

OC PESTICIDES IN THE NORWEGIAN ARCTIC ATMOSPHERE

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Introduction

The long-range atmospheric transport (LRAT) of organochlorine (OC) pesticides to places far removed from their initial point of release is a cause for global concern¹. Investigations into OC pesticides have found that natives of Arctic areas are often exposed to higher concentrations of these contaminants than those living in close proximity to usage areas. For example, Inuit populations living on Broughton Island were found to be subject to a daily chlordane intake of 5 µg/kg bw/day, whereas people living North America (an area of high use) were only subjected to intakes of 0.1 µg/kg bw/day^{2,3}. Monitoring campaigns run by the Norwegian Institute for Air Research (NILU) under the Arctic monitoring and Assessment Programme (AMAP) have systematically collected air samples at Zeppelin Mountain, Svalbard, Norway since the beginning of the 1900s. Here, twelve years data (1994-2005) on chlordanes (*cis*- and *trans*-), DDTs, and hexachlorocyclohexane (α -HCH and γ -HCH) is analysed with respect to long-term underlying trends, climatic influences, and source alterations. These chemicals are discussed separately throughout the paper for ease of reading.

Chlordanes

Chlordane was used extensively on crops, residential lawns and gardens and for termite control. Bans were introduced in the late 1980s with the US being the last to cease use in 1988⁴. The two main isomers in the technical formulation *trans*-chlordane (TC) and *cis*-chlordane (CC) are investigated here. The ratio of these isomers (TC/CC) in the US formulation is ~1.16⁵, although they can range from 1.26-1.35 in other areas⁶. These ratios can be used to indicate whether sources are from recent use or re-volatilisation from previously contaminated soils and vegetation⁷.

DDTs

The use of technical DDT ($\geq 80\%$ *p,p'*-DDT; $\geq 15\%$ *o,p'*-DDT) was widely banned in the 1970s, although use is still permitted under special licence for the control of disease vectors in e.g. Africa and South America, and in anti-fouling paints in China⁸. Dicofol, which is used to kill mites such as the red spider mite on crops, is made from DDT and can contain impurities (mainly *o,p'*-DDT and Cl-DDT) following synthesis reactions^{9,10}. In 1998-2000 the annual production of DDT in China was ~6 000 t (~80% for Dicofol production)¹¹. Ratios of DDT/DDE+DDD can be used to give an idea of the age of the source, and a ratio of *o,p'*-DDT/*p,p'*-DDT can be used to see if the source is from technical DDT or Dicofol.

Hexachlorocyclohexane (HCH)

HCH is an insecticide which has been extensively used on crops by many countries. Technical-HCH (53-70% α -HCH; 11-18% γ -HCH) was banned in many countries prior to 1980, however it is thought to be still in use in Russia¹². Lindane ($\geq 99\%$ γ -HCH), however, saw increased use in the 1980s and 90s, particularly in Canada, India and China. In Europe, France was a major user of lindane before a ban was implemented in 1998¹³. A notable 'step-down' in atmospheric concentrations of α -HCH was observed in the Canadian Arctic following bans on technical-HCH in 1983 in China, and 1992 in India^{14,15}. Ratios of γ -/ γ - + α -HCH *100 (i.e. the proportion of γ -HCH to the total) can indicate whether sources are from technical-HCH or lindane.

Methods

Atmospheric samples are collected weekly over a period of 48 hours at Ny-Ålesund, Svalbard, Norway (78°55'N/11°59'E). Details of the sampling and analysis can be found in an earlier publication by Oehme *et al.*¹⁶, and so are not discussed in detail here. Briefly, each sample is collected using a Hi-Volume sampler aspirating ~1 000m³ air, with particulate and vapour phases collected on glass fibre filters (GFFs) and

polyurethane (PUF) plugs, respectively. Samples are extracted separately and then combined (as <10% of these are found in the particulate phase) and quantified using GC-MS (operating in NCI mode).

Time trend analysis using dynamic harmonic regression (DHR)

DHR is a sophisticated time-series modelling tool, which uses stochastic time variable parameters (TVPs), thus enabling the tracking of changes in source strengths and types. This modelling technique has been described in detail elsewhere^{17,18,19}, and so is only described briefly here. The generic formula used by DHR is:

$$y_t = T_t + C_t + S_t + e_t$$

where y_t is the time series; T_t is a longer-term trend, or slow changing component; C_t is the cyclical component; S_t is the seasonal component, and e_t is an irregular or 'noise' component to cope with inherent variations in atmospheric data due to polluted air mass incursions and turbulence within the planetary boundary layer. Since the cyclic component is not being modelled directly, the model contains the trend, characterising changes slower than the annual variation; the seasonal component describing the annual seasonality and its evolution, and the faster changing irregular component.

Results and Discussion

The longer-term trends of the OC pesticides are displayed in Figure 1. This shows that, although all of these chemicals have been subject to restrictions and/or bans, concentrations in the Arctic atmosphere are not showing any appreciable decline, with the exception of the HCHs.

Chlordanes

The seasonality displayed by the two isomers shows subtle differences with TC concentrations characterised by distinct winter maxima and summer minima, whereas CC shows two distinct peaks in concentrations in Spring and again in Autumn together with a winter maximum. This could relate to the preferential photodegradation of TC relative to CC⁶. This theory is supported by the examination of TC/CC ratios, with average values of 0.28 in summer, and 0.68 in winter (excluding 2001, due to high values). Episodes of high TC/CC ratios, such as seen in 2001, could be attributed to applications of technical heptachlor containing TC and CC, as these higher ratios coincide with high heptachlor concentrations²⁰.

Although there appears to be a general decline in concentrations over the time period, the average concentrations recorded in 2005 for TC and CC ($0.25 \pm 0.13 \text{ pg m}^{-3}$ and $0.61 \pm 0.13 \text{ pg m}^{-3}$, respectively) are not statistically different from those recorded in 1994 ($0.7 \pm 0.57 \text{ pg m}^{-3}$ and $1.2 \pm 0.41 \text{ pg m}^{-3}$). In fact, when looking at the standard deviation around these averages, this pattern could relate secondary emissions from soils and vegetation taking over as the main source of these chemicals. Concentrations recorded in the spring of 1992 (TC: $0.55 \pm 0.23 \text{ pg m}^{-3}$; CC: $0.98 \pm 0.38 \text{ pg m}^{-3}$) and March-December of 1993 (TC: 0.53 pg m^{-3} ; CC: 1.09 pg m^{-3}) are also similar to those reported here^{16,21}.

DDTs

The most pronounced seasonality is displayed by *o,p'*-DDE, although all of the DDTs show a winter maxima and summer minima. Ratios of DDT/DDE+DDD show that DDT dominates during the Arctic summer, whilst the degradation products dominate in winter. This is in agreement with a previous investigation²² where this pattern was attributed to long-range transport from Asia during the winter. Another possibility is the association with particles and the occurrence of the Arctic Haze at this time²³. Ratios of *o,p'*-DDT/*p,p'*-DDT show a change in source from technical DDT to dicofol, with a general increase in ratio throughout the time-series.

Elevated concentrations of the majority of DDTs in 2004 (not *p,p'*-DDT) were apparent from June-December inclusive. The highest concentrations were recorded for *o,p'*-DDE, and so this isomer shows the trend from 1994-2003 alone. None of the DDTs (with the exception of *p,p'*-DDT) show a statistically significant decline in concentrations. In fact, *p,p'*-DDE shows no notable difference, with a hint of a possible future increase. This could be due to the fact that CL-DDT, an impurity in Dicofol, also degrades to *p,p'*-DDE⁹. The decline displayed by *p,p'*-DDT would support the fact that sources to the Arctic are now predominantly from Dicofol. The significant drop at the beginning of the time-series for *o,p'*-DDE is thought to be due to exceptionally high values in this year (~7 times greater than those in subsequent, or previous years²¹), although it could, possibly be

a longer, slower, cyclical effect, which will not become evident until there are several more years data available for analysis.

HCHs

A bimodal pattern in seasonality is evident for γ -HCH with elevated concentrations in April-May and October-November consistent with on-going use. On the other hand, α -HCH has one marked annual peak in concentrations evident in August, which is broadly in agreement with the temperature cycle, suggesting input from predominantly secondary sources. Differences in seasonality for α -HCH seen at Zeppelin and at Alert, the Canadian Arctic monitoring station, where a bimodal pattern similar to γ -HCH is seen, could indicate influences from climatic fluctuations such as the Arctic Oscillation²⁴. Since the extent of sea-ice is much less at Zeppelin, oceanic inputs of chemicals to the Arctic are much more evident here than at Alert²⁵.

Both isomers display a definite decline throughout the time-series, most evident for γ -HCH. Recent legislation governing use of lindane in France (1998), and Canada and Germany (2004), could be promoting an immediate response, as was evident for α -HCH concentrations reaching the Arctic in the early 1990s.

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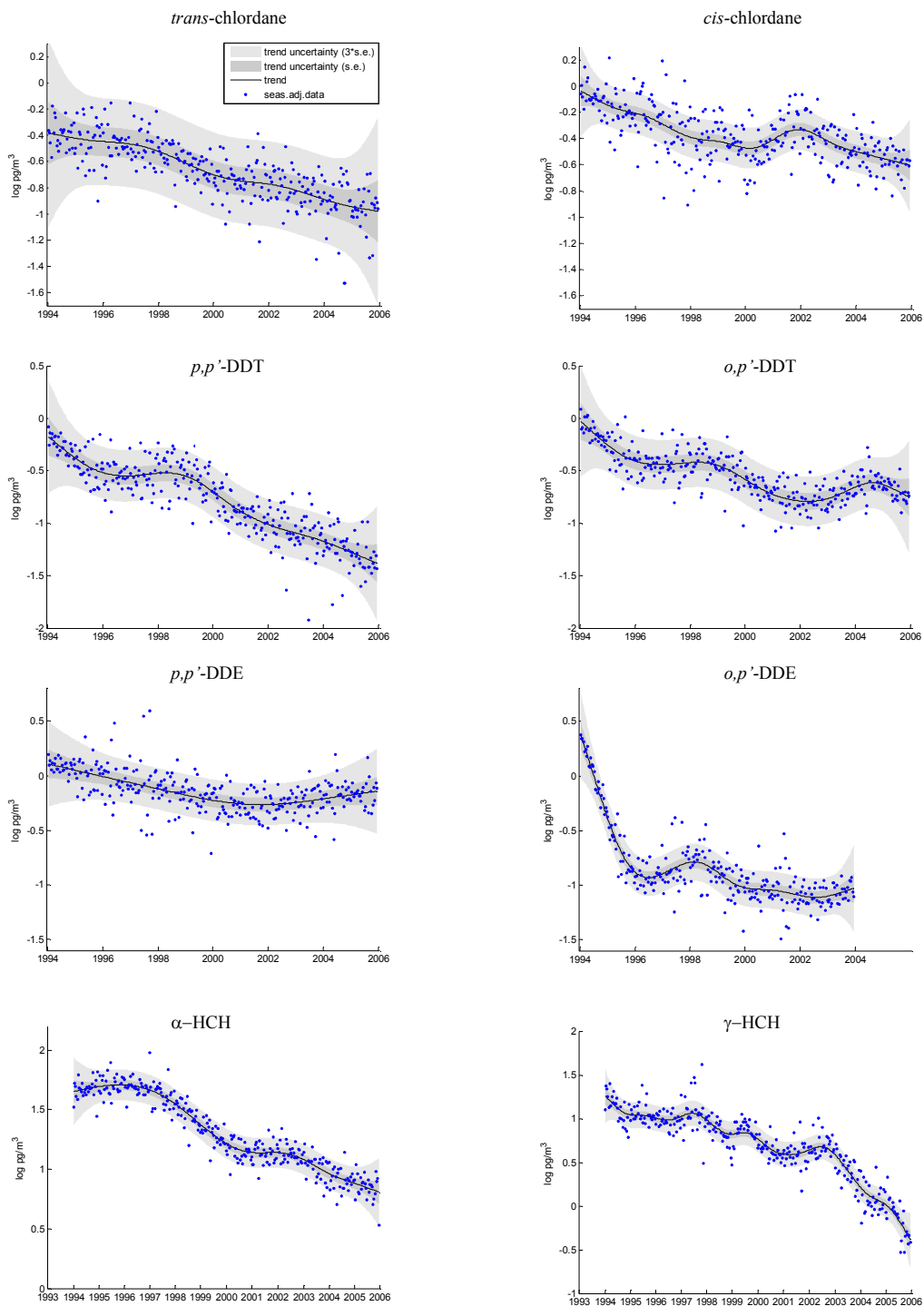


Figure 1: Longer-term trends of *trans*- and *cis*- chlordane; *p,p'*-DDT, *o,p'*-DDT, *p,p'*-DDE and *o,p'*-DDE; α - and γ -HCH.

Note: The time-series for *o,p'*-DDE stops at 2004 due to extremely high values reported in this year.

