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**Trends and  
variability in  
transport of  
persistent organic  
pollutants to the  
Arctic and possible  
relation to climate  
change**

Master thesis in  
Meteorology and  
Oceanography

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# Abstract

In this thesis, transport pathways, temporal trends and seasonality of persistent organic pollutants (POPs) in the Arctic are examined. These pollutants, which can be transported over long distances, constitute a great threat to humans and wildlife because they can accumulate in fatty tissue and lead to e.g. hormon production failure and even death.

Atmospheric POP measurements from the Zeppelin monitoring station in Ny-Ålesund, Svalbard, from 1993 to 2007 and an ice core collected from Kongsvegen glacier near Ny-Ålesund covering the years from 1994 to 2005 were analyzed for temporal variations in different POP concentrations. These data were then correlated to large scale atmospheric patterns (North Atlantic Oscillation and Arctic Oscillation) and transport pathways. The latter were estimated from the transport model FLEXPART, employing CO as an emission tracer.

Results show that seasonal variations of POPs are influenced by temperature, photochemistry, meteorology, application patterns and snow melt. It is also found that POP concentrations are generally declining, in accordance with the downward trends in POP emissions. Levels of HCB and high-chlorinated PCBs have increased since approximately 2005, probably because of the increasing number of boreal forest fires and because of temperature increase, leading to re-emissions from oceans and soil.

Continent analysis of POPs shows that in general, Europe is the continent associated with PCB events detected at Zeppelin. Pesticides, especially  $\gamma$ -HCH and chlordanes, are mainly transported to Svalbard from Asia because they are most heavily used there. North American events seldom lead to enhanced POP levels at Zeppelin because compounds are often washed out on the way. Correlations between NAO and PCBs and between AO and pesticides were found, though not very strong.

The data from the ice core were compared with the air measurements to examine the relationship between the two data sets. This has never before been done for ice cores collected in Svalbard. The analysis shows three "zones" in the ice core; a *surface layer*, containing low concentrations of POPs, an *accumulation zone*, showing significantly higher concentrations, and a *background level*, showing lower and more stable concentrations compared to the accumulation zone. Correlations between the data series in air and ice for  $\gamma$ -HCH and HCB were calculated, but no correlations were found.



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# Abbreviations

<b>AMAP</b>	Arctic Monitoring and Assessment Programme
<b>AO</b>	Arctic Oscillation
<b>ATSDR</b>	Agency for Toxic Substances and Disease Registry, U.S. Department of Health and Human Services
<b>C</b>	Concentration
<b>CD</b>	Chlordane
<b>CO</b>	Carbon monoxide
<b>CPC</b>	Climate Prediction Center
<b>DDD</b>	Dichloro-Diphenyl-Dichloroethane
<b>DDE</b>	Dichloro-Diphenyl-Dichloroethylene
<b>DDT</b>	Dichloro-Diphenyl-Trichloroethane
<b>ECMWF</b>	European Centre for Medium-Range Weather Forecasts
<b>EI</b>	Electron impact ionization
<b>EMEP</b>	European Monitoring and Evaluation Programme
<b>ENSO</b>	El Niño – Southern Oscillation
<b>GC</b>	Gas chromatography
<b>HCB</b>	Hexachlorobenzene
<b>HCH</b>	Hexachlorocyclohexane
<b>HLC</b>	Henry's Law constant
<b>IPCS</b>	International Programme on Chemical Safety, United Nations Environment Programme, World Health Organization
<b>ISTD</b>	Internal standard
<b>K<sub>oa</sub></b>	Octanol-air partition coefficient
<b>K<sub>ow</sub></b>	Octanol-water partition coefficient
<b>LOD</b>	Level of detection
<b>LOQ</b>	Level of quantification
<b>LRTAP</b>	Geneva Convention on Long-range Transboundary Air Pollution
<b>MetOs</b>	Department of Meteorology and Oceanography, University of Oslo
<b>MS</b>	Mass spectrometry
<b>m/z</b>	Mass-to-charge ratio
<b>NAO</b>	North Atlantic Oscillation
<b>NCI</b>	Negative ion chemical ionization
<b>NILU</b>	Norwegian Institute for Air Research
<b>NO</b>	Nonachlor
<b>NOAA</b>	National Oceanic and Atmospheric Administration

## *Abbreviations*

<b>NPI</b>	Norwegian Polar Institute
<b>OC</b>	Organochlorine compound
<b>OCN</b>	Octachloronaphtalene
<b>OH</b>	Hydroxyl radical
<b>PAH</b>	Polycyclic aromatic hydrocarbon
<b>PCB</b>	Polychlorinated Biphenyl
<b>PES</b>	Potential emission sensitivity
<b>POP</b>	Persistent organic pollutant
<b>PUF</b>	Polyurethane foam
<b>r</b>	Correlation coefficient
<b>R</b>	Recovery
<b>RF</b>	Response factor
<b>RRF</b>	Response factor, recovery standard
<b>RSTD</b>	Recovery standard
<b>RT</b>	Retention time
<b>SIM</b>	Selected ion monitoring
<b>S/N</b>	Signal-to-noise ratio
<b>SPE</b>	Solid-phase extraction
<b>TCN</b>	Tetrachloronaphtalene
<b>UN-ECE</b>	United Nations Economic Commission for Europe
<b>UNEP</b>	United Nations Environment Programme
<b>USEPA</b>	U.S. Environmental Protection Agency
<b>UTC</b>	Coordinated Universal Time



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# 1. Introduction

## 1.1. Background and previous studies

Persistent organic pollutants (POPs) constitute a group of synthetic substances for which the sources and pathways for release into the global environment vary to a great extent. The United Nations Environment Programme (UNEP) made, during the Stockholm Convention in 2001, a list of criteria for identification of POPs. The criteria are:

1. *Persistence*

The half-life of the chemical is long in water (>two months), soil (>six months) and sediment (>six months), which means that the chemical is highly resistant to both biological and chemical degradation.

2. *Ability to accumulate in fatty tissue*

The chemical is hydrophobic and attracts living tissue. It is found at much higher concentrations in living organisms than in the surrounding environment. The substance has the potential of increasing its concentration through a food chain.

3. *Potential for long-range transport*

High levels of the chemical are measured at locations far from the release area and imply transport via air, water and/or migratory species. The substance has chemical and physical properties which support semi-volatility.

4. *Toxicity*

There is evidence of toxicity and damage to human health or to the environment at small concentrations.

In the 1970s, studies found that some of these contaminants can be transported over long distances and be deposited in regions where they have never before been used or produced (Kerr, 1979). Rachel Carson's book *Silent Spring* from 1962, dealing with the release of pesticides into the environment, helped to launch the debate and consciousness about the effects POPs can have on the environment, even though their impact was not fully understood at that time. A protocol about persistent organic pollutants by the United Nations Economic Commission for Europe (UN-ECE) under the Geneva Convention on Long-range Transboundary Air Pollution (LRTAP) was signed in 1979. The objective of the agreement was to control, reduce or eliminate discharges, emissions and losses of POPs (UN-ECE, 1979). In 2001, the Stockholm Convention was signed in order to minimize POPs worldwide, and

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the treaty came into force in 2004 (UNEP, 2001). Increased understanding of the dangerous consequences of POPs on humans and wildlife have thus led to a profound decrease of primary emissions during the 1970s, 1980s and 1990s (*Breivik et al.*, 2007).

POPs have different physical-chemical properties which determine their behaviour and preferred medium during transport. They have the ability to accumulate in water, soil and lipids (AMAP, 2004) and can either be transported through air, ocean currents or migrating animals. In 1993, Wania and Mackay introduced the theory that POPs can travel to higher latitudes in several "jumps", the "grasshopper effect", because of sequential cold condensation from the atmosphere to water and soil, followed by re-evaporation back to the atmosphere (*Wania and Mackay*, 1993, 1996). The behaviour of some of the POPs is highly temperature dependent, and increasing temperatures and decreasing sea-ice cover increases re-evaporation and hence re-release to the atmosphere from water and soil.

Previous studies have concluded that chemical substances can be stored in forest canopies and released during forest fires (*Stohl et al.*, 2007), but *Eckhardt et al.* (2007) was the first study to show that this is indeed possible for POPs.

In this thesis, recent trends of POPs in the Arctic are analysed in detail. The Arctic was for a long time considered a clean environment, separated from contaminant sources related to industry and pesticide use in other parts of the world. A desire to monitor environmentally hostile compounds in the Arctic emerged when it was discovered that the Arctic in fact is closely connected to the rest of the world because organochlorines (OCs) were found in the Arctic marine environment (*Holden*, 1970; *Andersson et al.*, 1988). The Zeppelin monitoring station was built in Ny-Ålesund, Svalbard, in 1989, and the first POP measurements were performed in 1993. Even though primary emissions have decreased, high concentrations of POPs are still measured at Zeppelin, and focus is nowadays directed towards so-called secondary emissions (*Eckhardt et al.*, 2007; *Hung et al.*, 2005). These arise from re-emissions from soil, oceans or forests, while primary emissions are associated with long-range transport from countries still using and producing PCBs and organochlorine pesticides.

For more than 50 years, researchers have been acquainted with a peak in atmospheric pollution in the Arctic during winter and spring (*Quinn et al.*, 2007), but only now are the underlying factors, like seasonality in removal rates, photochemical processes and meteorology starting to get well understood. However, interannual changes on Arctic pollution levels are still less understood.

These interannual variations could be linked to certain climate patterns, like the North Atlantic Oscillation (NAO) and the Arctic Oscillation (AO). Such patterns have long been recognized (*Walker and Bliss*, 1932), but little research has been done to link these low-frequency atmospheric circulation patterns to pollution levels in the Arctic. One of the few existing studies is the one by *Eckhardt et al.* (2003), who found a connection between NAO and transport of passive tracers representative of anthropogenic emissions.

To increase our understanding of these relationships, the behaviour of "classical" POPs and their relationship to climate patterns is investigated further in this thesis.

The majority of the classical POPs is banned or severely restricted in most developed countries. These POPs give a good basis to investigate secondary emissions, since primary emissions have declined during the last decades. Studies show that the levels of classical POPs at Zeppelin have decreased over the last years (*Berg et al.*, 2004).

In addition, an ice core has been analysed with respect to POPs for this thesis. But why should one study ice cores? The concentrations of the pollutants are much smaller compared to those in fatty tissue, and what damage can the compounds do deep down in the ice? The answer is that ice cores give information about long-range atmospheric transport, since glaciers are generally located far away from industrial activity. Current detailed measurements of contaminants in the atmosphere do not extend many years back in time. Zeppelin data series for POPs are not long enough to get an impression of the long-term trend further back in time than 10 – 15 years. To get an impression of changes in the environment on a long-term perspective, ice cores provide an invaluable record (*Gregor et al.*, 1995). Ice cores are believed to contain detailed records of the concentration levels of pollution in the atmosphere through history. Levels of POPs in surface snow correspond to levels in the atmosphere at the time of snow fall, modified by subsequent dry deposition and losses, so by looking at ice cores one gains an insight into historical surfaces (*Wolff*, 1990).

So far, only few studies on PCBs and pesticides in ice cores in Svalbard have been done. *Hermanson et al.* (2005) analysed a core from Austfonna ice cap for several pesticides and found many compounds throughout the ice core dated from 1943 to 1998. *Isaksson et al.* (2003) analysed ice cores from Lomonosovfonna and Austfonna, Svalbard, for pesticides and found among others  $\alpha$ - and  $\gamma$ -HCH. To find pesticides like these in Svalbard ice cores can only mean that the compounds are transported through the atmosphere over long distances, since no insecticides have ever been used in Svalbard. The ice core analysed for POPs in this thesis was drilled at Kongsvegen glacier near Ny-Ålesund. This was done to investigate levels of POPs in the ice core relative to air measurements taken at the Zeppelin station.

## 1.2. Aim and structure of thesis

The aim of this thesis is to identify trends and variability in transport of POPs to the Arctic on a seasonal and interannual scale and to estimate how changes in the variability can be an implication of climate change. An attempt will be done to compare ice core POP data and continuous air measurements of POPs at Zeppelin, and to our knowledge this has not been done before.

Chapter 2 gives a description of the POPs analyzed in air and ice and their physical-chemical properties, which are decisive for their ability to undergo long-range transport and deposition. Some relevant mechanisms pollutants that may affect pollutants during transport are also explained. In Chapter 3, methods for preparation and analysis of POP measurements in air and in the ice core are described. In Chapter 4, quality control and method evaluation for the ice core preparation and

## *1. Introduction*

analysis are discussed. In Chapter 5, results from seasonality and trend analysis, continent analysis and correlation investigations performed to connect levels of POPs to NAO/AO are presented. In Chapter 6 the results are discussed, and conclusions and proposals for further research are given in Chapter 7.

## 2. POPs in the Arctic: Background

To investigate the behaviour of POPs on a seasonal and long-term basis, time series of "classical" POPs detected at the Zeppelin monitoring station in Ny-Ålesund, Svalbard, have been examined. Section 2.1 below gives an overview of the compounds investigated; their areas of application, emission sources, when they were banned or restricted and important physical-chemical properties. Selected physical-chemical properties for all POPs analysed are described in detail and summarized in Section 2.2. Knowledge about properties is essential for understanding the behaviour of POPs during long-range transport to Svalbard. The properties give insight to the compounds' abilities for interaction between air, oceans, soil and forest canopies. Section 2.3 takes a closer look on important mechanisms POPs are affected by on their journey to the Arctic. The chapter rounds off with Section 2.4, which explains consequences of POPs on humans and wildlife and why this topic is important to investigate.

### 2.1. Target compounds

Table 2.1 gives an overview of the POPs analysed in air at the Zeppelin station, together with a list of POPs analysed in the ice core drilled from Kongsvegen glacier. The following sections provide details of all target compounds.

Sampling location	PCBs	Pesticides
Zeppelin station, Ny-Ålesund	18, 28, 31, 33, 37, 47, 52, 60, 66, 74, 99, 101, 105, 114, 118, 122, 123, 128, 138, 141, 149, 153, 156, 157, 167, 170, 180, 183, 187, 189, 194, 206, 209	$\alpha$ -HCH, $\gamma$ -HCH, trans- chlordane, cis-chlordane, trans-nonachlor, cis- nonachlor, o,p'-DDE, p,p'- DDE, o,p'-DDD, p,p'-DDD, o,p'-DDT, p,p'-DDT, HCB
Kongsvegen glacier, Ny-Ålesund	18, 28, 31, 44, 52, 77, 81, 95, 99, 101, 105, 110, 114, 118, 123, 126, 128, 138, 146, 149, 151, 153, 156, 157, 167, 169, 170, 177, 180, 183, 187, 189	$\alpha$ -HCH, $\gamma$ -HCH, trans- chlordane, cis-chlordane, trans-nonachlor, cis- nonachlor, HCB

Table 2.1.: List of POPs analysed

### 2.1.1. $\alpha$ - and $\gamma$ -Hexachlorocyclohexane (HCH)

$\alpha$ -HCH is the most abundant component in the technical hexachlorocyclohexane mixture, which was used as an insecticide from 1943 to the 1970s. Technical HCH consists of the isomers  $\alpha$ -HCH (60-70 %),  $\beta$ -HCH (5-12 %),  $\gamma$ -HCH (10-15 %),  $\delta$ -HCH (6-10 %) and  $\epsilon$ -HCH (3-4 %) (ATSDR, 2005).

Lindane consists of >99 %  $\gamma$ -HCH (ATSDR, 2005) and replaced technical HCH at the end of the 1970s and the beginning of the 1980s after banning of technical HCH in western countries and Japan in the 1970s (Breivik *et al.*, 1999).  $\gamma$ -HCH is the only isomer in the technical HCH mix which has insecticidal properties and has been used as an insecticide on fruit, vegetables and forest crops and for treatment of head lice and scabies since the 1940s.  $\gamma$ -HCH can remain in the air for a long time and is favourable for long-range transport. It deposits to soil and water by rain fall-out or degradation by other components in the atmosphere (ATSDR, 2005).

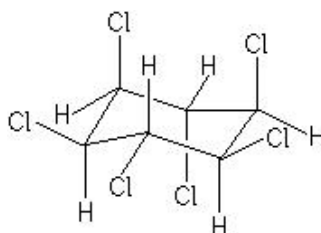


Figure 2.1.: Chemical structure of  $\gamma$ -HCH

Technical HCH is still assumed to be in use in Russia, despite of its banning in 1990 (Breivik *et al.*, 1999). The highest historical production and usage took place in China, India and the former Soviet Union (Li and Bidleman, 2003).

The largest producers and users of lindane during the 1990s were Canada, China, India, USA, France and other western and eastern European countries (Li and Macdonald, 2005), but usage has been banned or severely restricted in many countries in the last years. Usage was banned in France in 1998 and restricted in Canada in 2000, but lindane consumption in China and USA has continued and in many countries lack of information about usage makes the estimation of emissions problematic (Li and Bidleman, 2003). Both  $\alpha$ -HCH and lindane are considered for inclusion under the Stockholm Convention (UNEP, 2001).

The HCHs, especially  $\alpha$ -HCH, is quite soluble in water compared to other POPs, which make the ocean currents a major pathway for transport into the Arctic (Li *et al.*, 2004). See Table 2.2 for physical-chemical properties of  $\alpha$ - and  $\gamma$ -HCH.

### 2.1.2. Chlordane

Technical-grade chlordane is a mixture consisting of more than 140 related compounds. The major components are cis- and trans-chlordane, oxychlordane, hep-



tachlor, heptachlor epoxide and cis- and trans-nonachlor. The composition and amount of chemicals in technical-grade chlordane depend on the manufacturer (AMAP, 2004; ATSDR, 1994).

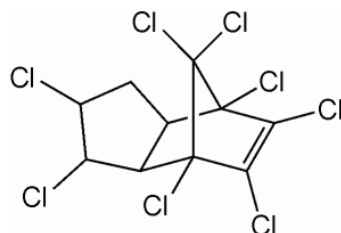


Figure 2.2.: Chemical structure of chlordane

Chlordane has mainly been used as an insecticide on vegetables, maize, potatoes, fruits and cotton and as a termiticide. USA was the largest producer and user of chlordane from 1947 until the end of the 1980s, but also western European countries, the former Soviet Union and tropical Asian countries were limited users. In 1997 USA stopped production and sale of chlordane, but Singapore and China are still producing (AMAP, 2004; Ritter *et al.*, 1995; IPCS, 1988). For information about the physical-chemical properties of chlordanes, see Table 2.2. Chlordane is one of the *Dirty Dozen* assessed by the Stockholm Convention (UNEP, 2001).

### 2.1.3. Hexachlorobenzene (HCB)

HCB is highly soluble in lipids, slowly degradable and one of the most persistent of the environmental pollutants (ATSDR, 2002b; IPCS, 1998; Ritter *et al.*, 1995).

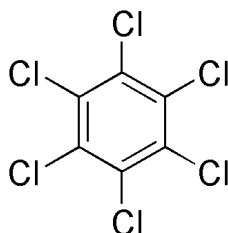


Figure 2.3.: Chemical structure of HCB

HCB was used as a fungicide in the 1960s, but had several other areas of use, e.g. the rubber industry and the ammunition producing industry. In the 1970s HCB production was stopped in many countries for these purposes because of suspicion of the damaging effects on the environment and human health. However, its use

## 2. POPs in the Arctic: Background

in combustion has continued, and it is formed as a by-product in the production of chlorinated solvents and pesticides.

Since it is released into the environment as an industrial by-product, reliable information about production, use and emissions of HCB is hard to achieve (AMAP, 2004; ATSDR, 2002b; IPCS, 1998; Pacyna *et al.*, 2003). None of the applications HCB has been used for in the past are currently practiced in North America or Western Europe, but Russia and China acknowledge the use of HCB in the production of solvents and military pyrotechnics. However, *EMEP Status Report 3/08* reports of HCB emissions from Spain, Russia, Ukraine and United Kingdom. The amount of HCB in use is however not known (Bailey, 2001).

In Table 2.2 physical-chemical properties of HCB are listed. HCB is one of the most volatile POPs and HCB concentrations are believed to be highly dependent on the temperature of the surrounding environment (Ma *et al.*, 2003). A big part of HCB measured in the atmosphere is believed to come from re-volatilization from soil from past contamination (Bailey, 2001). Studies have found good correlation between HCB air concentrations and El Niño – Southern Oscillation (ENSO). The ENSO phenomenon is associated with enhanced levels of HCB in air because of evaporation from soils due to high environmental temperatures (Ma *et al.*, 2003).

HCB is included under the Stockholm Convention (UNEP, 2001).

### 2.1.4. Dichloro-Diphenyl-Trichloroethane (DDT), Dichloro-Diphenyl-Dichloroethylene (DDE) and Dichloro-Diphenyl-Dichloroethane (DDD)

Technical-grade DDT consists of approximately 85 % p,p'-DDT, 15 % o,p'-DDT and trace amounts of o,o-DDT. It may also contain DDD and DDE, the two major metabolites and breakdown products of DDT in the environment (ATSDR, 2002a).

DDT is an insecticide which does not occur naturally in the environment. See Table 2.2 for property details.

DDT magnifies through the food web. Since it breaks down to DDE, levels of DDE in the body normally increase through life, except during periods of breast-feeding, when the mother passes on the substance to her child (ATSDR, 2002a). DDT was synthesized in 1874, but its insecticidal properties were not discovered before 1939. DDT is the world's most widely used insecticide between 1946 and 1972 (Li and Bidleman, 2003). It was first put to use during World War II to control malaria, typhus and other insect-borne diseases. Swiss chemist Paul Hermann Müller of Geigy Pharmaceutical was awarded the Nobel Prize in Physiology or Medicine in 1948 for his discovery of the insecticidal properties of DDT. After World War II, DDT was made available for agricultural use, and the production and use increased drastically (IPCS, 1979; Ritter *et al.*, 1995).

In 1962, Rachel Carson's book, *Silent Spring*, about the release of pesticides into the environment without fully understanding their effects was published. As a consequence of the book, DDT was banned for most areas of use in the United States in 1972. The compound was banned during the 1970s and 1980s for agricultural use

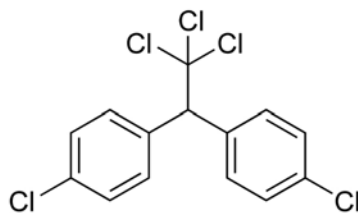


Figure 2.4.: Chemical structure of DDT

in most developed countries. Besides the United States, the former Soviet Union, China, Mexico and Brazil were the largest users of DDT in agriculture. Hungary was the first country to ban DDT in 1968 (*Li and Bidleman, 2003; Li and Macdonald, 2005*). DDT was banned for agricultural use under the Stockholm Convention in 2001. Application of DDT was in some tropical countries officially allowed again for the fight against malaria around 2000 after being banned for some years (*Kallenborn, 2009, pers.comm*). The largest users and producers in the world today are India and China (*AMAP, 2004*), even though DDT was banned in China in 1983 and severely restricted in India in 1995 (*Li and Bidleman, 2003*).

### 2.1.5. Polychlorinated Biphenyls (PCBs)

PCBs belong to a group of synthetic compounds which is banned under the Stockholm Convention (UNEP, 2001). 209 different PCB congeners with possible space for 2 – 10 chlorine atoms exist. The high-chlorinated PCBs are less volatile than the low chlorinated ones, and the ability to accumulate in lipids increases with increasing chlorine substitution (*Ritter et al., 1995*).

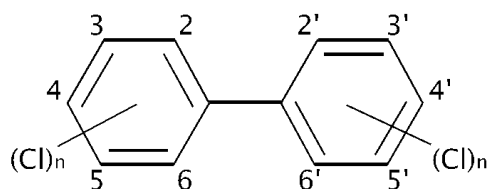


Figure 2.5.: Chemical structure of PCB

PCBs are insulating and highly resistant to heat and have thus been used as coolants in electrical equipment. They are chemically stable, even in the presence of oxygen or active metals at high temperatures (*IPCS, 1992; ATSDR, 2000*).

Most of the historical production of PCBs occurred in the United States, West

## 2. POPs in the Arctic: Background

Germany, former Soviet Union, France, United Kingdom, Japan, Czechoslovakia, China, Spain and Italy (Breivik *et al.*, 2002a, 2007). It is estimated that 97 % of the global, historical use of PCBs must be accounted for by countries in the northern hemisphere (AMAP, 2004).

Most of the intentional production of PCBs has stopped, but considerable amounts are still detected in the environment (Breivik *et al.*, 2002a). Countries of the former Soviet Union were relatively late to end the production of PCBs, and emissions are expected to continue for these countries because PCB containing equipment is still used and produced. Industrial waste is located within the territories of the Russian Federation (AMAP, 2000). Many European countries report of PCB emissions, e.g. the United Kingdom, Germany, France, Spain, Italy and the United States (EMEP, 2008).

There are high uncertainties connected to PCB emissions caused by industrial processes, and the atmospheric concentrations and congener distribution of PCBs are believed to be highly dependent on the environmental temperature (Breivik *et al.*, 2004, 2002b).

Only a small fraction of the total PCB burden can be found in the atmosphere, while the largest fraction is found in soils. Soil is very effective in uptake and retaining of PCBs, which make PCBs resistant to repeated air-soil exchange. Degradation of PCBs in soils is slow. Soil samples taken from rural sites on western United Kingdom and Norway in 1998 show that the lighter PCBs are found further north and away from source regions than the heavier PCBs. Heavier molecules struggle to travel long distances (Ockenden *et al.*, 2003). See Table 2.2 for physical-chemical properties of PCBs.

### 2.2. Physical-chemical properties of POPs

Table 2.2 gives a list of physical-chemical properties of POPs investigated in this thesis. Description of properties is taken from Mackay *et al.* (2006b) and listed below:

**Solubility, water** The solubility of a substance is the maximum capacity a solvent phase has for a dissolved chemical. In this thesis the solubility is expressed as the amount of the POP which can be dissolved in water at equilibrium, in milligrams per liter.

**Vapour pressure** The vapour pressure of a substance is the pressure that its vapour has in equilibrium with its non-vapour phases. The vapour pressure is an indication of a liquid's evaporation rate; its "solubility in air". The higher vapour pressure a substance has, the more volatile the substance is.

**log  $K_{ow}$**  The octanol-water partition coefficient  $K_{ow}$  provides an estimate of a compound's partitioning tendency from water to lipids. High log  $K_{ow}$  corresponds to high hydrophobicity and high ability for a substance to accumulate into fatty tissue.

### 2.3. Transport of persistent organic pollutants to the Arctic

**log  $K_{oa}$**  The octanol-air partition coefficient  $K_{oa}$  describes a substance's partitioning preference from the atmosphere to lipids like e.g. foliage and soils, which are the most important lipids considered in this thesis.

**Henry's Law constant** Henry's Law constant (HLC) for a compound is strongly related to the vapour pressure. Henry's Law constant is the ratio of a substance's partial pressure in air to its concentration in water. It expresses the relative air-water partitioning tendency. A high HLC means high tendency to partition into air.

**Half-life** Half-life is the time required for a substance to decay to half of its initial concentration. In this thesis, half-lives in different environments (air, surface water, soils) are presented as observations of the rate of disappearance without identifying the cause of loss.

## 2.3. Transport of persistent organic pollutants to the Arctic

Pollutants can be transported from southerly latitudes to the Arctic through the atmosphere, ocean currents, rivers, migrating animals and, to a lesser extent, ice (Melnikov *et al.*, 2003; Gustafsson *et al.*, 2005). Transportation is most rapid through the atmosphere, with a time scale of a few days to weeks. The ocean currents are slower. Transportation may take several years, but the oceans have on the other hand a much larger storage capacity than the atmosphere. The rivers which flow out in the Arctic Ocean transport contaminants from industrial areas of the northern parts of Russia and Canada (Macdonald *et al.*, 2003a).

Transport of pollutants can be affected by many factors and vary on shorter and longer time scales. Below is a presentation of some of the factors.

### 2.3.1. Atmospheric circulation patterns driving transport into the Arctic

Atmospheric transport in, out and within the Arctic takes place through winds associated with high and low pressure systems located in the Northern Hemisphere. The Icelandic Low produces westerly winds over North America and Europe and forces air from industrial areas in Europe and Russia into the Arctic with help from the Siberian High. The Aleutian Low forces air originating from Asia to cross the Pacific Ocean and reach North America (Macdonald *et al.*, 2003a). See Figures 2.6 and 2.7 for location of high and low pressure systems in the Northern Hemisphere during winter and summer.

## 2. POPs in the Arctic: Background

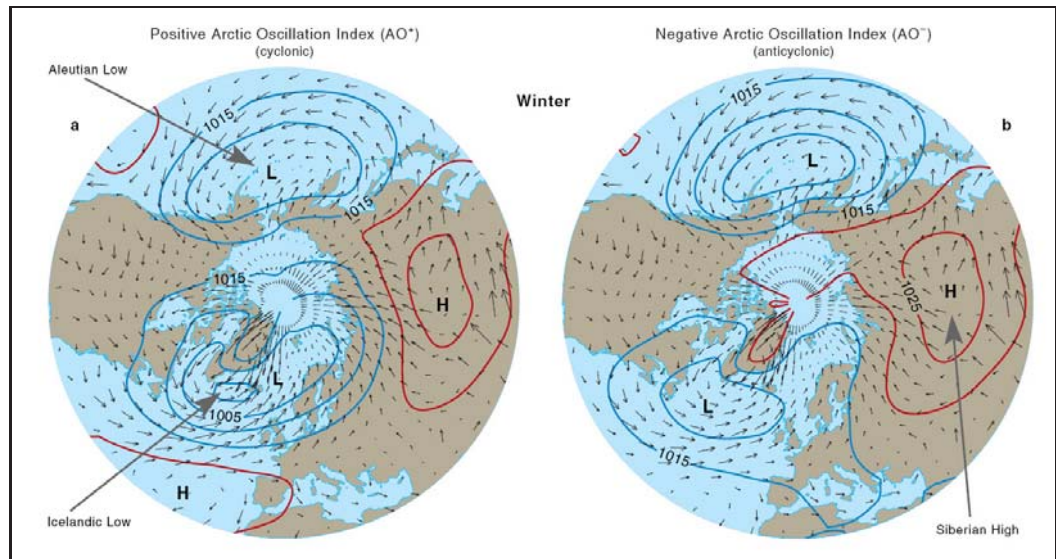


Figure 2.6.: Atmospheric pressure fields in the Northern Hemisphere during strong AO+ and AO- conditions in winter. From: *Macdonald et al. (003a)*

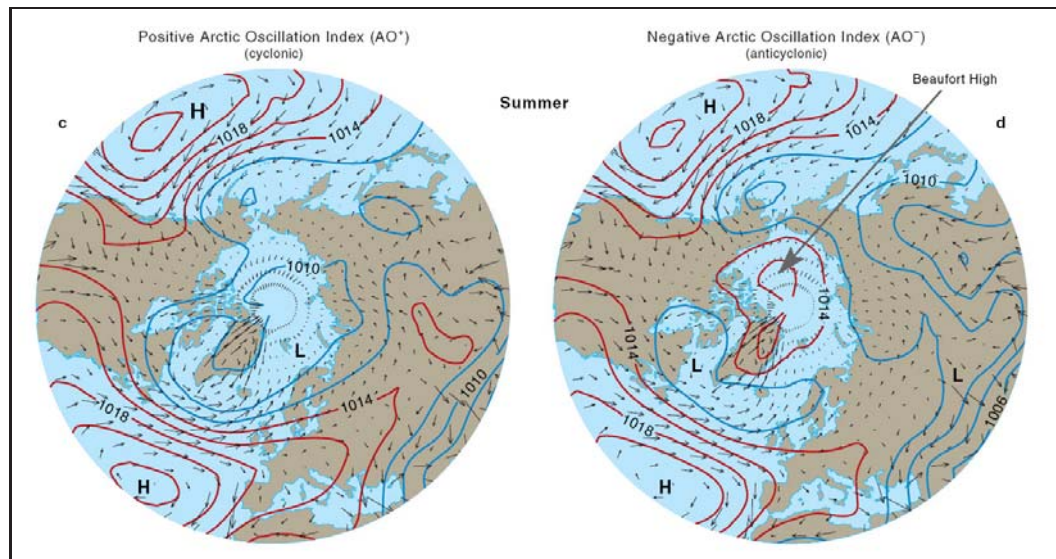


Figure 2.7.: Atmospheric pressure fields in the Northern Hemisphere during strong AO+ and AO- conditions in summer. From: *Macdonald et al. (003a)*



### 2.3.2. Change in position of the polar dome with season

The Arctic lower troposphere is isolated from more southerly latitudes by the polar front, which is the barrier between the cold Arctic air and the warm continental air. Surfaces of constant potential temperatures, *isentropes*, form closed "domes" over the Arctic. Transport of air masses takes place mostly along isentropes.

In summer, the Arctic front is located far north, making it difficult for air masses originating from industrial areas south of the Arctic to enter the Arctic. In winter, the Arctic front extends further south and encapsulates large industrial areas in especially Europe and Russia. This makes it easier for pollution to be transported into the Arctic during winter and spring (Stohl, 2006).

The strength of the polar dome varies with season. In winter the polar dome forms a strong transport barrier and forces the pollution to be concentrated closer to the ground. Hence, the polar dome separates North American and European sources, forcing European pollution to be transported in the lower troposphere and North American pollution higher up in the troposphere. However, diabatic cooling is more effective during winter, since air transported into the Arctic meets cold snow and ice covered surfaces. This makes the winter more favourable for cross-isentropic transport of pollution from higher to lower levels. During summer, pollution is mixed vertically to a greater extent than during winter, and cross-isentropic transport to higher levels in the troposphere is more common. This reduces the chances for pollution to reach low levels of the troposphere (Klonecki *et al.*, 2003).

Air pollution can be transported into the Arctic along three different pathways: 1) Low-level transport followed by ascent in the Arctic, 2) low-level transport alone or 3) uplift outside the Arctic, followed by descent in the Arctic. European pollution follows all three pathways of transport in winter and the first and last in summer. The last pathway is the most frequent for pollution coming from North America and Asia, since these areas are mostly located south of the polar front. Since the polar dome inhibits cross-isentropic transport, pollution from North America and Asia enter the Arctic at high altitudes (Stohl, 2006).

It is believed that faster warming of high latitudes compared to lower due to climate change will lead to a weakening of the polar dome. This will again lead to increased pollution transport to the Arctic because the polar dome will have a lower efficiency as a transport barrier (Law and Stohl, 2007).

### 2.3.3. Atmospheric transport mechanisms: Global fractionation and the grasshopper effect

In 1993 Wania and Mackay introduced the concept of global fractionation. This process occurs when organic compounds travel from lower to higher latitudes and condense at different ambient temperatures depending on their volatility (Wania and Mackay, 1993). POPs have the ability to travel through air, water and soil at ordinary environmental temperatures, but high temperatures in tropical and subtropical regions favour evaporation, and low temperatures in polar regions favour

## 2. POPs in the Arctic: Background

cold deposition. Low temperatures also weaken natural decomposition reactions and thus enhance the persistency of the substance (Wania, 1999).

Sometimes POPs travel towards higher latitudes in several jumps. This is referred to as the "grasshopper effect". A compound transported in the gaseous phase can get washed out via precipitation or temporarily deposited in water or soil and re-evaporate during warm weather conditions. It can then continue to migrate further north via the atmosphere. As a result of this some POPs are found at higher levels in the Arctic compared to regions close to the sources (Wania and Mackay, 1996; AMAP, 2004; Burkow and Kallenborn, 2000).

In addition, POPs have the ability to be re-emitted to the atmosphere during melting of the snow pack, ageing of the snow or during windy conditions (Halsall, 2004; Herbert *et al.*, 2006).

Studies report that forests have high capability of taking up semi-volatile organic compounds from the atmosphere. From the forest canopies the compounds are deposited to forest soil, increasing the soil as a storage reservoir. The deposition takes place by seasonal canopy wash-off and natural decomposition processes (Horstmann and McLachlan, 1998; Wania, 1999; Wania and McLachlan, 2001). Once taken up, the compounds have difficulties getting re-emitted to the atmosphere, except during forest fires (Eckhardt *et al.*, 2007).

A compound's ability to undergo global fractionation is determined by its physical-chemical properties, as described in Section 2.2.

### 2.3.4. North Atlantic Oscillation (NAO)

The North Atlantic Oscillation (NAO) is the normalized gradient of the sea-level pressure between the Azores High and the Icelandic Low and controls the strength of winds and storm tracks across the North Atlantic. The NAO index is high especially in winter and spring, affecting temperature changes, moisture distribution, wind direction and intensity of wind speed.

In winter, the Icelandic Low intensifies, which leads to a more rapid atmospheric transport from south to north compared to in summer. This is especially the case during strong NAO conditions, NAO+.

In summer, the Icelandic Low is weaker and the Siberian High disappears. During NAO- the Beaufort High blocks transport across the Arctic Ocean, but during NAO+ the high pressure system disappears and cross-Arctic transport is possible again (Macdonald *et al.*, 2003a).

During the period from the beginning of the 1980s to the mid 1990s the NAO index was in a continual, highly positive state, but the last ten years it has been in a more neutral state, see Figure 2.8.

Several studies have found a significant correlation between anthropogenic transport of chemical substances and NAO (Burkhart *et al.*, 2006; Eckhardt *et al.*, 2003).



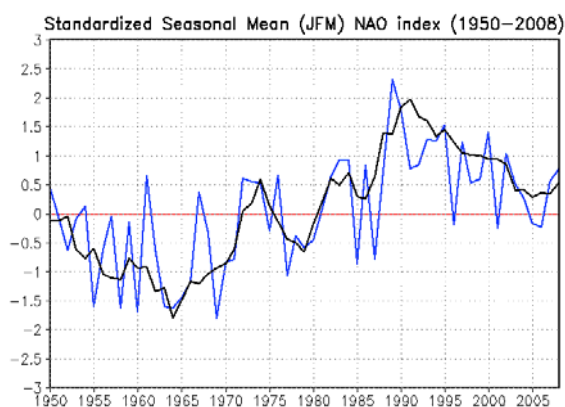


Figure 2.8.: Standardized seasonal mean of NAO index during cold season (blue line) and standardized five-year running means (black line), 1950 – 2008. Both curves are standardized using 1950 – 2000 base period statistics. From: CPC (2008).

#### 2.3.5. Arctic Oscillation (AO)

The Arctic Oscillation (AO) describes the variation in the strength of the polar vortex and gives a better estimate of the hemispheric variability than NAO. The polar vortex is believed to be closely related to interannual and long-term variability of climate (Macdonald *et al.*, 2005), but less related to short-term variations. AO is considered an important measure for Arctic climate change, but accounts for less of the variation of the atmospheric pressure field compared to NAO. AO and NAO are found to correspond well (Macdonald *et al.*, 2003a).

Some scientists argue that NAO is in fact an integrated part of the AO (Wallace, 2000), but some disagree and assert that they have clear distinctions (Ambaum *et al.*, 2001).

In this thesis correlations between POPs and both NAO and AO have been investigated.

#### 2.3.6. Midnight sun and polar night

The Arctic is special when it comes to light conditions. After polar sunrise, removal rates of organochlorines by photodegradation and depletion reactions with hydroxyl radicals (OH) increase, which results in lower levels of OCs in air during summer (Hung *et al.*, 2005).

During polar night photochemistry is switched off. The absence of OH production is enhancing atmospheric persistence of all organic compounds in higher latitudes

## 2. POPs in the Arctic: Background

(AMAP, 2004; Hermanson *et al.*, 2005).

### 2.3.7. Ice cover

The Arctic Ocean is covered, partly or completely, with sea ice throughout the year. Sea ice minimum around Svalbard occurs in September and maximum occurs in March (*Polarview*, 2009). The trend during the recent decades is that the sea ice extent of the Arctic Ocean has been decreasing. Some POPs partition strongly into water, e.g.  $\alpha$ - and  $\gamma$ -HCH. From approximately 1950 until 1990 a great amount of these compounds were transported into the Arctic through ocean currents and were trapped under the pack ice in the Arctic Ocean (*Li et al.*, 2002). Nowadays, oceans freeze later in the year than earlier, and melting occurs earlier in the year. Thus, re-evaporation from the oceans for longer periods of the year occurs.

## 2.4. Consequences of POP emissions

Many studies confirm that concentrations of POPs are high in Arctic carnivores and that concentrations accumulate through the food chains (AMAP, 2004). Evidence propose that bioaccumulation of toxic substances constitutes a great threat to human health and wildlife.

Some of the POPs, e.g. DDTs, show xenoestrogenic activity, that is; their chemical structure is similar to estrogens. This cause hormone production failure which results in, among others, malformations in reproductive organs, impaired mating behaviour, impaired eggshell quality, miscarriages and change of sex. The immune system, growth and metabolism can also be affected (AMAP, 2004; ATSDR, 2002a). It has been investigated if DDTs can cause cancer, but studies give conflicting conclusions (*Aronson et al.*, 2000; *Dorgan et al.*, 1999).

## 2.5. Impacts of climate change on contaminant pathways

Evidence suggests that global warming will alter the transportation of persistent organic pollutants over long distances (*Macdonald et al.*, 2003b). The Arctic has already undergone dramatic change during the recent years, e.g. change in atmospheric sea-level pressure, wind fields, permafrost, sea-ice drift, ice cover, length of melt season, precipitation patterns and ocean currents (*Macdonald et al.*, 2005).

Organochlorines (OCs) have a wide spectrum of physical-chemical properties, and volatility, phase partitioning and degradation kinetics are sensitive to changes in temperature and hydrology (*Macdonald et al.*, 2003a).

Transport of pollutants through physical pathways like the atmosphere, ocean currents and river run-off can change in response to the Arctic and North Atlantic Oscillation. During strong NAO (AO) conditions, especially NAO+ (AO+) conditions, the Arctic atmosphere gets a stronger connection with the western European and the

North American atmosphere. This can lead to more direct passage of air masses from industrial areas to the remote and clean Arctic and also a more rapid transport (Macdonald *et al.*, 2003a), as described in Sections 2.3.4 and 2.3.5.

More washout of pollutants from the atmosphere by rain can change the transport mode from atmospheric transport to transport by ocean currents. For compounds like the HCHs, which are semi-volatile, have a low HLC and partition strongly into cold water, a change in transport medium from the atmosphere to the ocean has been observed (Macdonald *et al.*, 2000). Between 1950 and 1990, when emissions were high, HCHs accumulated in the Arctic Ocean and was trapped under the ice pack. After reduction of HCH emissions the atmosphere contains less of the compounds, but the ocean has become the largest reservoir. Melting of multiyear ice caused by global warming can unleash HCH concentrations from the water masses trapped under the ice (Li *et al.*, 2002).

## 2.6. Summary

In this chapter, the POPs analysed in air at the Zeppelin station, Ny-Ålesund, and in ice drilled from Kongsvegen glacier were introduced, and information about production and usage, banning and areas of application of these compounds was given. In addition, some physical-chemical properties of POPs were described and set in conjunction with the compounds' abilities to undergo atmospheric transportation and to interact with oceans, soil and forest canopies. Atmospheric circulation patterns and variability connected to these patterns were also described in order to later be able to connect concentration levels to source areas.

The next chapter will describe sampling procedures, preparation and analysis methods used on air samples collected at the Zeppelin station and ice samples from the ice core collected from Kongsvegen glacier. Quality control for the analysis of air samples is included in the following chapter, but quality control and method evaluation for the preparation and analysis of the ice core samples are given in Chapter 4. Chapter 3 includes a description of FLEXPART, the transport model providing backward model runs of CO utilized in this thesis. Methods used in order to investigate seasonal and long-term trends of POPs are also presented.

## 2. POPs in the Arctic: Background

Compound	Solubility, water at 25° C [mg/L]	Vapor pressure at 25° C [Pa]	log $K_{oa}$	log $K_{ow}$	Henry's Law const at 25° C [Pa m <sup>3</sup> /mol]	Half-life: air, surface water, soils
$\alpha$ -HCH	96.85 <sup>[2]</sup>	0.245 <sup>[2]</sup>	7.464 <sup>[2]</sup>	3.94 <sup>[2]</sup>	0.741 <sup>[2]</sup>	3.3 - 4.4 yrs <sup>[11]</sup> , 1.7 - 77 d <sup>[9]</sup> , 7.1 - 8.2 yrs <sup>[10]</sup>
$\gamma$ -HCH	71.84 <sup>[2]</sup>	0.0759 <sup>[2]</sup>	7.74 <sup>[2]</sup>	3.83 <sup>[2]</sup>	0.309 <sup>[2]</sup>	4.3 - 9.1 yrs <sup>[11]</sup> , 10 - 138 d <sup>[9]</sup> , 14.5 - 16 yrs <sup>[10]</sup>
trans-CD	0.615 <sup>[1]</sup>	0.010 <sup>[1]</sup>	8.85 <sup>[1]</sup>	6.27 <sup>[1]</sup>	6.8 <sup>[1]</sup>	5.2 - 51.7 h <sup>[7]</sup> , 0.6 - 3.8 yrs <sup>[7]</sup> , 0.6 - 3.8 yrs <sup>[7]</sup>
cis-CD	0.402 <sup>[1]</sup>	0.0073 <sup>[1]</sup>	8.85 <sup>[1]</sup>	6.20 <sup>[1]</sup>	5.7 <sup>[1]</sup>	5.2 - 51.7 h <sup>[7]</sup> , 0.6 - 3.8 yrs <sup>[7]</sup> , 0.6 - 3.8 yrs <sup>[7]</sup>
trans-NO	-	-	-	6.35 <sup>[17]</sup>	-	-
cis-NO	-	-	-	6.08 <sup>[17]</sup>	-	-
HCB	0.398 <sup>[1]</sup>	0.094 <sup>[1]</sup>	7.21 <sup>[1]</sup>	5.64 <sup>[1]</sup>	65 <sup>[1]</sup>	15 - 29 yrs <sup>[11]</sup> , 2.7 - 5.7 yrs <sup>[7]</sup> , 11.7 - 48.7 yrs <sup>[10]</sup>
p'p-DDD	0.738 <sup>[1]</sup>	0.0023 <sup>[1]</sup>	10.03 <sup>[1]</sup>	6.33 <sup>[1]</sup>	0.5 <sup>[1]</sup>	17.7 - 177 h <sup>[7]</sup> , 2 - 15.6 yrs <sup>[7]</sup> , 2 - 15.6 yrs <sup>[7]</sup>
p'p-DDE	0.252 <sup>[1]</sup>	0.0034 <sup>[1]</sup>	9.70 <sup>[1]</sup>	6.93 <sup>[1]</sup>	4.2 <sup>[1]</sup>	< 1 day <sup>[8]</sup> , 1.9 yrs <sup>[9]</sup> , 17.2 - 40.9 yrs <sup>[10]</sup>
p'p-DDT	0.149 <sup>[1]</sup>	$4.8 \times 10^{-4}$ <sup>[1]</sup>	9.73 <sup>[1]</sup>	6.39 <sup>[2]</sup>	1.1 <sup>[1]</sup>	17.7 - 177 h <sup>[7]</sup> , 7 - 350 d <sup>[7]</sup> , 2 - 15.6 yrs <sup>[7]</sup>
PCB 18 (Tri)	0.780 <sup>[3]</sup>	0.033 - 0.0762 <sup>[5]</sup>	7.79 <sup>[16]</sup>	5.60 <sup>[4]</sup>	25.3 <sup>[6]</sup>	6.9 - 17 d <sup>[12]</sup> , <2.7 yrs <sup>[13]</sup> , -
PCB 52 (Tetra)	0.140 <sup>[14]</sup>	0.0120 <sup>[14]</sup>	8.22 <sup>[14]</sup>	5.91 <sup>[14]</sup>	25.12 <sup>[15]</sup>	62.5 d <sup>[15]</sup> , 3.4 yrs <sup>[15]</sup> , 10 yrs <sup>[15]</sup>
PCB 118 (Penta)	0.0223 <sup>[14]</sup>	$1.0 \times 10^{-4}$ <sup>[14]</sup>	9.36 <sup>[14]</sup>	6.69 <sup>[14]</sup>	14.45 <sup>[14]</sup>	16 - 48 d <sup>[12]</sup> , - -
PCB 153 (Hexa)	0.0111 <sup>[14]</sup>	$6.03 \times 10^{-4}$ <sup>[14]</sup>	9.44 <sup>[14]</sup>	6.87 <sup>[14]</sup>	19.95 <sup>[14]</sup>	250 d <sup>[15]</sup> , 14 yrs <sup>[15]</sup> , 18.8 yrs <sup>[15]</sup>

Table 2.2.: Physical-chemical properties of target compounds. From *Mackay et al.* (2006a,c); *Simpson et al.* (1995). For list of reference selection, see Table A.1 in Appendix A.

## 3. Materials and methods

In this chapter, methods for sampling, sample preparation and analysis used for the determination of POPs in air samples collected at the Zeppelin station and an ice core drilled from Kongsvegen glacier are described.

In Section 3.1, sampling procedures and methods used on the air samples are presented, together with quality control. Section 3.2 presents the method of solid-phase extraction (SPE) utilized on the ice core samples, together with procedures for quantification. In Section 3.3, the basics behind the transport model FLEXPART, which produces backward model runs of CO utilized in this thesis, is described. Finally, Section 3.4 describes methods used to investigate seasonality and long-term trends, together with calculations performed to investigate connections between POPs and NAO/AO. Statistical significance is also introduced in order to later evaluate the results.

### 3.1. Air samples from the Zeppelin station, Ny-Ålesund

#### 3.1.1. Sampling and storing

The Zeppelin station is located near Ny-Ålesund, Svalbard ( $78^{\circ}54'N$ ,  $11^{\circ}53'E$ ), and is considered suitable for POP measurements because of the following reasons. The measuring station is located 474 m above sea level, which places it above the boundary layer for most of the time. This makes the Zeppelin station suitable for measurements of long-range transport. Because of the wind direction (mostly from the south) the station is relatively unaffected by local contamination from Ny-Ålesund. There is a slightly lower pressure inside the station compared to outside, which makes clean, outdoor air flow in instead of contaminated, indoor air flow out when doors are opened. Indoor air is transported out through pipelines and released far away from the station and measuring inlets to avoid contamination when sampling. See Figure 3.1 for location of the Zeppelin station relative to Ny-Ålesund.

Monitoring of POPs in continuous time series has been performed at Zeppelin since 1993 for 10 PCB congeners,  $\alpha$ - and  $\gamma$ -HCH, chlordanes and HCB, since 1994 for DDT derivatives and since 1997 for 22 additional PCB congeners.

The Norwegian Institute for Air Research (NILU) operates a majority of the instruments performing air pollution measurements at the Zeppelin station, including the POP measuring device. The instrument is a high volume sampler which sucks air through a glass channel, a particle filter made of glass fibre and two plugs made of polyurethane foam (PUF) (11 cm (d)  $\times$  5 cm (h), density 25 kg/m<sup>3</sup>, Ekornes Industries). Each sampling period is 48 hours and sampling is carried out once a week.

### 3. Materials and methods

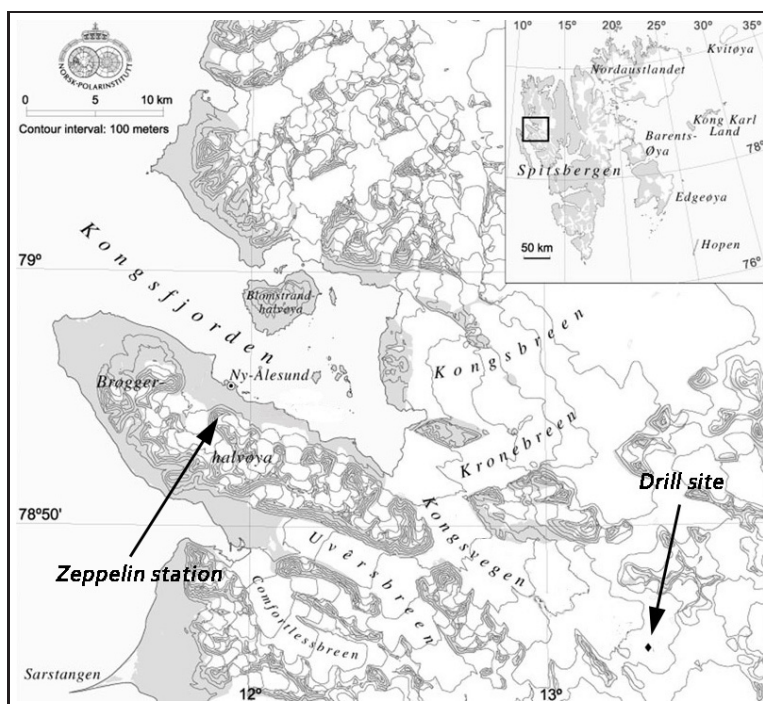


Figure 3.1.: Map showing the location of Ny-Ålesund and the drill site location on Kongsvegen. From: *Brandt et al. (2008)*

The PUF samples are handled with clean tweezers, packed in plastic bags and stored in a refrigerator until transport to the laboratory at NILU, Kjeller, Oslo, for analysis (*Hermansen, 2008, pers.comm.*).

#### 3.1.2. Sample preparation

Extraction of air samples is done by NILU in Kjeller, Oslo. The particle filter and the two PUF plugs are added internal standards and extracted with 250 – 300 ml diethyl ether : *n*-hexane (1:9) by Soxhlet extraction for 6 – 8 hours. The extracts are then concentrated by a Zymark TurboVap 500 System (Caliper, Hopkinton, MA, USA) to 0.5 ml and added 8 – 10 ml sulphuric acid (96 %, Merck no. 731) to remove other non-persistent components. Afterwards silica fractionation is performed, that is; letting the extract through a glass column filled with 4 g silica and eluted with 30 ml *n*-hexane : diethyl ether (9:1). The volume is again reduced to 0,5 ml, and a recovery standard, tetrachloronaphtalene (TCN), is added to the samples before analysis with GC-MS (*EMEP, 2001; Eckhardt et al., 2007*).

### 3.1.3. Analysis

The detection and quantification of POPs collected in the filter and PUF plugs are done with gas chromatography (GC) combined with a high resolution mass spectrometer (MS). The gas chromatograph used by NILU for analysis of POPs at Zeppelin from 1990 to 2003 was a Hewlett-Packard 5890II and from 2003 until today is a Hewlett-Packard 6890 (Hewlett Packard, Avondale, USA). The GC is coupled to an AutoSpec mass spectrometer from Micromass Waters, Manchester, UK (EMEP, 2001; Eckhardt *et al.*, 2007).

**Gas chromatographic conditions:** Separation is done on a 50 m × 0.22 mm (inner diameter) fused silica capillary column (8% phenylpolycarbonsiloxane) with film thickness 0.15 µm. Helium (4.5) was used as carrier gas at a column flow rate of 35 – 40 cm/s. Injection of 1 µL sample was performed at 280 °C using a splitless injector and a splitless time of 2 minutes. The initial column temperature was 90 °C. A temperature program was performed as follows. The initial temperature was held for 2 min followed by an temperature increase of 25 °C / min to 170 °C and a further increase of 3 °C / min to 300 °C.

**Mass spectrometer conditions:** A mass spectrometric detector was used in electron impact mode (EI) at 30 – 40 eV with selected ion monitoring (SIM) acquisition mode.

For more details about analytical equipment and procedures used by the Norwegian Institute for Air Research, see the EMEP Manual (EMEP, 2001).

### 3.1.4. Quality control

Sampling and sample storage are integrated parts of the overall quality control program followed by NILU. Both station personnel and laboratory personnel are trained to follow detailed routines to avoid contamination of samples.

Field blanks and control samples are taken according to standard procedure to ensure accuracy, precision and detection limits.

Limit of detection (LOD) is according to Eckhardt *et al.* (2007) determined by NILU by a signal-to-noise ratio (S/N) for field blank samples > 3:1 and according to the EMEP Manual determined as three times the standard deviation of the field blank.

Limit of quantification (LOQ) is defined by a signal-to-noise ratio of 10:1 or by a standard deviation of 10 of the field blank.

According to Roland Kallenborn (pers.comm.) the first monitoring station building built on the Zeppelin mountain in 1989 consisted of PCB containing materials. A new station was built in 1999, free of PCBs and other contaminating compounds. This makes the reliability of the PCB data before 1999 questionable, and thus these data are rejected from calculations in this thesis. Pesticide data were not affected by the properties of the old station.

For more information about quality control procedures followed by NILU, see the EMEP Manual (EMEP, 2001).



## 3.2. Ice core from Kongsvegen, Ny-Ålesund

### 3.2.1. Sampling and storing

The ice core was drilled from Kongsvegen glacier (78°45'N, 13°21'E) near Ny-Ålesund, Svalbard, by the Norwegian Polar Institute (NPI) in spring 2006. Figure 3.1 shows drilling location. The core was approximately 7.5 m long, and it was dated to cover the period from approximately autumn (Aut) 1994 to autumn 2005, see Figure B.1 and Table B.4 in Appendix B. The ice core was divided into nine samples with approximately one year resolution. Annual layers were taken to begin in autumn and to include the subsequent summer melt layer at the top of the annual layer. Table 3.1 gives an overview over the sample number and the corresponding sample period.

<b>Sample 1</b>	Aut 2005 – Aut 2004 / Aut 2004 – Aut 2003
<b>Sample 2</b>	Aut 2003 – Aut 2002
<b>Sample 3</b>	Aut 2002 – Aut 2001
<b>Sample 4</b>	Aut 2001 – Aut 2000
<b>Sample 5</b>	Aut 2000 – Aut 1999
<b>Sample 6</b>	Aut 1999 – Aut 1998 / Aut 1998 – Aut 1997
<b>Sample 7</b>	Aut 1997 – Aut 1996
<b>Sample 8</b>	Aut 1996 – Aut 1995
<b>Sample 9</b>	Aut 1995 – Aut 1994

Table 3.1.: Overview of samples and corresponding years.

The outer coat of the ice core was scraped off before it was cut into smaller pieces. The ice core pieces were put into zip-lock polyethylene bags, which again were put in plastic containers and stored in a zarges box. This was done to prevent cross-contamination between the samples or from the surroundings. The zarges box with the samples was sent by plane from Tromsø to Longyearbyen straight after cutting and stored in a freezer (-18 °C) until extraction.

### 3.2.2. Sample preparation

#### Solid phase extraction (SPE) with Si-C18 phase cartridges

Solid-phase extraction (SPE) was introduced in the beginning of the 1980s, but ten years ago SPE was improved and accepted as a reliable method in environmental analysis. It is included as an official method by the U.S. Environmental Protection Agency (USEPA) for determination of organochlorine (OC) pesticides and polychlorinated biphenyls (PCBs) (*Barcelo*, 2000). Studies show that SPE in combination with GC-MS, which both were methods used in this thesis, give acceptable recoveries and linearity for pesticides (*Patsias and Papadopoulou-Mourkidou*, 1996).

The concept of SPE is to let a sample pass through a cartridge which contains a stationary phase in order to elute the compounds of interest. The purpose of this



procedure is to concentrate large volume samples and elute compounds of interest in small volumes of solvent. Interfering sample matrix components are removed. Additionally, the solvent can be changed from the original solvent, in this case water, to a more suitable solvent for GC-MS analysis; hexane. Solvents used in GC-MS should be volatile and not contain water.

As a part of this thesis the ice core pieces were slowly melted and sucked through 500 mg IST isolute™ C18-phase SPE separation cartridges (International Sorbent Technology Ltd, Mid Glamorgan, UK) connected to a Phenomenex® vacuum manifold (Phenomenex, Cheshire, UK). Extraction was done with a speed of two droplets per second.

The cartridges were rinsed and conditioned before sample application, (Table 3.2), and internal standards were added, (Table 3.3). The cartridges were dried after rinsing, but were kept wet after conditioning to maintain the highest possible loading capacity. After extraction the cartridges were dried on the vacuum manifold, wrapped in aluminium foil to avoid cross-contamination and stored at  $-18^{\circ}\text{C}$  until elution.

Rinsing	Conditioning/activation
2 x 4ml Acetone	3 x 4ml Methanol
2 x 4ml n-Hexane	3 x 4ml Methanol:Milli-Q (1:200)

Table 3.2.: Rinsing and conditioning of Si-C18 phase cartridges

Internal standards	Volume [ $\mu\text{l}$ ]	Concentration [ $\text{ng}/\mu\text{l}$ ]
$^{13}\text{C}$ PCB 118 (ISTD)	10.0	4.0
$^{13}\text{C}$ trans-chlordane (ISTD)	10.0	4.0
Octachloronaphtalene, OCN (RSTD)	10.0	4.0

Table 3.3.: Internal standards added in solid-phase extraction

#### Clean-up, fractionation and concentration

Elution was carried out on the vacuum manifold by sucking solvents through the cartridges with a gentle vacuum pressure, and four different fractions were obtained (Table 3.4). Before fractionation a small amount of acetone:*n*-hexane (1:1) was added to the cartridges to wetten the stationary phase.

The volume of the sample fractions was reduced to approximately 100  $\mu\text{l}$  by Pierce Reacti-Vap evaporating unit (Thermo Scientific Inc, Rockford, USA) with nitrogen

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<b>Fraction 1</b>	4ml Acetone : <i>n</i> -Hexane (1:1)
<b>Fraction 2</b>	4ml Acetone : <i>n</i> -Hexane (1:1)
<b>Fraction 3</b>	4ml <i>n</i> -Hexane
<b>Fraction 4</b>	4ml <i>n</i> -Hexane

Table 3.4.: Fractionation of Si-C18 phase cartridges

(5.0) (AGA, Oslo, Norway). This was done with low nitrogen stream pressure to prevent the volatile compounds from evaporating. The sample fractions were then transferred to 350  $\mu$ L GC injection vials (Cronus, Gloucester, UK) and added recovery standard (RSTD, see Table 3.3) for analysis by GC-MS.

After elution, some of the sample fractions contained water and needed to be filtered through sodium sulfate, Na<sub>2</sub>SO<sub>4</sub>.

A recovery test and four method blank tests were performed for quality assurance of the results. Blank tests were added internal standards (see Table 3.3) and the recovery test was added recovery solution (see Table B.1).

The method of solid-phase extraction is described in *Font et al.* (1993), *Berrueta et al.* (1995) and *Barcelo* (2000).

#### 3.2.3. Analysis

##### Instrumental parameters

Due to GC-MS instrument problems at UNIS the quantification of POPs in ice core samples was moved to the NILU laboratories at the Polar Environmental Centre in Tromsø. Analysis of ice core samples was done by Roland Kallenborn and Linda Hanssen. The instrument used was a 6890 capillary GC with a 5975 quadrupole mass sensitive detector (MSD) (Agilent Technologies, USA).

**Gas chromatographic conditions:** Separation was done on a 30 m Agilent J&W Scientific DB-5 column (Agilent Technologies, USA) with an inner diameter of 250  $\mu$ m and a film thickness of 0.25  $\mu$ m. DB-5 is a fused silica capillary column with a 5/95 % phenyl/methylpolysiloxane stationary phase. Helium (5.5) (Hydrogas, Porsgrunn, Norway)) was used as carrier gas at a column flow rate of approximately 55 ml/min. Injection of 1  $\mu$ L sample was performed at 280 °C using a splitless injector and a splitless time of 2 minutes. The initial column temperature was 70 °C. A temperature program was performed as follows. The initial temperature was held for 2 min followed by an temperature increase of 15 °C / min to 180 °C and a further increase of 5 °C / min to 280 °C.

**Mass spectrometer conditions:** A mass spectrometric detector was used in electron impact mode (EI) for PCBs and with negative ion chemical ionization (NCI) for

pesticides. MS detection was performed with SIM acquisition mode.

In the beginning, in the middle and in the end of each batch injections of quantification standards at different concentrations were performed for the PCBs, and the standards were also injected separately in between samples. For the pesticides injections of two standards at different concentrations were performed in the beginning and in the end, and also five times in between samples. Prior to standard quantification the corresponding instrument blank was determined (n-hexane). After the standard quantification, two additional blanks were analysed in order to identify possible cross-contamination during the injection sequence.

### Quantification

Compounds were identified by their characteristic fragment masses (Table B.5 in Appendix B) and ion ratios. Software used for quantification of POPs in this thesis was Xcalibur™ version 1.4 from Thermo Electron Corporation.

Preferably, quantification is performed using internal standards. It can also be carried out by using an external standard.

Quantification by external standard is carried out like listed below:

$$f_i = \frac{C_{i(s)}}{A_{i(s)}} \quad (3.1)$$

$$C_{i(p)} = f_i \cdot A_{i(p)} \quad (3.2)$$

where  $f_i$  is the response factor of analyte  $i$  in the standard,  $C_{i(s)}$  and  $C_{i(p)}$  are the concentrations of analyte  $i$  in the injected standard volume and sample volume, respectively, and  $A_{i(s)}$  and  $A_{i(p)}$  are the areas of signal  $i$  in the standard and sample chromatogram, respectively (Oehme, 2007).

Quantification by internal standard is carried out like listed below:

$$RF = \frac{\text{amount}(\text{sample}) \times \text{signal area}(\text{ISTD})}{\text{amount}(\text{ISTD}) \times \text{signal area compound}(\text{sample})} \quad (3.3)$$

RF is the relative response factor based on  $^{13}\text{C}$  PCB 118 and  $^{13}\text{C}$  trans-chlordane.

Concentration; C:

$$C = \left( \frac{\text{amount}(\text{ISTD}) \times \text{signal area compound}(\text{sample})}{RF \times \text{signal area}(\text{ISTD})} \right) / \text{volume sample} \quad (3.4)$$

$$RRF = \frac{\text{amount}(RSTD) \times \text{signal area}(ISTD)}{\text{amount}(ISTD) \times \text{signal area}(RSTD)} \quad (3.5)$$

RRF is the response factor based on the recovery standards, OCN (ice) and TCN (air).

Recovery; R(%):

$$R(\%) = \frac{\text{amount}(RSTD) \times \text{signal area}(ISTD) \times 100}{RRF \times \text{amount}(ISTD) \times \text{signal area}(RSTD)} \quad (3.6)$$

Recovery is the percentage share of internal standard relative to the recovery standard, OCN, found after sample treatment.

### 3.3. Transport calculations

FLEXPART is a Lagrangian model which calculates long-range and mesoscale dispersion of air pollutants from point sources forward or backward in time. FLEXPART produces multiple atmospheric trajectories which provide a trajectory field. This gives information about the emission tracers' location relative to the sampling spot backward or forward in time. Meteorological input data from the European Centre for Medium-Range Weather Forecasts (ECMWF) are used for the POP modelling on the data collected from the Zeppelin station. FLEXPART is based on the programming language FORTRAN 77 (Stohl *et al.*, 2007, 2005).

In this master thesis backward model runs from the FLEXPART model with respect to carbon monoxide, CO, have been utilized. The model runs cover the time period from 1995 to 2007 and were performed by Andreas Stohl and David Hirdman, NILU. The emission inventory of CO has turned out to correlate well with the emission inventory of POPs, since the sources are similar. CO is considered a tracer for human activity, and POP emissions a result of human activity since POPs do not occur naturally in the environment (Eckhardt *et al.*, 2003; Eckhardt, 2007, pers.comm.). CO is a passive tracer because it is transported without being affected by chemical or depositional processes. Highest correlations are naturally expected between CO and POPs which are transported substantially through the atmosphere.

In this thesis statistics from footprint distributions of potential emission sensitivity (PES) have been utilized. Emission sensitivity is proportional to the residence time of the particles over a unit area, and footprint residence time is the residence time of the particles averaged over the lowest 150 m of the troposphere. Anthropogenic emissions are mostly located at the surface, so footprint residence time gives information about where the emissions are likely taken up. Assuming no chemical transformation and no deposition, this is the response an emission release of unit source strength would have at the measurement point (Stohl, 2008).

The footprint distributions have been utilized to retrieve information about age spectrum and origin continent of CO calculated backwards from the Zeppelin station. The age spectrum time series show the different ages of the emission tracer, CO, arriving at Zeppelin and the continent spectrum time series show the origins of the CO. The Arctic age is the time a particle has spent continuously north of 70°N (Stohl, 2006). The continent spectra give information about air masses originating from South America, Europe, Australia, North America, Africa and Asia. For each day of the month, age and continent spectra are calculated backwards 20 days. In addition, biomass burning CO contributions have been utilized to check for fire hot spot locations.

FORTTRAN 95 was used to calculate averages of the concentrations, and MATLAB was used for plotting of data.

## 3.4. Statistical calculations

The analyses performed in this thesis were done using MATLAB and MINITAB. Correlations were calculated using Pearson's correlation coefficient. Seasonality and long-term trends of POPs were looked into using Holt-Winters' method and running mean, respectively.

The North Atlantic Oscillation and Arctic Oscillation indices are downloaded from the website of Climate Prediction Center (CPC), a part of the National Weather Service and under the National Oceanic and Atmospheric Administration (NOAA) in the United States (CPC, 2008).

### 3.4.1. Holt-Winters' method

Holt-Winters' method is an exponential smoothing procedure which calculates dynamic estimates for three components; trend, level and seasonal. The method can be used for data sets with both trend and seasonality present. There are two model types: Additive and multiplicative model. The additive model is used when the seasonal pattern in the data set does not depend on the size of the data, that is; when it does not change as the series level goes up or down. This model is used for seasonality investigations of POPs looked into in this thesis.

Three smoothing parameters are used to update the components at each period, one for the level, one for the trend and one for the seasonal component. The values of the smoothing weights are in the range between 0 and 1. Initial values for the level and trend components are obtained from a linear regression on time, while initial values for the seasonal component are obtained from regression with seasonal indicators (MINITAB, 2009). The fitted values are estimated as shown below:

$$V_t = L_{t-1} + T_{t-1} + S_{t-p} \quad (3.7)$$

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where  $V_f$  is the fitted value,  $t$  is time,  $p$  is the seasonal period,  $L$  is the level,  $T$  is the trend and  $S$  is the seasonal component. The smoothing equations for  $L$ ,  $T$  and  $S$  are:

$$L_t = \alpha(D_t - S_{t-p}) + (1 - \alpha)[L_{t-1} + T_{t-1}] \quad (3.8)$$

$$T_t = \gamma[L_t - L_{t-1}] + (1 - \gamma)T_{t-1} \quad (3.9)$$

$$S_t = \delta(D_t - L_t) + (1 - \delta)S_{t-p} \quad (3.10)$$

where  $D$  is the data value,  $\alpha$  is the level weight,  $\gamma$  is the trend weight and  $\delta$  is the weight for the seasonal component.

In this thesis weight 0.2 for the seasonal component was chosen, and the seasonal period was set to one year.

Seasonal estimates for all POPs were performed using monthly averaged values of Zeppelin POP time series. The Holt-Winters' method in MINITAB does not allow missing values in the data series, so in cases where there were missing data for a whole month, the average of the previous and next month was used. If data was missing for several months in a row, the average of the previous and the next years' equivalent month was used. See Table A.5 in Appendix A for a complete list of interpolated values used in seasonality calculations.

#### 3.4.2. Running mean

Running mean was performed using MINITAB. One year running means were calculated to examine long-term trends for POPs. As for the seasonality calculations, interpolated monthly averaged values were used, see Table A.5 in Appendix A.

#### 3.4.3. Pearson's correlation coefficient

Correlations between CO/POPs and the climate variability patterns are calculated using the standard Pearson's correlation coefficient,  $r$ .

$$r = \frac{1}{n-1} \sum_{i=1}^n \left( \frac{x_i - \bar{x}}{s_x} \right) \left( \frac{y_i - \bar{y}}{s_y} \right)$$

where  $x$  and  $y$  are the variables we want to investigate the linear relationship between,  $s$  is the standard deviation, and  $\bar{x}$  and  $\bar{y}$  are the means of  $x$  and  $y$ , respectively (Moore *et al.*, 2006).

The correlations were calculated using MINITAB.

#### 3.4.4. Statistical significance

A significance test is a procedure where observed data are compared with a hypothesis to assess the truth of it. The hypothesis is a statement about the parameters in a population. A test of statistical significance finds the probability of

getting an outcome as extreme or more extreme than the actual observed outcome, that is; to assess if the effect measured is real or not.

The statement being tested in a test of significance is called the *null hypothesis*. The null hypothesis is usually a statement of "no effect" or "no connection". In this master thesis the null hypothesis is:

$H_0$ : There is no linear relationship between the data sets

The next step in the statistical significance test is to state an *alternative hypothesis*, which we hope is true instead of  $H_0$ . In this thesis the alternative hypothesis is:

$H_a$ : There is a linear relationship between the data sets

To test the significance of the correlations calculated in this thesis *P-values* were computed. P-values range from 0 to 1 and determine the extent of which the null hypothesis can be rejected. The smaller the P-value, the stronger the evidence against  $H_0$  provided by the data and the more significant the result is.

The last step is to compare the P-values with a fixed value regarded as decisive, a *significance level*,  $\alpha$  (Hopkins, 2000).

In this thesis statistical significance is tested for the calculated correlations between CO and measured POPs, CO and NAO/AO, age CO and NAO and between measured POPs and NAO/AO. Hopkins (2000) states that there are problems connected to P-values and that some scientific work with statistically non-significant effects never gets published even though it should be. In this thesis  $\alpha$  is chosen to be 0.05, the standard value for P. However, P-values are in this thesis presented at different levels of  $\alpha$  for all correlations higher than 0.3. P-values for monthly correlations are calculated using MINITAB.

### 3.5. Summary

In this chapter, procedures and methods used for the determination of POPs in air and ice were presented. In addition, description of the transport model FLEXPART, showing transport pathways for CO, a pollution tracer, in form of backward trajectory fields from Zeppelin, was given. Techniques and methods for the processing of air data were presented. The term *statistical significance* was introduced. This was done to later be able to evaluate the significance of the correlations which is calculated and presented in Chapter 5.

Quality control measures employed on the air data was discussed in this chapter, while quality assurance and evaluation of SPE and GC-MS analysis performed on the ice core samples will be presented and discussed in Chapter 4. This is an important part of the analysis of the ice cores because estimation of reliability of the results is crucial in order to interpret the data.





## 4. Quality control and method evaluation: POPs in ice

In Chapter 3, the course of the methods utilized in the laboratory work performed by NILU and by myself was described. In this chapter, quality control measures employed on the ice core preparation and analysis performed in this thesis are presented. To investigate reliability of the results obtained is essential in order to do further analyses.

Section 4.1 displays the results from the testing of three stationary phases for SPE. This was necessary to find the most suitable phase and to ensure the most reliable results possible. The subsequent section, Section 4.2, states three identification criteria and three quantification criteria that are applied to the SPE method. Two instrument tests and a recovery test are also performed to ensure reliable results from the GC-MS analysis and to detect loss of analyte during the different steps of the method. General uncertainties which must be taken into account are listed in Section 4.3. Finally, conclusions and evaluation of the method are given in Section 4.4.

### 4.1. Testing of method and choice of stationary phase

Three different stationary phases for SPE were tested with respect to recovery rates; Oasis® HLB Extraction Cartridge, BAKERBOND spe™ Extraction Column and IST isolate™ C18-phase cartridge. The IST isolate™ C18-phase gave highest recoveries (>95 %) and was chosen as the stationary phase in the further experimental work. Table 4.1 summarizes average recovery rates for the three phases tested.

Internal standard	Oasis®	BAKERBOND spe™	IST isolate™
<sup>13</sup> C PCB 118	10.9	12.4	95.4
<sup>13</sup> C trans-chlordane	65.3	46.5	95.5

Table 4.1.: Recovery rates in percent for the three phases tested.

A fractionation test was also performed in order to determine which of the four sample fractions contained the analytes after elution. Both PCBs and pesticides eluted mostly in the first fraction.

## 4.2. Quality control criteria

Quality control criteria taken into account for the treatment of the ice core samples in this thesis were three identification criteria, three quantification criteria, two instrument tests and a recovery test. These are described in detail below:

### 4.2.1. Identification criteria

Three common identification criteria are applied for quality control in mass spectrometry (*Oehme*, 2007). Firstly, intensity ratios between fragment ions should be within 20 % of the theoretical value determined by a reference compound. Intensity ratios for all sample analytes can be determined by calculating the fraction of the quantification ion signal area to the reference ion signal area. Ion ratios are then compared with ion ratios for the corresponding analytes in the standards. If the limit of 20 % is exceeded either the quantification ion or the reference ion is disturbed by matrix related compounds and identification and quantification must be considered less certain. Calculating ion ratios is done to verify that the identified compounds found in the samples are equal to the target compounds. In addition, all masses must have identical signal shape in the mass spectrum.

Secondly, retention times compared to an internal standard or an external standard solution must be within certain limits. *Oehme* (2007) states that the retention time of an analyte must be  $\pm 2 - 3$  seconds compared to an external standard solution and  $\leq 0.3$  % relative to an internal standard.  $^{13}\text{C}$ -labelled compounds elute 2 – 3 seconds before their corresponding compounds.

Thirdly, detection limits must be based on a minimal signal-to-noise ratio in the chromatogram. Limit of detection (LOD) is the lowest analyte signal detectable by the instrument with an acceptable degree of certainty. The LOD can be defined by a signal-to-noise ratio (S/N) of 3:1 (*Oehme*, 2007) or by a standard deviation of 3 of the field blank (*Long and Winefordner*, 1983). S/N ratio is determined by integrating the noise corresponding to ten times the signal width at half height (*Bröker et al.*, 1998).

Ion ratio deviations for a majority of the PCBs were more than 20 %. PCB 18 showed acceptable deviations in all samples. PCB 28/31 showed deviations around 50 %, that is; above the acceptable limit but still lower than the deviations for many of the other PCBs. PCB 180 and PCB 189 showed acceptable ion ratio deviations for many of the samples. Ion ratio deviations for PCB 18, PCB 28/31, PCB 180, PCB 189,  $\gamma$ -HCH, HCB and cis-nonachlor are listed in Table 4.2.

Too high (>50 %) deviations from the reference were obtained for most PCBs. These were PCB 52, 95, 99, 105, 110, 138, 153, 157 and 167. These PCBs were excluded from further quantification. High deviations indicate that the compounds are co-eluted together with other compounds resulting in multiple peaks which are not possible to separate. Co-elution made these compounds impossible to quantify accurately. By looking at mass spectra for these compounds one can clearly see that their signal

Sample	PCB 18	PCB 28/31	PCB 180	PCB 189	$\alpha$ -HCH	$\gamma$ -HCH	HCB	cis-NO
Sample 1	15	49	46	62	nf	0	1	6
Sample 2	16	75	15	36	nf	2	5	5
Sample 3	16	77	68	3	85	8	13	0
Sample 4	15	18	65	74	nf	12	5	1
Sample 5	11	47	62	66	nf	6	10	7
Sample 6	14	63	53	58	nf	0	14	nf
Sample 7	17	62	10	33	81	24	26	nf
Sample 8	20	77	27	46	nf	1	10	1
Sample 9	17	65	29	40	86	26	22	nf
Blank 1	17	69	62	58	nf	10	9	nf
Blank 2	15	33	9	30	nf	9	nf	nf
Blank 3	13	73	57	62	nf	7	9	nf
Blank 4	13	68	42	50	nf	2	4	nf

Table 4.2.: Ion ratio deviations of PCB 18, PCB 28/31, PCB 180, PCB 189,  $\alpha$ -HCH,  $\gamma$ -HCH, HCB and cis-NO in percent relative to reference compounds in standard solutions. Red numbers: Deviation < 20 %. Blue numbers: Deviation < 50 %. nf = not found in sample.

shapes are not equal to the other compounds. Thus, the criterion for identical signal shape compared to the standard is not fulfilled.

For the pesticides, all analytes' retention times deviated maximum 0.2 seconds from the external standard solution. For the PCBs the maximum deviation was 0.6 seconds.

The software used for quantification, Xcalibur, calculates S/N ratios for all signal peaks in the chromatograms automatically. No signal areas with S/N < 3:1 (<LOD) calculated by Xcalibur were used in calculations and plots. In addition, LOD was determined by 3 times the standard deviation of blanks. The LODs for all analytes are given in Table 4.3.

#### 4.2.2. Quantification criteria

Many different quantification criteria are applied in organic trace analysis and chromatographic methods coupled to mass spectrometric detection. In this thesis limit of quantification (LOQ), blank determination and values and quantity relation between ISTD and measured concentration are looked into.

LOQ for an analyte is the minimum quantity of a compound that can be determined with acceptable accuracy. It is defined by an S/N ratio of 10:1 (*Oehme, 2007*) or by a standard deviation of 10 of the field blank (*Long and Winefordner, 1983*).

Blanks are divided into field blank and method blank. Method blank is for testing the whole method without sample or standards. The field blank gives, in addition to that, information about sampling and storage. The method blank test is performed in the laboratory, while the field blank requires that the extraction medium has gone through the same transport, storing and pre-treatment procedures as the real

#### 4. Quality control and method evaluation: POPs in ice

Compound	LOD [pg]	LOQ [pg]
PCB 18	3.56	11.87
PCB 28/31	0.61	2.03
PCB 44	0.13	0.42
PCB 52	0.83	2.77
PCB 95	374.7	1245.6
PCB 99	65.4	217.9
PCB 101	0.82	2.72
PCB 105	51.4	171.2
PCB 110	217.2	723.9
PCB 114	0.45	1.49
PCB 118	0.70	2.33
PCB 123	1.21	4.04
PCB 126	0.16	0.54
PCB 128	0.35	1.16
PCB 138	27.9	93.0
PCB 146	0.12	0.39
PCB 149	0.02	0.07
PCB 153	4.32	14.4
PCB 156	1.21	4.04
PCB 157	29.9	99.7
PCB 167	0.92	3.08
PCB 169	0.68	2.26
PCB 170	0.21	0.69
PCB 177	0.22	0.74
PCB 180	9.93	33.1
PCB 183	0.42	1.39
PCB 187	0.16	0.53
PCB 189	6.42	21.4
$\alpha$ -HCH	0.09	0.31
$\gamma$ -HCH	0.93	3.09
tr-CD	0.01	0.03
cis-CD	0.01	0.03
tr-NO	0.01	0.04
cis-NO	0.13	0.45
HCB	0.08	0.25

Table 4.3.: Limit of detection (LOD) and limit of quantification (LOQ) for target compounds calculated from the standard deviation of the blanks 1, 3 and 4.

sample (*Oehme*, 2007). Blank tests are performed to monitor and control possible contamination during transport and laboratory work.

According to the European Standard EN 1948, blank values should be equal to LOD or be at least ten times lower than the lowest concentrations measured in real samples (*Bollmacher*, 2001; *Bröker et al.*, 1998).

According to *Oehme* (2007), one blank per twenty samples is needed if the measured concentrations in the samples are more than two orders of magnitude above the blanks. If the measured sample concentrations are about one order of magnitude above the blanks one to five blanks are needed per five samples.

An internal standard has to fulfil certain criteria. It must not be present in the sample initially, but its chemical behaviour and properties must be as equal to the analytes' as possible. The ISTD must not react with analytes in the sample and it must be added at similar concentrations as the analytes (Oehme, 2007). The ISTDs  $^{13}\text{C}$  PCB 118 and  $^{13}\text{C}$  trans-chlordane both fulfilled the criteria for an internal standard. Quantity of added ISTD must not be too small. If it is too small the measuring uncertainty rises. A minimum criterion is an S/N ratio of 20:1 (Oehme, 2007). However, the amount of ISTD cannot be very much higher than the amount of analyte, because then the ISTD does not necessarily behave in the same way as the analyte.

In this thesis, four method blank tests were performed. The method blanks were spiked with internal standards  $^{13}\text{C}$  PCB 118 and  $^{13}\text{C}$  trans-chlordane.

A majority of the compounds found in the samples were also found in the method blanks. As for the samples, ion ratios for many of the compounds found in the blanks deviated substantially from the standard ion ratios. These compounds were excluded from further investigations. Therefore, only the compounds with acceptable ion ratio deviations were taken into account. Ion ratio deviations of PCB 18, PCB 28/31, PCB 180, PCB 189,  $\gamma$ -HCH and HCB for the four blanks are given in Table 4.2. Limit of quantification (LOQ) for compounds PCB 18, PCB 28/31, PCB 180, PCB 189,  $\gamma$ -HCH and HCB is given in Table 4.3.

Xcalibur calculates LOQ directly from the chromatograms, and no signal areas with  $\text{S/N} < 10:1$  (<LOQ) were used in calculations and plots. LOQ was also calculated as ten times the standard deviation of blanks 1, 3 and 4 and is given in Table 4.3.

The levels for compounds quantified in the real samples were all above LOQ in the blanks. It is reasonable to believe that the blanks have experienced cross-contamination from the samples, since samples and blanks share the same distribution pattern and because samples and blanks were stored together in the freezer. Cross-contamination may also come from transfer of compounds between samples because of the use of pipettes, syringes or the evaporating unit. This makes the quantification less reliable. Blank levels were lower than sample levels, but the two criteria for blanks according to EN 1948 are not fulfilled. Analyte concentrations are higher than LOD and not at least ten times lower than the lowest concentrations measured in the samples were found in all blanks.

The amount of added ISTD was within the range of expected analyte concentrations, and all ISTD signal areas had S/N ratios  $> 20:1$ .

#### 4.2.3. Instrument tests

Calculating instrument linearity is a way of evaluating the instrument's ability to perform the analysis. The purpose of linearity calculations is to ensure that the signal area of the chromatographic peak is directly correlated to the amount of analyte present in the sample. Linearity is evaluated by calculating the square of correlation,  $r^2$  (Oehme, 2007). When  $r^2 > 0.90$  the method is considered to have acceptable linearity. When linearity is acceptable, the *response factor* can be calculated relative

#### 4. Quality control and method evaluation: POPs in ice

to the internal standard. The response factor makes it possible to calculate unknown concentrations of a target analyte by applying linear regression.

In this thesis, three different calibration standard levels were injected; 50 pg/ $\mu$ l, 100 pg/ $\mu$ l and 200 pg/ $\mu$ l. Accurate concentrations of analytes in the calibration standards are listed in Tables B.2 and B.3 in Appendix B. An average of the signal areas for 50 pg/ $\mu$ l, 100 pg/ $\mu$ l and 200 pg/ $\mu$ l injections throughout the batch was used in the linearity calculations. The GC-MS analysis showed acceptable linearity for all PCBs,  $^{13}\text{C}$  PCB 118 and OCN; see Table B.6 in Appendix B. Only two calibration standard levels of pesticides were injected, thus it was not possible to determine the linearity of the pesticides and  $^{13}\text{C}$  trans-chlordane.

Another instrument test is to check the instrument repeatability throughout the batch. This is done by calculating the concentrations detected by the GC-MS for all components in the standard calibrations throughout the batch and investigate the development.

The 100 pg/ $\mu$ l level was chosen to do calculations regarding instrument repeatability for both PCBs and pesticides. Change in concentrations throughout the batch was plotted for five injection points for the PCBs and for six injection points for the pesticides; see Figure 4.1. The same standards were used for all injections.

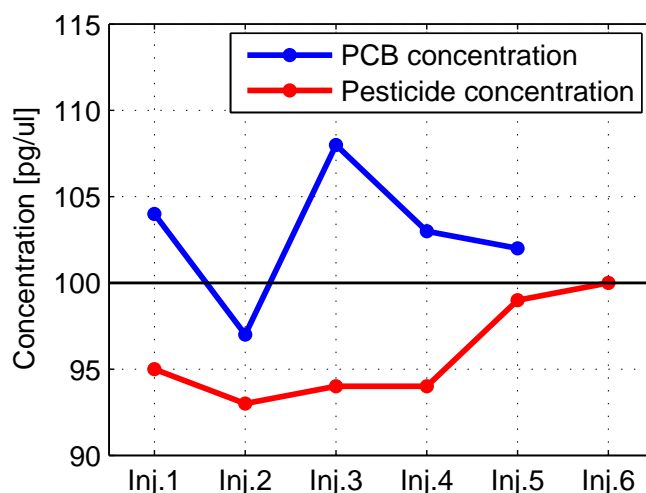


Figure 4.1.: Repeatability testing through the batch for PCBs and pesticides. Presented are average values for PCBs and pesticides for 5 and 6 injection points, respectively.

The figure shows that the repeatability of the instrument is acceptable. Throughout the series, the variation of the PCB concentration is between 97 pg/ $\mu$ l and 108 pg/ $\mu$ l, and the variation of the pesticide concentration is between 93 pg/ $\mu$ l and 100 pg/ $\mu$ l;

that is, within  $\pm 10\%$ . The concentration of the pesticide standard injection increases towards the end of the series, which indicates that evaporation of solvent may have occurred, but to a small extent.

#### 4.2.4. Recovery test

Recovery is calculated to detect loss of analyte through different steps of a method. A common procedure for detecting recovery is to add known amounts of analyte to the samples. Recovery of added internal standards should be 60 – 80 % as a lower limit (Oehme, 2007).

Recoveries of added ISTD in samples relative to the recovery standard, OCN, are listed in Table 4.4. They are below the limit of 60 – 80 % and are thus overall unacceptable. The blank recoveries were higher, however, but for some of the blanks recoveries of more than 100 % were obtained which was considered to be too high.

Sample	<sup>13</sup> C PCB 118 [%]	<sup>13</sup> C TC [%]
Sample 1	46.4	3.5
Sample 2	8.1	14.5
Sample 3	19.6	18.3
Sample 4	1.7	2.9
Sample 5	7.1	12.0
Sample 6	32.2	32.0
Sample 7	17.2	18.3
Sample 8	30.8	32.1
Sample 9	12.5	31.2
Blank 1	116.5	95.3
Blank 3	96.7	115.0
Blank 4	120.9	123.4

Table 4.4.: Recovery of <sup>13</sup>C PCB 118 and <sup>13</sup>C trans-chlordane relative to RSTD in all samples and blanks

Quantification by internal standards has many advantages. The volume of the sample extract does not need to be determined. The ratio between the analyte and the internal standard is the area of interest, and evaporation of solvent is of no concern. In addition, determination of recovery of the internal standard is a quality control criterion for each single sample.

The method of external quantification requires that the volumes of the sample and the external standard are determined with great precision. Quantification based on external standards may be more inaccurate than quantification based on internal standards because the analytes behave somewhat different with interference from a sample matrix. However, an added internal standard will not bind to the matrix the same way as an analyte, which is a drawback of the method of quantification with internal standards.

#### 4. Quality control and method evaluation: POPs in ice

At first, quantification was done by using the two internal standards,  $^{13}\text{C}$  PCB 118 and  $^{13}\text{C}$  trans-chlordane. Because of the low recoveries of the ISTDs obtained in samples and the recovery test, internal standard quantification gave unreliable results. Because of that, quantification was done with external standards instead. By choosing to quantify by external standards, the advantages with ISTD quantification was lost and especially the fact that small volume differences did not have to be considered. Most likely the methods' accuracy decreased.

Recoveries of all target compounds relative to added ISTD were calculated in a recovery test. All recoveries were within acceptable limits, except for  $\alpha$ - and  $\gamma$ -HCH; see Table 4.5. However, also in the recovery test the recoveries of the internal standards were lower than 40 % and hence not acceptable.

The reason for low recoveries is most likely the long period of storage between sample preparation and analysis. The lids of the vials used for containing the samples are not completely tight, and evaporation occurred even in the freezer. Some of the samples dried out completely during storing. In addition, loss during volume reduction or transfer between the different sample preparation steps may have occurred, but to check this recoveries after each step of the method must have been performed. Since the recoveries of the analytes compared to the ISTD are acceptable (Table 4.5), both analytes and ISTD are affected by the processes of loss.

### 4.3. General uncertainties

#### 4.3.1. Sampling and storing

The ice core was collected by the Norwegian Polar Institute (NPI) in spring 2006 and put into polyethylene bags. No other information about sampling procedures was given. No gloves were used during cutting of the ice core into smaller pieces. The ice core pieces were stored at  $-18\text{ }^{\circ}\text{C}$  for approximately a year before extraction.

Samples were stored at  $-18\text{ }^{\circ}\text{C}$  in insert vials with volume  $300\text{ }\mu\text{l}$  for approximately 5 months after sample preparation and before analysis on GC-MS. Samples, blank tests and the recovery test were stored together in a freezer, and no other contamination sources (e.g. biological material) were located in the same freezer. Since the time of storage was so long, refill of the samples with *n*-hexane was necessary several times because of evaporation. Unfortunately, during times when it was impossible to check the sample vials, some of the sample fractions dried completely. Still, they were refilled and analysed on GC-MS.

#### 4.3.2. Sample preparation

During handling of sample vials, the vial containing fraction 1 of sample 4 was knocked over, and approximately half of the content was spilled. Sample 4 contained significantly lower levels of ISTD than the other samples. Ideally, the ISTD should



Compound	Recovery [%]
PCB 18	78.9
PCB 28/31	82.2
PCB 44	87.0
PCB 52	82.6
PCB 95	83.0
PCB 99	79.6
PCB 101	83.3
PCB 105	85.8
PCB 110	81.7
PCB 114	81.1
PCB 118	79.2
PCB 123	83.3
PCB 126	83.2
PCB 128	73.0
PCB 138	76.8
PCB 146	76.7
PCB 149	101.6
PCB 153	78.0
PCB 156	80.0
PCB 157	86.1
PCB 167	72.5
PCB 169	88.2
PCB 170	81.9
PCB 177	78.7
PCB 180	81.4
PCB 183	75.1
PCB 187	73.6
PCB 189	86.6
$\alpha$ -HCH	154.0
$\gamma$ -HCH	153.0
tr-CD	85.5
cis-CD	90.1
tr-NO	86.1
cis-NO	102.5
HCB	96.2
$^{13}\text{C}$ PCB 118	34.4
$^{13}\text{C}$ tr-CD	13.4

Table 4.5.: Recovery of all target compounds relative to added internal standard. Recoveries of  $^{13}\text{C}$  PCB 118 and  $^{13}\text{C}$  trans-chlordane are relative to recovery standard, OCN. Results from recovery test.

correct for volume loss, but since quantification was based on external standards, quantification of sample 4 must be considered less accurate than for the other samples.

#### 4.3.3. Analysis

By reasons not known, not all sample fractions and standards were analysed by GC-MS at NILU in Tromsø. Fraction 4 of samples 2 and 3 were not injected. Since

both PCBs and pesticides are believed to elute mostly in the first fraction, the lack of fraction 4 for these samples was however considered to be negligible. For the analysis of both PCBs and pesticides, only the second fraction of blank number 2 was injected. All 4 fractions of three other blanks were injected, and hence the incomplete analysis of blank 2 was considered negligible.

Fraction 1 of sample 1 was not analysed for pesticides. This makes the results for the pesticides in sample 1 (years 2005/2004/2003) more inaccurate and probably underestimated. Injection of the highest calibration standard level of pesticides (200 pg/ $\mu$ L) was not performed. Hence linearity calculations for pesticides were not possible, since at least three calibration levels are needed for these calculations. Thus, the linearity of the method could not be determined for pesticides.

#### 4.4. Method evaluation: Conclusions and suggestions for improvement

Recoveries of ISTDs compared to RSTD were too low, which is often a drawback of the solid-phase extraction method utilized in this thesis. However, when testing the Si-C18 phase, excellent recoveries for both  $^{13}\text{C}$  trans-chlordane and  $^{13}\text{C}$  PCB 118 were obtained; see Table 4.1. In addition, other studies have concluded that SPE gives acceptable recoveries for OCs (e.g. *Patsias and Papadopoulou-Mourkidou*, 1996). The long period of storing between sample preparation and GC-MS analysis is probably the reason for low recoveries. This means that the SPE method using Si-C18 phase cartridges may be a good method for the determination of OCs and PCBs. However, this could not be verified in this thesis.

The GC-MS method used showed acceptable linearities for all PCBs,  $^{13}\text{C}$  PCB 118 and OCN. Unfortunately, linearity for the pesticides was not possible to calculate. Hence, no guarantee for acceptable linearities during the pesticide run on GC-MS is given. However, instrument repeatability during both runs were acceptable.

High deviations the reference value for the ratio between quantification ions and reference ions obtained from the standard is a problem for many of the compounds detected in both samples and blanks. This implies co-elution of compounds. No knowledge about handling of the ice core during drilling and storing before it was cut into pieces was obtained, which may be a huge source of error. Concentration levels of target compounds are quite high in all four blanks, which indicates cross-contamination from samples to blanks during storing between sample preparation and GC-MS analysis. Some of the sample concentrations are below LOD and LOQ for some of the years according to LOD and LOQ calculated from standard deviations of blanks, but all are above LOQ according to Xcaliburs estimations. LOD and LOQ calculated from standard deviations of blanks must be considered too high, since contamination evidently has occurred.

Suggestions for improvement must be to perform GC-MS analysis straight after sample preparation in order to avoid loss of analytes and internal standards because of evaporation. This was not possible during this thesis work because of unexpected

instrument problems. In addition, to verify a method several replicates should be analysed to ensure reproducibility of a method. This was not possible during this thesis work because the levels of POPs in each sample are rather low, so splitting of the sample volumes into smaller volumes in order to get replicates may result in that no target compounds are detected. An alternative is to analyse additional ice cores from approximately the same drilling location. Another way to ensure reliable results is to analyse samples with another independent method.

## 4.5. Summary

In this chapter, different quality control parameters for the SPE method and GC-MS analysis were presented and deployed on the methods. The SPE method showed low recoveries, probably as a result of the long storing period between sample preparation and analysis. Because of this, the method could not be verified for the determination of OCs and PCBs in this thesis. Method blanks contained rather high analyte concentrations, suggesting that cross-contamination from samples probably occurred. GC-MS analysis was verified as a good method for the quantification of POPs. Ion ratio deviations relative to a reference value were high for a majority of the PCBs, which implied co-elution with other compounds. Only the compounds showing acceptable ion ratios were included in further analysis. The levels of these POPs in the ice core are presented in Chapter 5. In Chapter 5, results from analyses of air data are also displayed.



## 5. Results

This chapter is divided into two part. Results from analyses of POPs in air with respect to seasonality, trends, connections with NAO/AO and different origin continents are presented in the first part. Results from analyses of POPs in ice with respect to spatial distributions and connections with air measurements are presented in the second part.

### 5.1. POPs in air

The following sections are related to concentrations of POPs in air. Section 5.1.1 describes three events picked out and investigated for elevated concentrations, while Section 5.1.2 presents seasonality plots of all target compounds obtained by Holt-Winters' method. Trend plots of POPs obtained by running mean calculations are given in Section 5.1.3. In Section 5.1.4, connections between CO and measured POPs, CO and NAO/AO, age CO and NAO and between measured POPs and NAO/AO are presented using correlation calculations. In Section 5.1.5, continent spectrums of CO and POPs at Zeppelin are presented. In this thesis, continent spectrum analysis of CO focuses on the fractions of CO coming from the three continents Europe, Asia and North America for all months of the year, while continent spectrum analysis of POPs is based on the forcing of the various POPs from the three continents during strong transport events, regardless of time of year.

#### 5.1.1. Transport events

Three different time periods were picked out and investigated with respect to transport episodes. The time of the episodes is listed in Table 5.1.

Year	Week number	Date of FLEXPART output	Time of day (UTC)
1997	33/34	August 17	1800
1997	37-41	September 15	0900
		September 22	1800
2007	3	January 15	0600

Table 5.1.: List of transport events investigated

## 5. Results

### Event 1: Week 33/34, 1997

Just before the event in August 1997 air pollution at Zeppelin originate from areas close to Greenland and North Atlantic Ocean. From the 17<sup>th</sup> to the 19<sup>th</sup> of August, the retroplume sweeps further southeast, indicating that pollution from eastern parts of Russia, Northern and Eastern Europe is transported into the Arctic, see Figure 5.1. On the 19<sup>th</sup> of August and later, the retroplume returns to Greenland again. Elevated levels of PCBs, especially the lighter ones, and  $\alpha$ -HCH was the result of this event.

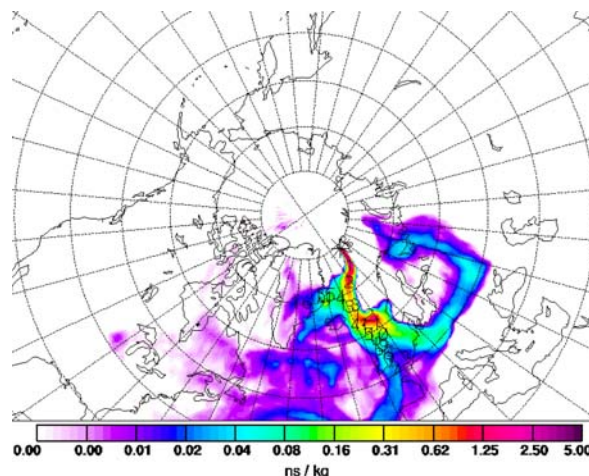


Figure 5.1.: Footprint potential emission sensitivity (PES) distribution derived from FLEXPART 20 days backward simulation, 17.08.97, 18.00 UTC. Number of days backward in time shown in figure.

### Event 2: Week 37–41, 1997

The event picked out in September 1997 consists of a series of transport episodes. Until the 14<sup>th</sup> of September, air masses arriving at Zeppelin are Arctic air. From the 15<sup>th</sup> to the 17<sup>th</sup>, a pronounced retroplume covering eastern parts of Russia and northern parts of Europe appears, see Figure 5.2(a). The plume moves eastwards until it reaches north-eastern parts of Asia on the 19<sup>th</sup>, see Figure 5.2(b).

This episode was recognized by elevated levels of PCBs, especially the lighter ones,  $\gamma$ -HCH, cis-chlordane, cis-nonachlor and DDTs. For the PCBs, the transport is most pronounced in week 37, but it is also noticeable in week 38.  $\gamma$ -HCH and the DDTs experience a prominent increase in week 38. HCB also experience an increase, but not before week 40 and 41, when the retroplume sporadically meets northern parts of Russia. See Figure 5.3.

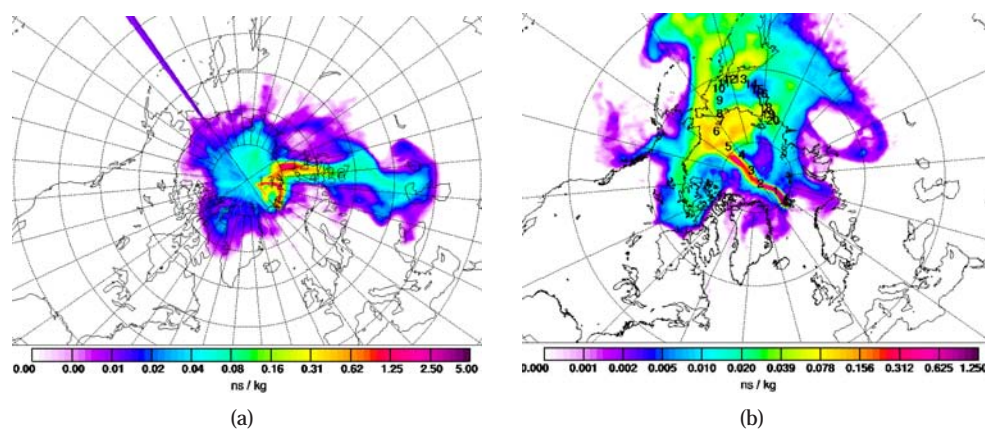


Figure 5.2.: Footprint potential emission sensitivity (PES) distribution derived from FLEXPART 20 days backward simulation for a) 15.09.97, 09.00 UTC and b) 22.09.97, 18.00 UTC.

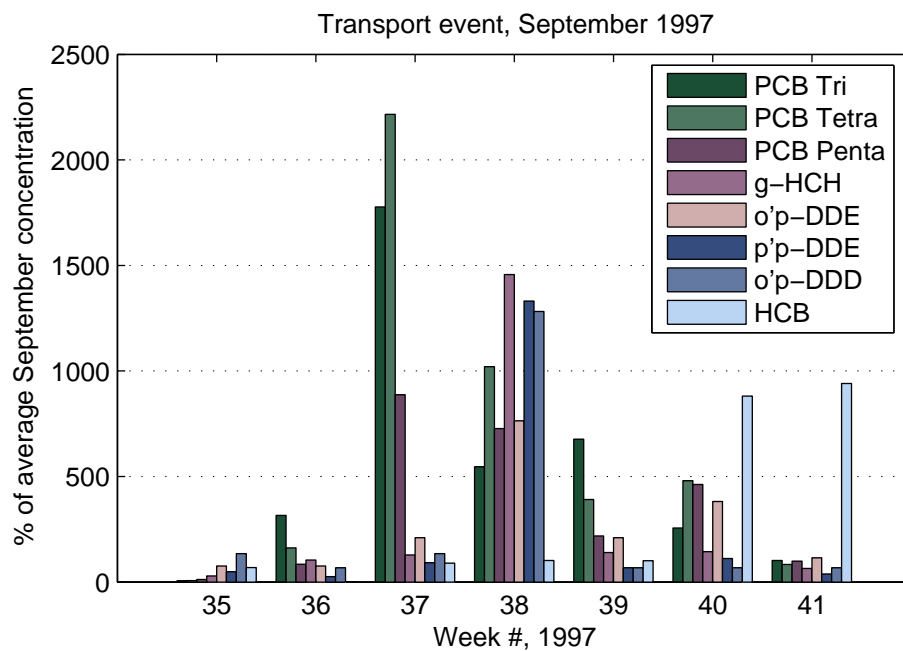


Figure 5.3.: Development of POP concentration during the transport event in September 1997.

## 5. Results

### Event 3: Week 3, 2007

The profound increase in POP concentrations in the beginning of 2007 is a result of a long-lasting occurrence of a distinct retroplume located over Russia and Eastern Europe from the 12<sup>th</sup> to the 19<sup>th</sup> of January, see Figure 5.4. The POPs affected are the heavier PCBs, trans- and cis-nonachlor and the DDTs. See Figures 5.5(a) and 5.5(b) for this transport episode's impact on the measurements of PCB Penta and cis-nonachlor at Zeppelin.

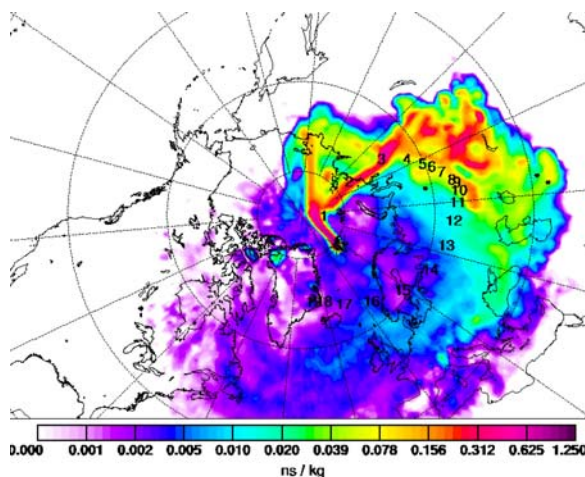


Figure 5.4.: Footprint potential emission sensitivity (PES) distribution derived from FLEXPART 20 days backward simulation, 15.01.07, 06.00 UTC.

#### 5.1.2. Seasonal variations

$\alpha$ -HCH, trans-chlordane, cis-nonachlor (Figure 5.5(b)) and the DDT derivatives show a clear seasonal cycle just by looking at the weekly measurements. The seasonality of all compounds were investigated using Holt-Winters' method.

Many of the components show decreasing fluctuations with time. This is the case especially for  $\alpha$ -HCH,  $\gamma$ -HCH, HCB and the PCBs. DDD and DDE also show the same decreasing pattern, except for in the end of the period, when dramatic transport events take place.

Seasonality plots of POPs not presented in this section can be viewed in Appendix C.

#### HCHs

$\alpha$ - and  $\gamma$ -HCH show a similar seasonal pattern.  $\alpha$ -HCH changes behaviour somewhat during the time period from 1993 to 2007.  $\alpha$ -HCH experiences two peaks per year.



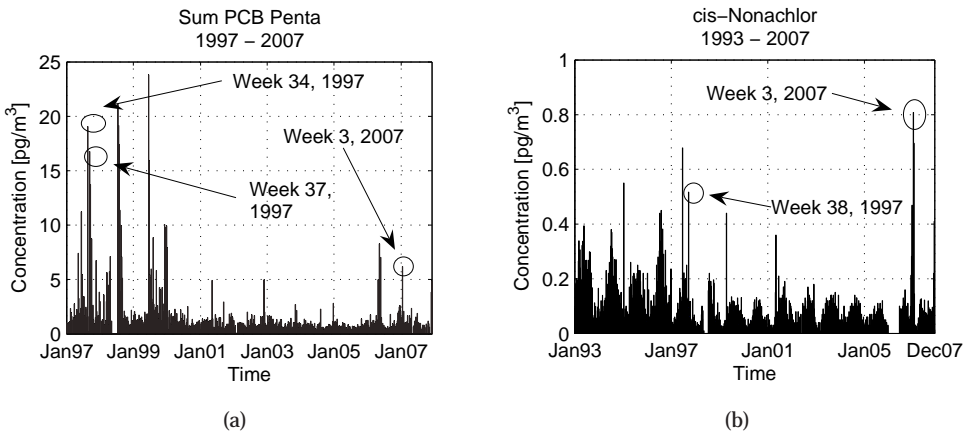


Figure 5.5.: Weekly measurements from Zeppelin of a) Sum PCB Penta, 1997 – 2007, and b) cis-Nonachlor, 1993 – 2007.

Until 2002, the two peaks occur from October to January and from February to April. Minimum concentrations are found in June. After 2002 the autumn peak starts earlier in the year, in July. Thus, the peak gets wider, but smaller in amplitude. The peak in the spring gets smaller compared to the peak in the autumn.

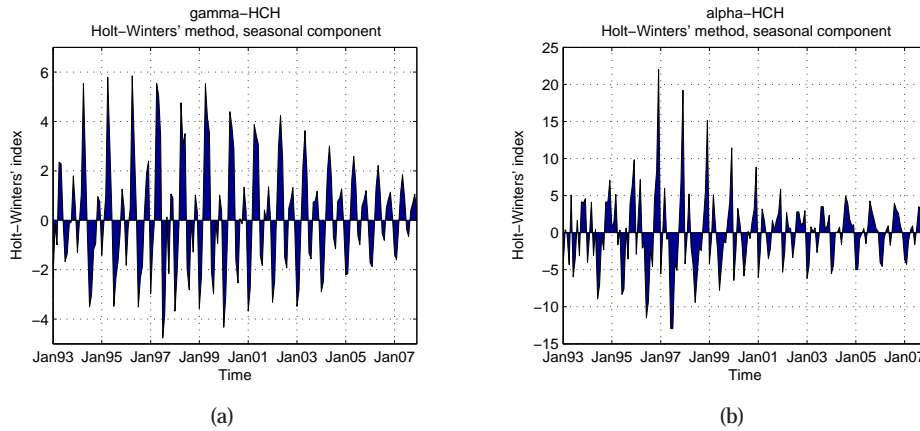


Figure 5.6.: Seasonal variations of a)  $\gamma$ -HCH and b)  $\alpha$ -HCH computed by Holt-Winters' method.

$\gamma$ -HCH experiences one peak from September to December and one from March to June. Also for this POP, the autumn peak grows compared to the spring peak towards the end of the time series. For a presentation of the seasonality of  $\alpha$ - and  $\gamma$ -HCH, see Figure 5.6.

## 5. Results

### Chlordanes

Cis-chlordane and trans-nonachlor share the same concentration distribution pattern. They experience a change in seasonality during the period of measure. In the beginning of the period, three distinct peaks can be noticed, one between March and May, one in July-August and one in November-December. During the period the three peaks grow more and more together. First, the spring and summer peaks merge and dominate over the winter peak. After 2002 the summer and winter peaks merge and form the dominant peak of the year. See Figure 5.7(a) for seasonal variations for cis-chlordane.

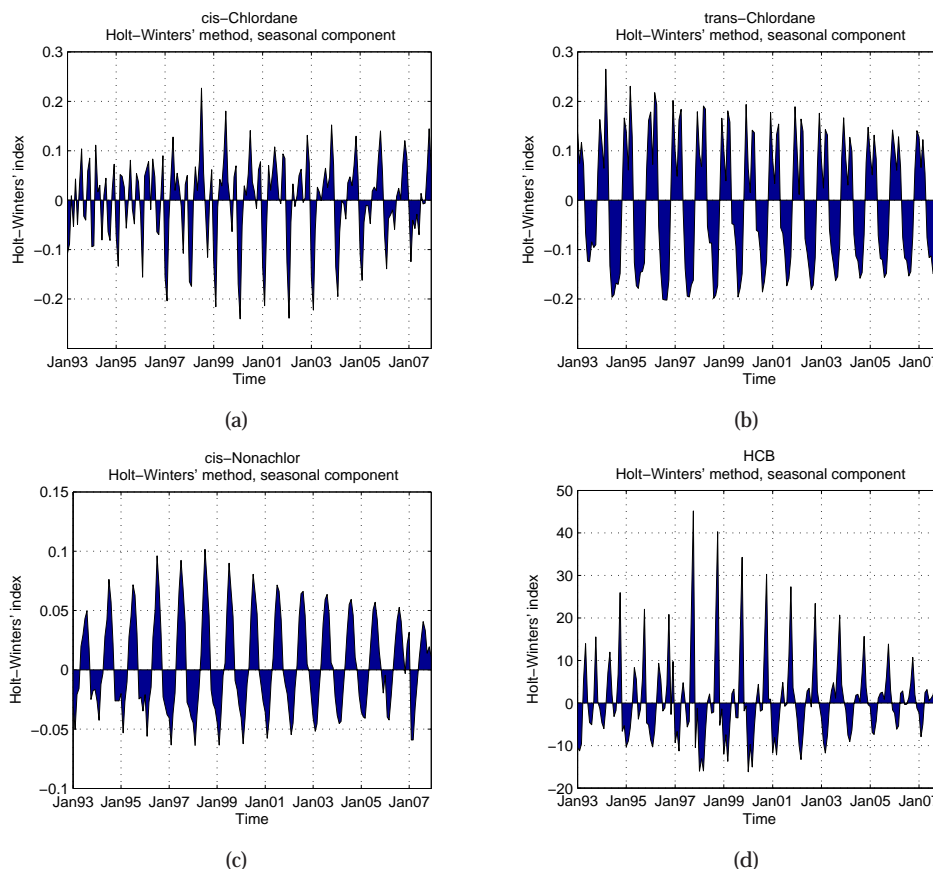


Figure 5.7.: Seasonal variations of a) cis-chlordane, b) trans-chlordane, c) cis-nonachlor and d) HCB computed by Holt-Winters' method.

Trans-chlordane has maximum between October and April and minimum in August. However, the maximum peak is divided into two peaks, with a local minimum in February. Cis-nonachlor has maximum from April to September and

minimum in February. The maximum peak widens during the time period. See Figures 5.7(b) and 5.7(c) for seasonal variations for trans-chlordane and cis-nonachlor.

## HCB

HCB experiences two peaks of maximum concentrations per year, and they merge together with time. The first peak occurs in spring, from March to June, and the second one appears in autumn, from August to November, early in the data series. This peak gets broader with time. Minimum occurs at the turn of the year. See Figure 5.7(d).

## DDT derivatives

Figure 5.8(a) shows the behaviour of the sum of the DDT derivatives. Sum DDT experiences one prominent peak per year which occurs from October to April. In addition, a smaller peak appears in June-July. This smaller peak is very little compared to the larger one from 1994 to 1996, but from 1996 to 2002 it gets bigger before it again shrinks from 2003 and until today. Especially for the DDDs and p'p-DDT the peak in early summer gets bigger after 1998, see Figures 5.8(b) and 5.8(c). For other DDT derivatives, see Figures C.4 and C.5 in Appendix C. Minimum concentrations for DDT derivatives are reached in May and September/October.

## PCBs

PCBs behave quite similarly when it comes to seasonality. All PCB groups experience concentration peaks twice a year, a smaller peak in November-December and a more pronounced peak between May and August; see Figure 5.8(d). The summer peak becomes smaller with time compared to the December peak for the heavier PCBs. The lighter PCBs experience a minor peak in April, before the summer peak comes into force. For other PCB groups, see Figures C.1 and C.2 in Appendix C.

### 5.1.3. Trends

Trend was investigated closely by calculating one year running means. In general, the sum of POPs shows a decreasing trend, see Figure 5.9(a).  $\alpha$ -HCH,  $\gamma$ -HCH, the low-chlorinated PCBs, trans- and cis-chlordane, trans- and cis-nonachlor, o'p-DDE, o'p-DDD, o'p-DDT and p'p-DDT show a general decrease over time during the time period measured. Trend plots of POPs not presented in this section can be viewed in Appendix D.

## HCHs

Both  $\alpha$ - and  $\gamma$ -HCH experience a decreasing trend from 1993 to 2007; see Figure 5.9(b) for  $\alpha$ -HCH. The concentration level is however quite high, especially for  $\alpha$ -HCH.

## 5. Results

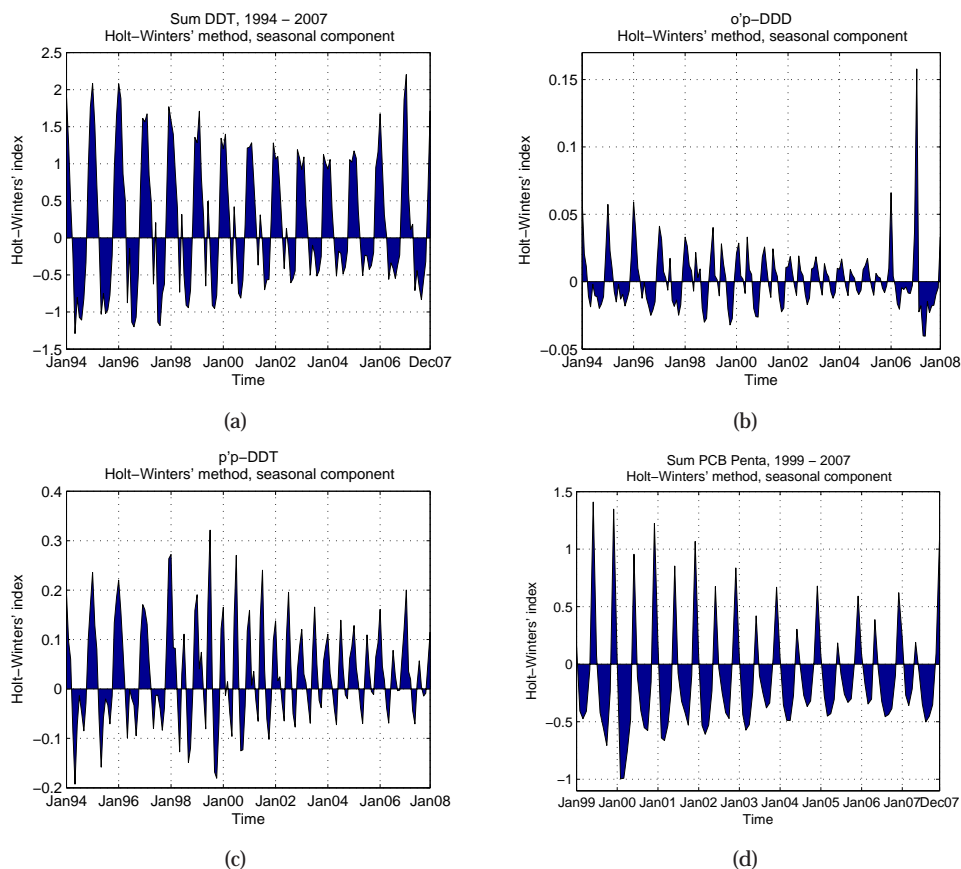


Figure 5.8.: Seasonal variations of a) sum DDT, b) o'p-DDD, c) p'p-DDT and d) sum PCB Penta computed by Holt-Winters' method.

### Chlordanes

Both trans- and cis-chlordane experience a decreasing trend from 1993 to 2007; see Figure 5.9(c) for trans-chlordane. Cis- and trans-nonachlor show a more complex pattern. Cis-nonachlor experiences a decrease throughout the period, except for the last two years, when the compound experiences an upswing; see Figure 5.9(d). Trans-nonachlor also undergoes decrease, but to a lesser extent; see Figure D.3(a) in Appendix D.

### HCB

HCB experiences a decrease in concentration level from 1993 to approximately 2004, but after 2004 the concentration level rises; see Figure 5.10(a).

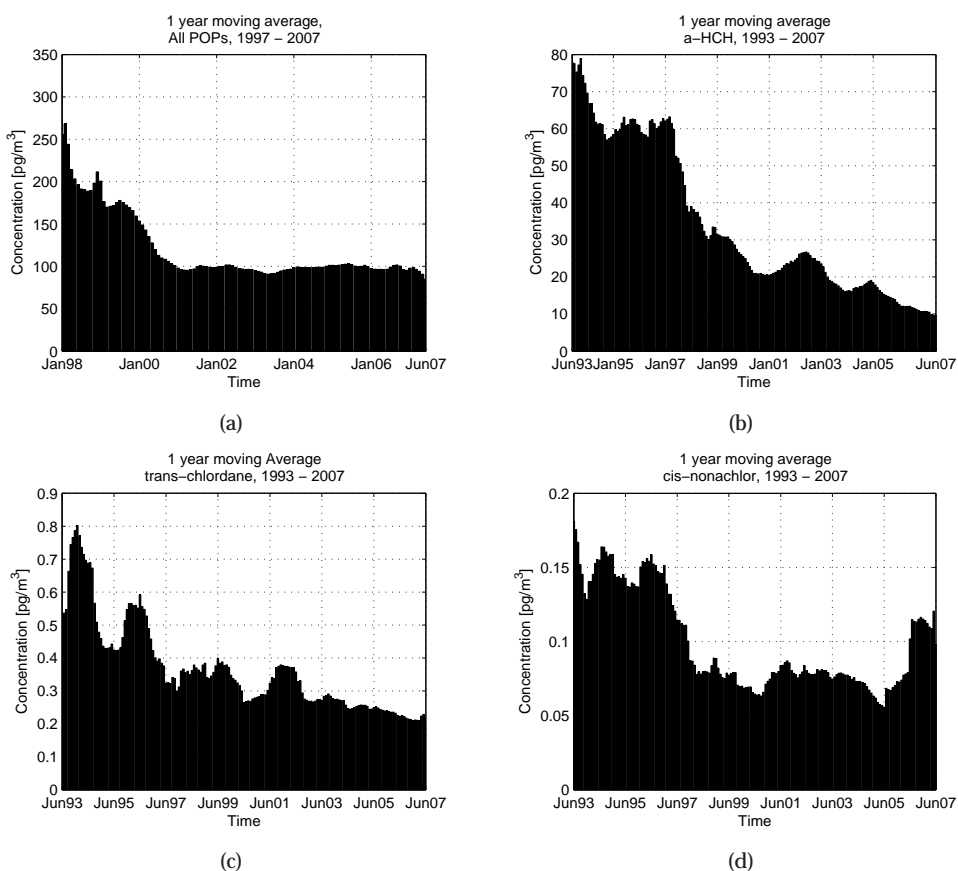


Figure 5.9.: One year moving average of a) sum of all POPs, 1997 – 2007, b)  $\alpha$ -HCH, 1993 – 2007, c) trans-chlordane, 1993 – 2007 and d) cis-nonachlor, 1993 – 2007.

### DDT derivatives

Some of the DDT derivatives experience a downward trend in the beginning of the time period, while others do not, see Figures 5.10(c) and 5.10(d). In general, the decrease of DDT derivatives is less pronounced compared to other POPs. In the DDD and p'p-DDE data series, a peak develops in the end of the period.

### PCBs

All PCB groups experience a sharp decrease in concentrations in the beginning of the data series before the concentration level stabilizes. The heavier PCBs (PCB Penta, Hexa and Hepta group) experience an increase in the end of the period, from 2005

## 5. Results

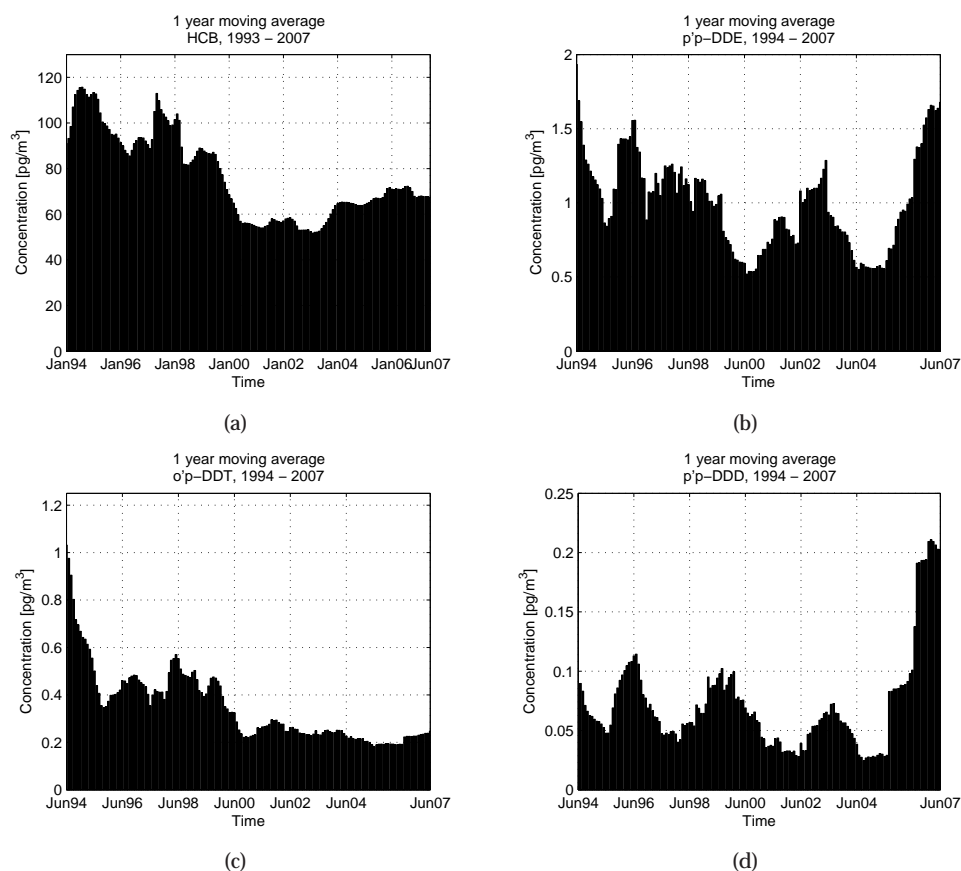


Figure 5.10.: One year moving average of a) HCB, 1993 – 2007, b) p'p-DDE, 1994 – 2007, c) o'p-DDT, 1994 – 2007 and d) p'p-DDD, 1994 – 2007.

and until today, see Figure 5.11(b). For the lighter PCBs this pattern is not as clear as for the heavier ones, see Figure 5.11(a).

### 5.1.4. Connections between North Atlantic Oscillation / Arctic Oscillation and POPs

#### CO and POPs

Carbon monoxide (CO) concentrations are believed to be highly connected with POP concentrations because they are both representative of anthropogenic emissions (*Eckhardt et al.*, 2003; *Eckhardt*, 2007, pers.comm.). Correlations between CO and the different POPs during the annual cycle were computed in order to estimate if the POPs are likely to behave accordingly to the trajectory files for CO given in the

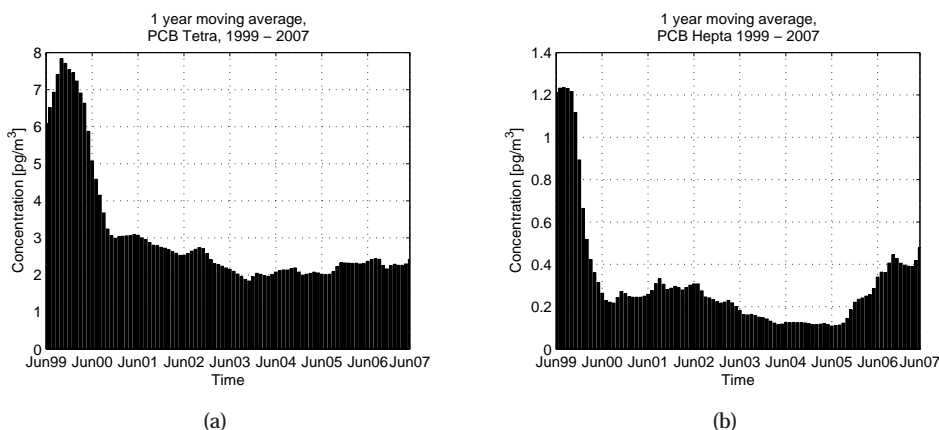


Figure 5.11.: One year moving average of a) sum PCB Tetra and b) sum PCB Hepta, 1999 – 2007.

FLEXPART output. Average values for each month of the year calculated from 1998 to 2006 were used. See Table 5.2 for correlations based on monthly averages and P-values for correlations higher than 0.30.

The yearly cycle of trans-chlordane, o'p-DDE, p'p-DDE, o'p-DDD and o'p-DDT is highly correlated with CO levels, and p'p-DDT also shows fairly good correlation.

### CO and NAO/AO

Correlations between CO and NAO/AO for each month of the year were calculated over the time period from 1997 to 2005; see Table 5.3. This was done to study a connection between high concentrations of a passive tracer and high NAO/AO index.

It can be seen that correlations are highest for NAO, but they are generally low, except for January. It is also evident that NAO and CO are more correlated in the winter/spring months. P-values for correlations higher than 0.30 are given in Table 5.3.

### Agespectrum of CO and NAO/AO

The majority of the air pollution arriving at Zeppelin have an Arctic age of air of more than 13 days; see Figure 5.12. However, monthly distributions of age of air differ a bit. From November to March air younger than 13 days is more represented than during the other months of the year.

Age of CO was correlated with NAO and AO. Of the two indices, NAO correlated best with less aged air; see Table 5.4. The highest correlations were achieved for January, March and April. The highest correlations were found between NAO and CO with age between approximately 2 and 12 days. AO gives better correlation with CO of higher age, 10 – 16 days. See Table 5.5 for P-values for correlations higher

Compound	Correlation, <i>r</i> , with CO	P-value
PCB Tri	-0.630	
PCB Tetra	-0.538	
PCB Penta	-0.220	
PCB Hexa	-0.422	
PCB Hepta	-0.474	
a-HCH	-0.627	
g-HCH	-0.640	
tr-CD	<b>0.819</b>	<b>0.001</b>
cis-CD	-0.258	
tr-NO	0.006	
cis-NO	-0.686	
o'p-DDE	<b>0.933</b>	<b>0.000</b>
p'p-DDE	<b>0.928</b>	<b>0.000</b>
o'p-DDD	<b>0.670</b>	<b>0.017</b>
p'p-DDD	-0.178	
o'p-DDT	<b>0.937</b>	<b>0.000</b>
p'p-DDT	<b>0.422</b>	<b>0.171</b>
HCB	-0.441	

Table 5.2.: Correlations between the yearly cycle of CO and POPs, with corresponding P-values for correlations higher than 0.30. Black numbers:  $r > 0.3$ , blue numbers:  $r > 0.5$ , red numbers:  $r > 0.7$ .

than 0.30. Figure 5.13 shows the averaged time series of age CO for the winter/early spring months compared to the NAO index for the corresponding years.

#### Persistent organic pollutants and NAO/AO

Table 5.6 shows correlations between measured POPs at Zeppelin and NAO/AO. PCBs correlate best with NAO and pesticides correlate best with AO. February is the month of the year with best correlations with both NAO and AO. Fairly good correlations are achieved in August for many of the POPs. NAO also correlates well with most of the POPs in March. Table 5.7 shows the P-values for correlations higher than 0.30.

#### 5.1.5. Continent analysis

##### Continent spectrum of CO at Zeppelin

CO from South America, Australia and Africa contributes practically nothing to the CO budget at Zeppelin; see Figure 5.14. This is consistent with previous studies (*Stohl*



	NAO, r	NAO, P-value	AO, r	AO, P-value
Jan	<b>0.827</b>	<b>0.006</b>	0.286	
Feb	-0.262		-0.490	
Mar	<b>0.358</b>	<b>0.344</b>	-0.015	
Apr	<b>0.325</b>	<b>0.394</b>	-0.634	
May	0.017		-0.227	
Jun	<b>0.408</b>	<b>0.276</b>	<b>0.543</b>	<b>0.131</b>
Jul	<b>0.640</b>	<b>0.063</b>	0.015	
Aug	-0.497		0.0003	
Sep	-0.016		-0.465	
Oct	<b>0.559</b>	<b>0.118</b>	0.223	
Nov	0.019		-0.059	
Dec	-0.282		-0.491	

Table 5.3.: Correlations between CO and NAO/AO, 1997 – 2005, with corresponding P-values for correlations higher than 0.30. Black numbers:  $r > 0.3$ , blue numbers:  $r > 0.5$ , red numbers:  $r > 0.7$ .

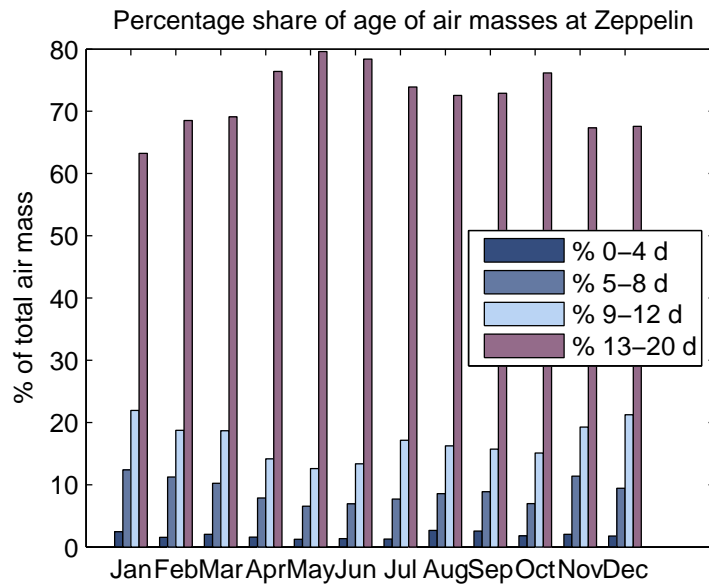


Figure 5.12.: Percentage share of Arctic age of air for CO at Zeppelin, average 1996 – 2007.

## 5. Results

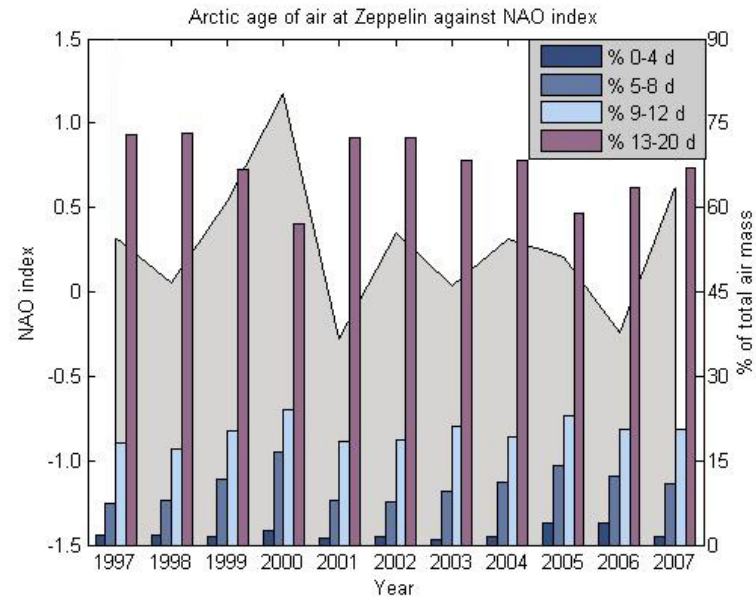


Figure 5.13.: Arctic age of air at Zeppelin against NAO. Average of December – March, 1997 – 2007. NAO index in gray shaded area curve.

	% 0-2 d	% 2-4 d	% 4-6 d	% 6-8 d	% 8-10 d	% 10-12 d	% 12-14 d	% 14-16 d	% 16-20 d
Jan	<b>0.543</b>	<b>0.675</b>	<b>0.764</b>	<b>0.614</b>	<b>0.612</b>	<b>0.304</b>	-0.462	-0.603	-0.609
Feb	-0.152	-0.059	<b>0.431</b>	<b>0.414</b>	0.114	0.267	<b>0.680</b>	0.207	-0.398
Mar	<b>0.364</b>	<b>0.525</b>	<b>0.649</b>	<b>0.699</b>	<b>0.718</b>	<b>0.774</b>	0.270	-0.525	-0.823
Apr	<b>0.472</b>	<b>0.736</b>	<b>0.580</b>	<b>0.570</b>	<b>0.657</b>	<b>0.579</b>	0.100	-0.629	-0.600
May	-0.116	-0.184	-0.108	0.158	<b>0.342</b>	<b>0.610</b>	<b>0.495</b>	<b>0.332</b>	-0.289
Jun	-0.397	<b>0.523</b>	<b>0.345</b>	-0.030	-0.304	-0.481	-0.141	0.124	0.014
Jul	-0.410	<b>0.390</b>	<b>0.499</b>	<b>0.353</b>	0.087	0.212	<b>0.782</b>	<b>0.651</b>	-0.545
Aug	-0.193	0.025	0.283	<b>0.355</b>	<b>0.413</b>	<b>0.327</b>	0.104	0.221	-0.370
Sep	-0.172	0.153	<b>0.538</b>	<b>0.699</b>	<b>0.684</b>	<b>0.709</b>	<b>0.576</b>	0.109	-0.773
Oct	0.262	<b>0.356</b>	0.291	<b>0.359</b>	<b>0.482</b>	<b>0.428</b>	<b>0.338</b>	-0.160	-0.413
Nov	-0.155	-0.119	-0.125	-0.344	-0.574	-0.317	-0.001	0.189	<b>0.367</b>
Dec	0.054	0.249	0.230	0.007	0.020	0.251	<b>0.479</b>	0.117	-0.273

Table 5.4.: Correlation between percentage share age CO and NAO, 1997 - 2007. Black numbers:  $r > 0.3$ , blue numbers:  $r > 0.5$ , red numbers:  $r > 0.7$ .

	% 0-2 d	% 2-4 d	% 4-6 d	% 6-8 d	% 8-10 d	% 10-12 d	% 12-14 d	% 14-16 d	% 16-20 d
Jan	0.084	0.023	0.006	0.044	0.045	0.364			
Feb			0.213	0.234			0.030		
Mar	0.272	0.097	0.031	0.017	0.013	0.005			
Apr	0.142	0.010	0.062	0.067	0.028	0.062			
May					0.303	0.046	0.122	0.319	
Jun		0.099	0.299						
Jul		0.235	0.118	0.286			0.004	0.030	
Aug				0.314	0.236	0.356			
Sep			0.131	0.014	0.017	0.012	0.078		
Oct		0.280		0.259	0.139	0.151	0.224		
Nov									0.411
Dec							0.257		

Table 5.5.: P-values of correlations higher than 0.30 for percentage share age CO and NAO, 1997 – 2007. Black numbers:  $r > 0.3$ , blue numbers:  $r > 0.5$ , red numbers:  $r > 0.7$ .

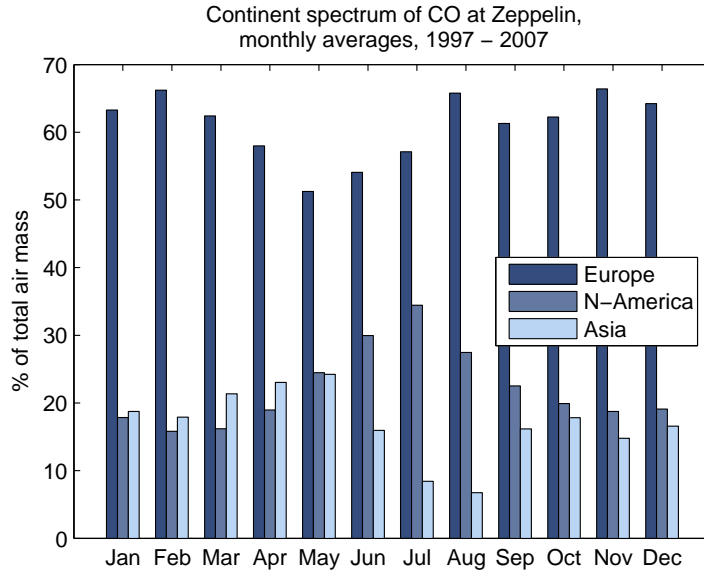


Figure 5.14.: Continent spectrum of CO at Zeppelin, monthly averages, 1997 – 2007.

## 5. Results

*et al.*, 2002). Africa is the continent with the highest percentage of contributions of the three, but contributions rarely exceed more than a few percent of the total budget, and this happens during unusually strong transport episodes where the transport retroplume modelled in FLEXPART extends exceptionally far south.

On a monthly average, European contributions are bigger than both North American and Asian for all months of the year, see Figure 5.14. Asian contributions outnumber North American ones from January to April, but from June and throughout the rest of the year North American contributions are higher on average. In summer, air from Europe and Asia contributes less to the total budget, and the percentage of air from North America increases.

Even though North American contributions are smaller than the European for all months of the year, they are episodically quite substantial and outnumber European contributions frequently, especially during summer. Figure 5.15 shows European and North American contributions throughout the year 2000, Asian contributions left out.

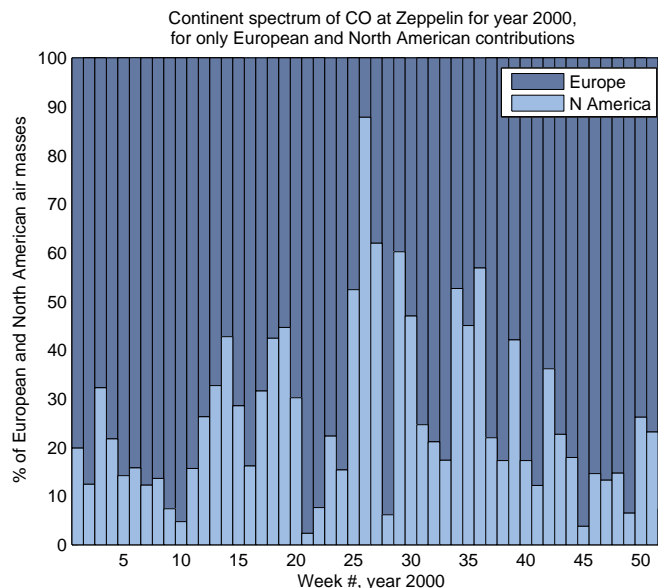


Figure 5.15.: Continent spectrum of CO at Zeppelin for year 2000, weekly averages. European and North American contributions only.

### Continent spectrum of POPs at Zeppelin

The previous section presented the origin continents of CO arriving at Zeppelin. This section will try to connect the levels of the various POPs arriving at Zeppelin to the different continents. Figure 5.16 shows the increase/decrease of PCBs, DDTs and the

rest of the pesticides in percent of standard concentrations, respectively.

To link which kinds of POPs experience elevated concentration levels from which continents, all strong transport episodes from Europe, North America and Asia which occurred between 1997 and 2007 was picked out. The criteria required for an event to be considered strong was:

**Europe :**

- Episode > 2 days duration
- > 95 % of the contribution must be from Europe during the majority of the period

**North America :**

- Episode > 2 days duration
- > 80 % of the contribution must be from North America during the majority of the period

**Asia :**

- Episode > 1 day duration
- > 80 % of the contribution must be from Asia during the majority of the period

European contributions were set to be > 95 % because they are usually strongly represented at Zeppelin throughout most of the year. The criterion for duration of Asian strong events were set to be > 1 day, since pollution from Asia has greater difficulties getting transported into the Arctic. This is especially the case for pollution from south and east Asia (Stohl, 2006). Transport events considered exclusively European, North American and Asian are listed in Tables A.2, A.3 and A.4 in Appendix A, respectively.

Standard values for POPs were determined for each month of the year by calculating three months moving average of the time series. Especially before year 2000 the average monthly concentrations vary considerably from year to year, so by calculating running mean representative values for all POPs were determined for all months.

It is clear from Figure 5.16(a) that during strong transport episodes from Europe, PCB concentrations increase compared to standard concentrations. During events from North America, PCB concentrations decrease. During Asian events, the PCB Penta group shows an increase.

Asian events account for the highest increase of DDT derivatives in Zeppelin air on average; see Figure 5.16(b). This concerns p'p-DDE and the DDDs. Europe also contributes to higher concentrations of DDDs, but to a lesser extent. Strong North

## 5. Results

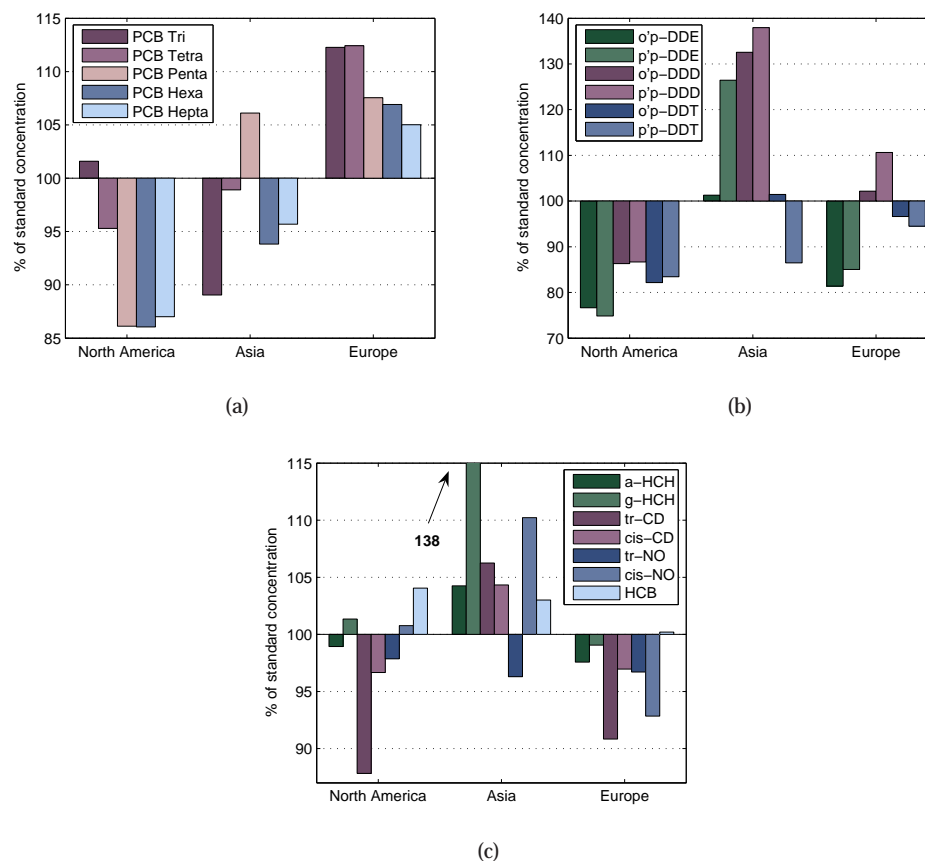


Figure 5.16.: Continent spectrum of a) PCBs, b) DDTs and c) HCHs, chlordanes and HCB arriving at Zeppelin during events bringing air substantially from North America, Europe and Asia in percent of standard concentrations.

American events represent decrease in DDTs in average compared to DDT levels during events from other continents.

Strong Asian events give a strong, positive contribution to  $\gamma$ -HCH measured at Zeppelin; see Figure 5.16(c). The majority of the other pesticides, particularly cis-nonachlor, also shows elevated concentration levels at Zeppelin during Asian events. The other pesticides do not show elevated levels during strong events from neither Europe nor North America.

## 5.2. POPs in ice

The following sections deal with POP concentrations in ice. In Section 5.2.1, a presentation of the ice core's spatial distributions of the POPs that showed acceptable ion ratios is given. In Section 5.2.2, scatter plots showing concentrations in ice relative to the concentrations of POPs in air for the years 1995 to 2000 are presented.

### 5.2.1. Spatial distribution of POPs

Concentration levels of PCBs and pesticides in the ice core show the same distribution pattern. The sample taken closest to the surface shows quite low concentrations for all compounds quantified. The next three samples analysed, corresponding to years 2003/2002, 2002/2001 and 2001/2000, show significantly higher concentrations. The last five samples, corresponding to years 2000/1999, 1999/1998/1997, 1997/1996, 1996/1995 and 1995/1994, show lower, more stable concentrations. See Figures 5.17 and 5.18.

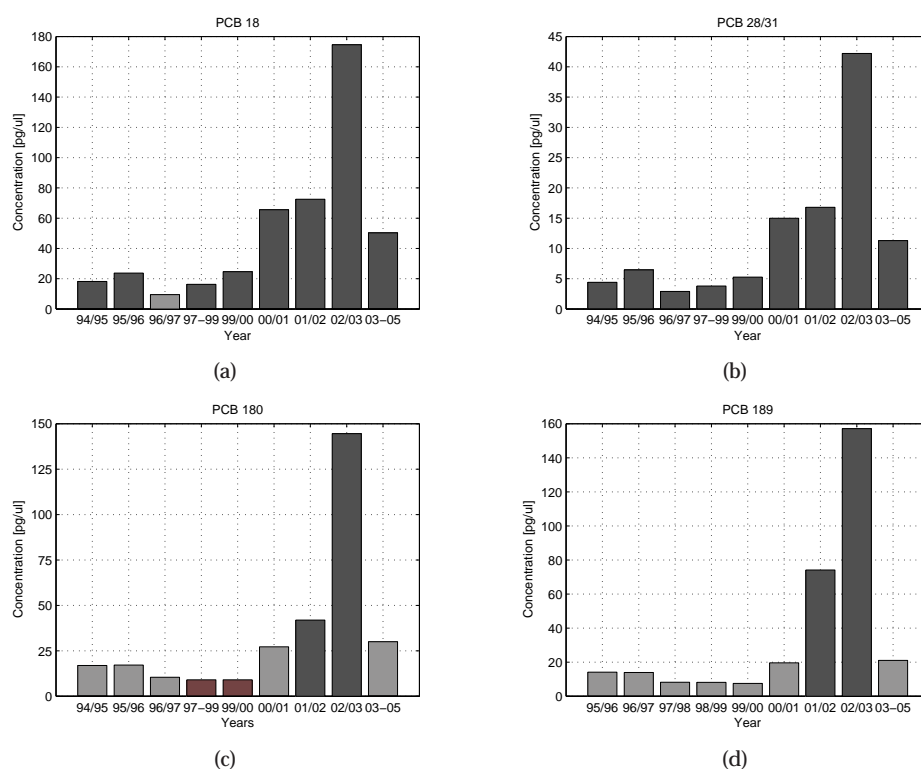


Figure 5.17.: Spatial distributions of a) PCB 18, b) PCB 28/31, c) PCB 180 and d) PCB 189 in ice core. Dark grey bars: C > LOQ. Light grey bars: C > LOD. Red bars: C < LOD.

## 5. Results

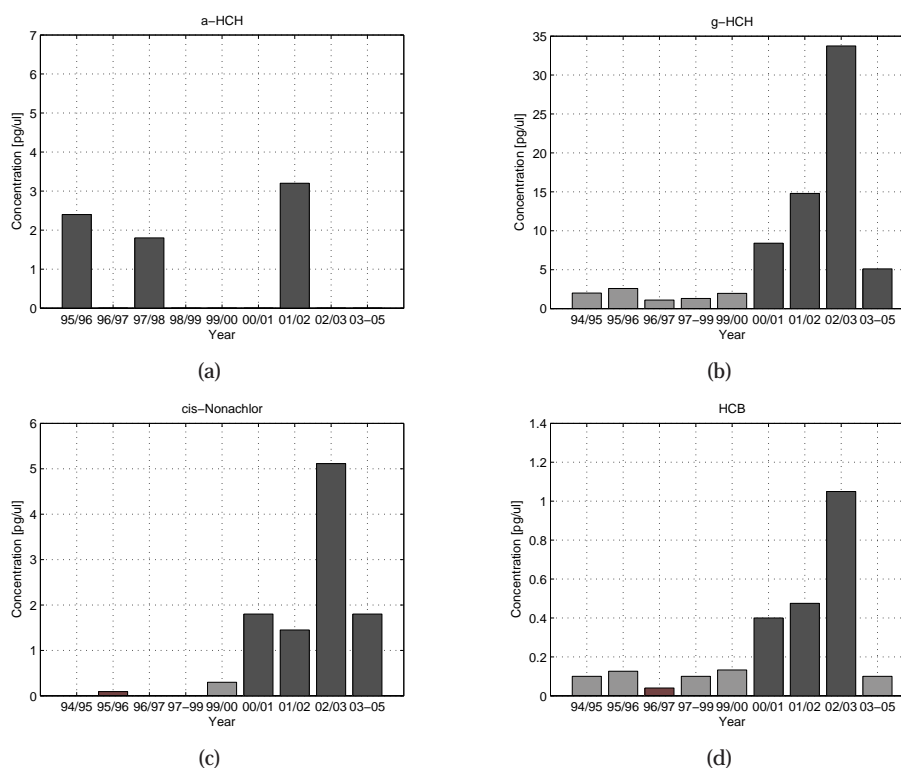


Figure 5.18.: Spatial distributions of a)  $\alpha$ -HCH, b)  $\gamma$ -HCH, c) cis-nonachlor and d) HCB in ice core. Dark grey bars: C > LOQ. Light grey bars: C > LOD. Red bars: C < LOD.

### 5.2.2. Comparison with POP concentration levels in air

An attempt was made to correlate POP concentrations in air and ice. Levels in the ice core from 2000 and earlier, when concentrations were quite stable, were estimated to be most suitable for comparison with air concentrations. The reason for this is discussed in Section 6.2.3. Since PCB measurements at Zeppelin before 1999 are considered unreliable because of contamination, no correlations between PCBs in air and ice could be performed. HCB and  $\gamma$ -HCH were the only two POPs examined in this thesis which show data points in both air and ice for all years between 1995 and 2000. However, no correlations were obtained for these compounds in air and ice. Scatter plots for  $\gamma$ -HCH and HCB showing the relations in air and ice are given in Table 5.19.



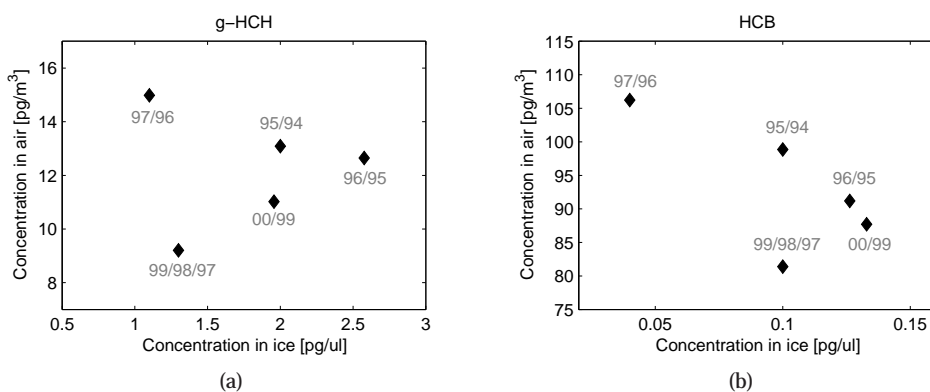


Figure 5.19.: Scatter plots of concentrations in air and in ice from 1993 to 2000 for a)  $\gamma$ -HCH and b) HCB. Data points are labelled with the equivalent year.

### 5.3. Summary

In this chapter, results from seasonality and trend calculations were presented, together with correlations between POPs and NAO/AO. Continent spectrums of CO and POPs at Zeppelin were also displayed. In addition, three transport events were looked into in order to link altered concentration levels to specific continents.

The general trend for POPs during the period from 1993 to 2007 is decline, except for high-chlorinated PCBs and HCB, which show a small increase the last four years. POPs show quite different seasonality patterns. PCBs show positive correlations with NAO, and pesticides show positive correlations with AO. The continent spectrum of CO shows that Europe accounts for most of the CO contributions all year round, but North American contributions are high during summer. The continent spectrum of POPs shows that Asia accounts for contributions of  $\gamma$ -HCH and chlordanes, while Europe accounts for PCBs. During North American events, no elevated levels of POPs are detected at Zeppelin, except for a small HCB increase. The decreasing trends for most POPs and increasing trends for PCBs and HCB, seasonality patterns, positive correlations between NAO/AO and POPs and continent spectrums are discussed in Chapter 6 in elucidation of physical-chemical properties and other mechanisms introduced in Chapter 2.

Table 5.6.: Correlations between POPs and NAO/AO. Black numbers:  $r > 0.3$ , blue numbers:  $r > 0.5$ , red numbers:  $r > 0.7$ .

NAO	PCB Tetra	PCB Hexa	PCB Hepta	a-HCH	g-HCH	tr-CD	dis-CD	Sum DDT	HCB
Jan	-0.290	0.014	0.004	-0.454	-0.372	-0.224	-0.251	-0.163	-0.207
Feb	0.782	0.328	0.534	0.472	0.637	0.386	0.096	0.018	0.218
Mar	0.503	0.394	0.413	0.307	0.243	0.040	0.030	0.597	0.084
Apr	-0.449	-0.273	-0.198	-0.658	-0.721	-0.154	-0.127	-0.228	-0.165
May	-0.054	0.039	0.200	0.0814	0.186	0.186	0.323	0.241	-0.147
Jun	-0.413	0.366	0.443	-0.237	-0.302	0.436	-0.044	-0.206	-0.258
Jul	-0.126	-0.319	-0.382	-0.166	-0.245	-0.245	-0.171	-0.438	-0.288
Aug	0.492	0.167	0.252	0.653	0.504	0.443	0.198	0.195	-0.233
Sep	0.293	-0.330	-0.152	-0.142	0.195	0.237	0.169	-0.006	0.219
Oct	0.062	0.305	0.317	-0.024	0.084	0.593	0.209	0.194	-0.243
Nov	-0.457	0.029	0.250	-0.448	-0.473	0.205	0.182	-0.097	-0.086
Dec	0.243	0.535	0.373	-0.250	-0.045	0.168	0.074	0.162	0.507

AO	PCB Tetra	PCB Hexa	PCB Hepta	a-HCH	g-HCH	tr-CD	dis-CD	Sum DDT	HCB
Jan	0.032	0.014	0.248	-0.379	-0.401	0.308	0.346	0.367	0.038
Feb	0.658	0.354	0.585	0.664	0.794	0.428	0.021	0.309	0.424
Mar	0.348	0.123	0.378	0.169	-0.104	-0.022	0.013	0.283	-0.252
Apr	-0.150	0.057	0.189	0.105	0.075	0.487	0.420	0.336	-0.071
May	-0.593	-0.064	0.067	-0.565	-0.414	-0.433	-0.347	-0.111	-0.521
Jun	-0.396	0.257	0.357	-0.314	-0.331	0.289	-0.143	-0.199	-0.143
Jul	-0.230	-0.074	0.017	-0.123	-0.178	-0.090	-0.145	-0.030	0.167
Aug	0.267	0.391	0.108	0.205	0.475	0.421	0.499	0.407	0.071
Sep	-0.007	-0.613	-0.420	-0.548	-0.229	-0.205	-0.264	-0.367	-0.057
Oct	-0.017	0.141	0.148	-0.037	-0.088	0.322	0.070	0.086	-0.165
Nov	-0.159	-0.240	-0.093	-0.285	-0.354	0.209	0.125	-0.377	0.052
Dec	0.237	0.594	0.564	0.040	0.006	0.001	-0.068	0.428	0.621

NAO	PCB Tetra	PCB Hexa	PCB Hepta	a-HCH	g-HCH	tr-CD	cis-CD	Sum DDT	HCB
Feb	<b>0.004</b>	<b>0.299</b>	<b>0.192</b>	<b>0.168</b>	<b>0.048</b>	<b>0.271</b>			
Mar	<b>0.115</b>	<b>0.230</b>	<b>0.207</b>	<b>0.388</b>				<b>0.053</b>	
May							<b>0.363</b>		
Jun		<b>0.298</b>	<b>0.200</b>			<b>0.208</b>			
Aug	<b>0.125</b>			<b>0.029</b>	<b>0.114</b>	<b>0.172</b>			
Oct		<b>0.362</b>	<b>0.342</b>			<b>0.054</b>			
Dec		<b>0.090</b>	<b>0.259</b>						<b>0.055</b>

AO	PCB Tetra	PCB Hexa	PCB Hepta	a-HCH	g-HCH	tr-CD	cis-CD	Sum DDT	HCB
Jan						<b>0.357</b>	<b>0.298</b>	<b>0.266</b>	
Feb	<b>0.028</b>	<b>0.285</b>	<b>0.059</b>	<b>0.036</b>	<b>0.006</b>	<b>0.218</b>		<b>0.385</b>	
Mar	<b>0.294</b>		<b>0.251</b>						
Apr						<b>0.154</b>	<b>0.227</b>	<b>0.342</b>	
Jun			<b>0.311</b>						
Aug		<b>0.234</b>			<b>0.140</b>	<b>0.197</b>	<b>0.118</b>	<b>0.214</b>	
Oct						<b>0.334</b>			
Dec		<b>0.054</b>	<b>0.071</b>					<b>0.189</b>	<b>0.135</b>

Table 5.7.: P-values for correlations higher than 0.30 between POPs and NAO/AO.  
Black numbers:  $r > 0.3$ , blue numbers:  $r > 0.5$ , red numbers:  $r > 0.7$ .



## 6. Discussion

In Chapter 5, results from seasonality and trend calculations of POPs, together with connections between POPs and NAO/AO, were given. Three transport events showing elevated POP concentrations were also looked into. Continent analyses of CO and POPs at Zeppelin were presented, and origins for CO throughout the year and origins for POPs during strong transport events were identified. Spatial distribution of POPs in the ice core, together with correlations between  $\gamma$ -HCH and HCB time series in air and in ice were presented.

This chapter will treat the results in elucidation of the compounds' application patterns, sources, physical-chemical properties, atmospheric circulation patterns and photochemistry, which were factors introduced in Chapter 2. As for Chapter 5, this chapter will also be divided in two parts; one part concerning air data and one part concerning ice data.

### 6.1. POPs in air

Section 6.1.1 connects concentration levels of POPs measured at Zeppelin to continents during the three transport events by taking application patterns into account. In Section 6.1.2, seasonal patterns are discussed in connection with application patterns, physical-chemical properties, atmospheric circulation patterns and photochemistry. Trends are investigated in Section 6.1.3 and seen in connection with application patterns and climate related issues affected by physical-chemical properties and atmospheric circulation patterns. Correlations between POPs and NAO/AO are explained in Section 6.1.4. Finally, Section 6.1.5 treats continent spectrums of CO and POPs in light of change of the polar dome with season, application patterns and physical-chemical properties.

#### 6.1.1. Transport events

##### Event 1: Week 33/34, 1997

The elevated PCB levels detected during this event is a result of the location of the retroplume shown in the FLEXPART output in Figure 5.1. The plume sweeps through areas known for PCB usage in Europe; United Kingdom, Germany, France and Italy (EMEP, 2008). The lighter PCBs are most represented, since they are more volatile than the heavier ones and thus more capable of undergoing long-range atmospheric transportation. This is consistent with previous studies (*Wania and Mackay, 1996; Gioia et al., 2006*) and with the physical-chemical properties of PCBs listed in Table 2.2 in

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section 2.2. Increased  $\alpha$ -HCH concentrations are most likely a result of technical HCH use in Russia (Breivik *et al.*, 1999).

### Event 2: Week 37–41, 1997

PCBs undergo the strongest increase during the beginning of this period, in week 37; see Figure 5.3. Pollution is transported into the Arctic from Russia. Russia reports PCB emissions because of use of PCB containing equipment and storage of industrial waste (AMAP, 2000).

$\gamma$ -HCH and DDTs experience an upswing in week 38. This is most likely a consequence of transport from China, one of the largest users and producers of DDT and lindane in the world (AMAP, 2004).

HCb is a compound whose sources are harder to identify. By looking at the footprint distributions achieved by FLEXPART, the picture is not completely clear. The retroplume points towards areas located in high latitudes in Russia. Russia reports HCB use in tracer bullets and can hence be a reason for the elevated HCB levels, but the levels for week 40 and 41 in 1997 are higher than any other level detected in the time period of measurements at Zeppelin, 1993 – 2007. Concentration distribution and patterns of HCB are discussed further in section 6.1.2.

### Event 3: Week 3, 2007

Elevated levels of DDT and cis- and trans-nonachlor during this transport episode is most likely a result of emissions from China. The PCB amounts may have been transported to Zeppelin from Russia. FLEXPART output shows that several forest fires took place in Russia at that time, see Figure 6.1. A study relating atmospheric PCB enhancements and biomass burning concludes that biomass burning is an important source of PCBs in the atmosphere (Eckhardt *et al.*, 2007). More issues related to boreal forest fires will be discussed in section 6.1.3. Emissions together with favourable atmospheric circulation conditions were the reasons for elevated POP levels. By looking at the FLEXPART output, one can see that the retroplume extends extraordinary far south during this episode, to areas with substantially higher environmental temperatures, see Figure 5.4. High temperatures favour re-evaporation, making it more likely for compounds with high HLC to re-volatilize.

#### 6.1.2. Seasonal variations

In this section, seasonal patterns for the target compounds are discussed in connection with application patterns, physical-chemical properties, atmospheric circulation patterns and photochemistry. Five main categories of seasonal patterns are found:

**A** Peaks following the annual temperature cycle (higher concentrations in summer)

**B** Peaks following light conditions (higher concentrations in winter)

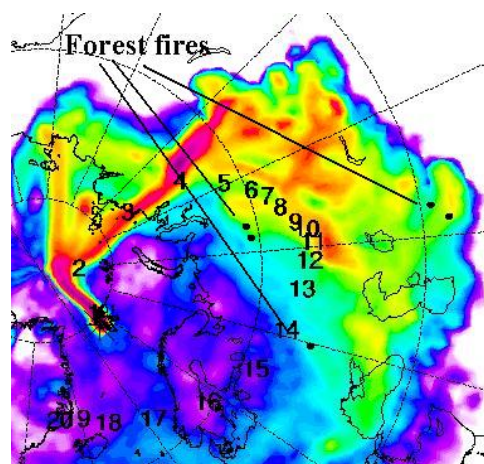


Figure 6.1.: Footprint potential emission sensitivity (PES) distribution derived from FLEXPART 20 days backward simulation, 15.01.07, 12.00 UTC, showing the location of forest fires in Russia (black dots) compared to the location of the retroplume.

- C Peaks following meteorological patterns (higher concentrations during winter and spring)
- D Peaks following application patterns (higher concentrations during ploughing in spring and autumn)
- E Peaks because of release during snow melt, "spring pulse" (higher concentrations during late spring)

The following sections describes in detail the seasonal patterns and points out which patterns are associated with which target compound.

## HCHs

Primary emissions of HCH are largest in spring, when agricultural activity takes place. This agrees with seasonality calculations of HCHs done using Holt-Winters' method. However, it is the autumn peak that is the biggest peak of the year for  $\alpha$ -HCH, and it is also the autumn peak for both  $\alpha$ - and  $\gamma$ -HCH which experience increase with time; see Figure 5.6. Therefore, secondary emissions of HCHs are an interesting object for further investigation.

During recent years, average temperatures in the Arctic have been considerably higher compared to a couple of decades ago. Higher temperatures have led to longer melting seasons and less sea ice. A less ice-covered Arctic Ocean favours

## 6. Discussion

re-evaporation of contaminants, and longer ice-free periods prolong the period a compound can be re-emitted to the atmosphere from the oceans.

During the 1980s net deposition of  $\alpha$ -HCH from the atmosphere to the oceans took place because of high levels in air and high solubility in cold water for  $\alpha$ -HCH. During the 1990s net volatilization back to the atmosphere took place. The ocean can be considered a large reservoir for  $\alpha$ -HCH, and when the Arctic Ocean is ice free for longer periods of the year, the contaminants are no longer trapped under the pack ice, but are released to the atmosphere instead. HCHs are highly temperature dependent, which facilitates high evaporation during high temperatures (*Su et al.*, 2006).

There are reasons to believe that  $\alpha$ - and  $\gamma$ -HCH experience a change in the concentration distribution pattern because of change in sea-ice cover and temperature. Figure 5.6 supports the theory of ocean currents being an important physical pathway for the HCHs into the Arctic. The peak in autumn because of re-evaporation is the most pronounced peak for all years for  $\alpha$ -HCH.

The peak in spring for  $\gamma$ -HCH may be explained by the "spring pulse", a term first mentioned by *Gouin et al.* (2002), which explains increased spring concentrations by chemical deposition into the snowpack in winter and release of the chemicals into the atmosphere again during snowmelt.

### Chlordanes

The chlordanes show different seasonality patterns. Trans-chlordane follows a pattern with higher concentrations during polar night; see Figure 5.7(b). The most probable explanation for this is that trans-chlordane is highly degradable by sunlight (*Kallenborn*, 2009, pers.comm). Hence, it is reasonable that the lowest levels of trans-chlordane are found in summer, when photochemistry is most effective. In addition, trans-chlordane has a high  $\log K_{oa}$ , which means that the compound's ability to be absorbed in foliage in summer is high. Both cis- and trans-chlordane also show high ability to absorb into soil (*Harner et al.*, 2001).

Before 2002 the spring peak is the dominant one for cis-chlordane and trans-nonachlor, but from 2003 and later on it becomes smaller compared to the autumn peak; see Figure 5.7(a) for cis-chlordane. When looking at the development of winter seasonal mean (December, January and February) from 1993 to 2007, NAO is in an almost continuously positive state until 2003. From 2003 and until today NAO turns more neutral, see Figure 2.8 in section 2.3.4. Hence, the development of seasonal variations for cis-chlordane and trans-nonachlor is consistent with the development of NAO. The increase of the autumn peak is most likely also connected to emissions from secondary sources due to temperature increase the last years.

The seasonal distribution of cis-nonachlor follows the annual temperature cycle, with higher concentrations in summer; see Figure 5.7(c). The widening of the summer peak suggests that cis-nonachlor contributes to the atmospheric concentrations measured at Zeppelin by secondary emissions and that later freezing in the autumn expands the period of re-evaporation from oceans. According to *Simpson et al.* (1995) cis-nonachlor has the highest  $\log K_{ow}$  of the chlordanes and thus has the highest ability



to dissolve in water. This explains the inverted pattern of trans-chlordane and cis-nonachlor.

However, it is hard to find a good explanation for why all four chlordanes show such different seasonal patterns. They are all constituents of technical chlordane, where trans- and cis- chlordane are the major components, and thus should show the same application pattern. Physical-chemical properties for the nonachlors are hard to find, which makes it difficult to investigate seasonality differences relative to trans- and cis-chlordane. *Jantunen and Bidleman* (2006) reports of a HLC of  $32 \text{ Pa m}^3/\text{mol}$ , highest of all chlordanes, for trans-nonachlor, which is significantly higher than the HLC values for chlordanes taken from *Mackay et al.* (2006c) utilized in this thesis. However, in the same paper HLCs for trans- and cis-chlordane are similarly reported to be much higher than the HLCs reported in *Mackay et al.* (2006c). Therefore it is difficult to compare values. However, the HLCs given by *Jantunen and Bidleman* (2006) have the same proportions as the HLCs given by *Mackay et al.* (2006c), which indicates that trans-nonachlor has the highest HLC of the chlordanes analysed. This is consistent with the seasonal pattern associated with cis-nonachlor, which shows high concentrations in summer.

*Becker et al.* (2009) also reports of different seasonality patterns for trans- and cis-chlordane.

## HCB

The peak in late spring for HCB, see Figure 5.7(d), can be explained by the "spring pulse" regarding chemical deposition of chemicals into the snowpack and release into the atmosphere during snowmelt (*Gouin et al.*, 2002). Since snowmelt in Ny-Ålesund takes place quite late in the spring, this can account for the late spring peak of HCB. When looking at standard temperatures for Ny-Ålesund on a monthly basis, June is the first month of the year with an average temperature above  $0^\circ \text{C}$  (*eKlima*, 2009), but snow melt starts earlier because of radiation from the sun. HCB shows elevated concentration levels already from March, which is not a period known for high melting rates. It is possible that this is a result of HCB being released from melting of snow packs at more southerly latitudes and transported into the Arctic (*Hung et al.*, 2005).

The autumn peak is most likely a result of re-volatilization of HCB from soils and water. The widening of this peak can be explained by the latest years' shrinking ice-cover and permafrost decline.

HCB at Bjørnøya, another Arctic monitoring station, shows high values from October to May, almost the opposite of Zeppelin. *Kallenborn et al.* (2007) state that lack of photochemical degradation is the reason for high values of HCB in Bjørnøya in winter. This is not consistent with the seasonality pattern for HCB found in this thesis, and reasons for different patterns are not entirely clear. Light conditions in Bjørnøya and Ny-Ålesund are quite similar, even though Ny-Ålesund is located further north. Both Bjørnøya and Ny-Ålesund are in close proximity to oceans, which suggests that evaporation from oceans should be of equal importance in both locations.

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### DDT derivatives

DDTs experience the concentration peaks in late autumn, winter and early spring, and thus follow the annual cycle of light conditions in the Arctic (AMAP, 2004); see Figure 5.8(a). During polar night, photochemistry in the Arctic is not present. Low summer concentrations are thus a result of photochemical degradation.

The smaller peak in June-July is most likely a result of release of DDTs during melting of the snowpack.

### PCBs

Behaviour of PCBs is highly temperature dependent (Breivik *et al.*, 2004, 2002b), and the largest fraction of PCBs in the environment is found in soils (Ockenden *et al.*, 2003). Hence it stands to reason that PCB concentrations follow the annual temperature cycle with highest concentrations in summer because of re-volatilization during high temperatures; see Figure 5.8(d).

The peak in November-December may be explained by the location of the polar front. The polar front is dynamic and changes position throughout the year. It would be reasonable to expect a peak which extends further into the winter (see section 2.3.2), but it may be that the polar front covers some source areas in December which are important for PCB emissions and that more long-range atmospheric transport events take place during that time (Kallenborn, 2009, pers.comm.).

The small peak in April for the lightest PCBs may be explained by the "spring pulse". Volatility is an assumption for evaporation of compounds from the snow pack during spring melting, and the lightest PCBs are the most volatile.

### 6.1.3. Trends

Trend investigations performed on POP data in the Arctic give conflicting results. Some studies conclude with a downward trend (Hung *et al.*, 2005), but other studies cannot find clear trends for all POPs because of the short time frame (Berg *et al.*, 2004). Becker *et al.* (2009) found increase for HCB.

The limited length of data series is clearly a drawback when it comes to trend investigations of POPs from atmospheric data detected at Zeppelin. As mentioned in section 3.1.1 and 3.1.4, POP data series at Zeppelin reach 10 – 15 years back in time, a rather short period to draw conclusions about trends. Some campaign-based measurements during spring at Zeppelin and three stations on the Norwegian mainland were performed in 1982 – 1984 and 1992 (Oehme *et al.*, 1995). Comparison of the 1992 campaign to the 1982 – 1984 campaigns indicated a decrease in  $\alpha$ -HCH and chlordanes and an increase in  $\gamma$ -HCH with time. However, it is hard to draw conclusions about trends in air concentrations in Zeppelin air during the 1980s based on just a few 4 – 6 weeks periods in 1982 – 1984. Trends found in this thesis are discussed in the sections below.

## HCHs

The downward trend of  $\alpha$ - and  $\gamma$ -HCH coincides with intentional restrictions and banning of these substances, but concentrations are still quite high; see Figures 5.9(b) and D.2(b). The high concentration levels are, as mentioned earlier, connected to the physical-chemical properties of  $\alpha$ - and  $\gamma$ -HCH, since HCHs are among the most water soluble POPs. Since  $\alpha$ - and  $\gamma$ -HCH have been deposited to the oceans from the atmosphere during times of high emission rates, they are now released back to the atmosphere because of warmer climate (*Li et al.*, 2002, 2004).

$\alpha$ - and  $\gamma$ -HCH, together with HCB, show the most elevated levels of POPs measured at Zeppelin. These are the compounds with the highest vapour pressure, see Table 2.2, and hence the most volatile compounds. HCHs are thus favourable for long-range transport.

## Chlordanes

Chlordanes show a decrease, especially after 1997 (see Figures 5.9(c) and 5.9(d)) when the largest manufacturer, USA, stopped producing. However, chlordanes are still produced in Singapore and China (*AMAP*, 2004).

Trans- and cis-chlordane show a more distinct decrease than trans- and cis-nonachlor. In return, cis-nonachlor shows an increase in the end of the period, but this is a result of the strong transport episode in the beginning of 2007, see Figure 5.5(b). Trans- and cis-chlordane are the major constituents of technical-grade chlordane, and because of reduced usage of this insecticide it is reasonable that these are the chlordanes which are decreasing the most.

When looking at the levels of chlordanes both cis-chlordane and cis-nonachlor show higher levels than trans-chlordane, the major constituent of technical chlordane. This may indicate either higher rates of re-emissions from oceans and soil, or that fresh emissions arise from the use of other technical mixtures (*Becker et al.*, 2009).

*Berg et al.* (2004) report of no distinct trend for chlordanes at Zeppelin. However, the time series utilized only covered the period from 1993 to 2003. *Becker et al.* (2009) report of a declining trend of cis- and trans-chlordane, which agrees with results found in this thesis.

## HCB

HCB is a complicated compound to analyse since there is so little knowledge about usage and emissions and because HCB is produced unintentionally as an industrial by-product (*AMAP*, 2004; *Pacyna et al.*, 2003). It is reasonable to believe that decline in HCB concentration until 2004 is a result of a decline in emissions; see Figure 5.10(a). The small upward trend during the latest years may, as for the HCHs, be because of re-emissions from soil and sediments (*Bailey*, 2001; *Su et al.*, 2006). The high volatility of HCB and temperature dependent behaviour makes this possible now during times of warming of the environment.

### DDT derivatives

DDT was banned in most countries in the 1970s and 1980s, before the beginning of the data series utilized in this thesis. Thus, the decline in concentrations is not so pronounced as for other POPs (Figure D.5(b)). The peak in the end of the period for DDDs and p'p-DDE is most likely related to the strong transport event in the beginning of 2007; see Figure 5.10(b).

DDT was reintroduced in tropical countries in Asia and Africa around 2000, and thus, fresh emissions from direct application can be expected (*Kallenborn, 2009, pers.comm.*). DDD and DDE are breakdown products of DDT, and DDE is found at higher levels than DDT; see Figures 5.10(b) and 5.10(c). At first sight, it is easy to draw the conclusion that little fresh emissions of DDTs are released to the atmosphere, but *Becker et al. (2009)* reports that p'p-CI-DDT, present in the technical mixture dicofol, may be a source of p'p-DDE. Dicofol is produced in southern Europe, India, China, Israel and Brazil. This explains why such high levels of DDE compared to DDT is present in the atmosphere. The trend picture of DDT derivatives at Zeppelin thus indicates that fresh emissions are still added to the environment.

### PCBs

As for the other POPs, PCB decline seems connected to production drop (*Breivik et al., 2002a; Gioia et al., 2006*).

However, concentrations in air for heavier PCBs have increased slightly during the last three years; see Figure 5.11(b). This is most likely not a consequence of atmospheric circulation changes, as can be explained as follows; The highest amounts of PCBs in the air at Zeppelin are from the lighter compounds. This is consistent with the fact that lighter compounds are more volatile and more available for long-range atmospheric transport (*Wania and Mackay, 1996*). If the PCB increase was because of change in atmospheric transport patterns, there would primarily be an increase in the lighter and more volatile PCBs.

One explanation for this increase may be that during recent years global temperature increase has led to more re-evaporation from soils. According to *Ockenden et al. (2003)*, soils are a good reservoir for PCBs. When first deposited into soil, PCBs are resistant to degradation and soil-air exchange. However, during the right conditions, especially regarding temperature, PCBs can volatilize from soil. *Breivik et al. (2002b)* state that emissions and atmospheric concentrations of heavier PCBs in particular are affected by temperature. The warming of the climate during the recent years can hence explain the recent upswing in high-chlorinated PCBs.

Another theory is that this increase has to do with the largely increasing number of boreal forest fires during recent years (*Eckhardt et al., 2007; Stohl et al., 2007*). Considering the physical-chemical properties of PCBs, it is obvious that high chlorination represents high ability to bioaccumulate. Pine needles and bark have cuticles containing lipids which attract hydrophobic substances. The higher the chlorination of PCBs, the higher the octanol-air coefficient, and as a result heavier PCBs are released in great numbers during forest fires (*Kallenborn, 2009; Wania, 1999*).

#### 6.1.4. Connections between North Atlantic Oscillation / Arctic Oscillation and POPs

This section treats connections between POPs and NAO/AO in light of meteorology and sources. First, correlations between the pollution tracer, carbon monoxide (CO), and POPs are discussed in order to determine if the POPs are likely to behave accordingly to the trajectory field of CO given by FLEXPART. Then, correlations between CO and NAO/AO are examined, before investigations of ages of CO during periods of the year associated with high NAO/AO indices are performed. Finally, correlations between POPs and NAO/AO are discussed. The section rounds off with some final remarks concerning P-values and statistical significance.

##### CO and POPs

As expected, highest correlations are achieved between carbon monoxide (CO) and POPs which are highly insoluble in water; see Table 5.2. These POPs are transported to the Arctic substantially through the atmosphere and show little "grasshopper behaviour". This is evident by looking at physical-chemical properties of the POPs listed in Table 2.2 in Section 2.2.

##### CO and NAO/AO

Comparing the correlations of CO concentration with both the NAO and the AO index, correlations are higher for NAO; see Table 5.3. This is to be expected, since AO is considered more important for variability on a longer scale than NAO and captures more of the hemispheric variability. NAO instead captures the variability of the difference between the Icelandic Low and the Azores High, which controls air moving in a direct pathway to Svalbard and Ny-Ålesund.

Good correlations in winter and spring between NAO and CO indicate that this is the time of year when CO concentrations are most affected by NAO. This is reasonable, since NAO is at its highest at this time of year.

##### Agespectrum of CO and NAO/AO

Less aged air is more represented at Zeppelin from November to March than for other times of the year; see Table 5.4. This is most likely a consequence of NAO. NAO is in its most positive state in winter and spring, when the Icelandic Low is much more intense compared to summer. This leads to stronger and more rapid transport of air into the Arctic, hence a lower age of Arctic air.

Age of CO achieved higher correlations with NAO than with AO. This is reasonable, since NAO accounts for the strength of transport in the Atlantic part of the Arctic on an episodic scale. Less than 2 days is too short a time for the age of CO to be related with NAO. Even though strong NAO conditions are associated with rapid pollution transport, episodes where pollution transport from outside the Arctic takes barely ever less than 2 days.

## 6. Discussion

Air with age higher than 14 days does not show significant correlations with NAO for any of the months. These air masses may have arrived in the Arctic by weak transport episodes from locations outside the Arctic not indicated by trajectories (Sharma *et al.*, 2006).

It is clear just by looking at the averaged time series in Figure 5.13 that NAO affects the age of air. E.g. in 2000, when the NAO index was high, percentage share of air that was 13 – 20 days old and 5 – 8 days olds is approximately 60 % and 16 %, respectively. In 2002, when the NAO index was low, percentage share of air 13 – 20 days old jumps to almost 75 %, and 5 – 8 days old air drops to 8 %.

### Persistent organic pollutants and NAO/AO

Although a majority of the correlations between the concentrations of POPs and NAO/AO is quite low, it is obvious that POP concentrations are influenced by the two climate variation patterns; see Table 5.6. This agrees with previous studies (Eckhardt *et al.*, 2003).

A seasonal pattern can also be noticed. Highest correlations are achieved between NAO and the lighter and most volatile PCBs in February and March, with higher correlations during strong NAO conditions. This high correlation in late winter and early spring seems reasonable when one considers other processes that may influence measured concentrations of POPs, namely; re-evaporation, photochemical degradation and seasonality in emissions. Re-volatilization due to evaporation from oceans and soils happens during summer and autumn, when temperatures are at their maximum and ice cover at its minimum, and these aspects influence the concentration levels to a great extent. Photochemical degradation happens only with sufficient sunlight, in late spring, summer and early autumn. Many of the pesticides analysed are emitted in spring, summer and autumn because of agricultural activity. This makes it most likely for POP measurements to be most correlated with NAO/AO in the winter and early spring months, when there is less interference from other mechanisms.

Why NAO correlates best with PCBs and AO correlates best with pesticides can be explained by emissions and pathways into the Arctic. NAO describes the variability in the winds to the Arctic from Europe, where PCB emissions are frequently occurring. AO describes more of the hemispheric variability and would therefore capture transport directed to the Arctic by the Siberian High as well, that is; pollution coming from Asia. Asia is known for its pesticide use, especially DDTs and chlordanes, which is correlated well with AO.

High correlations are also achieved in August between NAO and low-chlorinated PCBs,  $\alpha$ -HCH,  $\gamma$ -HCH and trans-chlordane and between AO and high-chlorinated PCBs,  $\gamma$ -HCH, trans-chlordane, cis-chlordane and DDT. Pesticide concentrations are increased in autumn because of ploughing, and water soluble compounds with high volatility evaporates to the atmosphere during periods of ice-free oceans. However, NAO and AO are not particularly strong in autumn. This makes the good correlations in August difficult to explain.



### Statistical significance of correlations

As mentioned in Section 3.4.4, statistical significance is controversial and often misinterpreted, and caution should be taken when making use of this kind of test (Hopkins, 2000). Level of statistical significance in this thesis is generally high for high correlations. Since this subject is controversial, no correlations are rejected on basis of their p-values.

### 6.1.5. Continent analysis

In the following sections, continent spectrums of CO and POPs at Zeppelin are discussed in terms of meteorology and sources. Focus in on the three continents North America, Asia and Europe.

#### Continent spectrum of CO at Zeppelin

Consistent with previous studies, Europe is the largest contributor of pollution transport to Svalbard (Stohl, 2006; Klonecki *et al.*, 2003); see Figure 5.14. Pollution is transported most effectively from Europe into the Arctic since source areas are located close to the Arctic and often north of the Arctic front, and because transportation takes place along a direct route in the lower troposphere, close to the ground. European contributions become significantly smaller in summer, since the same direct low-level transport as in winter is not possible in summer. This is because of weakening of the polar dome and hence more vertical mixing in the troposphere (Klonecki *et al.*, 2003; Stohl, 2006; Eckhardt *et al.*, 2003).

North American air is more likely to experience uplift across isentropes because of its pathway to the Arctic across the Atlantic Ocean. The Atlantic Ocean is relatively warm because of the Gulf Stream, it heats the air on its way to the Arctic. This leads to uplift and more vertical mixing and makes it harder for North American pollution to enter the Arctic lower troposphere. Asia is located at even higher potential temperatures than North America, which makes it difficult for Asian pollution to enter the lower troposphere in the Arctic.

Stohl (2006) presents potential emission sensitivity (PES) for CO with different ages for winter and summer in the Arctic, and PES in winter shows larger extension towards northern parts of Eurasia and even northern parts of Asia than towards North America. However, the time it takes for air pollution to be transported from Asia to the Arctic is quite long.

In summer, PES shows higher propensity towards North America. PES is also high for northern parts of Eurasia, but to a lesser extent than in winter. This is consistent with the findings in this thesis; Asian contributions are higher than North American in the first four months of the year, but for the rest of the year, especially during summer, North American pollution outnumbers Asian.

By taking a closer look at North American and European contributions in Figure 5.15 it is obvious that North American pollution can have large influence on the total air mass budget, especially during summer. This has to do with the strength

## 6. Discussion

of the polar dome and vertical mixing with height as described in Section 2.3.2. In summer, the direct, low-level transportation of pollution from Europe that takes place in winter, does not occur, and the pathways for European and North American air masses are more similar.

However, even though PES for North America is higher in summer and even more pronounced than for Europe, and North America contribute quite a lot to the total continent spectrum of CO in summer, not much pollution enters the Arctic with North America as source. This will be discussed in the following section.

### Continent spectrum of POPs at Zeppelin

Transport events from Europe, Asia and North America contribute to higher or lower concentrations of POPs in Zeppelin air compared to standard concentrations, depending on several aspects. These are :

- 1) Emission rates from different continents
- 2) Tendency for wash-out of components on the pathway to the Arctic
- 3) Positioning of the polar dome and vertical mixing
- 4) Travel distance from emission site to the Arctic

All the above mentioned issues are already explained in earlier sections. However, they will now be discussed in light of POP concentrations measured in connection with transport episodes from different continents.

### North America

Overall, transport events from North America do on average not contribute to significantly higher concentrations of any of the POPs at Zeppelin; see Figure 5.16.

EMEP (2008) reports continued PCB emissions from the United States. North American events contribute little to pollution levels at Zeppelin. They represent more forcing of the lighter PCBs than the heavier ones, even though the forcing is small. This is because the lighter PCBs have a higher vapour pressure and are thus more volatile. PCB Tri has the highest HLC of all PCB groups and thus a stronger tendency to partition into air; see Table 2.2 in Section 2.2. This makes the lighter PCBs more available for atmospheric transport into the Arctic without getting washed out on the way.

The fact that no more DDT is used in North America nowadays (*Li and Bidleman, 2003*) explains the low concentrations of DDT and its metabolites compared to standard concentrations.

Strong North American events lead to a slight forcing of  $\gamma$ -HCH in Zeppelin air. Since lindane usage and production are known to take place in the United States and Canada (*Li and Bidleman, 2003*), one should expect greater forcing on  $\gamma$ -HCH concentrations at Zeppelin. The most likely explanation for why this is not the case



is that  $\gamma$ -HCH is washed out before entering the Arctic.  $\gamma$ -HCH has a quite low HLC (see Table 2.2) which implies high tendency to partition into water. The pathway that North American air follows on its way to the Arctic across the Atlantic Ocean explains the wash-out. The relatively cold air masses meet the warm ocean, and cold condensation and wet scavenging of pollutants occur (Klonecki *et al.*, 2003).

As long as lindane production and usage continues in North America, this process will feed the North Atlantic Ocean with  $\gamma$ -HCH.  $\gamma$ -HCH is transported with ocean currents rather than with the atmosphere to the Arctic. In the Arctic,  $\gamma$ -HCH will evaporate from the oceans back to the atmosphere, making the transportation cycle of  $\gamma$ -HCH from North America to the Arctic a considerably slower process compared to an all atmospheric transport route. The result of this is that even if the production of  $\gamma$ -HCH were to stop completely, it will still be detected at Arctic measuring stations for many years ahead.

HCB is the POP with the strongest forcing during North American events. Estimated emissions of HCB from North America are believed to be quite small and strongly decreasing with time. However, emissions of HCB are difficult to estimate and the uncertainties are high. This is mainly because most of the HCB measured in the atmosphere is believed to come from re-volatilization from soil. HCB has a high HLC (see Table 2.2 in Section 2.2) and is the most volatile of the POPs analysed in this thesis. The high HLC makes HCB little available for wash-out. Ma *et al.* (2003) report that the known usage of HCB cannot account for observed HCB concentrations in air in the United States, so it is obvious that HCB behaviour is difficult to map.

North America represents little forcing of chlordanes compared to Asia, since the United States stopped production in 1997 (AMAP, 2004).

## Asia

On average, PCB Penta experiences increased measured concentrations at Zeppelin during strong Asian events in average; see Figure 5.16(a). Light PCBs, PCB Tris, experience a quite strong decrease in concentrations during these events. Asian pollution undergoes a long transportation route to the Arctic, and it would be natural to expect a greater forcing by the lightest PCBs. The fact that the heavier PCBs are more represented may be because of forest fires, as mentioned in Section 6.1.3. Forest fires release mostly the heavier PCBs, but because of the long transportation route from Asia to the Arctic, the heaviest ones are not able to travel the whole distance. This may be the reason why the PCB Penta group gives the strongest forcing.

Asia represents very strong forcing of DDDs and p,p'-DDE, substantially higher than both Europe and North America; see Figure 5.16(b). Singapore and China are still producing DDT, but the amount of fresh DDT emissions is not so high. DDD and DDE are metabolites of DDT, and as long as DDT is released into the environment as fresh emissions it will break down to DDE and DDD. The metabolites both have significantly higher vapour pressure and HLC than DDT. This is evident by looking at Table 2.2. Therefore, DDE and DDD are more volatile than DDT and are more available for long-range atmospheric transportation.

It is obvious from Figure 5.16(c) that strong Asian events contribute most to  $\gamma$ -HCH concentrations. This is also the case for chlordanes, which are still produced in

## 6. Discussion

China and Singapore, and for  $\alpha$ -HCH, which is still produced in India (*Li and Bidleman*, 2003; *AMAP*, 2004). HCHs have high vapour pressures and are among the most volatile POPs analysed in this thesis (see Table 2.2), which makes them favourable for long-range atmospheric transport and hence transport from Asia to the Arctic.

### Europe

Europe is located close to the Arctic, and many of the pollution source areas in Europe are located within the Arctic front. As mentioned in Section 2.1.5, Russia and other European countries report PCB emissions. A consequence of this is that the measured concentrations of all PCB groups experience a positive forcing during European transport events; see Figure 5.16(a). This is especially the case for the lighter and more volatile PCBs.

European transport events give little contributions to concentrations of DDT derivatives measured at Zeppelin, except for a small contribution of p'p-DDD; see Figure 5.16(b). As mentioned earlier, DDD is a breakdown product of DDT, so even though DDT is not known to be produced in Europe anymore, DDD is still emitted from Europe to the atmosphere.

When looking at Figure 5.16(c), European events are neither particularly associated with higher HCH, chlordane nor HCB concentrations at Zeppelin. European countries do not report any HCH or chlordane usage, but HCB usage is reported. HCB emissions are quite complicated to estimate. *EMEP Status Report 3/08* reports European emissions, so it would be natural to expect forcing of HCB during European emissions, especially because of the short distance and direct route to the Arctic. But as mentioned above, HCB is a complicated compound when it comes to the distribution profile. HCB is found to correlate rather poorly with CO, see Table 5.2. Since the FLEXPART model runs utilized in this thesis are based on CO as emission input it is likely that the emission inventory of HCB cannot be explained completely by the emission inventory of CO.

## 6.2. POPs in ice

In Chapter 5, plots of spatial distributions of PCB 18, PCB 28/31, PCB 180, PCB 189,  $\alpha$ - and  $\gamma$ -HCH, HCB and cis-nonachlor were presented. These results are discussed in more detail in this section. Section 6.2.1 explains the concentration levels of POPs listed in Section 5.2.1 in terms of quality control. Section 6.2.2 contains interpretations of the concentration levels of POPs found in the ice core with respect to physical-chemical properties. Concentrations in ice are attempted to be linked to concentrations in air in Section 6.2.3.

### 6.2.1. Concentration levels from a quality control view

Ion ratios showing small deviations from a reference value (< 20 %) is an important quality control criterion. This ensures reliable concentrations after quantification of compounds. PCB 18,  $\gamma$ -HCH, HCB and cis-nonachlor show acceptable ion ratios,

see Table 4.2 in Section 4.2.1. The other compounds that were quantified show less acceptable ion ratios for all or some samples, and these concentrations should be considered less accurate.

All sample concentrations displayed in the plots are above LOQ according to Xcalibur. According to LOD and LOQ calculated from standard deviations of the blanks, some of the concentrations are below both LOD and LOQ. Which concentrations this concerns is shown in Figures 5.17 and 5.18. However, it is obvious that the method blanks have been exposed to cross-contamination from the samples, so LOD and LOQ calculated from the blanks must be considered too high for many of the compounds.

### 6.2.2. Spatial distribution of POPs

#### Three zones: Surface layer, accumulation zone and background level

Three "zones" are identified in the ice core in terms of concentrations of POPs; a surface layer containing low concentrations of POPs, an accumulation zone showing significantly higher concentrations and a background level showing lower and more stable concentrations compared to the accumulation zone. POPs are found in quite small amounts in the surface layer where snow and ice have direct contact with the atmosphere. This is because they are re-volatilized due to strong winds or snow ageing. In the surface layer, pollutants are either transported downwards in the ice or released back to the atmosphere. POPs have different physical-chemical properties which is decisive for their behaviour at this stage. The high concentration zone can be referred to as an "accumulation zone" where compounds are taken up before migrating further down in the ice.

Concentration levels in the ice core below the accumulation zone (approximately year 2000 and earlier) are more stable and may be more of a "background level".

#### Appearance of POPs in ice in terms of physical-chemical properties

PCB 18 and PCB 28/31 are found in the ice core in high amounts since these are the most water soluble PCBs. This is consistent with results from a study on an ice core collected from the Agassiz ice cap in Canada covering layers from the mid 1960s until the mid 1990s (*Gregor et al.*, 1995). At first hand surprising, PCB 180 and PCB 189 are also found in high amounts. PCB 180 and PCB 189 are among the least volatile and water soluble PCBs, and still they are found at such high levels. These are, together with PCB 138 and PCB 153, the most common PCB congeners related to particulate matter and biologic material (*Corsolini et al.*, 1995, e.g.). PCB 138 and PCB 153, together with other PCBs, were probably also present in the ice core, but because of co-elution with other compounds quantification was not possible. These compounds may have entered the ice by long-range atmospheric transport as a consequence of boreal forest fires, as explained in Section 6.1.3, or by local contamination from e.g. cruise ships frequently travelling the west coast of Svalbard during summer.

## 6. Discussion

$\alpha$ -HCH was only found in some samples, and a clear distribution pattern is hard to confirm. In addition, ratios between quantification and reference ions in all three samples in which  $\alpha$ -HCH is detected are not within the acceptable limit of 20 %. Hence, concentrations are questionable. Co-elution with another unidentified compound is likely.

The most surprising compound to detect in the ice core was cis-nonachlor. Cis-nonachlor is the one of the chlordanes with the lowest concentration level detected at Zeppelin. Little information about physical-chemical properties of trans- and cis-nonachlor is available, but according to *Simpson et al.* (1995), cis-nonachlor is the one of the chlordanes with the lowest  $\log K_{ow}$  and hence is the most water soluble. No traces of other chlordanes components were found.

### Fate of POPs in the surface layer

To investigate closer which POPs are more prone to re-volatilization to the atmosphere once deposited to snow and ice, the ratio between concentrations corresponding to the years 2003/2002 and 2005/2004/2003 was calculated for PCB 18, PCB 28/31, PCB 180, PCB 189,  $\gamma$ -HCH, HCB and cis-nonachlor. Ratios are given in Table 6.1 and relate two different layers in the ice core; the surface layer and the accumulation layer. A high ratio corresponds to large concentration differences between the two layers and hence high ability of the compound to evaporate from the surface layer when deposited.

PCB 18	PCB 28/31	PCB 180	PCB 189	$\gamma$ -HCH	HCB	cis-NO
3.5	3.7	4.8	7.5	6.6	10.5	2.8

Table 6.1.: Ratio between concentrations corresponding to the years 2003/2002 and 2005/2004/2003 for PCB 18, PCB 28/31, PCB 180, PCB 189,  $\gamma$ -HCH, HCB and cis-nonachlor.

It is obvious that the degree of re-volatilization is dependent on the compounds' physical-chemical properties. The compound with the highest ratio is HCB, but  $\gamma$ -HCH and PCB 189 also show high ratios. HCB has, as mentioned before, a high HLC and is thus an airborne compound which easily re-volatilizes.  $\gamma$ -HCH shows high water solubility properties, but it is also one of the most volatile of the POPs analysed. Its high volatility is the reason for the high ratio.

*Wania* (1997) modelled the fate of  $\gamma$ -HCH and HCB in an ageing snow pack during three phases: snow settling, snow melting and snow firnification. The conclusion of the study was that 97 – 99 % of HCB and  $\gamma$ -HCH deposit into the snow after snow pack settling. After one year of firnification 90 % of HCB and 40 % of  $\gamma$ -HCH are lost by evaporation from the snow pack, while after melting 85 % of HCB is evaporated back to the atmosphere and 95 % of  $\gamma$ -HCH is lost by draining. This is consistent with HCB's significantly lower concentrations in ice compared to air. It also supports the concentration levels of  $\gamma$ -HCH, since this compound migrates downwards with the

melt water.

The high ratio of PCB 189 is more difficult to explain, since this POP shows low volatility. The ion ratios for PCB 189 detected in these two samples are above the acceptable limit, which makes the concentrations a bit inaccurate. This may be an explanation for the high ratio.

In the same study by Wania (1997) p'p-DDT was estimated to be sorbed on the interface by almost 100 % after firnification and partitioned on organic carbon by approximately 85 % after melting. p'p-DDT was not analysed in the Kongsvegen ice core, but its behaviour can be compared to the behaviour of PCB 180 and PCB 189, which have even lower water solubilities and vapour pressures than p'p-DDT. *Gregor et al.* (1995) report loss of PCBs from Agassiz ice cap, but less than for HCHs. This makes the spatial distribution of PCB 180 and PCB 189 more questionable, since it seems like the compounds are lost by either evaporation or draining like the lighter PCBs.

It must be taken into account that the sample corresponding to years 2005/2004/2003 was not analysed for pesticides for the first and most important fraction, which may cause the calculated ratio between years 2005/2004/2003 and 2003/2002 to be higher than it is in reality.

### 6.2.3. Concentrations of POPs in ice compared to in air

#### Comparison of levels

At Zeppelin, HCB, sum of PCBs and sum of HCHs are of the same order of magnitude. The lighter PCBs are more represented than the heavier ones, and  $\alpha$ -HCH is more represented than  $\gamma$ -HCH. This was compared to the concentrations found in the ice core.

As mentioned in the previous section, lighter PCBs are more represented in the ice core, and this is consistent with air measurements.

$\gamma$ -HCH is found in relatively high amounts, even though the earliest five samples contain  $\gamma$ -HCH below LOQ. Why is  $\gamma$ -HCH found at much higher concentrations than  $\alpha$ -HCH?  $\alpha$ -HCH is more soluble in water than  $\gamma$ -HCH, so it would be reasonable to expect more of this compound in ice. However,  $\alpha$ -HCH is also more volatile, and most likely this compound is re-volatilized back to the atmosphere rather than migrating down in the ice to a larger extent than  $\gamma$ -HCH. *Hermanson et al.* (2005) also found  $\gamma$ -HCH in higher amounts than  $\alpha$ -HCH in an ice core collected from a Svalbard glacier.

The level of HCB is substantially lower in ice than in air. This is a result of HCB's much higher HLC compared to other POPs. HCB is very volatile and not very water soluble, which makes HCB an airborne pollutant.

Cis-nonachlor is actually found at higher concentrations in the accumulation zone than in air. This may be because of its solubility, but the findings related to chlordanes in this thesis raise many questions, and it is hard to get the whole picture.

### Ice cores – historical records of POPs?

The part of the ice core referred to as the "background level" may in theory be correlated to air concentrations for the corresponding period of time. Unfortunately, the time series from the ice core is quite short, and the measured time series in air at Zeppelin is even shorter. Hence, no correlations were found between concentrations in air and ice for  $\gamma$ -HCH and HCB.

One year resolution for the ice core may be too detailed. In the dating of the core two years are missing, 2004/2003 and 1998/1997. Unusually warm summers in Svalbard have led to a melting of the winter accumulation. The height at which the core of the glacier was collected is not known. What is hard to say is if the snow layer has disappeared or migrated further down into the ice and mixed with previous years (Isaksson, 2007, pers.comm.).

There are only few previous studies on PCBs and pesticides in ice cores. More commonly analyzed ice core species are ions. *Simoes and Zagorodnov* (2001) and *Pohjola et al.* (2002) analysed ice cores from different glaciers in Svalbard for ions and concluded that many ions travel downwards in the ice during melting. *Vehvilainen et al.* (2002) analysed an ice core from Lomonosovfonna for naphthalene, a polycyclic aromatic hydrocarbon (PAH), in addition to ions, but this compound showed less movements compared to the ions. *Hermanson et al.* (2005) report a melt index for Austfonna which may cause the summer melt to penetrate as much as 5 years down into the ice, and *Vehvilainen et al.* (2002) report 2 – 3 years of percolation for Lomonosovfonna. Even though the exact height for the core drilling at Kongsvegen is not known, both Austfonna and Lomonosovfonna are located at higher altitudes than Kongsvegen, so the same (and perhaps higher) level of melting is expected to take place at Kongsvegen. Exactly how many years the summer melt can percolate downwards can be determined by calculating the melting index for the glacier (*Hermanson et al.*, 2005; *Isaksson et al.*, 2003).

Another reason for the high concentrations in the accumulation zone compared to the lower concentrations in previous layers may be that POPs are lost further down in the core due to degradation. If this is the case, treating ice cores as records of historical trends is difficult to justify. This is despite of the fact that decomposition processes slow down in ice, helping preservation of compounds (*Isaksson et al.*, 2003).

Based on the findings in this thesis, ice cores cannot be seen as records of historical surfaces which reflect POP concentrations present in the atmosphere. Compound levels in the ice core reflect their physical-chemical properties which determine a compound's volatility and partitioning preference into air or water. Hence, concentration levels of POPs in ice cores may be considered deposition and uptake records rather than trend records.

## 7. Conclusions and perspectives

In this thesis, behaviour of POPs detected at the Zeppelin station, Ny-Ålesund, has been investigated in order to identify seasonal patterns, trends, connections with NAO and AO and origin continents of transportation. Seasonal patterns were examined using Holt-Winters' method, and trends were identified using running mean calculations. Connections between POPs and NAO/AO were investigated by correlation calculations.

An ice core drilled from Kongsvegen glacier near Ny-Ålesund was analysed for POPs using the methods of SPE and GC-MS in order to identify spatial distributions of compounds in the core. The distribution was expected to reflect POP levels in air, and thus, correspond to a historical record of POPs. Levels in air and ice were compared.

The following section summarizes the findings obtained by these analyses. Section 7.2 proposes suggestions for improvement of experiments, together with ideas for further research in order to enhance the understanding of the behaviour of POPs on their journey to the Arctic.

### 7.1. Conclusions

**Transport events:** Concentration distributions of POPs measured at the Zeppelin station are highly influenced by episodes of long-range atmospheric transport. Some of the events are so prominent that they influence both trend and seasonality calculations, and during such events some of the POPs reach concentrations 1000-2000 times bigger than average for that time of year.

**Seasonal variations:** When it comes to seasonal variations, five main categories of patterns are found; peaks following the annual temperature cycle (**A**), light conditions (**B**), meteorological patterns (**C**), application patterns (**D**) and snow melt (**E**). Some of the POPs are affected by more than one pattern. Table 7.1 gives an overview of different POPs and what mechanisms they are influenced by, together with preferred transportation medium.

**Climate related trends:** The downward trend of many POPs detected in air at Zeppelin during the last 15 years responds to the banning and restricted use of these compounds. Less pollution released to the atmosphere at the emission sites leaves less pollution to be transported to the Arctic. However, high-chlorinated PCBs and



## 7. Conclusions and perspectives

POP	A	B	C	D	E	Continent	Air	Water	Biota
$\alpha$ -HCH	+		+	+		As	+	+	
$\gamma$ -HCH	+		+	+	+	As	+	+	
tr-CD		+	+			As		+	+
cis-CD			+	+		As		+	+
tr-NO			+	+		As		+	+
cis-NO	+			+		As		+	+
HCB	+		+		+	N-A, As	+		
DDTs		+			+	As			+
PCBs	+		+			Eu	+		+

Table 7.1.: Overview of factors the different POPs are influenced by on a seasonal basis, together with continent origin and preferred medium. Letters A – E corresponds to influencing factors mentioned above, As = Asia, N-A = North America, Eu = Europe.

HCB have experienced an increase in recent years. Higher temperatures and less ice-cover have led to re-emissions from oceans and soil, and an increasing number of boreal forest fires has led to re-emissions from foliage.

During the last decades, the Earth's climate has warmed significantly, particularly in the Arctic. This has led to melting of sea ice and more open water in areas that used to be covered with ice. For some pollutants, their physical pathways from southern latitudes to the Arctic has changed because of climatic changes there. Oceans can be considered large reservoirs for water soluble POPs because net deposition of POPs from the atmosphere occurred until the 1990s, during times of high emission rates. Since oceans have much larger storage capacity and ocean currents are much slower than atmospheric currents, Arctic monitoring stations are likely to detect POPs for many years ahead.

Changes in seasonal patterns are also affected by a smaller ice-covered area. Many compounds experience a strengthening and widening of peaks in summer and autumn because re-volatilization from oceans and soil now takes place during longer periods of the year.

**Connections between levels of POPs and NAO/AO:** Correlations between CO and POPs were highest for the least water soluble POPs. Some POPs showed no connections with CO through the yearly cycle. This implies that investigations done on POPs in this thesis with FLEXPART output as a basis may not necessarily explain all concentration patterns detected at Zeppelin.

Less aged CO is more represented at Zeppelin between November and March, and age of CO between approximately 2 and 12 days correlates best with NAO. Hence, NAO affects age of air because it leads to stronger and more rapid transport into the Arctic.



Even though some correlations are quite low, POPs are obviously influenced by the North Atlantic Oscillation and Arctic Oscillation. Highest correlations are found in winter/spring between NAO and PCBs and between AO and pesticides. The reason for this is that NAO captures the variability of transport from Europe to the Arctic, and AO captures in addition to that the variability of transport from Asia to the Arctic. Europe stands for a large fraction of PCB emissions worldwide and Asia is known for pesticide usage.

**Continent spectrum:** Table 7.1 also lists continents POPs that are detected at Zeppelin are generally transported. European transport events contribute in general to increased concentrations of lighter PCBs.

During summer, North American pollution events often outnumber European events. However, increased POP concentrations during North American events are seldom noticed. This is a result of the transport pathway the pollution must follow from North America to Svalbard. Pollution is transported to Svalbard across the warm North Atlantic Ocean and compounds are washed out on the way. This mechanism contributes to the oceans being reservoirs for POPs and supports the unfortunate outcome of POPs being released to the atmosphere long after the emissions have stopped. HCB is the only compound which contributes to elevated concentrations measured at Zeppelin during North American events. This is because HCB is an airborne compound which is barely soluble in water.

Asian potential pollution sources are located south of the Arctic front and at higher potential temperatures than e.g. European sources. This makes it difficult for pollution coming from Asia to enter the lower Arctic troposphere. The increased number of boreal forest fires in Eurasia during recent years has led to increased concentrations of heavier PCBs, and because of insecticide usage in Asia, Asian transport events accounts for increased concentrations of DDTs,  $\gamma$ -HCH and chlordanes.

**Spatial distributions of POPs in ice:** The Kongsvegen ice core analysed for POPs shows low levels of POP concentrations in the surface layer close to the surface and higher concentrations below the surface layer. The compounds' physical-chemical properties are decisive for their destiny after snow settling. In the surface layer, compounds are either re-volatilized to the atmosphere because of strong winds, evaporated, drained or partitioned on organic carbon during firnification or melting. Further down in the ice core a "background concentration" level is present, which in theory may be correlated to air concentrations. An attempt to compare ice core POP data and air measurements of POPs was done. However, no correlations between the data series in ice and in air were found. Concentration levels of POPs in ice cores may be considered deposition and uptake records rather than trend records.

## 7.2. Perspectives and recommendations for further research

It is obvious that the changing behaviour of some POPs is caused by climate changes. The rate of precipitation is expected to increase with a warmer climate. The Arctic is considered very dry, and more snow or rain would alter the deposition rates of POPs significantly. POPs may be scavenged from the air and deposit into snow and ice in greater amounts. This pattern of more precipitation will most likely be visible more and more in air measurements and in ice and snow.

Verification of solid-phase extraction with Si-C18 cartridges as a successful method for determining OCs in ice was not possible during this thesis work, even though other studies have done this successfully. However, POP determination of replicates using other independent methods, e.g. Soxhlet/Erhardt extraction with glass columns filled with XAD-2 resin, would be useful to ensure reliable results, especially since target compounds in this thesis work probably were co-eluted with compounds originating from the adsorbent in the Si-C18 cartridge.

Comparison of Svalbard ice cores with ice cores collected from Russia, Canada and Greenland, preferably using the same analysis method, would reveal regional differences of POP records and may shed light on differences in meteorology, secondary emissions and application patterns.

Few studies on POPs in ice cores have been performed, and more research is needed to get the whole picture. Choosing glaciers located at high altitudes where the melting level is held at a minimum is advantageous when investigating ice cores as historical pollution records.

Ice cores covering longer periods of time than the Kongsvegen ice core investigated in this thesis are most favourable for pollution record investigations. Comparison with air measurements is hard to do yet because POP monitoring on a regular, yearly basis only has been carried out at Zeppelin for 10 – 15 years. Hence, it is very important to continue atmospheric measurements. Some trends are indeed possible to be investigated by using the data collected until today, but longer data series are preferred. With longer time series, POP levels may also be correlated better with North Atlantic Oscillation or Arctic Oscillation, since these indices are available from 1950 and until today.

This thesis has focused substantially on secondary emissions and their impact on atmospheric measurements of an Arctic monitoring station and concluded that water soluble and volatile compounds are re-emitted to the atmosphere during the recent years' temperature rise. A suggestion for further research is to try to connect strong HCB and PCB events to changes in local temperatures. HCB and PCBs are compounds believed to be emitted to a great extent from soils and sediments during high temperature events. This can be done with supplementary FLEXPART backward model runs to see origin continents of the compounds.

FLEXPART output based on CO as an emission inventory turned out to be quite explanatory for the behaviour of POPs. However, as mentioned in the previous section and experienced during the course of this thesis, this is not always true.

## *7.2. Perspectives and recommendations for further research*

Andreas Stohl, NILU, has done some model runs with PCB-153 as an emission inventory, covering the years from 2000 to 2003. To get PCB model runs for a longer time period, both before year 2000 and after year 2003, would be highly useful in the further mapping of transport pathways for PCBs. What would also be useful would be model runs with other POPs as emission inventories.



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## A. Air analysis parameters

Table A.1.: List of reference selection from Mackay *et al.* (2006b,a).

#	Reference
[1]	L. Shen and F. Wania, 2005, "Compilation, evaluation, and selection of physical-chemical property data for organochlorine pesticides," <i>J Chem Eng Data</i> , vol. 50, pp. 742-768.
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Table A.1 – Continued

#	Reference
	Pesticide and PCB Concentrations in Air near the Great Lakes," <i>Environmental Science &amp; Technology</i> , vol. 38, no. 2, pp. 414 - 422.
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<b>Time period of event</b>	<b>Week number</b>
08.-12.07.1997	28-1997
20.-30.07.1997	30/31-1997
03.-07.09.1997	37-1997
23.-28.04.1998	17/18-1998
03.-04.05.1998	19-1998
02.-03.07.1998	27-1998
21.07-03.08.1998	30-32-1998
04.-11.08.1998	33-1998
17.-24.08.1998	34/35-1998
22.-24.02.1999	8-1999
10.-13.08.1999	32-1999
22.-25.05.2000	21-2000
18.-20.11.2000	46/47-2000
19.-21.06.2001	25-2001
22.-26.07.2001	30-2001
28.07-02.08.2001	31-2001
11.-14.08.2001	32/33-2001
28.-30.09.2001	39-2001
12.-14.07.2002	28-2002
28.06-01.07.2003	27-2003
28.01-04.02.2004	5-2004
13.-20.03.2004	11/12-2004
03.-07.07.2004	28-2004
22.-24.07.2004	30-2004
08.-15.08.2004	33-2004
29.-31.07.2005	31-2005
30.08-11.09.2005	35/36-2005
09.-12.04.2006	15-2006

Table A.2.: List of transport events considered exclusively European after criteria in section 5.1.5. Date of event taken from continent spectrum FLEXPART output, week number is corresponding period of time in POP data.

Time period of event	Week number
03.-05.06.1997	23-1997
28.06-01.07.1998	27-1998
11.-16.06.1999	23/24-1999
29.06-05.07-2000	26/27-2000
22.-23.07.2000	29-2000
04.-07.09.2000	36-2000
21.-25.05.2001	21-2001
23.-24.09.2001	38/39-2001
17.-20.05.2002	20/21-2002
01.-03.07.2002	27-2002
07.-10.07.2002	28-2002
07.-08.09.2002	36-2002
24.-28.05.2003	21/22-2003
31.12.2003-03.01.2004	1-2004
30.05-02.06.2004	23-2004
08.-12.06.2004	24-2004
09.-15.07.2004	28/29-2004
29.10-02.11.2004	44/45-2004
21.-24.02.2005	8-2005
23.-28.07.2005	29/30-2005
06-09.08.2005	31/32-2005
22.-25.10.2005	42/43-2005
20.-23.06.2006	25-2006
04.-05.07.2006	27-2006
10.-14.07.2006	28-2006
25.-28.07.2006	30-2006
23.-25.08.2006	34-2006
19.-22.12.2006	51-2006

Table A.3.: List of transport events considered exclusively North American after criteria in section 5.1.5. Date of event taken from continent spectrum FLEXPART output, week number is corresponding period of time in POP data.

<b>Time period of event</b>	<b>Week number</b>
13.-16.04.1997	15/16-1997
20.09.1997	38-1997
08.10.1998	41-1998
22.-24.06.2000	25-2000
26.-30.03.2001	13-2001
28.-30.06.2001	26-2001
29.-31.03.2002	13-2002
24.-26.05.2002	21-2002
10.-11.05.2003	19-2003
11.-13.06.2003	24-2003
16.09.2004	38-2004
07.-08.03.2005	10-2005
10.-12.05.2005	19-2005
?-01.03.2006	9-2006
26.-27.03.2006	12-2006
28.-31.03.2006	13-2006
17.-21.05.2006	20-2006
23.-24.05.2006	21-2006
25.-27.05.2006	21-2006
18.-20.09.2006	38-2006
07.-11.04.2007	14/15-2007
18.-20.06.2007	25-2007

Table A.4.: List of transport events considered exclusively Asian after criteria in section 5.1.5. Date of event taken from continent spectrum FLEXPART output, week number is corresponding period of time in POP data.

A. Air analysis parameters

	<b>Jun-98</b>	<b>Jan-06</b>	<b>Feb-06</b>	<b>Mar-06</b>	<b>Apr-06</b>	<b>May-06</b>	<b>Dec-07</b>
$\alpha$ -HCH	28.73	12.43	9.64	11.03	14.15	14.54	
$\gamma$ -HCH	9.77	2.44	1.86	2.09	2.60	2.67	
tr-CD	0.39	0.41	0.36	0.38	0.25	0.15	
cis-CD	0.86						
tr-NO	0.66	0.70	0.59	0.64	0.53	0.58	
cis-NO	0.10	0.73	0.52	0.59	0.55	0.58	
o'p-DDE	0.14	0.19	0.04	0.03	0.06	0.07	
p'p-DDE	0.97	0.22	0.18	0.13	0.07	0.03	
o'p-DDD	0.07	2.88	1.09	0.82	1.78	0.71	
p'p-DDD	0.03	0.37	0.04	0.06	0.02	0.01	
o'p-DDT	0.61	0.68	0.05	0.07	0.02	0.02	
p'p-DDT	0.72	0.49	0.36	0.26	0.19	0.09	
HCB		0.37	0.14	0.15	0.07	0.06	64.46

Table A.5.: Interpolated values used in seasonality and trend calculations.

## B. Ice core analysis parameters

Compound	Stock solution [ng/ $\mu$ l]	Volume [ $\mu$ l]	Actual conc. [pg/ $\mu$ l]
PCB-mix, 32 isomers	10.0	5	100.0
$\alpha$ -HCH	1.0	50	100.1
$\gamma$ -HCH	1.0	50	100.0
cis-Chlordane	1.0	50	102.2
trans-Chlordane	1.0	50	102.0
cis-Nonachlor	1.0	50	98.9
trans-Nonachlor	1.0	50	103.7
HCB	1.0	50	100.0
$^{13}\text{C}$ PCB 118	4.0	12.5	100.0
$^{13}\text{C}$ trans-chlordane	4.0	12.5	100.0
Octachloronaphtalene, OCN	4.0	12.5	100.8

Table B.1.: Recovery solution. Concentration: 100pg/ $\mu$ l. Volume: 500 $\mu$ l

		Cal 1	Cal 2	Cal 3	Cal 1	Cal 2	Cal 3
Compound	Stock solution [ng/ $\mu$ l]	Vol added [ $\mu$ l]			Actual conc [pg/ $\mu$ l]		
PCB-mix (32)	10.0	3	5	10	60.0	100.0	200.0
$^{13}\text{C}$ PCB 118 (ISTD)	4.0	6	13	25	48.0	104.0	200.0
OCN (RSTD)	4.0	6	13	25	48.0	104.0	200.0

Table B.2.: PCB calibration. Volume: 500 $\mu$ l. Three levels: 50 pg/ $\mu$ l, 100 pg/ $\mu$ l, 200 pg/ $\mu$ l.

## B. Ice core analysis parameters

		Cal 1	Cal 2	Cal 3	Cal 1	Cal 2	Cal 3
Compound	Stock solution [ng/ $\mu$ l]	Vol added [ $\mu$ l]			Actual conc [pg/ $\mu$ l]		
$\gamma$ -HCH	1.0	15	24	30	50.0	80.0	100.0
$\alpha$ -HCH	1.0	15	24	30	50.1	80.1	100.1
trans-Chlordane	1.0	15	24	30	51.0	81.6	102.0
cis-Chlordane	1.0	15	24	30	51.0	81.8	102.2
trans-Nonachlor	1.0	15	24	30	51.9	83.0	103.7
cis-Nonachlor	1.0	15	24	30	49.4	79.1	98.9
HCB	1.0	15	24	30	50.0	80.0	100.0
$^{13}\text{C}$ trans-Chlordane (ISTD)	4.0	4	6	7.5	53.3	80.0	100.0
OCN (RSTD)	4.0	4	6	7.5	53.8	80.6	100.8

Table B.3.: Pesticide calibration, Volume: 300 $\mu$ l

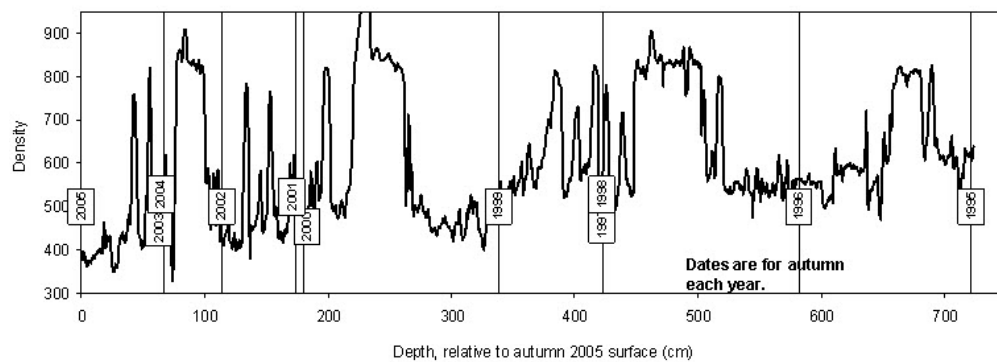


Figure B.1.: Dating of ice core by looking at density changes with depth. Done by Elisabeth Isaksson and Jack Kohler, Norwegian Polar Institute.

<b>Year</b>	<b>Depth [cm]</b>
2005	0
2004	66
2003	66
2002	113
2001	175
2000	180
1999	338
1998	423
1997	423
1996	582
1995	721

Table B.4.: Dating of ice core and defining of depths, done by Elisabeth Isaksson and Jack Kohler, Norwegian Polar Institute. Depth is relative to the surface; the autumn 2005 layer.

*B. Ice core analysis parameters*

<b>Compound</b>	<b>Quantification ion [m/z]</b>	<b>Reference ion [m/z]</b>	<b>Retention time [min]</b>
PCB 18	256	258	13.19
PCB 28			14.50
PCB 31			14.50
PCB 44	291.9	289.9	16.06
PCB 52			15.49
PCB 95	325.9	323.9	17.40
PCB 99			18.33
PCB 101			18.19
PCB 105			21.13
PCB 110			19.34
PCB 114			20.61
PCB 118			20.26
PCB 123			20.14
PCB 126			22.19
PCB 128	359.8	361.8	22.83
PCB 138			21.92
PCB 146			20.77
PCB 149			20.12
PCB 153			21.00
PCB 156			23.69
PCB 157			23.85
PCB 167			22.94
PCB 169			25.03
PCB 170	393.8	395.8	25.23
PCB 177			23.41
PCB 180			24.26
PCB 183			22.62
PCB 187			22.43
PCB 189			26.29
$\alpha$ -HCH	254.8	252.8	12.37
$\gamma$ -HCH	254.8	252.8	13.20
tr-CD	407.8	409.8	18.29
cis-CD	407.8	409.8	18.71
tr-NO	443.65	441.65	18.82
cis-NO	443.65	441.65	20.89
HCB	283.8	285.8	12.46
$^{13}\text{C}$ PCB 118	338	268	20.26
$^{13}\text{C}$ tr-CD	417.8	419.8	18.28
OCN	403.8	332	28.87

Table B.5.: Compounds and ions with corresponding retention times.



<b>Compound</b>	<b><math>r^2</math></b>	<b>Response factor</b>
PCB 18	0.962	0.0051
PCB 28/31	0.961	0.0017
PCB 44	0.957	0.0053
PCB 52	0.968	0.0048
PCB 95	0.960	0.0053
PCB 99	0.953	0.0045
PCB 101	0.957	0.0048
PCB 105	0.963	0.0036
PCB 110	0.954	0.0038
PCB 114	0.957	0.0036
PCB 118	0.955	0.0035
PCB 123	0.953	0.0036
PCB 126	0.965	0.0037
PCB 128	0.965	0.0056
PCB 138	0.967	0.0050
PCB 146	0.959	0.0050
PCB 149	0.954	0.0050
PCB 153	0.959	0.0050
PCB 156	0.970	0.0038
PCB 157	0.974	0.0035
PCB 167	0.967	0.0037
PCB 169	0.976	0.0040
PCB 170	0.973	0.0064
PCB 177	0.968	0.0064
PCB 180	0.972	0.0054
PCB 183	0.968	0.0055
PCB 187	0.966	0.0056
PCB 189	0.972	0.0045
$\alpha$ -HCH	-	0.0234
$\gamma$ -HCH	-	0.0227
tr-CD	-	0.0050
cis-CD	-	0.0097
tr-NO	-	0.0043
cis-NO	-	0.0067
HCB	-	0.0010
<sup>13</sup> C PCB 118	0.938	0.737
<sup>13</sup> C tr-CD	-	1.764
OCN	0.993	-

Table B.6.: Linearity and response factors of target compounds and internal standards. Linearity is given as the square of the correlation. The response factor given is the average of 3 (2) levels for PCBs (pesticides).



## C. Seasonality plots

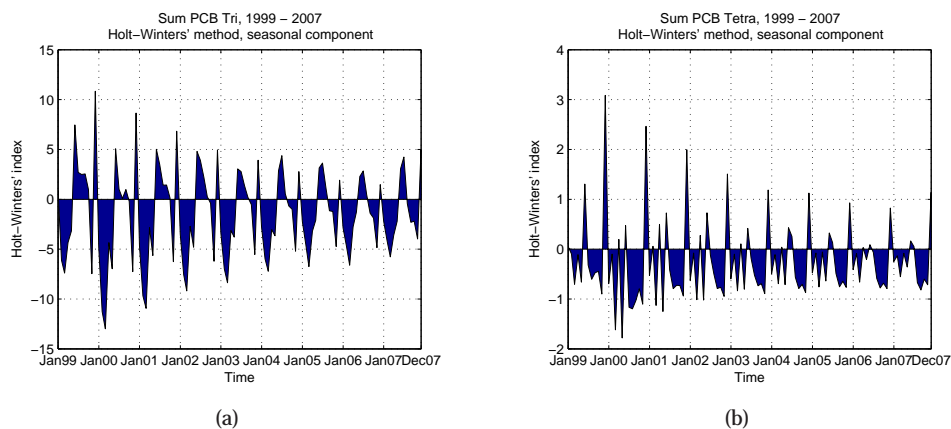


Figure C.1.: Seasonal variations of a) PCB Tri and b) PCB Tetra computed by Holt-Winters' method, 1999 – 2007.

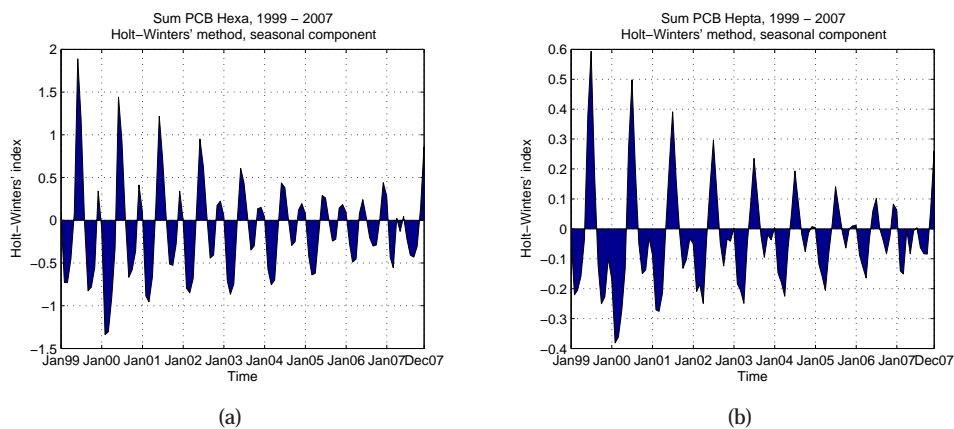


Figure C.2.: Seasonal variations of a) PCB Hexa and b) PCB Hepta computed by Holt-Winters' method, 1999 – 2007.

### C. Seasonality plots

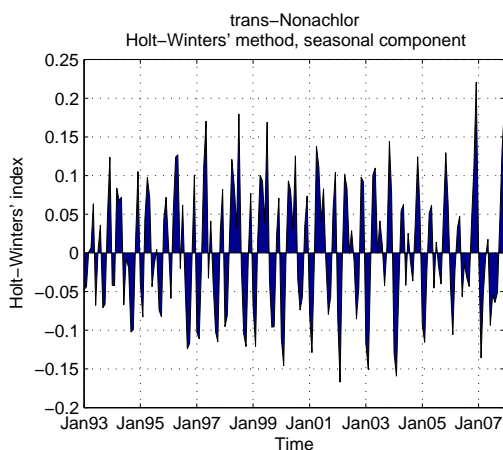
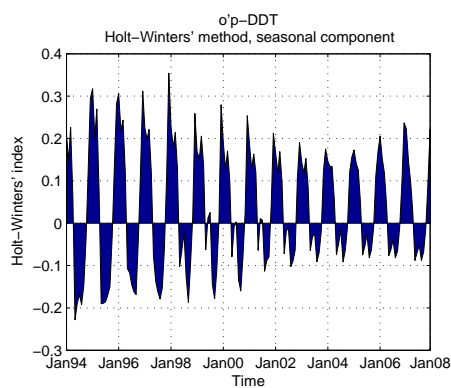
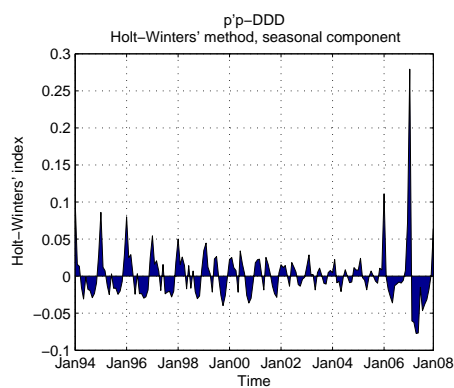


Figure C.3.: Seasonal variations of trans-nonachlor computed by Holt-Winters' method, 1993 - 2007.

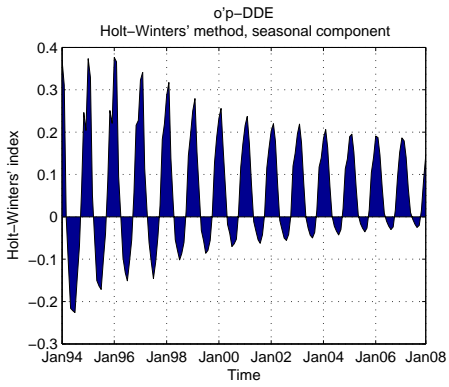


(a)

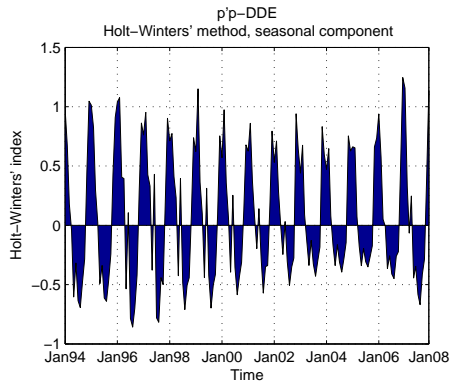


(b)

Figure C.4.: Seasonal variations of a) o'p-DDT and b) p'p-DDD computed by Holt-Winters' method, 1994 - 2007.



(a)



(b)

Figure C.5.: Seasonal variations of a) o'p-DDE and b) p'p-DDE computed by Holt-Winters' method, 1994 – 2007.



## D. Trend plots

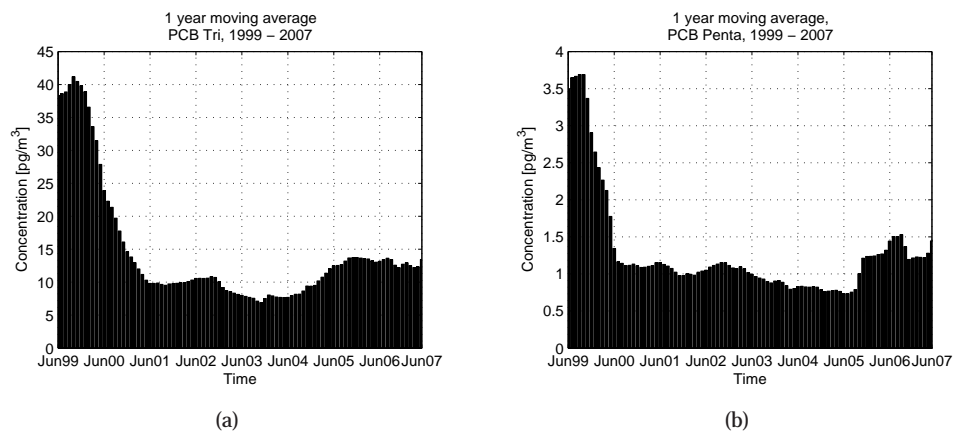


Figure D.1.: One year moving average of a) PCB Tetra and b) PCB Penta, 1999 – 2007.

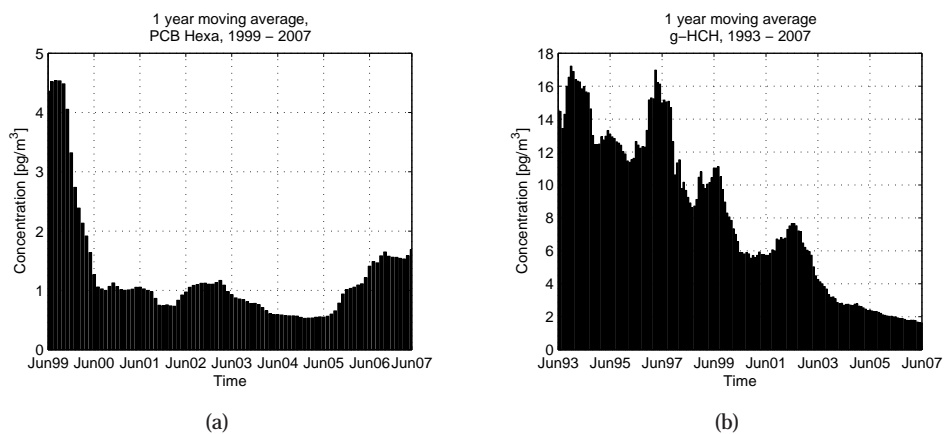


Figure D.2.: One year moving average of a) PCB Hexa, 1997 – 2007, and b)  $\gamma$ -HCH, 1993 – 2007.

#### D. Trend plots

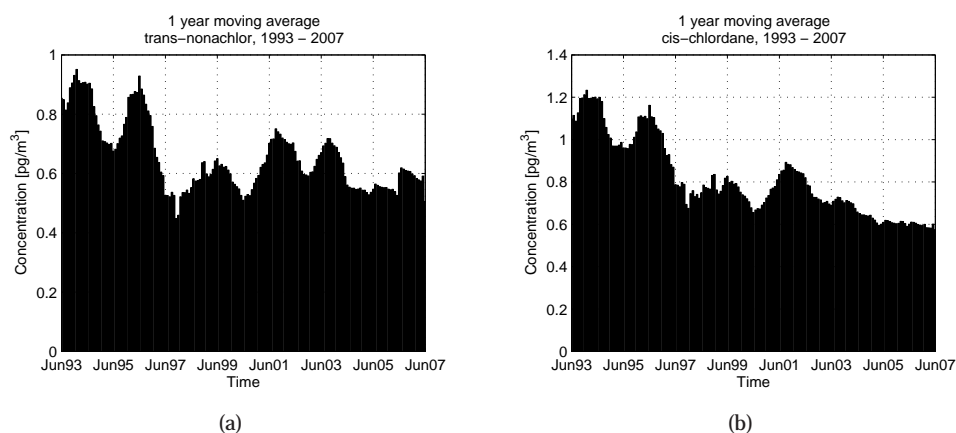


Figure D.3.: One year moving average of a) trans-nonachlor and b) cis-chlordane, 1993 – 2007.

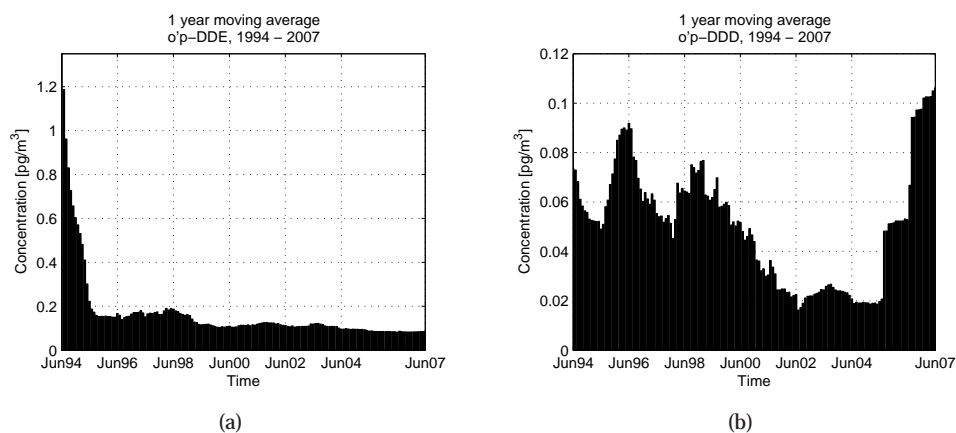
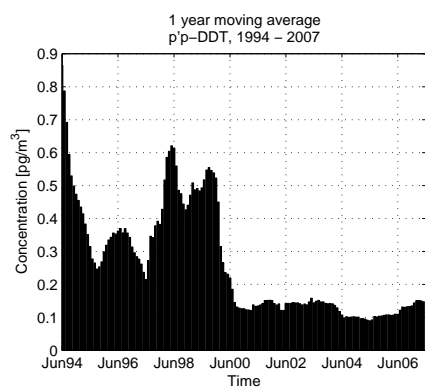
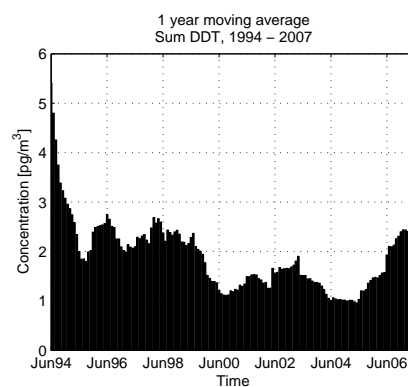


Figure D.4.: One year moving average of a) o'p-DDE and b) o'p-DDD, 1994 – 2007.





(a)



(b)

Figure D.5.: One year moving average of a) p'p-DDT and b) sum DDT, 1994 – 2007.