THE ENVIRONMENTAL RELEVANCE OF LABORATORY MEASURED TOXICITY THRESHOLD CONCENTRATIONS OF p,p'-DDE IN ANTARCTIC KRILL (*EUPHAUSIA SUPERBA*); A MODELING ASSESSMENT BASED ON MEASURED ENVIRONMENTAL LEVELS

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Introduction

Measurements of the dominant DDT metabolite p.p'-DDE in the Southern Ocean near Antarctica have revealed low lipid-based concentrations in wild krill (*Euphasia superba*) populations, in the order of 10^{-8} mol/m^3 lipid.[1] These levels are well below toxic threshold lipid-based concentrations of p.p'-DDE at which behavior modification has been observed in krill in laboratory experiments of approximately 0.37 mol/m^3 lipid[2]. This discrepancy of many orders of magnitude ostensibly suggests that there exists little likelihood of observing toxic effects of p.p'-DDE in wild populations of krill in Antarctica.

Modelling persistent organic pollutants (POPs) such as DDE in plankton populations in the natural environment poses particular problems due to seasonal changes in population sizes. The strong seasonal variation in photosynthetically available radiation (PAR) experienced by coastal marine ecosystems in polar regions induces the largest variations in phytoplankton biomass on the planet, and consequently grazer populations such as krill experience large seasonal fluctuations in biomass. Rigorous modelling of DDE and other POP distributions in Antarctic marine biota therefore requires careful treatment of 'growth dilution' and 'digestive concentration' processes. Here we use a mass-conserving dynamic fugacity model of POP movement in Antarctic marine plankton ecosystems[3] to simulate the distribution of p,p'-DDE in Antarctic food webs.

We assess the likelihood of wild krill populations accumulating *p,p'*-DDE in their lipid to levels associated with toxic responses in Antarctic krill under laboratory conditions. Abiotic environmental *p,p'-DDE* data is limited to one publication from McMurdo Sound, Antarctica, where relatively high levels of p.p'-DDE (4×10^{-5} mol m^{-3} dry weight) have been measured in sediments.[4] Antarctic krill are thought to spend winter periods of low food supply on the continental shelf[5] and have been observed feeding on detritus associated with bottom sediments[6]. We therefore examined the sensitivity of our results to different assumptions regarding the feeding ecology of the krill[7]. Our results suggest that it is feasible that sub-lethal toxic levels of p,p'-DDE could be reached in populations of krill feeding at highly contaminated sites.

Materials and methods

We simulated the distribution of p,p'-DDE in the environment beside the ice dock at McMurdo Station where p,p'-DDE sediment concentrations of 4.0-4.7 ng g^{-1} (dry weight) have been measured.[4] We modelled p,p'-DDE dynamics in a one square metre column composed of air (1,000 m high), water (33 m deep) and sediment (0.1 m deep) that did not allow fluxes of p,p'-DDE across its boundaries. The model domain contained a mass of 4×10^{-6} mol of p,p'-DDE reflecting the concentrations measured in the sediment in McMurdo Sound.

Parameter values for the ecosystem dynamics component of the model were obtained by modifying literature values so that model predictions of chlorophyll-a matched a 10-year climatology of chlorophyll-a measurements in McMurdo Sound measured by the MODIS TERRA satellite sensor. The ecosystem submodel was forced with a climatology of photosynthetically active radiation (PAR) and sea surface temperature (SST) also measured by MODIS TERRA. The ecosystem submodel is coupled to a fugacity submodel that calculates the fugacity of p,p'-DDE in the air, water, sediment compartments, the phytoplankton and zooplankton populations, and detritus. The flux expression describing the time dependance of p,p'-DDE 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 Z_p, and f_p are the fugacity capacity (mol Pa^{-1} m^{-3}) and fugacity (Pa) of p,p'-DDE in phytoplankton and V_p, and ρ_p are the phytoplankton lipid volume (m^3) and density (mgN m^{-3} lipid) respectively and P is the phytoplankton population (expressed as mgN m^{-3}).. The penultimate term corrects p,p'-DDE fugacity in phytoplankton (f_p) for changes in phytoplankton biomass and the last term corrects Z_p for changes in temperature. Degradation processes were not included in this model as they are insignificant over the time scales we simulate. These expressions for krill include dietary uptake of p,p'-DDE from phytoplankton, which increases the mass of p,p'-DDE in the krill. The concentration of p,p'-DDE in krill (denoted by subscript Z for zooplankton) as a result of feeding may increase or decrease depending on its change in volume. Expansion of the volume correction term, using volumes derived from the ecosystem model, reveals that the change in concentration depends on the relative concentrations in the phytoplankton and krill:

$$V_Z Z_Z \frac{df_Z}{dt} = D_{ZW}\left(f_W - f_Z\right) + \left(f_P r_P Z_P - f_Z r_Z Z_Z\right) j\,PZ - V_Z f_Z \frac{dZ_Z}{dt}$$

Here, the middle term on the right hand side reveals the dependency of the changes in the fugacity of p,p'-DDE in krill on the relative concentrations in the krill and phytoplankton. Here, φ is an encounter rate for zooplankton grazing on phytoplankton. A similar term may be included to describe krill feeding on detritus.

The fugacity model was forced by a 30-year air temperature climatology measured at the McMurdo Station and the 10-year SST climatology measured by MODIS TERRA. The Van't Hoff relationship[8] was used to correct temperature dependent parameters [Henry's law constant (H), the octanol/water partition coefficient (K_{OW}) and the sub-cooled liquid vapour pressure (P^s_l)] as described by Shen and Wania[9] and Bogillo and Bazylevska [10] using a reference temperature of 298K and the internal phase transfer energies of p,p'-DDE.

The coupled ecosystem-fugacity model was used to investigate the uptake of p,p'-DDE into plankton, the seasonal changes in partitioning of p,p'-DDE between biota and air, water and sediment, and the biomagnification of p,p'-DDE in zooplankton. Here, biomagnification is defined as the ratio between the concentration p,p'-DDE in zooplankton to its concentration in phytoplankton. We also examined the sensitivity of the p,p'-DDE concentration in krill to changes in the fraction of detritus in contact with the sediment and the rate at which krill grazed upon detritus.

Results and discussion

The simulation results show that the seasonal variation induced in the plankton by seasonal changes in light and temperature (Figure 1, left panel) cause noticeable seasonal variations in the concentrations of p,p'-DDE in all phases apart from sediment (Figure 2), and in the krill biomagnification factor (Figure 1, right panel).

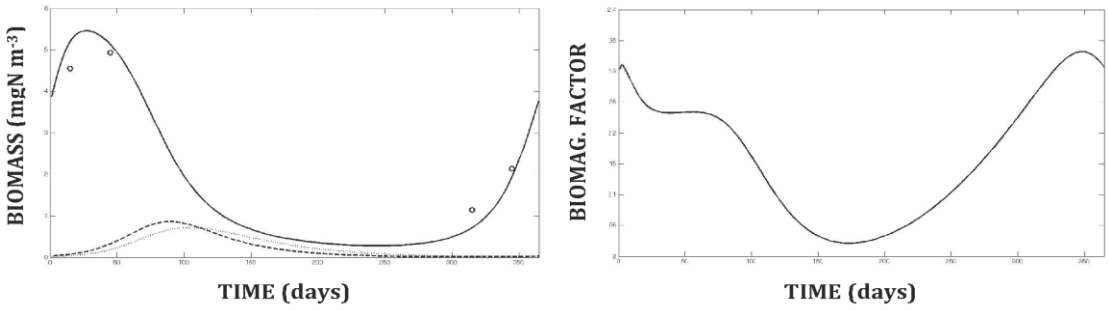

Figure 1. Seasonal variations in plankton dynamics (left panel): phytoplankton biomass from model (solid line) and satellite (dots); krill (dashed line) and detritus (dotted line). Right panel shows seasonal variation of biomagnification of p,p'-DDE in krill.

The majority (over 99%) of the p,p'-DDE is in the sediment, where seasonal variations are also induced, but are not obvious in Figure 2, and in field measurements would likely be overwhelmed by spatial variation. The seasonal variations in the environment however result in a small fraction of the sediment burden moving into the

water column, and thence into the phytoplankton, and then krill, as a result of the spring phytoplankton bloom. This results in the noticeable seasonal cycles of p,p'-DDE concentration in the biota, where lipid concentrations vary by approximately ±20% of the annual mean. The steady state concentrations in Figure 2 show that p,p'-DDE concentrations in biota are several orders of magnitude greater than those of the physical compartments.

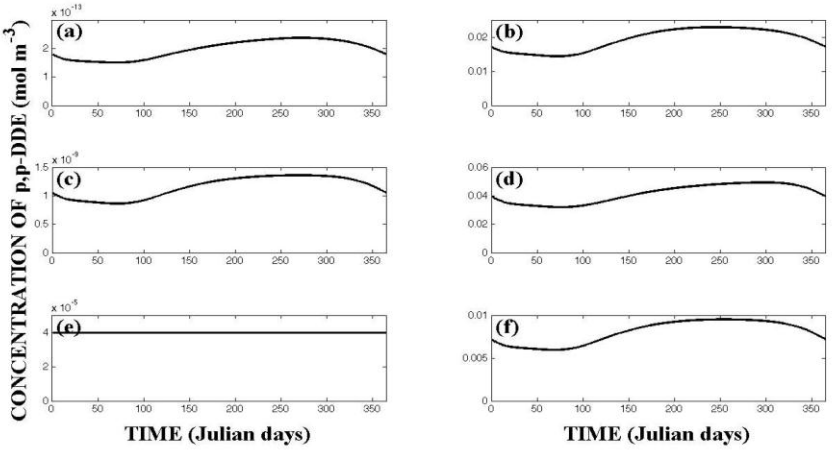

Figure 2. Concentration of p,p'-DDE in air (a), water (c), sediment (e), phytoplankton (b), krill (d), detritus (f).

The model simulations shown in Figure 3 that started with zero p,p'-DDE burden in the biota at the start of the spring phytoplankton bloom (simulating uncontaminated biota moving into a contaminated area) reveal that phytoplankton reach their maximum p,p'-DDE concentration in a matter of days, as they rapidly equilibrate with the fugacity of p,p'-DDE in the surrounding water via diffusion-like processes. Similarly, p,p'-DDE concentration in the detritus increase rapidly in this scenario as a result of the production of high-concentration waste by phytoplankton and zooplankton. We observe that the introduction of the biota induces some differences in the seasonal dynamics in the water compartment (cf Figures 2 and 3) due to the transient dynamics introduced by the biota, but the two simulations are identical after the first year.

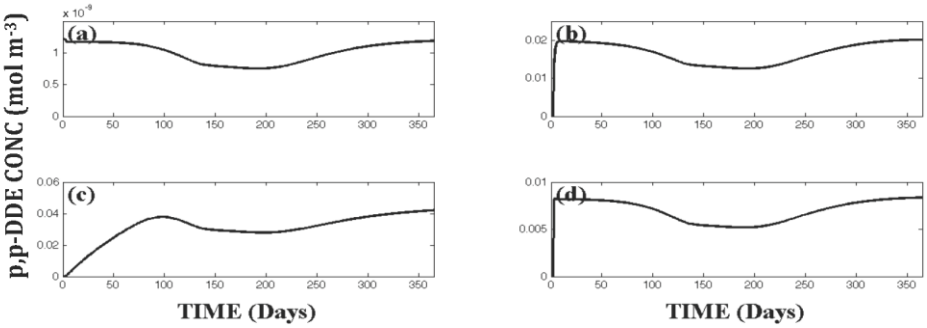

Figure 3. Concentration of p,p'-DDE in water (a), phytoplankton (b), krill (c) and detritus (d) showing the rate of uptake into the food chain. Phytoplankton, krill and detritus have zero p,p'-DDE burden at day zero, which is Julian day 245, when the modeled phytoplankton population is at its minimum.

Maximum p,p'-DDE concentrations in krill are achieved more slowly than those in phytoplankton, reflecting that the major pathway of p,p'-DDE into krill is via dietary intake. However, the simulations indicate that the krill p,p'-DDE concentration can reach close to its maximum level in approximately 100 days, suggesting that krill populations that only move inshore to feed in summer could achieve concentrations similar to those shown to produce sub-lethal toxic effects in the laboratory.

The feeding ecology and overwintering strategy of Antarctic krill are still poorly understood, but it appears that feeding on detritus may be an important component of the strategy[7]. The potential for such ecological dynamics

to affect the partitioning of POP in an environment depends on the characteristics of the particular chemical. An analysis of the sensitivity of the annual average krill p,p'-DDE concentration to krill consumption of detritus (c) and the fraction of detritus in contact with bottom sediments (Ω), reveals that moderate consumption of suspended detritus has the potential to increase the annual average concentration of p,p'-DDE in krill significantly (Figure 4). Note that Figures 2 and 3 do not include krill feeding on detritus ($c = 0$) and there is no contact between detritus and bottom sediments ($W = 0$).

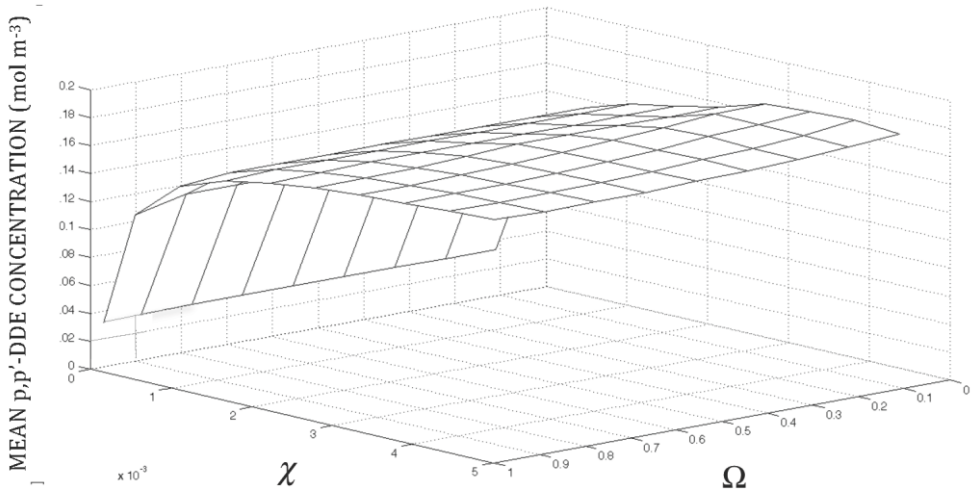

Figure 4. Sensitivity of annual average concentration of p,p'-DDE in Antarctic krill to different assumptions of the fraction of detritus in contact with bottom sediments (Ω) and the rate of consumption of detritus by krill (c).

However, if krill don't feed on detritus ($c = 0$), and all detritus makes contact with bottom sediments ($W = 1$), then the annual average p,p'-DDE concentration in krill may be reduced. Note the concentrations predicted for krill feeding on detritus approach the concentration observed to cause toxic effects in krill in laboratory experiments (0.37 mol m^{-3} lipid). This is a reasonable result given that the acceptable level of model skill in this field is within an order of magnitude[11]. The results of this heuristic modelling study suggest that it is not unreasonable to postulate that wild populations of krill that reside in or seasonally visit bays in Antarctica that are heavily polluted by p,p'-DDE may experience toxic effects. These model predictions may be improved by the availability of additional measurements of POP concentrations and processes in Antarctica, and by an improved understanding of krill ecology.

References:

1. Bengtson Nash S, Poulsen A, Kawaguchi S, Vetter W, Schlabach M. (2008) *Sci Tot Environ*. **407**: 304-314
2. Poulsen A, Kawaguchi S, Kukkonen J, Leppänen M, Bengtson Nash S. (2012) *Environ Poll*. **160**: 185-191
3. Cropp R, Kerr G, Bengtson Nash S, Hawker D. (2011) *Environ Chem*. **8**: 263-280
4. Risebrough R, de Lappe B, Younghans-Haug C. (1990) *Mar Poll Bull.* **21** (11): 523-529
5. Nicol S. (2006) *Biosci.* **56**(2): 111-120
6. Clarke A, Tyler P. (2008) *Curr Biol.* **18**: 282-285
7. Meyer, B. (2012) *Polar Biol.* **35**: 15-37
8. Schwarzenbach R, Gschwend P, Imboden D. (2003) *Environmental Organic Chemistry*. 2nd Edition, Hoboken: John Wiley & Sons
9. Shen L, Wania F. (2005). *J Chem Eng Data.* **50**: 742-768
10. Bogillo, V, Bazylevska, M. (2008)*Variations of Organochlorine Contaminants in Antarctica.*, in *The Fate of Persistent Organic Pollutants in the Environment*, Mehmetli E, Koumanova, B.,Eds. 2008, Springer: Dordrecht, Netherlands: Springer.
11. Kelly B, Ikonomou M, Blair J, Morin A, Gobas F. (2007) *Science* **317**: 236 - 239