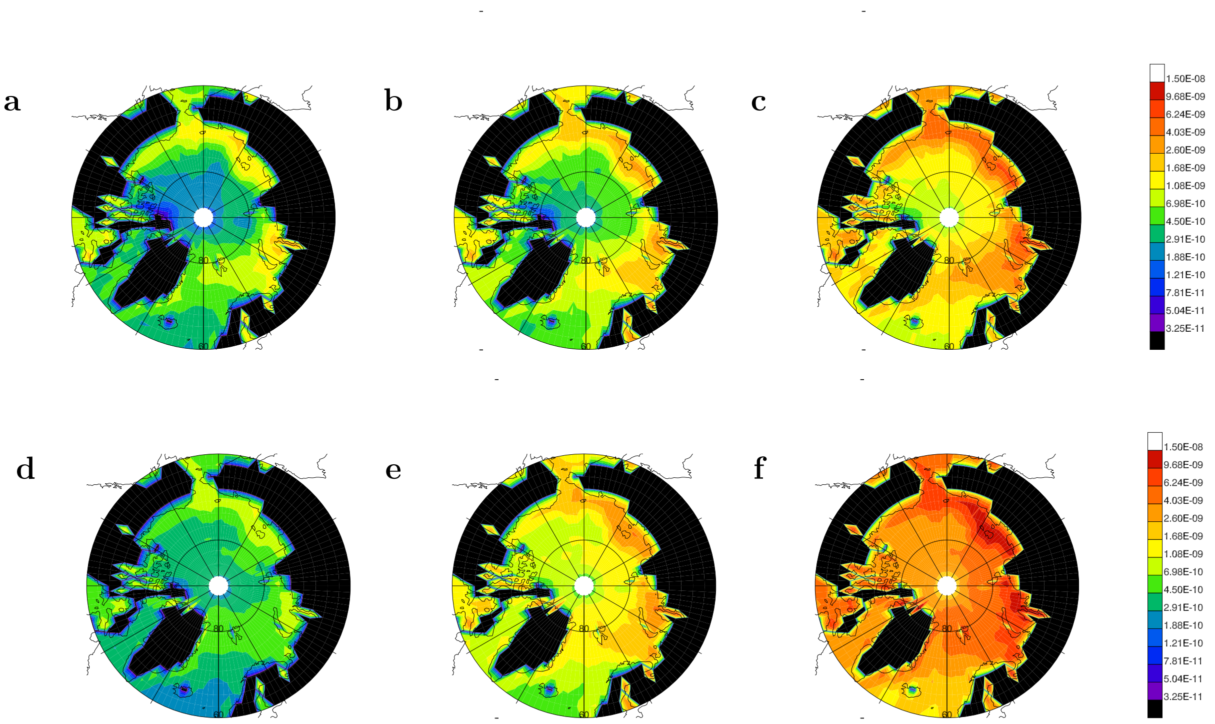

Figure 5.10: Surface ocean burden $[kgm^{-2}]$ of DDT (a, d) γ- (b, e) and α-HCH (c, f) in presence (a, b, c) and absence (d, e, f) of the sea-ice cover. Average over 10 years.

effect leads to an increase of the retaining capacity of the ocean underneath. As, for the simulated scenarios, the ocean budget is mostly depositional, the ocean surface concentration is, locally, slightly higher when the ice cover is absent, due to direct deposition. The compartmental distribution of γ-HCH and DDT does not experiences drastic changes in absence of the sea-ice cover. The amount that would be stored in the sea-ice compartment is in this case distributed to soil and ocean.

As mentioned in the introduction, the presence of sea-ice compartment may translate in a delay of the atmospheric deposition in reaching the ocean waters. The most quantitatively significant release of the compound via ice melting occurs at the boundary of the seasonally varying ice cover. In comparison to the case of absence of sea-ice, a release in a region where the temperature is more favourable for volatilisation implies a more intensive cycling. This explains a smaller residence time in ocean and a higher persistent in adjacent non mobile compartments when the ice cover is in the model. This effect is appears more pronounced in case of DDT.

Transport mechanisms

In Fig.5.11 are shown the migration processes for semivolatile organic compounds. One of the transport mechanisms hypothesized for semivolatile organic compounds is the so-called *grasshopping* [33], [135].

Semivolatile organic compounds may reside, based on their vapour pressure, in the atmosphere temperature range, both in condensed and gaseous phases. Their persistence prevents them from rapid breakdown, upon atmospheric deposition, in ground compartments. According to the global temperature distribution, the intercompartmental cycling of SOCs can occur as a sequence of volatilisation, transport in the atmosphere, deposition and transport in the ocean, i.e. as a sequence of *hops*. This peculiar behaviour may translate into a net poleward transport, the *cold condensation* (Bidleman et al., 1990[17], Wania and Mackay, 1993[133]) of compounds accumulating in areas where the revolatilisation is not favoured.

Clearly, the number of factors playing a significant role in such cycling patterns, as deposition and characteristics of the recipient compartment (retentive capacity) as well as local conditions, and the derived complexity in a description of the system, particularly in the depiction of the interactions between compartments, are much higher than in the case of compounds classified as single-hop[4] [127].

The fate of these latter is, in fact, mainly influenced (apart from emission patterns and environmental factors) by their persistence in atmosphere.

Multi-hop compounds, due to their vapour pressure and lipophilicity, readily shift their distribution between gas-phase and condensed phases (organic substrates of soil and vegetation, aerosols, marine phases, water) in response to changes in environmental temperature and phase composition, and therefore can travel long distances in repeated cycles of evaporation and deposition [133]. This could determine an enhancement of the long-range transport potential.

This study is to be considered the natural evolution of a previous global modelling study (Semeena and Lammel, 2005[108]) performed with a model previously introduced in 4, the 2DO model.

As a three-dimensional ocean model, coupled with the atmospheric GCM, replaced the bidimensional mixed layer in the preexisting setup, for the first time here the grasshopper effect is studied with a three-dimensional representation of the global ocean.

Model setup and simulation scenario

The model setup employed is analogous to the one described in Chapter 3.

An agricultural emission scenario was employed for DDT and $\gamma-$HCH as in Chapter **??**.

The compounds DDT and lindane are continuously applied all year long in equal amount.

In order to investigate the meridional transport mechanism, the first environmental cycle

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[4] Defined as chemicals which are so involatile or so water-insoluble that they can undergo LRT only by piggybacking on suspended solids in air and water (UNEP, 2003[127]).

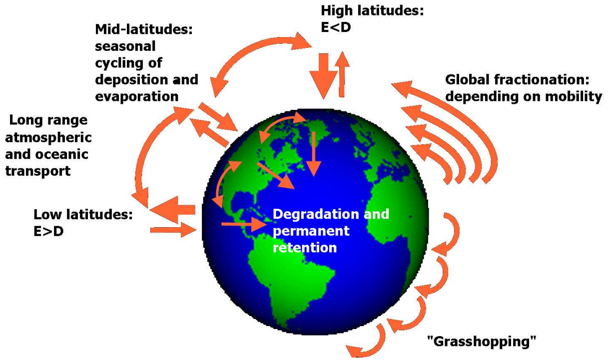

Figure 5.11: SOCs migration processes[1]

in atmosphere and ocean has been disconnected by the subsequent cycles (in Table 5.4 a schematic, more detailed description of the scenarios).
For all the compounds and scenarios, the duration of the simulations is 10 years.

Results

Having disconnected the first environmental cycle from the subsequent ones allows to acknowledge the multi-hopping nature of DDT and γ-HCH.
The results show that, for both substances, the compounds reach the Arctic within the first month upon application, by means of the sole atmospheric transport (first cycle). However, a closer look allows to appreciate the differences between the two compounds, for which the cycles have different importance.

In Figures 5.12 and 5.13 the zonal average of the mixing ratio in the atmosphere (a, b) and the concentration in ocean (c, d) during the 8^{th} year of simulation.
At this stage the atmosphere is already in pseudo-steady state, whereas the ocean is still accumulating, with faster pace in case of DDT (cf Fig.5.2).
Similar behaviour in the atmosphere is traceable for both substances. Already upon first volatilisation from terrestrial compartments (first hop), the atmospheric transport spreads the compounds along the latitude, clearly to the Arctic (visible since the first months of run). The substances, in spite of the inner-tropical convergence zone, reach also the southern hemisphere (via trade winds and winter monsoon). This is particularly evident for DDT. For this compound, the application over India and central America, three orders of magnitude higher than the ones taking places in Africa and South America, contribute to the plume extending up to 20°S. The atmospheric mixing ratio experiences seasonal variations; it peaks in the northern hemisphere in summer (volatilisation).
The single-hop reaches for lindane higher in the atmosphere (even trespassing, for a small fraction, the tropopause) than the subsequent hops.
The two compounds behave also different in their first atmospheric cycle: in northern

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[a] adapted from Wania and Mackay, 1996[135]

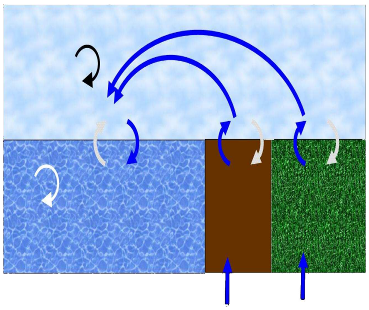
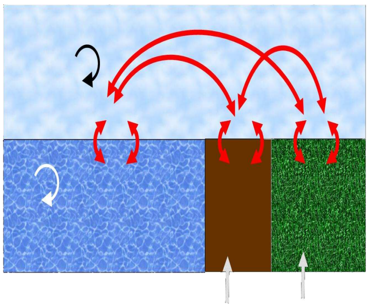
scenario	scheme	description
Single-hop		The compounds are directly applied on soil and vegetation from where they can volatilise (or be permanently stored). Transport in the atmosphere and deposition redistribute SOCs to terrestrial compartments and ocean. In the latter compartment, transport, sinking and revolatilisation occur, concluding the first cycle of SOCs in the environment. The input to the atmosphere due to revolatilisation from soil, vegetation and ocean is part of subsequent cycles and therefore not considered.
Multi-hop		The scenario only considers the environmental cycles subsequent to the first one. Input to the system are the only determined by revolatilisation from ocean (and sea-ice) as calculated in the single-hop scenario (introduced above). Once entering the atmosphere, the substances can cycle multiple times through all compartments.

Table 5.4: Description of the *single−* and *multi−hop* model setup. Blue (for single-hop) and red (for multi-hop) arrows indicate processes considered in the setup. The ice compartment is considered as part of the ocean compartment in the diagram. Degradation processes occur in all compartments, using the same rates for both scenarios. For this reasons they do not appear in the diagram.

summer lindane experiences a marked peak (visible in Fig.5.13) centered at $300hPa$, arising from the plume over India, where the applications, spread mainly between 30°N and 50°N, also have their maximum (but no seasonality). In the same season, the deposition reaches, in the southern hemisphere, up to Antarctica.
The atmospheric multiple cycles of γ-HCH also cross the equator. For DDT the volatilisation from southern hemisphere appears very pronounced.
Unlike the case of γ-HCH, richer in atmosphere in its first cycle, the amount of DDT in single- and multi-hop is comparable.

In the ocean, the difference in the vertical gradients in the tropics between the two agrochemicals is striking. DDT clear reaches deeper in higher amounts in a region in which as shown previously, due to the abundance of organic phases, the gravitational settling associated with particles is more important than elsewhere.

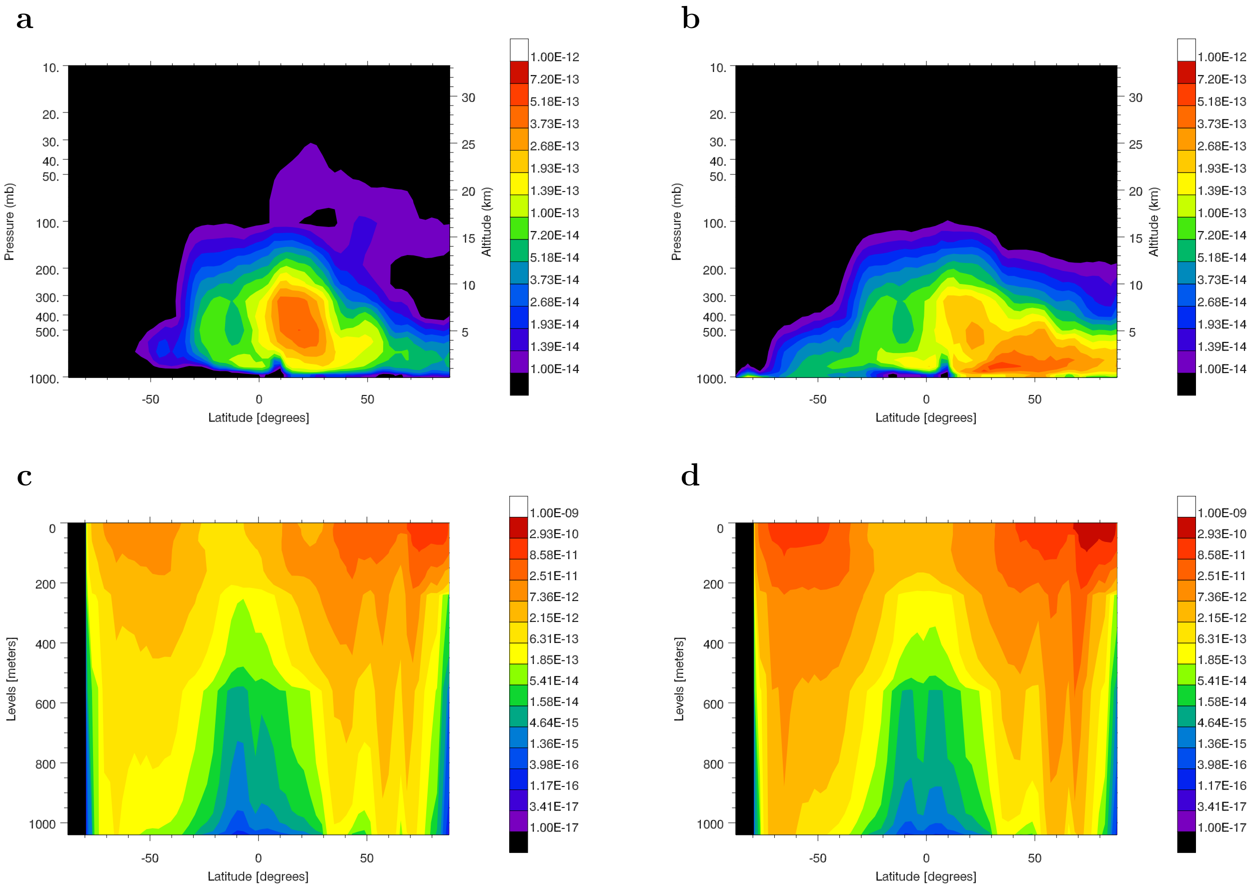


Figure 5.12: DDT in atmosphere $[kg\ kg^{-1}]$(a, b) and ocean $[kg\ m^{-3}]$ (b, c) single- (left) and multi-hop (right). Zonal average of the 8^{th} year of simulation.

Ocean single-hop is generally richer in DDT than in lindane (applied in higher amount, more soluble, but efficiently degraded). For this latter compound already within the first year compounds are found in the southern hemisphere (atmospheric transport).
The multiple cycles' ocean burden is richer in DDT, whereas for the other compound the masses and the gradients in single and multi-hop ocean are comparable. The reason is the higher persistence of DDT.

In Fig.5.14 the contribution of single- and multi-hop to the total environmental burden. After three years of run, recycled DDT exceeds the amount present in the environment upon application and the gap increases with time. For γ-HCH the first hop, for most of the simulation richer than the multi-hop, almost equals it in ten years.

Fig.5.15 shows how single and multiple cycles contribute to the burden of the different compartments (global sums) in time. The two chosen compounds show different behaviour.
At first glance can be seen that for DDT the multiple cycles are responsible for the most part of the burden in all compartments, whereas for γ-HCH the first cycle is very strong.

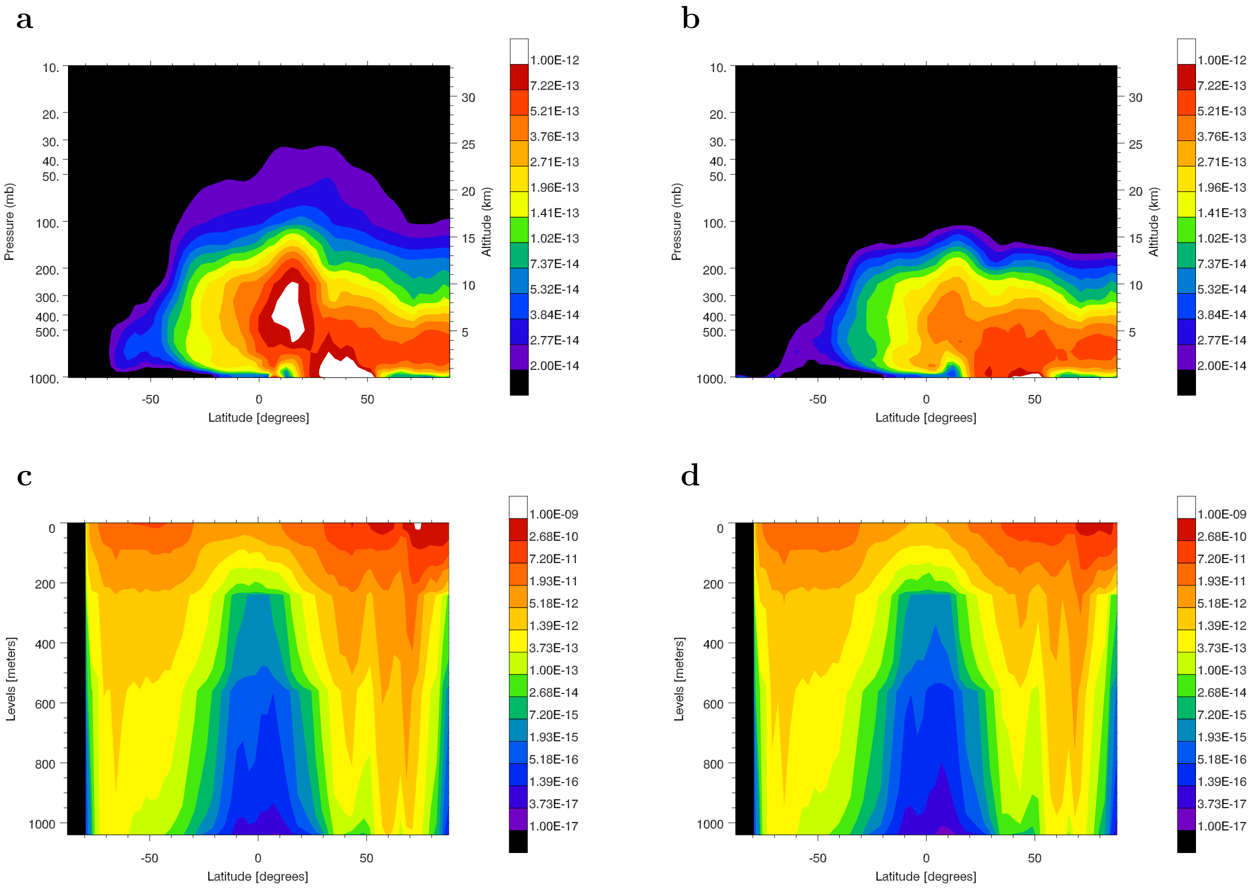


Figure 5.13: γ-HCH in atmosphere $[kg\ kg^{-1}]$ (a, b) and ocean $[kg\ m^{-3}]$ (b, c) single- (left) and multi-hop (right). Zonal average of the 8^{th} year of simulation.

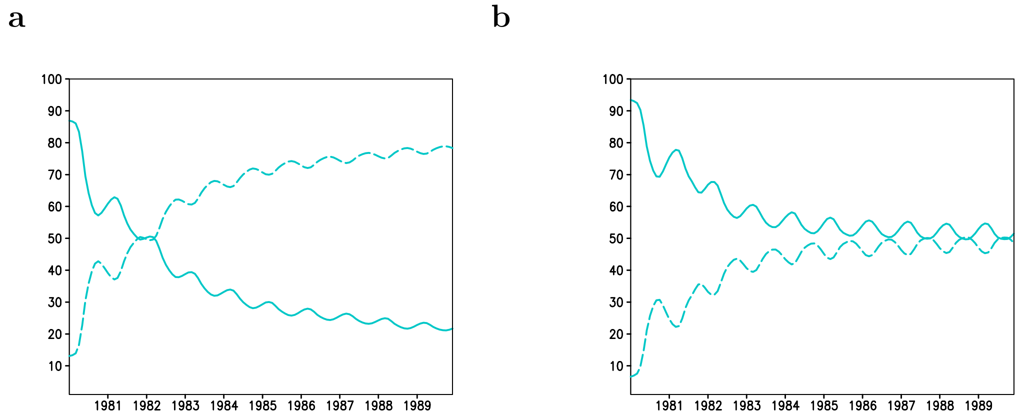


Figure 5.14: DDT (left column) and γ-HCH (right) fractions [%] of total environmental burden in single-hop (full line) and multi-hop (dashed line). Time series of a global sum.

More quantitatively, in the atmosphere the fraction recycled equals, after 3 years, the emitted amount for DDT. This feature, compared to the temporal trend of the atmospheric burden, shows how the deposition influences the seasonality of the concentration. For γ-HCH the effects of the degradation are obvious. The recycled amount is never enough to come close to the amount remaining in the atmosphere upon initial volatilisation.

For the vegetation compartment, the multi-hop DDT fraction is higher than single-hop (60% vs 40 %) and for γ-HCH again the opposite.

The soil is the only compartment, clearly eventually accumulating in all runs, exhibiting, similarly for both substances, higher recycled contribution. As expected, due to its higher environmental persistence, the recycled fraction is higher for DDT.

The higher fugacity in ocean of DDT explains the behaviour in this compartment. The compound is available for further cycles more than a more soluble compound as γ-HCH.

Finally, the sea-ice compartment appears to follow the general trend for both substances, being richer in lindane in its burden deriving from the single-hop and in DDT for the subsequent cycles.

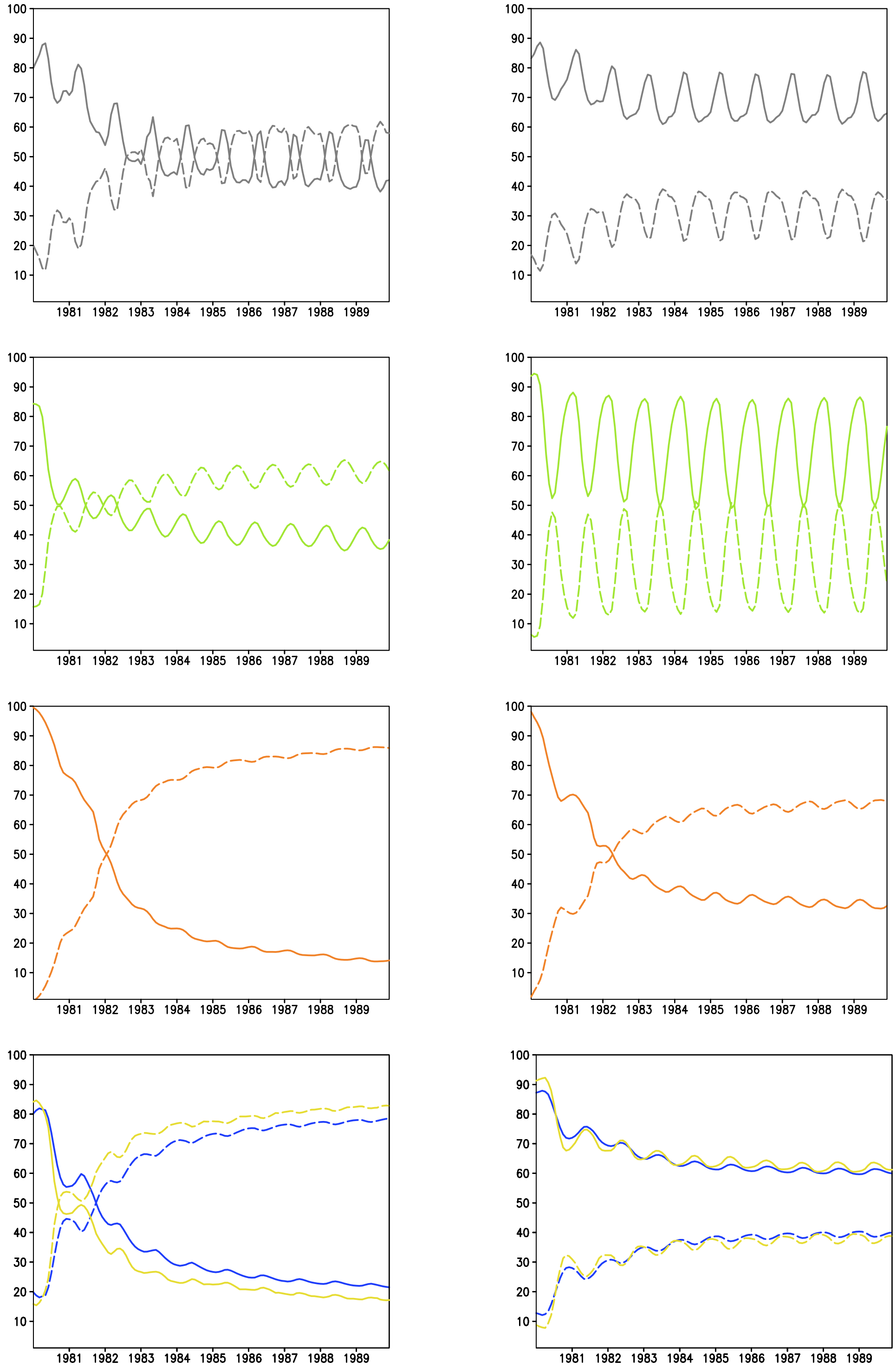


Figure 5.15: DDT (left column) and γ-HCH (right) fractions [%] in atmosphere (gray), vegetation (green), soil (orange), ocean (blue), sea-ice (yellow) in single-hop (full line) and multi-hop (dashed line). Time series of a global sum.

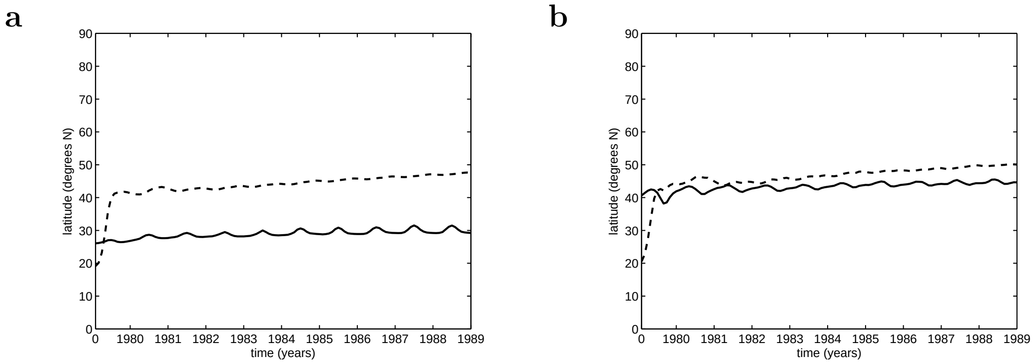


Figure 5.16: DDT (a), γ-HCH (b): latitudinal migration of the centre of gravity of the total burden. Single- (full line) and multi-hop (dashed line).

A further step into the knowledge of the relevance of the hopping mechanism is the quantification of the contribution of single- and multi-hop, considered separately, to the long-range transport. In Fig.5.16 the latitudinal migration of the centre of gravity of the total environmental burden for single- (full line) and multi-hop is shown.
For both compounds the curve referring to the first cycle is, obviously, due to the continuous application scenario which distributes the compounds onto non-mobile substrates, strongly bound to the application latitudes (cf. Table 5.2) and moves only few degrees north in ten years. The recycled burden, on the other hand, after an initial drop due to the contribution of fast atmospheric transport of re-volatilised mass, lies above, i.e. further north, the curve describing the first-hop, and its pace increases in time. For DDT the two curves lie over 2000 km apart, a longer gap in comparison to the 600 km of γ-HCH.

As the atmosphere carries compounds in a few days all over the world, a look to the separate first and multiple cycles allows, furthermore, to evaluate the efficiency of the global ocean as a meridional transport vector. Fig.5.17 shows the centre of gravity of the ocean burden, of its main source process (atmospheric deposition) and of its sinks (volatilisation and, for γ-HCH, degradation) for the single-hop scenario.

In case of γ-HCH, the ocean burden moves further north, in the course of the simulation, increasing its distance from the deposition. Degradation (accounting for over 70% of the sinks) and volatilisation are higher at warmer latitudes, therefore their COG does not move northwards to the same extent. The other compound (for which the degradation, only taking place in sediments, is non significant, being less than 1% of the sinks, and thus not shown) does not show, on global burden scale, any relevant meridional migration of the COG of the ocean burden.

Discussion

Having disconnected the first environmental cycle from the subsequent ones allows to acknowledge the multi-hopping nature of DDT and γ-HCH. The meridional transport is, for

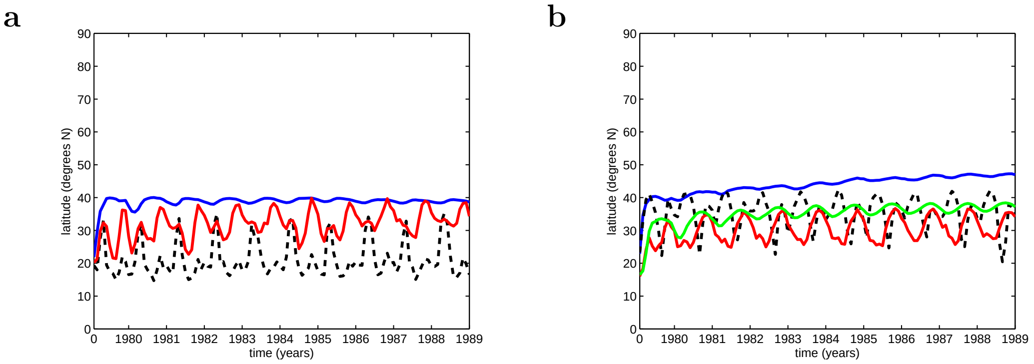


Figure 5.17: DDT (a), γ-HCH (b): latitudinal migration of the COG of ocean burden (blue), deposition (black, dashed), volatilisation (red), degradation (green) in the first environmental cycle.

both compounds indeed, of multi-hopping type. This confirms the outcome of previous studies [108]. The fact that γ-HCH as well is transported in multiple cycles, on the other hand, specifically contradicts a classification, based on the properties of the compound, labelling it as a *swimmer* [72].

As explained by the persistence of the substance, recycled DDT exceeds the amount present in the environment upon application from the third year onward. The gap increases with time. For γ-HCH the first hop, for most of the simulation richer in compound than the multi-hop, almost equals it in ten years.

Only exceptions to the general trend (single hop more frequent in γ-HCH and vice versa for DDT, to different extents for different compartments) are the atmospheric burden of DDT, which only toward the end of the run is enriched in recycled burden and, most clearly, the soil burden of lindane, where the recycled portion is prevailing to the first applied one. This could be due to the deposition, upon atmospheric transport, to colder areas. Nevertheless, for this compound, it is its higher tendency to remain in the aqueous phase, where degradation is faster, which prevents it to exchange to other compartments, determining its total burden behaviour. These results are also in agreement with the outcome of the sole ocean experiment in the previous chapter. As DDT is clearly more persistent in the environment, the compound accumulates so that what is recycled between the compartments exceeds the emissions, i.e. the compartments may represent significant secondary sources (which would be evident if the emissions stopped). The degradation, mostly in atmosphere and soil makes, on the other hand, high environmental concentration of γ-HCH not so dependent on recycling.

As in the previous study (Semeena and Lammel, 2005[108]), the single-hop reaches higher in the atmosphere and effectively transports compounds to the Arctic and, in the southern direction, beyond the equator.

The comparability between the two studies is limited, however, as descends from 4, as the differences (mostly in the representation of the ocean, but also in the atmospheric GCM and in the sea-ice compartment) in the setup influence the compartmental distribution.

No other global modelling studies of the compounds studied has been performed so far.
The movement of the centre of gravity by ocean transport appears to be more effective in case of the most soluble γ-HCH. Based on results, for this compound the absence of degradation, a sink process concurrent to volatilisation, would probably determine a shift toward north of the COG.
For both compounds the curve referring to the recycled burden lies increasingly above, i.e. further north, the one describing the migration of the compound in its first cycle, strongly bound to the application latitudes (cf. Table 5.2).
Whereas for DDT, the northward shift of the total burden is a result of the multi-hopping, in case of γ-HCH the transport experiences the contribution of the mass of single- and multi-hopping in comparable extents. Meridional migration is always a combination of different processes. A net northward shift of the COG of a compound on the global scale could be determined by lack of sinks, rather than by actual transport. Anyway, the results show that, for both DDT and γ-HCH, the occurrence of the multi-hopping behaviour effectively enhances the long-range transport potential.

Summary

For the first time a three-dimensional modelling approach, based on the coupling of two GCMs has been used to describe the multicompartmental cycling of γ-HCH, α-HCH and DDT in the global environment. The outcome of the experiments studying the multicompartmental cycling shows that, on a decadal scale, the compounds accumulate mostly in soil. The soluble lindane is also found in comparable amount in ocean. DDT, the most persistent compound chosen, has the highest residence time in almost all compartments. α-HCH, the only compound applied with seasonal variations, appears to be the most prone to reach pseudo-steady state. Furthermore, the last compartment added to the model setup, the sea-ice, does not appear to bear a significant influence on the global compartmental distribution, only allowing deviations at the high latitudes of the Northern Hemisphere in the soil, vegetation and, clearly, ocean burdens.

As only a modelling study promises to unravel the individual processes and contributions to fate and transport determining the global environmental exposure, in this study, this potential has been made use of one step forward, namely by addressing the contribution to meridional transport of atmosphere and ocean separately. The results show that global transport is determined by the fast atmospheric circulation. At low latitudes the transport in the ocean is traceable, even after just a few months of run. There, the substances result more uniformly distributed with respect to the depositional patterns. Net meridional transport taking place in the ocean is, however, effective, as seen in the previous chapter, mostly on local scale (western boundary currents) and for persistent compounds, for which, DDT only a small amount is found in the Arctic upon applications at mid-latitudes. On a global scale, the actual northward advection is barely appreciable. What appears to be a northward shift of the centre of gravity for lindane, results always from a combination of actual transport and sinks processes, as degradation and (much less significant) volatilisation.

DDT and HCH are environmental contaminants of concern in Arctic [76], [16]. Model results show a more effective accumulation of γ-HCH in the Arctic, where the differences from DDT in compartmental distribution are more pronounced than on a global scale.

In order to investigate the meridional transport mechanism, the first environmental cycle in atmosphere and ocean has been disconnected by the subsequent cycles. The meridional transport for both DDT and γ-HCH is of multi-hopping type. As shown also in previous studies with a AGCM based model [108], an atmospheric single hop travels higher and is already sufficient to reach the Arctic (being based the emissions in the Northern Hemisphere). For γ-HCH the first cycle (continuously fueled by the applications) burden is an extremely high fraction of the total burden and only toward the end of the run the contribution of the recycled amount is comparable to it. On the other hand, for the persistent DDT the multiple cycles are responsible for the most part of the burden in all compartments from the third year onward. Conclusion, is, furthermore, that the occurrence of the multi-hopping behaviour might enhance the long-range transport potential for both DDT and γ-HCH.

Chapter 6

Conclusions

Semivolatile Organic Compounds (SOCs), which are slowly degrading and have adverse effects on living beings, represent a major threat for the Earth System.
Models are an indispensable tool to describe the dynamics and resolve the complexity of processes and budget mass cycling of such substances. As several multicompartmental model solutions have been suggested, often emphasizing the atmosphere, a modelling tool for the fate and distribution of HCH and DDT, based on the coupling of atmospheric and oceanic General Circulation Models has been developed and used for the **first time**.
The system encompasses as well a description of the dynamics of semivolatile organic compounds (SOCs) in all other relevant environmental compartments as soil, vegetation and sea-ice. The model has been designed and used in order to address specific questions.
The main objectives pursued in this work (and their outcome) are:

- As the tool developed and used descends from a model (MPI-MTCM[107]) bearing a simplified, off-line, two-dimensional representation of the ocean, estimate of the impact of three-dimensional ocean approach on the simulated fate and distribution of SOCs.
  The outcome of the comparison shows that a model setup with a higher degree of resolution in ocean processes affects the compartmental distribution and the environmental cycling of both substances. The residence times in the ocean and in the whole system are significantly higher when the three-dimensional approach is used.

- Investigate the relevance of partitioning to organics.
  A fundamental process for SOCs in sea-water is partitioning to organics. The distribution of organic phases, hence of partitioning substrates, is very inhomogeneous in the global ocean. This bears, in turn, equally spatially high resolved effects on other processes, as the volatilisation, which results inhibited, as the ocean retaining capacity increases. For DDT this effect reaches up to 35%.
  To a certain extent, on the local scale, sorption to organic phases in the ocean influences as well the migration of the compounds to the deep ocean. The sinking is, however, a combination of biogeochemistry (gravitational settling with particles) and dynamics (vertical transport of water), and is obviously favoured by persistence. DDT is the most persistent and lipophilic substance among the ones selected for this

study and reaches the deep ocean in higher amounts everywhere. Ocean dynamics proved to be more important than sinking associated with particulate matter. In both cases, volatilisation is clearly inhibited in case of subduction of ocean waters. Vice versa, if upwelling or overturning occur (again dynamical phenomena) the compounds are again available for volatilisation (identified even more as a very sensitive and therefore fundamental process). At least for persistent compounds as DDT, vertical export does not necessarily represent a loss process anymore.

- Investigate the global meridional transport, of the role of the ocean in it and of its mechanism.
  DDT and HCH are environmental contaminants of concern in Arctic [76], [16], because of the hazard they pose to the pristine environment. Model results show that global transport is determined by the fast atmospheric circulation. At low latitudes the transport in the ocean is traceable, even after just a few months of run. There, the substances result more uniformly distributed by tropical currents, with respect to the depositional patterns. Net meridional transport taking place in the ocean is, as well, effective, as seen in Chapter 4, mostly on the local scale (western boundary currents) and for persistent compounds, for which only a small amount is found in the Arctic upon applications at mid-latitudes. On the global scale, the actual northward advection is barely appreciable. What appears a northward shift of the centre of gravity of the ocean burden of lindane, results always from a combination of actual transport and sink processes, as degradation and (much less significant) volatilisation. If the ocean were the only transport vector, the most persistent compound in the reservoir, namely DDT, would be transported more efficiently, as the results of a sole-ocean experiment show. However, as the atmosphere is the fastest vector towards the Arctic, γ-HCH is transported in higher amount to the higher latitudes, in spite of its more efficient degradation in all compartments. In the Arctic region, the differences from DDT in compartmental distribution are more pronounced than on a global scale.
  According to the global temperature distribution, the intercompartmental cycling of SOCs can occur as a sequence of volatilisation, transport in the atmosphere, deposition and transport in the ocean, the so called *grasshopping*. As the potential for several cycles makes the global environmental exposure particularly difficult to assess, a modeling study is especially significant. Results show that the meridional transport for both DDT and γ-HCH is, indeed, of multi-hopping type. As shown also in previous studies with a AGCM based model [108], an atmospheric single hop travels higher and is already sufficient to reach the Arctic (being based the emissions in the Northern Hemisphere).
  For γ-HCH the first cycle burden constitutes most of the total burden and only toward the end of the run the contribution of the recycled amount is comparable to it. On the other hand, for the persistent DDT multiple cycles are responsible for the most part of the burden in all compartments from the third year onward. Conclusion, is, furthermore, that the occurrence of the multi-hopping behaviour enhances the long-range transport potential for both DDT and γ-HCH.

- Analyse the multicompartmental cycling and effects of the sea-ice.
  The cycling of γ-HCH, α-HCH and DDT was studied in the global environment. The outcome of the experiments studying the multicompartmental cycling show that the compounds accumulate mostly in soil. The soluble lindane is also found in comparable amount in ocean. DDT, the most persistent compound chosen, has the highest residence time in almost all compartments. α-HCH, the only compound applied with seasonal variations, appears to be most prone to reach pseudo-steady state. The sea-ice compartment does not appear to bear a significant influence on global the distribution of DDT and γ-HCH in the simulated scenarios. In its absence, its share of the total burden is distributed to soil and ocean. The sea-ice cover inhibits volatilisation regionally by two-three orders of magnitude.

Other questions which remain to be investigated, as well as suggestion of further improvements of the model, are introduced and discussed in Chapter 7.

Chapter 7

Outlook

The three-dimensional ocean version of the multicompatmental chemistry-transport model (MPI-MTCM) simulates the multicompartmental fate and distribution of DDT and HCH and is able to address furthermore scientific question related to the partitioning to organics and to the meridional transport.
Here follows a brief lists of other questions to be faced, in terms of experiments to be performed, of processes to focus on, to introduce or improve.

- As the multiyear fate of both the α- and γ-HCH, can be simulated, an experiment with historical applications of the two isomers present in technical hexachlorocyclohexane could be performed. Such an experiment is of importance for the different response of the 2 species to environmental conditions which allows to compare their ratio to the gradients in observational data available literature (Iwata e al., 1993[50], Jantunen and Bidleman, 1998[51], Lakaschus et al., 2002[60]).

- Volatilisation is a key process, influenced by several factors and itself determining a substantial fraction of the exchange between compartments. Its spatial resolution as well as its dependencies need to be further investigated in order to generally improve and, if the case, adapt to new compounds' studies the parameterisations.

- Shelf seas are high productivity areas due to their particular characteristic such as limited depth, hydrodynamical and meteorological features and coastal (rivers, air emissions) input of organic matter. They may therefore play a significant role in the dynamics of SOCs, at least on the local scale. They are underrepresented in the current version of the model. As for the more chlorinated congeners shelves can constitute a more significant removal sink, phenomena like the remobilisation of pollutants hosted in sediments may occur. Therefore even after the compounds have been banned, they can be still present for decades afterwards(Jöensson et al., 2003[52]). Moreover, as the current version of the model does not include any input from the rivers, the inflow of pollutants from the major rivers (south American rivers, Siberian) could be introduced. They may play a significant role in determining the concentrations in the coastal seas as in the Arctic (Halsall, 2004[35]). The question whether this may have repercussion on their global fate is debated [25], [127].

- As partitioning is a crucial process, the use of higher resolution could provide a more accurate representation of the different dimensional classes of particulate organic carbon based on biogeochemistry [81]. Furthermore, as the gravitational settling occurs currently with fixed rate, dynamically calculated velocity, based on the different dimensional classes, would add realism to the process, as it could be crucial in determining the rate of concentration decline after the phasing out the use of SOCs [127].

  In order to address the last two questions, assimilation of satellite derived product, in terms of suspended particulate matter data, could improve the resolution in the shelf seas.

- As the ice could have effects on long-range and fate of SOCs [114], the global ice compartment, presently limited to the sea-ice (introduced in this study) needs to be extended to consider other significant ice covered regions as Antarctica. Antarctica ice sheet, as is the main sink for pollution reaching the Antarctic continent from other continents (Wolff, 1992[147]), could be an important sink for SOCs. Ice effects on long-range and fate [114]. The photolysis at the surface and in water ice can, furthermore, be relevant as degradation process (Klán and Holoubek, 2002[56]).
  On the other hand, the very peculiar behaviour of mountain glaciers (Villa et al., 2003[129], among other studies), could be more appropriately faced with regional modelling approaches. The consideration of a content in organic matter within the snow-pack would allow partitioning of the compounds to this phase, leading to a differential release, (the so called 'first flush' effect for more water soluble compounds) with melting water. The effects, if any, of this latter inclusion on the long term retentive capacity of the reservoir have to be investigated.

Glossary

Notation	**Description**
2DO	model in which a bidimensional surface is used to describe the ocean compartment.
3DO	model in which the three-dimensional MPIOM-HAMOCC model is used to describe the ocean compartment.
COG	centre of gravity, long-range transport indicator (Leip and Lammel, 2004[66]), corresponding to the 50^{th} percentile (i.e. the median) of the zonal and meridional cumulated distribution.
multi-hop	all environmental cycles after the first one.
residence time τ	the persistence the longevity of a chemical in the environment can be expressed by the residence time of the substances in the system. The residence time of a compound in a single compartment τ_i (or in the entire earth system or so-called overall environment τ_{ov}) can be derived as in Leip and Lammel, 2004[66] iteratively from the conservation equation: $\frac{\Delta c}{\Delta t} = E - \frac{c}{\tau}$ so that $\tau = \frac{c}{E - \frac{\Delta c}{\Delta t}}$. The term E refers to the emissions in the compartment (or system) whereas c is the mass and $\frac{\Delta c}{\Delta t}$ refers to the net uptake of the compartment (or system), i.e. to the sum of all inflow and outflow fluxes.
S	spatial scale, long-range transport indicator (Leip and Lammel, 2004[66]), $S = \frac{\sqrt{ZW+MW}}{2}$,where the ZW and MW are the distances of the 5% fringes of the distribution, respectively in north-south and west east direction.

Notation	**Description**
single-hop	first environmental cycle.
SS	spatial spreading, long-range transport indicator (Leip and Lammel, 2004[66]), is $SS = S_t - S_{t^0}$,the differences between two (time dependent) values of the spatial spreading S.
ZS	zonal spreading, long-range transport indicator (Leip and Lammel, 2004[66]). ZS refers to the 90% interquartile distance $ZS = ZW_t - ZW_{t^0}$. Where $ZW = lat_{95} - lat_{05}$. ZS quantifies the tendency of a distribution to spread in meridional direction.

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Acknowledgements

I would like to thank my supervisor Prof. Gerhard Lammel for the constant support he has given me, inspiring my work and teaching me throughout these years.

The support of Prof. Hartmut Grassl and the advice of Dr. Ernst Maier-Reimer are greatly appreciated.

Without my friends of the Aerosol Chemistry Group, it would have been much harder to accomplish this work. Thank you all, far from Hamburg or still here in the trenches.

The Max Planck Institute for Meteorology and the International Max Planck Research School on Earth System Modeling gave me the possibility to pursue my doctoral studies providing financial support, computing resources, help, educational events and friendly atmosphere.

I am also very thankful to all who, directly or indirectly, have been there for me during this work. Many conversations with many people helped me to keep focused and not to loose hope.

Special thanks to my parents and siblings for their unconditional love and support.

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