Investigating the long-term trends of atmospheric POPs in the Canadian and Norwegian Arctic: a spatial comparison

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Introduction

PAHs, OC pesticides and PCBs have been routinely measured in air samples collected at several arctic locations including Alert in the Canadian High Arctic (82°30'N, 62°20'W) and Ny-Ålesund on Svalbard in the Norwegian Arctic (78°55'N, 11°56'W) These respective monitoring programmes provide baseline data to allow elucidation of chemical behaviour and assessment of temporal patterns; both short and longer-term trends. As long-range atmospheric transport is a major source for many of these pollutants to the Arctic then international agreements/legislation aimed at controlling emissions in source regions may be realised by studying these arctic databases.

To-date, much of the effort into resolving longer-trends for POPs has stemmed from analysis of the Alert database[1,2]. However, unlike similar POP databases collected from temperate regions such as the Great Lakes, the inherent seasonality and scatter within these data have required the application of statistical time-series analysis tools to clarify underlying trends. As a result, levels of many OC pesticides and the lower chlorinated PCB congeners have been shown to be declining in the Canadian Arctic, in line with trends reported from the Great Lakes and elsewhere [e.g 3].

In a similar monitoring programme to Alert, data from the Zeppelin Mountain station at Ny-Ålesund are available for the years 1993-2001. Analytes include selected PCB congeners, OC pesticides and PAHs. This dataset will allow contaminant trends to be examined in the context of the European Arctic and allow a spatial comparison to be conducted with Alert. This will confirm whether declining levels for some chemicals observed in the Canadian Arctic are also occurring in the Norwegian Arctic.

To extend the scope of analysis for the Alert database, PAH trends are examined in this study using a time-series analysis tool called Digital Harmonic Regression (DHR)[4]. Additionally, trends for several of the OC pesticides observed at Ny-Ålesund will also be examined and discussed in relation to the Canadian Arctic.

Methodology

Air sampling, chemical analysis, quality controls and data management for the respective arctic databases are coordinated and organised through national programmes by the Meteorological Services of Canada (MSC) (Alert data) and the Norwegian Institute of Air Research (NILU) (Ny-Ålesund data). Details of respective air monitoring programmes can be found in Fellin*et al*.[5] and Oehme *et al.*[6]. Subtle differences between the two programmes are apparent which may affect interpretation of the chemical data. For example, air samples collected at Ny-Ålesund are acquired over a 48 h period each week, as opposed to an integrated 7-day period at Alert. Furthermore, air concentrations determined at Alert are adjusted to standard temperature and pressure and method detection limits (MDLs) are found to vary from year to year and between the two locations for a particular analyte.

Trend analysis Dynamic Harmonic Regression(DHR)is a statistical time series tool used in the modelling of environmental data to provide overall trend information and forecast scenarios[4]. DHR is similar to Digital Filtration (DF), a statistical tool successfully applied to the Alert datasets (PCBs and OC pesticides)[1,2].

The DHR model is described by equation (1):

$$Y_t = T_t + C_t + S_t + e_t \quad (1)$$

where Y_t is the observed time series; T_t is the underlying trend or low-frequency component within the data; C_t is the sustained cyclical or quasi-cyclical component (e.g. occurrence of Arctic haze within the winter season, that may have a periodicity differing from a typical seasonal trend); S_t is the seasonal component and e_t is the irregular component defined by a normally distributed Gaussian sequence with zero mean value and variance σ^2 e.g. the 'white noise' component.

The most important of these components given in equation (1) are the cyclical(C_t) and seasonal components (S_t) where;

$$C_t = \sum_{i=1}^{R_c} (\alpha_{i,t} \cos(f_i t) + \beta_{i,t} \sin(f_i t)) \quad (2)$$

$\alpha_{i,t}$and $\beta_{i,t}$ are stochastic time variable parameters (TVPs) and $f_i t$ = 1,2,…R_c, andR_c is the fundamental and harmonic frequencies associated with the cyclical component (usually spanning shorter time periods than the seasonal component); and

$$S_t = \sum_{i=1}^{R_s} (a_{i,t} \cos(\omega_i t) + b_{i,t} \sin(\omega_i t)) \quad (3)$$

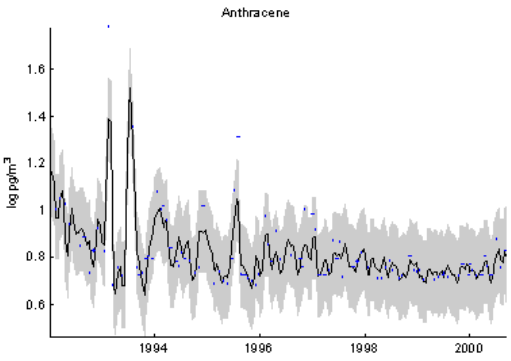
where$a_{i,t}$ and $b_{i,t}$ are stochastic TVPs and ω_it = 1,2…R_s, and R_s are the frequencies associated with the seasonal component. Equations (2 and (3) ensure that the model fits the observed data reasonably well and this fit generally improves when the white noise component is relatively small and the seasonality is pronounced and regular.

The DHR model, while similar to DF, incorporates not only 'seasonal' and 'cyclical' components, but also a 'white noise' component, which enables the underlying trend to be identified above the background noise often inherent in atmospheric data. 'White noise' may arise due to erratic air mass movements and/or local/regional sources. The utilisation of stochastic TVPs inherent in the DHR model allows for the seasonality in the POPs data to be removed (or filtered) and also enables interpolation over missing or erroneous data points. Furthermore, DHR allows for the evolution of 'seasonalities' and prevents 'end effects' where the final data in a time-series may skew the underlying trend. As such DHR provides greater confidence when displaying longer-term year-on-year trends in air data.

Results and Discussion

Figure 1 displays the time series of two PAHs measured at Alert; anthracene (a) and benzo[*a*]pyrene (b). Air concentrations (vapour and particle) were first $\log_{10}$ transformed prior to analysis using DHR and the shaded areas in each plot represent the uncertainty in the model fit (solid black line) to one and three standard deviations respectively. Anthracene, a relatively reactive, lower molecular weight PAH, does not exhibit the regular seasonal 'component' displayed by benzo[*a*]pyrene. The pronounced peaks in the early years of the anthracene time-series can be attributed to local combustion events at Alert, but the lack of the cyclical wintertime increases in concentrations serve to highlight the contrasting nature of these two PAHs. The DHR model fit is stronger for benzo[a]pyrene (r^2=0.33) than anthracene (r^2=0.18) due to the strong seasonal component evident in the benzo[*a*]pyrene database.

a)



b)

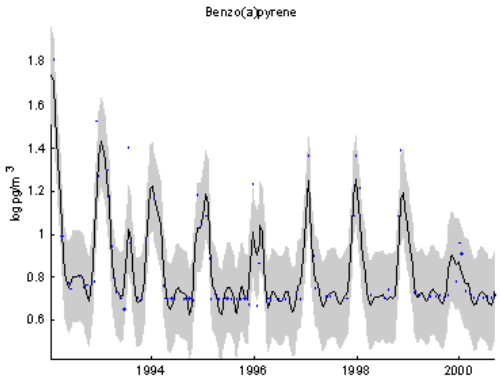


Figure 1. DHR time-series model fit (solid line) to anthracene and benzo[*a*] pyrene data (dots) from Alert.

To illustrate the underlying trend, Figure 2 shows the seasonally adjusted or 'filtered' data and trend line for both anthracene and benzo[*a*]pyrene. Many of the higher MW PAHs show a more pronounced decline in the early 1990's, followed by a 'levelling off' in concentrations from the mid-1990's onwards. This observation is similar to the trends exhibited by a number of basic air pollutants and heavy metals also monitored at Alert[7]. These authors concluded that reductions in industry in the former Soviet Union in the early 1990's may have been responsible for the reduction in these air pollutants. This may also be the case for particle-bound PAHs and has implications regarding the major PAH source types to be impacting the Arctic over the last two decades. Prior to the 1990's, PAHs in the arctic atmosphere appear to be dominated by industrial sources, rather than through general combustion related to space heating and transport - the latter maintaining concentrations through the mid-1990s onwards.

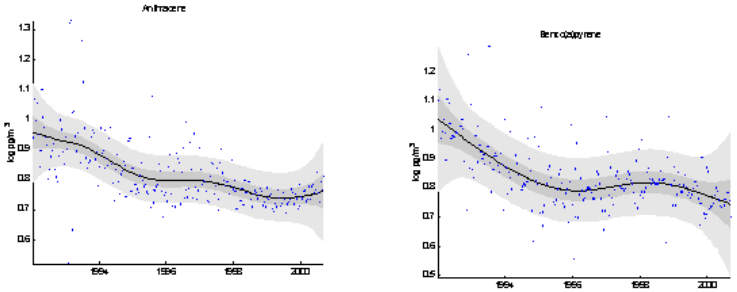


Figure 2. Long-term trends of anthracene and benzo[a] pyrene at Alert.

DHR has also been applied to the OC pesticide database from Ny-Alesund. For the HCHs, cyclical components include the increase in concentrations during the spring months for both α- and γ-HCH, which corresponds to findings from Alert. The underlying trend shows a reduction in concentrations for both HCH isomers, although a steeper decline is evident for α-HCH. Figure 3 illustrates the observed data (1993-2001) for α-HCH (a) and γ-HCH (b). Again, the long-term trends are concurrent with findings from the Canadian Arctic, suggesting that differences in regional sources between the Canadian and European Arctic

are not apparent and that levels of both HCHs appear to be declining uniformly at the two sites.

a) b)

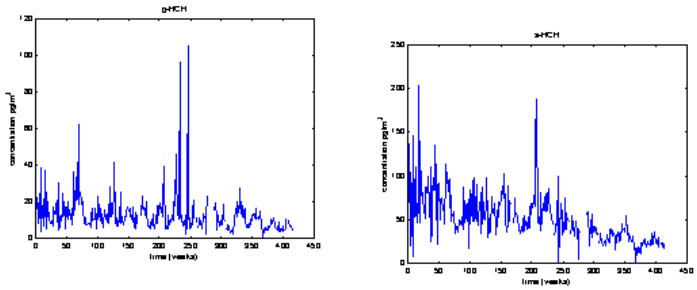


Figure 3. Concentrations of γ-HCH (a) and α-HCH (b) measured at Ny-Ålesund (1993-2001)

References

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