MODELLING OF THE SEASONAL DISTRIBUTION AND BEHAVIOUR OF PCBs IN A DYNAMIC ANTARCTIC PLANKTON ECOSYSTEM

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Introduction

Persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs) are found in the Antarctic environment largely as a result of long-range atmospheric transport from lower latitudes[1]. A series of successive condensation/ volatilization processes known as cold trapping eventually results in polar-regions becoming a sink for such compounds[2,3]. POPs including PCBs were first found in Antarctic biota in the 1960s and 1970s and subsequent investigation has found a widespread distribution in biotic and abiotic components of this environment, albeit usually at relatively low concentrations compared to those found in analogous samples from more temperate locations[4-6].

By definition, PCBs are regarded as persistent organic compounds. Under Antarctic conditions of low temperature and winter darkness, the rates of any transformation processes particular congeners may undergo would be expected to be minimized[7]. It is claimed that polar organisms have developed comparatively few mechanisms to deal with xenobiotic substances[7], thus exposure to relatively low concentrations of PCBs could be problematic, particularly because of the simple Antarctic food webs. Organisms at the top of food chains depend on only a few species such as Antarctic krill (*Euphausia superba*). Krill in turn feed on phytoplankton and therefore any chemical impact on plankton could have serious consequences for the entire ecosystem[7,8].

With potential climate change, condensed PCBs may be volatilized and redistributed in the Antarctic[9]. Thus, it is important to understand the factors governing their distribution and behaviour. Multi-compartment fugacity-based models are useful tools in this regard[10]. Van den Brink et al.[11] have recently concluded that concentrations of PCBs are declining in pelagic species in Antarctica such as seabirds, but not in benthic organisms leading to speculation that the total environmental burden may not be declining at all. Therefore models should consider PCB levels in sediment and detritus. Polar marine environments are also characterized by strong, seasonal variations in light and temperature that drive plankton blooms in the spring and summer months and play a major role in biogeochemical cycling. Models also need to accommodate these factors. Cropp et al. [8] recently developed a mass conserving fugacity-based model comprising a dynamic plankton food web model coupled to a model of the physical environment for this purpose.

In this work, we apply the model of Cropp et al. to investigate and compare the behavior of 9 different PCB congeners over a 12-month period in a plankton-based ecosystem in a representative region of the Southern Ocean, on the Antarctic continental shelf. Not only are PCBs worthy of such investigation in their own right, they possess a range of physicochemical properties such as log K_{OW} and Henry's Law Constants (H) that enable any systematic influence of such properties on chemical behavior to be discerned.

Materials and methods

PCB congeners considered were PCB-3, -15, -31, -52, -101, -105, -118, -153 and -180, that is, ranging from monochloro- to heptachlorinated compounds. Values of log K_{OW}, H, vapor pressure and the internal energies of phase transfer necessary to estimate the values of these properties at different temperatures are taken from Li et al.[12]. Values of K_{OW} increase by a factor of over 300 in going from PCB-3 to PCB-180 while vapor pressures decrease by a factor of over 4000. Uptake rate constants (k_u) with phytoplankton are taken from Dachs et al.[13,14]. There is little kinetic data for PCBs in zooplankton so uptake rate constants were derived from an empirical relationship between k_u and log K_{OW} for PAHs[15] by interpolation with PCB log K_{OW} data.

The model is described in detail in Cropp et al.[8]. The physical domain is a $1m^2$ column of air, water and

sediment, that is open to fluxes of energy but is closed to PCB fluxes. The vertical depths of these compartments are 1000, 100 and 0.05 m respectively. The seasonal phytoplankton biomass cycle was derived from SeaWiFS satellite measurements of chlorophyll-a (**Figure 1**). Lipid content was assumed to be 10% for phytoplankton and 4.5% for zooplankton. A detritus compartment comprising dead plankton and their respiration products was also included in the model. Sea surface temperatures from the satellite based Advanced Very High Resolution Radiometer and monthly mean air temperatures, sourced from a thirty year archive measured at the Dumont D'urville base located just south of the study region, were used to generate annual temperature profiles for sea and air respectively[8].

The flux expression describing the time dependance of PCB mass in phytoplankton is of the form:

$$V_p Z_p \frac{df_p}{dt} = Inputs - Outputs - f_p Z_p \rho_p \frac{dP}{dt} - f_p \rho_p P \frac{dZ_p}{dt}$$

where V_p, Z_p, ρ_p and f_p are volume, fugacity capacity constant, density (lipid basis) and PCB fugacity in phytoplankton respectively. The penultimate term corrects PCB fugacity in phytoplankton (f_p) for changes in phytoplankton biomass and the last term corrects Z_p for changes in temperature. Expressions for zooplankton and detritus are analogous, but those for air, water and sediment compartments do not include a volume correction term. For comparative purposes, an equimolar amount of each PCB congener of interest was injected into the model environment. Degradation processes were not considered.

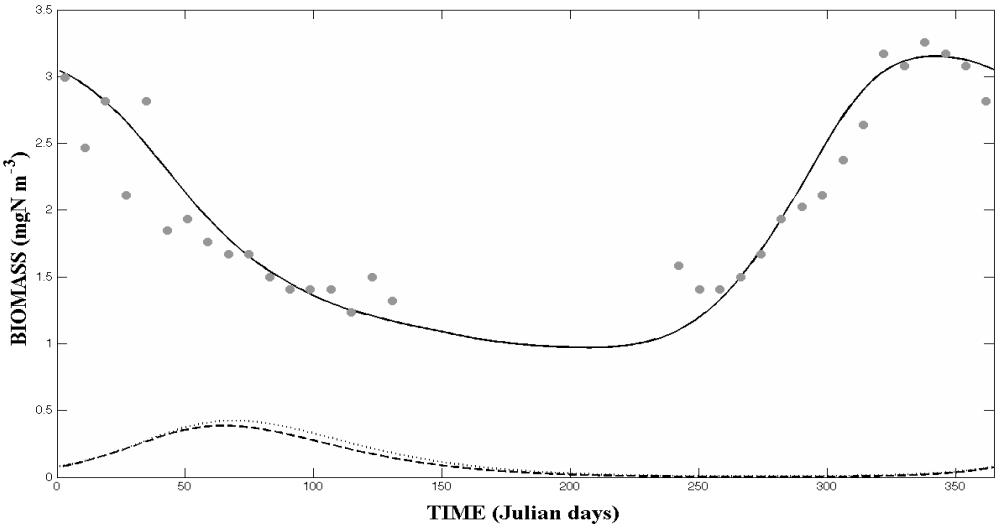

Figure 1. Calibrated annual phytoplankton biomass (mgN m^{-3}) derived from SeaWiFS chlorophyll-a data (dots) using Redfield ratios. The solid line is phytoplankton biomass, zooplankton biomass is shown by the dashed line, and detritus mass by the dotted line.

Results and discussion

The trends in congener K_{OW} and vapour pressure values are reflected in relative congener concentrations in air and water phases. There is little annual variation in air concentrations and mean values for the various PCBs fall by a similar amount to vapor pressure. Maximum concentrations in water tend to be observed between 150 and 200 (Julian) days, although again, annual variation is not large (less than a factor of 3). Mean concentrations for PCB-3 are 1000 times less than those for PCB-180. For sediment, there is typically less than a 1% change in concentration throughout the year for all PCBs investigated. Further, mean concentrations increase by only 30% from PCB-3 to PCB-180. This is also the compartment that has the highest mass for all congeners, typically accounting for 99.9% of the mass of PCB. The sediment reservoir is sufficiently large that PCB exchange with water through diffusion and deposition and resuspension of particles does not significantly affect the relative concentration. These results indicate physicochemical properties of PCBs influence concentrations in air, water and sediment rather than seasonal variations in plankton levels. For hexachlorobenzene, it was also shown that

temperature rather than plankton dynamics was responsible for most of the seasonal concentration variation in these phases[8]. It might therefore be expected that sustained changes in temperature would similarly affect PCBs in polar regions, which has implications for future climate change effects.

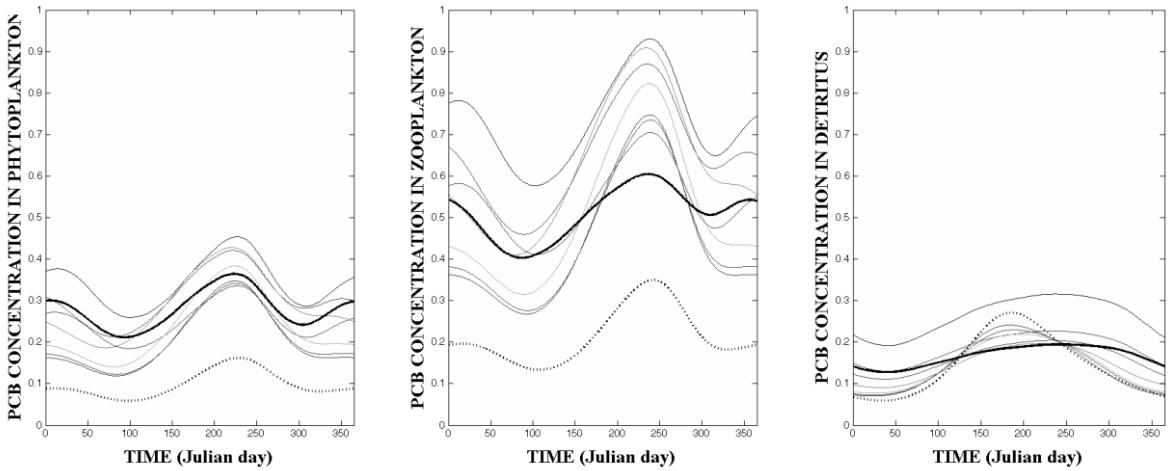

Figure 2. Seasonal variations in relative concentrations of PCB congeners in phytoplankton, zooplankton and detritus in a dynamic Antarctic plankton ecosystem. PCB-3 is shown as the dark solid line, PCB-180 as the dark dotted line, and the other congeners as the gray lines.

More interesting features emerge on comparison of temporal trends of PCBs and their relative concentrations in phytoplankton, zooplankton and detritus (**Figure 2**). These compartments have the highest concentrations, at least an order of magnitude higher than those found in the sediment. For phytoplankton, lesser-chlorinated species show a bimodal pattern with peak concentrations around the beginning of the year (Julian day zero) and the biggest around July-August. The latter corresponds to the time period when plankton biomass reaches a minimum during the year. As the size of PCBs increase, the pattern changes to one very dominant peak, slightly later in the year. Contrary to what might be expected on the basis of their log K_{OW} values, maximum phytoplankton concentrations do not increase with chlorine number. Diffusive uptake rates from water increase, but it appears that PCB losses from the population as a result of diffusive loss, mortality and grazing increase by factors at least as great. Peak PCB concentrations in zooplankton lag behind those in phytoplankton. Overall, plankton concentrations can change by up to 300% during the year. Detritus concentrations are typically lower those in phytoplankton with peak levels observed in late winter or early spring when minimum detritus mass occurs. Despite being an abiotic phase, detritus concentration trends are governed by plankton dynamics.

Concentrations in zooplankton are invariably greater than those in phytoplankton, regardless of congener and season. This may be quantified by a biomagnification factor expressed as the ratio of the concentration in zooplankton over that in phytoplankton, both expressed on a lipid weight basis. Annual trends in biomagnification factors for the smallest and largest congeners under consideration (PCB-3 and PCB-180) are compared in **Figure 3**. For both, peak values are observed in the Antarctic autumn and spring with the largest predicted in spring. What is striking is that there is little difference the magnitude of these maximal values (2.1 and 2.5 respectively) despite hydrophobicity as measured by $\log K_{OW}$ increasing from 4.65 to 7.16.

There has been uncertainty as to the biomagnification of other POPs by zooplankton in Antarctic marine food webs. Kelly et al.[16] suggested that for high K_{OW}, high K_{OA} compounds such as most PCBs, biomagnification for water respiring organisms could be predicted from K_{OW} alone. This approach correctly estimates the maximum biomagnification factors for PCB-180 and -153 of approximately 2.5. However, it appears to underestimate values for less chlorinated congeners and does not account for temporal variation. In contrast, several field based studies report little biomagnification of POPs[17].

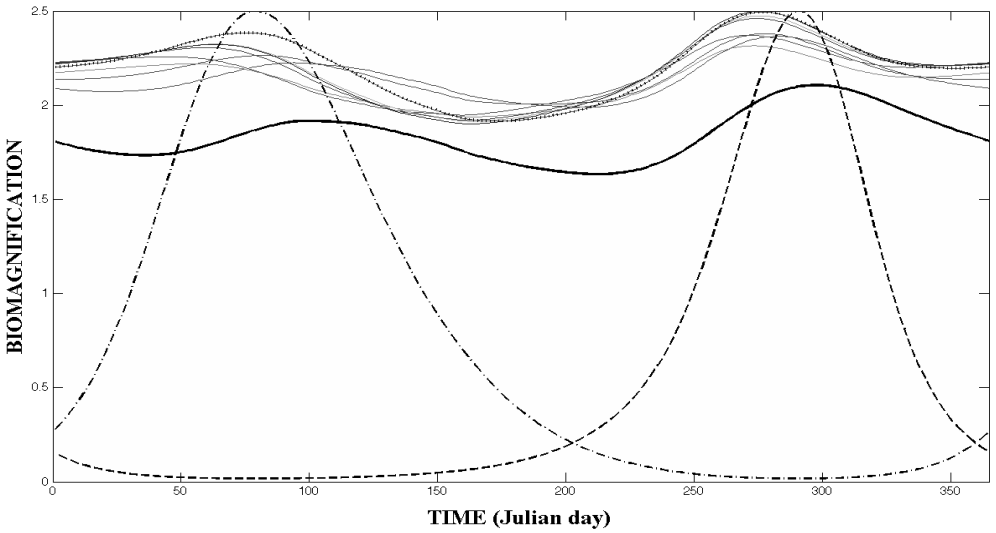

Figure 3. A comparison of seasonal biomagnification factor trends for PCB congeners. PCB-3 is shown by the solid dark line, PCB-180 by the dark dotted line and the other PCB congeners by the gray lines. The dashed lines represent the plankton biomass ratios: *Z/P* (left peak) and *P/Z* (right peak).

Our work reveals some of the basis for this uncertainty. While compound specific physicochemical factors may play some role in controlling the distribution of POPs in the marine environment, biological drivers are equally, if not more, important. Seasonal variation in the zooplankton biomagnification factor as shown in **Figure 3** is likely and may therefore be sensitive to when it is measured. Measurements made in summer, as they typically are in polar marine environments, may underestimate the maximum biomagnification factor by up to 25%.

In summary, seasonal temperature and light forcing of Antarctic plankton ecosystems within which a range of PCBs are distributed allow insights into factors influencing distribution and behavior. Air, water and sediment concentrations appear governed by compound-specific parameters such as $\log K_{OW}$ and temperature, but only subtly influenced by plankton dynamics. This situation is reversed for PCBs in plankton and detritus.

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