Accessory publication

A dynamic biophysical fugacity model of the movement of a persistent organic pollutant (POP) in Antarctic marine food webs

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Fugacity model of the physical environment

The physical model simulates the partitioning of POPs between air, water and sediment. Chemical transformation of POPs is not considered as they typically have residence times in the physical environment much longer than the time scales simulated in this study.[1] The physical model is based on the fugacity concept developed by Mackay,[2] extended to adopt a Level IV approach – a dynamic model. Accommodating the effect of temperature on fugacity capacity constants the model may initially be described by Eqns 1–3, which represent the movement of POPs as a result of diffusion and transport when attached to particles between the air (*A*), water (*W*) and sediment (*S*) phases respectively:

$$V_\mathrm{A} Z_\mathrm{A} \frac{\mathrm{d}f_\mathrm{A}}{\mathrm{d}t} = D_\mathrm{AW}\left(f_\mathrm{W} - f_\mathrm{A}\right) - f_\mathrm{A} U_\mathrm{q} Q \Phi A_\mathrm{W} Z_\mathrm{x} - f_\mathrm{A} U_\mathrm{p} \Phi A_\mathrm{W} Z_\mathrm{x} - V_\mathrm{A} f_\mathrm{A} \frac{\mathrm{d}Z_\mathrm{A}}{\mathrm{d}t} \quad (1)$$

$$\begin{aligned} V_\mathrm{W} Z_\mathrm{W} \frac{\mathrm{d}f_\mathrm{W}}{\mathrm{d}t} = {} & D_\mathrm{AW}\left(f_\mathrm{A} - f_\mathrm{W}\right) + D_\mathrm{SW}\left(f_\mathrm{S} - f_\mathrm{W}\right) + f_\mathrm{A} \Phi A_W (U_\mathrm{q} Q + U_\mathrm{p}) Z_x \\ & + f_\mathrm{S} U_\mathrm{r} A_\mathrm{S} Z_\mathrm{S} - f_\mathrm{W} U_\mathrm{d} A_\mathrm{S} Z_\mathrm{W} - V_\mathrm{W} f_\mathrm{W} \frac{\mathrm{d}Z_\mathrm{W}}{\mathrm{d}t} \end{aligned} \quad (2)$$

$$V_\mathrm{S} Z_\mathrm{S} \frac{\mathrm{d}f_\mathrm{S}}{\mathrm{d}t} = D_\mathrm{SW}\left(f_\mathrm{W} - f_\mathrm{S}\right) + f_\mathrm{W} U_\mathrm{d} A_\mathrm{S} Z_\mathrm{W} - f_\mathrm{S} U_\mathrm{r} A_\mathrm{S} Z_\mathrm{S} - V_\mathrm{S} Z_\mathrm{S} \frac{\mathrm{d}Z_\mathrm{S}}{\mathrm{d}t} \quad (3)$$

where:

$$D_\mathrm{AW} = k_\mathrm{v} A_\mathrm{W} Z_\mathrm{W} \quad (4)$$

$$D_\mathrm{SW} = k_\mathrm{t} A_\mathrm{S} Z_\mathrm{W} \quad (5)$$

The model is implemented in an idealised column of air, water and sediment that is open to fluxes of energy but is closed to fluxes of mass, and therefore has zero flux of POPs across the external boundaries. The model must therefore conserve the mass of a POP, implying the conservation of mass equation in a constant temperature environment of:

$$V_\mathrm{A} Z_\mathrm{A} f_\mathrm{A} + V_\mathrm{W} Z_\mathrm{W} f_\mathrm{W} + V_\mathrm{S} Z_\mathrm{S} f_\mathrm{S} = POP_\mathrm{T} \Leftrightarrow V_\mathrm{A} Z_\mathrm{A} \frac{\mathrm{d}f_\mathrm{A}}{\mathrm{d}t} + V_\mathrm{W} Z_\mathrm{W} \frac{\mathrm{d}f_\mathrm{W}}{\mathrm{d}t} + V_\mathrm{S} Z_\mathrm{S} \frac{\mathrm{d}f_\mathrm{S}}{\mathrm{d}t} = 0 \quad (6)$$

Eqn 6 demonstrates that conservation of mass implies that the right-hand sides of Eqns 1–3 must sum to zero, and perforce if the right-hand sides of model equations sum to zero, the system conserves mass. This property provides an important analytic check on the model equations, and also provides a simple check on numerical solutions to the model that can be useful to identify programming errors.

The physical model represents the movement of POPs between the air, water and sediment that results from diffusion and association with particles that are moved through the environment by physical transport processes. Movement between air and water is as a result of three processes – diffusion and wet and dry deposition of atmospheric aerosols and dust.[2] Air–water diffusion is controlled by the air–water diffusion mass-transfer coefficient k_V (m h^{-1}), the surface area available for diffusive exchange A_w (m^2) and the fugacity capacity of water Z_W (mol m^{-3} Pa^{-1}), resulting in diffusion terms $k_v A_W Z_W f_{A,W}$ with dimensions of moles per hour.[2] Wet deposition is governed by a rain rate U_q (m h^{-1}), a scavenging ratio Q, the volume fraction of aerosols Φ, the surface area available for deposition A_W (m^2) and the fugacity capacity of aerosols Z_x (mol m^{-3} Pa^{-1}), giving a deposition term $U_q Q \Phi A_W Z_x f_A$ (mol h^{-1}).[3] Dry deposition is governed by a deposition rate U_p (m h^{-1}), the volume fraction of aerosols, the surface area available for deposition and the fugacity capacity of aerosols giving a deposition term $U_p \Phi A_W Z_x f_A$ (mol h^{-1}).[3]

The exchange of POPs between the water and sediment occurs through diffusion or the exchange of particles through deposition and resuspension. Water–sediment diffusion is described analogously to air–water diffusion by a mass transfer coefficient k_t (m h^{-1}), the surface area available for diffusive exchange A_S (m^2) and the fugacity capacity of the water Z_W (mol m^{-3} Pa^{-1}).[2] Deposition represents POPs attaching to suspended particles that sink into the sediment due to gravity, and is described by the deposition rate U_d (m h^{-1}), the surface area available for sediment deposition A_S (m^2), and the fugacity capacity of the suspended sediment, which is assumed to be the same as Z_S (mol m^{-3} Pa^{-1}). Resuspension is the opposite process to sedimentation, where particles with POPs attached are transported from the sediment and into the water column by turbulence. Resuspension of POPs is described by a resuspension rate U_r (m h^{-1}), the surface area available for sediment resuspension A_S (m^2), and the fugacity capacity of the sediment Z_S (mol m^{-3} Pa^{-1}).[2] All parameters and their values are described in Tables 1 and 2.

Fugacity steady-state

Steady-state describes the state of the system when there is no change in fugacity over time, that is df_i/dt for all $i = A, W, S$.[4] The steady-state solution of the physical system (f_i^*) is given by:

$$f_{\mathrm{A}}^{*}=\frac{f_{\mathrm{W}}^{*}D_{\mathrm{AW}}}{D_{\mathrm{AW}}+U_{\mathrm{q}}Q\Phi A_{\mathrm{W}}Z_{\mathrm{x}}+U_{\mathrm{p}}\Phi A_{\mathrm{W}}Z_{\mathrm{x}}} \quad (7)$$

$$f_{\mathrm{W}}^{*}=\frac{f_{\mathrm{A}}^{*}\left(D_{\mathrm{AW}}+U_{\mathrm{q}}Q\Phi A_{\mathrm{W}}Z_{\mathrm{x}}+U_{\mathrm{p}}\Phi A_{\mathrm{W}}Z_{\mathrm{x}}\right)+f_{\mathrm{S}}^{*}\left(D_{\mathrm{SW}}+U_{\mathrm{r}}A_{\mathrm{S}}Z_{\mathrm{S}}\right)}{D_{\mathrm{AW}}+D_{\mathrm{SW}}+D_{\mathrm{PW}}+D_{\mathrm{ZW}}+D_{\mathrm{DW}}+U_{\mathrm{d}}A_{\mathrm{S}}Z_{\mathrm{W}}} \quad (8)$$

$$f_{\mathrm{S}}^{*}=\frac{f_{\mathrm{w}}^{*}\left(D_{\mathrm{SW}}+U_{\mathrm{d}}A_{\mathrm{S}}Z_{\mathrm{W}}\right)}{D_{\mathrm{SW}}+U_{\mathrm{r}}A_{\mathrm{S}}Z_{\mathrm{S}}} \quad (9)$$

These equations describe the fugacities of POPS in the air, water and sediment after the effect of an initial input of POPS (usually through the air) has been eliminated.[2] These equations do not provide a closed form solution for the steady-state fugacities and must be solved iteratively. This is consistent with the fact that the fugacities of the compartments at steady-state describe the partitioning of POPS between the three physical compartments. To obtain the actual amount of POPS in the air, water and sediment at steady-state, these fugacities must be applied to the conservation of mass equation.[6]

Ecosystem model

The biological model represents a simple Antarctic plankton ecosystem where the biomasses of phytoplankton and zooplankton are simulated. The model is based on a simplified version of the plankton ecosystem model of Moloney and Field[5] with the addition of detritus as represented by Edwards[6] to give a nutrient–phytoplankton–zooplankton–detritus (NPZD) model (round compartments and arrows labelled 1–5 in Fig. 1). The model is given by Eqns 10–13 where all state variables (*N, P, Z* and *D*) are expressed in terms of their atomic nitrogen concentration (mg N m^{-3}):

$$\frac{\mathrm{d}N}{\mathrm{d}t}=\upsilon D-\mu\frac{N}{N+\kappa}P \quad (10)$$

$$\frac{\mathrm{d}P}{\mathrm{d}t}=\mu\frac{N}{N+\kappa}P-\varphi PZ-\sigma_{\mathrm{P}}P \quad (11)$$

$$\frac{\mathrm{d}Z}{\mathrm{d}t}=\varphi(1-\psi)PZ-\sigma_{\mathrm{Z}}Z \quad (12)$$

$$\frac{\mathrm{d}D}{\mathrm{d}t}=\sigma_{\mathrm{P}}P+\sigma_{\mathrm{Z}}Z+\varphi\psi PZ-\upsilon D \quad (13)$$

The ecosystem model is applied in the same closed system as the physical model, with no flux of nitrogen across the boundaries, and so must also conserve mass, implying the conservation equation:

$$N+P+Z+D=N_{T} \quad \Leftrightarrow \quad \frac{\mathrm{d}N}{\mathrm{d}t}+\frac{\mathrm{d}P}{\mathrm{d}t}+\frac{\mathrm{d}Z}{\mathrm{d}t}+\frac{\mathrm{d}D}{\mathrm{d}t}=0 \quad (14)$$

where N_T is the total amount of atomic nitrogen in the ecosystem. This conservation condition again provides a useful consistency check on both the model equations and the numerical solutions of the NPZD submodel.

The growth of phytoplankton on dissolved inorganic nutrient is described by Michalis–Menten dynamics ($\mu N/(N + \kappa)$), where μ is the maximum rate of nitrogen uptake by P (h^{-1}) and κ is half-saturation constant for P uptake of nitrogen (mg N m^{-3}). Zooplankton grazing on phytoplankton is represented by Lotka–Volterra interaction term (φPZ) controlled by an encounter rate of φ (m^3 mg^{-1} N h^{-1}). A proportion (ψ) of zooplankton feeding is utilised for respiration, and the remainder serves to increase zooplankton biomass. Dead phytoplankton and zooplankton ($\sigma_P P$ and $\sigma_Z Z$) and respiratory products such as zooplankton faecal pellets ($\varphi\psi PZ$) become detritus, which feeds back into the nitrogen pool through bacterial remineralisation represented by υD, where υ is the detritus remineralisation rate (h^{-1}).[6] Detritus remineralisation rates in water and sediment are assumed to be the same.

Ecosystem seasonal forcings

The model's physical domain is subject to substantial environmental forcings resulting from seasonal changes in solar irradiance, temperature and upper ocean mixing that strongly affect plankton ecosystem dynamics in Antarctic regions.[7] These forcings change the average irradiance field and temperature that the plankton experience, and can have a significant effect on phytoplankton growth rates.[8,9] The seasonal variability of the environment may also affect the transport of POPs between physical phases.[10]

The seasonal forcings are incorporated into the coupled fugacity–ecosystem model described above by replacing the maximum phytoplankton growth rate (μ) that is a constant in Eqns 10 and 11, with a time-dependant term:

$$\hat{\mu} = R_L R_T \mu \quad (15)$$

where R_L and R_T represent the effects of light limitation and temperature on phytoplankton growth respectively. The average photosynthetically active radiation (the portion of the electromagnetic spectrum between 400 and 700 nm) in the upper mixed layer of the ocean (I_{AV}) is given by:

$$I_{AV} = I_0 \int_{z=0}^{z=MLD} e^{-k_L z} dz = \frac{I_0}{k_L MLD}\left(1 - e^{-k_L MLD}\right) \quad (16)$$

where I_0 is the daily average sea surface photosynthetically active radiation (Einsteins m^{-2} d^{-1}) measured by the Sea-viewing Wide Field-of-view Sensor (SeaWiFS) satellite, k_L is the light attenuation coefficient of seawater (m^{-1}) also measured by SeaWiFS, and MLD is the depth of the mixed layer (m) from the World Oceanographic Atlas (WOA98). The effect of changes in the average irradiance on phytoplankton growth is then given by[11]:

$$R_{\mathrm{L}} = \frac{I_{\mathrm{AV}}}{I_{\mathrm{SAT}}\sqrt{1+\left(\frac{I_{\mathrm{AV}}}{I_{\mathrm{SAT}}}\right)^2}} \quad (17)$$

where I_{SAT} is the phytoplankton saturating irradiance.

The temperature dependence of phytoplankton growth used in the model is based on the estimate of Eppley[8]:

$$R_{\mathrm{T}} = e^{0.063(T-T_{\mathrm{MAX}})} \quad (18)$$

where T is the ambient temperature (°C) and T_{MAX} is the maximum annual temperature (°C), both measured by the AVHRR satellite sensor.

Ecosystem steady-state

The steady-state solutions for the NPZD model are given by:

$$P^* = \frac{\sigma_Z}{\varphi(1-\psi)} \quad (19)$$

$$Z^* = \frac{\mu N^*}{\varphi\left(N^*+\kappa\right)} - \frac{\sigma_{\mathrm{P}}}{\varphi} \quad (20)$$

$$D^* = \left[\frac{\sigma_{\mathrm{Z}}}{\upsilon\left(1-\psi\right)}\right]\left(\frac{\sigma_{\mathrm{P}}}{\varphi}+Z^*\right) \quad (21)$$

$$N^* = \frac{-\beta-\sqrt{\beta^2-4\gamma}}{2} \quad (22)$$

where

$$\beta = \kappa - N_T + \left(1+\frac{\sigma_{\mathrm{P}}}{\upsilon}-\frac{\sigma_{\mathrm{P}}\psi}{\upsilon}\right)P^* + \left(\frac{\mu-\sigma_{\mathrm{P}}}{\varphi}\right)\left(1+\frac{\sigma_{\mathrm{Z}}}{\upsilon}\right) + \frac{\varphi\psi}{\upsilon}P^* \quad (23)$$

$$\gamma = \kappa\left[\left(1+\frac{\sigma_{\mathrm{P}}}{\upsilon}-\frac{\sigma_{\mathrm{P}}\psi}{\upsilon}\right)P^* - N_{\mathrm{T}} - \frac{\sigma_{\mathrm{P}}}{\varphi}\left(1+\frac{\sigma_{\mathrm{Z}}}{\upsilon}\right)\right] \quad (24)$$

The stability of the steady-state of the NPZD model is determined by the eigenvalues of the Jacobian matrix of the system (i.e. the linearised system) at the location of the steady-state described by Eqns 19–22. It was shown by Kolmogorov[12] that predator–prey systems, such as NPZ systems, typically have oscillatory dynamics, whereas Edwards[6] showed that the addition of detritus to an NPZ model, when zooplankton did not graze on the detritus, did not alter the dynamics of the NPZ system. NPZD models therefore generally have oscillatory dynamics that either come to a steady-state or repeatedly oscillate with fixed amplitude. The NPZD model described here has a stable steady-state for the parameter values used in this analysis.

Coupled fugacity–ecosystem model

The coupled fugacity model includes the fugacities of the phytoplankton (f_P), zooplankton (f_Z) and detritus (f_D) in addition to the fugacities of the air, water and sediment. The fundamental difference between the physical and biological compartments in the coupled model is that the volumes of the biological compartments change over time, whereas the volumes of the physical compartments are constant. Coupling of the physical and biological models therefore requires that the effect of the change in volume of the biological compartments on the fugacity of the compartment be correctly described. It is common in fugacity models of, for example, fish to include a growth dilution term to account for the effect of the change in volume. This approach is a reasonable approximation for a fish that is modelled in the linearly increasing part of its growth. However, it is not appropriate for plankton populations that grow nonlinearly and exhibit significant increases and decreases in biomass over an annual cycle.

The coupled fugacity–ecosystem model is applied in the same closed environment as the physical fugacity and ecosystem models, and must therefore also conserve mass. The mass conservation equation for nitrogen for the coupled model is the same as that for the ecosystem model (Eqn 14), but the equation for conservation of mass of POPS for the coupled model is:

$$V_A Z_A f_A + V_W Z_W f_W + V_S Z_S f_S + V_P Z_P f_P + V_Z Z_Z f_Z + V_D Z_D f_D = POP_T \quad (25)$$

where V_P, V_Z and V_D are the volumes of phytoplankton, zooplankton and detritus, Z_P, Z_Z and Z_D are the fugacity capacities of phytoplankton, zooplankton and detritus respectively, and POP_T is the total amount of POP in the system. As the ecosystem model is a population model, the volumes of phytoplankton, zooplankton and detritus will vary as the populations grow and decline over a season, and this will affect the fugacity of the biological compartments. Differentiating Eqn 25 with respect to time gives:

$$V_A \frac{\mathrm{d}(Z_A f_A)}{\mathrm{d}t} + V_W \frac{\mathrm{d}(Z_W f_W)}{\mathrm{d}t} + V_S \frac{\mathrm{d}(Z_S f_S)}{\mathrm{d}t} + \frac{\mathrm{d}\left(V_P Z_P f_P\right)}{\mathrm{d}t} + \frac{\mathrm{d}\left(V_Z Z_Z f_Z\right)}{\mathrm{d}t} + \frac{\mathrm{d}\left(V_D Z_D f_D\right)}{\mathrm{d}t} = 0$$

(26)

Application of the product rule of differentiation reveals that in order for a dynamic biological fugacity model to conserve mass, in contrast to the physical fugacity model and ecosystem model described above, the right hand sides of the equations describing how fugacity changes over time do not sum to zero:

$$\begin{aligned}
&V_{\mathrm{A}}Z_{\mathrm{A}}\frac{\mathrm{d}f_{\mathrm{A}}}{\mathrm{d}t}+V_{\mathrm{W}}Z_{\mathrm{W}}\frac{\mathrm{d}f_{\mathrm{W}}}{\mathrm{d}t}+V_{\mathrm{S}}Z_{\mathrm{S}}\frac{\mathrm{d}f_{\mathrm{S}}}{\mathrm{d}t}+V_{\mathrm{P}}Z_{\mathrm{P}}\frac{\mathrm{d}f_{\mathrm{P}}}{\mathrm{d}t}+V_{\mathrm{Z}}Z_{\mathrm{Z}}\frac{\mathrm{d}f_{\mathrm{Z}}}{\mathrm{d}t}+V_{\mathrm{D}}Z_{\mathrm{D}}\frac{\mathrm{d}f_{\mathrm{D}}}{\mathrm{d}t}\\
&=-\frac{\mathrm{d}Z_{\mathrm{A}}}{\mathrm{d}t}V_{\mathrm{A}}f_{\mathrm{A}}-\frac{\mathrm{d}Z_{\mathrm{W}}}{\mathrm{d}t}V_{\mathrm{W}}f_{\mathrm{W}}-\frac{\mathrm{d}Z_{\mathrm{S}}}{\mathrm{d}t}V_{\mathrm{S}}f_{\mathrm{S}}-\frac{\mathrm{d}Z_{\mathrm{P}}}{\mathrm{d}t}V_{\mathrm{P}}f_{\mathrm{P}}-\frac{\mathrm{d}Z_{\mathrm{Z}}}{\mathrm{d}t}V_{\mathrm{Z}}f_{\mathrm{Z}}-\frac{\mathrm{d}Z_{\mathrm{D}}}{\mathrm{d}t}V_{\mathrm{D}}f_{\mathrm{D}}\quad(27)\\
&-\frac{\mathrm{d}V_{\mathrm{P}}}{\mathrm{d}t}Z_{\mathrm{P}}f_{\mathrm{P}}-\frac{\mathrm{d}V_{\mathrm{Z}}}{\mathrm{d}t}Z_{\mathrm{Z}}f_{\mathrm{Z}}-\frac{\mathrm{d}V_{\mathrm{D}}}{\mathrm{d}t}Z_{\mathrm{D}}f_{\mathrm{D}}
\end{aligned}$$

Eqn 27 identifies that corrections must be made to the right-hand sides of the equations describing the fugacities of the biological compartments. These corrections, of the form $(\mathrm{d}V_{\mathrm{i}}/\mathrm{d}t)Z_{\mathrm{i}}f_{\mathrm{i}}$, represent the change in fugacity of the compartment that occurs as a result of a change in volume. These terms perform the same function as growth dilution terms that represent reductions in fugacity due to increase of the volume of the host organism in some dynamic fugacity models,[13] and digestive concentration terms that represent increases in fugacity of food due to digestion within the gut of an organism.[14] These terms typically use constant rates of growth or digestion, and provide reasonable representations of the effects of these processes in fugacity models of large, monotonically growing individual organisms such as fish. However, these terms are not appropriate for plankton population models as these systems are highly dynamic over a seasonal cycle, with periods of relative stasis over winter interspersed with short periods of rapid growth or mortality. Further, as indicated by Eqn 27, dilution or concentration terms based on constant rates cannot conserve mass, a fundamental property of any model seeking to simulate the movement of POPs in the environment. While growth dilution is a reasonable description of how fugacity changes when a population is growing, when members of a population die or are eaten they take their burden of POP with them, and the remaining population does not increase its concentration of POP as a result of their death. The change in volume, however, influences the partitioning of POP within the system, and the fugacity of POP in the population changes to reflect this change in partitioning. The $(\mathrm{d}V_{\mathrm{i}}/\mathrm{d}t)Z_{\mathrm{i}}f_{\mathrm{i}}$ terms in a population model are therefore most appropriately described as fugacity correction terms.

The magnitude of the change in volume of the biotic compartments $(\mathrm{d}V_{\mathrm{i}}/\mathrm{d}t)$ as a result of the ecosystem dynamics is derived from the ecosystem Eqns 10–13 by converting the rate of change of the population (measured as a mass concentration) to a rate of change of population volume by applying a mass to volume conversion (γ_{i}, m^3 *i* m^3 W mg^{-1} N) based on constant Redfield ratios and typical phytoplankton carbon volume concentrations, a lipid fraction (ξ_{i}) and scaling by the volume of the water compartment (V_{W}).[15]

The fluxes of POP that moves through the phytoplankton as a result of ecosystem processes such as natural mortality ($\sigma_P P$) and grazing by zooplankton (φPZ) are calculated by converting fluxes of biomass determined by the ecosystem model to a flux of POP contained in an equivalent volume of lipid as only the fraction of the plankton that is lipid is considered in the fugacity model. As the state variables in the ecosystem model have units of milligrams of N per cubic metre the volume of plankton is multiplied by the volume of water being simulated in the physical model, so that each term in the biological fugacity model has the dimensions of moles per hour:

$$\begin{aligned} V_P Z_P \frac{\mathrm{d}f_P}{\mathrm{d}t} &= f_W k_{pu} V_P Z_W - f_P k_{pd} V_P Z_P - f_P \xi_P \gamma_P V_W Z_P \varphi P Z \\ &\quad - f_P \xi_P \gamma_P V_W Z_P \sigma_P P - f_P \frac{\mathrm{d}V_P}{\mathrm{d}t} Z_P - f_P \frac{\mathrm{d}Z_P}{\mathrm{d}t} V_P \end{aligned} \quad (28)$$

Phytoplankton exchange POPs with the surrounding water through diffusion, governed by the uptake rate constant k_{pu} (h^{-1}) and depuration rate constant k_{pd} (h^{-1}).[16] These rate constants are multiplied by the volume of phytoplankton (V_P) (m^3) and the fugacity capacity of water Z_W or phytoplankton Z_P as appropriate to calculate the amount of POPs that phytoplankton exchange with the water per hour, given by the terms $k_{pu} V_P Z_W$ and $k_{pd} V_P Z_P$. Finally, the correction for the change in fugacity that results from the change in volume ($(\mathrm{d}V_P/\mathrm{d}t) Z_P f_P$) must be included in order for the system to conserve mass. The rate of change of volume of the phytoplankton population ($\mathrm{d}V_P/\mathrm{d}t$) is derived from the ecosystem model:

$$\frac{\mathrm{d}V_P}{\mathrm{d}t} = \xi_P \gamma_P V_W \frac{\mathrm{d}P}{\mathrm{d}t} = \xi_P \gamma_P V_W \left(\mu \frac{N}{N+\kappa} P - \varphi P Z - \sigma_P P \right) \quad (29)$$

Substituting Eqn 29 into Eqn 28 gives the phytoplankton fugacity equation:

$$V_P Z_P \frac{\mathrm{d}f_P}{\mathrm{d}t} = D_{PW} \left(f_W - f_P \right) - f_P \rho_P Z_P \left(\mu \frac{N}{N+\kappa} P \right) - f_P \frac{\mathrm{d}Z_P}{\mathrm{d}t} V_P \quad (30)$$

The fugacity of zooplankton is determined by diffusive exchange with water, uptake through consumption of phytoplankton (φPZ), and losses due to respiration ($\varphi \psi PZ$) and mortality ($\sigma_Z Z$), and a correction for the change in fugacity that results from the change in volume ($(\mathrm{d}V_Z/\mathrm{d}t) Z_Z f_Z$) of the zooplankton population. Zooplankton biomass from the ecosystem model is converted to a volume of lipid analogously to the conversion for phytoplankton described above. The diffusive exchange of POPs between zooplankton and water is controlled by the uptake and depuration rate constants (k_{zu} and k_{zd} respectively, h^{-1}). The expressions for zooplankton exchange with water are $k_{zu} V_Z Z_W$ and $k_{zd} V_Z Z_Z$, where V_Z is the volume of zooplankton (m^3). Once again applying explicit dynamics corrections for zooplankton volume drawn from the ecosystem model gives the zooplankton fugacity equation:

$$\begin{aligned} V_{\mathrm{Z}} Z_{\mathrm{Z}} \frac{\mathrm{d}f_{\mathrm{Z}}}{\mathrm{d}t} &= D_{\mathrm{ZW}}\left(f_{\mathrm{W}} - f_{\mathrm{Z}}\right) + f_{\mathrm{P}} \rho_{\mathrm{P}} Z_{\mathrm{P}} \varphi P Z - f_{\mathrm{Z}} \rho_{\mathrm{Z}} Z_{\mathrm{Z}} \varphi \psi P Z \\ &\quad - f_{\mathrm{Z}} \rho_{\mathrm{Z}} Z_{\mathrm{Z}} \sigma_{\mathrm{Z}} Z - f_{\mathrm{Z}} \rho_{\mathrm{Z}} Z_{\mathrm{Z}} \frac{\mathrm{d}Z}{\mathrm{d}t} - f_{\mathrm{Z}} \frac{\mathrm{d}Z_{\mathrm{Z}}}{\mathrm{d}t} V_{\mathrm{Z}} \\ &= D_{\mathrm{ZW}}\left(f_{\mathrm{W}} - f_{\mathrm{Z}}\right) + \left(f_{\mathrm{P}} \rho_{\mathrm{P}} Z_{\mathrm{P}} - f_{\mathrm{Z}} \rho_{\mathrm{Z}} Z_{\mathrm{Z}}\right) \varphi P Z - f_{\mathrm{Z}} \frac{\mathrm{d}Z_{\mathrm{Z}}}{\mathrm{d}t} V_{\mathrm{Z}} \end{aligned} \qquad (31)$$

Finally, the fugacity of detritus in the model is determined by diffusive exchange with water, input of POP due to the accumulation of dead phytoplankton ($\sigma_{\mathrm{P}}P$) and zooplankton ($\sigma_{\mathrm{Z}}Z$) and respiration products from zooplankton ($\varphi\psi PZ$), and a correction for changes in fugacity that result from changes in volume ($(\mathrm{d}V_{\mathrm{D}}/\mathrm{d}t)Z_{\mathrm{D}}f_{\mathrm{D}}$). Detritus is assumed to be composed entirely of organic carbon, and therefore does not have a conversion to lipid fraction (ξ). It loses mass due to bacterial remineralisation (υD) and it is assumed that remineralised nitrogen does not have any POP attached. Therefore, the only losses of POP from the detritus occur by diffusive exchange with the water and sediment. We treat detritus sinking and subsequent incorporation into bottom sediments analogously to Patwa et al.[17] by representing the proportion of detritus in contact with sediment by the dimensionless parameter ω. The fugacity equations for detritus and water therefore include terms $D_{\mathrm{DW}}(1 - \omega)(f_{\mathrm{W}} - f_{\mathrm{D}})$ to represent diffusive exchange between these compartments, and for detritus–sediment exchange $D_{\mathrm{DS}}\omega(f_{\mathrm{S}} - f_{\mathrm{D}})$ where D_{DS} represents diffusive exchange with sediment via molecular diffusion through water-filled pore spaces. This D value is given by $(B_{\mathrm{W}}(1 - V_{\mathrm{F}})^{1.5})/(\ln 2\ h_{\mathrm{S}})\ A_{\mathrm{S}}Z_{\mathrm{W}}$ after Wania et al.[18] where diffusivity in water (B_{w}) is also taken from this source and V_{F}, the volume fraction of solids in the sediment matrix is taken to be 0.5.Again including explicit dynamic variation in volume from the ecosystem model gives the detritus fugacity equation:

$$\begin{aligned} V_{\mathrm{D}} Z_{\mathrm{D}} \frac{\mathrm{d}f_{\mathrm{D}}}{\mathrm{d}t} &= D_{\mathrm{DS}} \omega\left(f_{\mathrm{S}} - f_{\mathrm{D}}\right) + D_{\mathrm{DW}}\left(1 - \omega\right)\left(f_{\mathrm{W}} - f_{\mathrm{D}}\right) + f_{\mathrm{Z}} \rho_{\mathrm{Z}} Z_{\mathrm{Z}} \varphi \psi P Z \\ &\quad + f_{\mathrm{P}} \rho_{\mathrm{P}} Z_{\mathrm{P}} \sigma_{\mathrm{P}} P + f_{\mathrm{Z}} \rho_{\mathrm{Z}} Z_{\mathrm{Z}} \sigma_{\mathrm{Z}} Z - f_{\mathrm{D}} \rho_{\mathrm{D}} Z_{\mathrm{D}} \frac{\mathrm{d}D}{\mathrm{d}t} - f_{\mathrm{D}} \frac{\mathrm{d}Z_{\mathrm{D}}}{\mathrm{d}t} V_{\mathrm{D}} \\ &= D_{\mathrm{DS}} \omega\left(f_{\mathrm{S}} - f_{\mathrm{D}}\right) + D_{\mathrm{DW}}\left(1 - \omega\right)\left(f_{\mathrm{W}} - f_{\mathrm{D}}\right) + \left(f_{\mathrm{P}} \rho_{\mathrm{P}} Z_{\mathrm{P}} - f_{\mathrm{D}} \rho_{\mathrm{D}} Z_{\mathrm{D}}\right) \sigma_{\mathrm{P}} P \\ &\quad + \left(f_{\mathrm{Z}} \rho_{\mathrm{Z}} Z_{\mathrm{Z}} - f_{\mathrm{D}} \rho_{\mathrm{D}} Z_{\mathrm{D}}\right)\left(\varphi \psi P Z + \sigma_{\mathrm{Z}} Z\right) + f_{\mathrm{D}} \rho_{\mathrm{D}} Z_{\mathrm{D}} \upsilon D - f_{\mathrm{D}} \frac{\mathrm{d}Z_{\mathrm{D}}}{\mathrm{d}t} V_{\mathrm{D}} \end{aligned} \qquad (32)$$

Completion of the coupling of the biological fugacity model to the physical fugacity model is achieved by including terms in the fugacity equation for water and sediment that represent diffusive exchange between the biological components and these physical compartments:

$$
\begin{aligned}
V_{\mathrm{W}}Z_{\mathrm{W}}\frac{\mathrm{d}f_{\mathrm{W}}}{\mathrm{d}t} &= D_{\mathrm{AW}}\left(f_{\mathrm{A}}-f_{\mathrm{W}}\right)+D_{\mathrm{SW}}\left(f_{\mathrm{S}}-f_{\mathrm{W}}\right)+D_{\mathrm{PW}}\left(f_{\mathrm{P}}-f_{\mathrm{W}}\right)\\
&\quad +D_{\mathrm{ZW}}\left(f_{\mathrm{Z}}-f_{\mathrm{W}}\right)+D_{\mathrm{DW}}\left(1-\omega\right)\left(f_{\mathrm{D}}-f_{\mathrm{W}}\right)+f_{\mathrm{A}}U_{\mathrm{q}}Q\Phi A_{\mathrm{W}}Z_{\mathrm{x}}\\
&\quad +f_{\mathrm{A}}U_{\mathrm{p}}\Phi A_{\mathrm{W}}Z_{\mathrm{x}}+f_{\mathrm{S}}U_{\mathrm{r}}A_{\mathrm{S}}Z_{\mathrm{S}}-f_{\mathrm{W}}U_{\mathrm{d}}A_{\mathrm{S}}Z_{\mathrm{W}}
\end{aligned}
\quad (33)
$$

$$
\begin{aligned}
V_{\mathrm{S}}Z_{\mathrm{S}}\frac{\mathrm{d}f_{\mathrm{S}}}{\mathrm{d}t} &= D_{\mathrm{SW}}\left(f_{\mathrm{W}}-f_{\mathrm{S}}\right)+D_{\mathrm{DS}}\omega\left(f_{\mathrm{D}}-f_{\mathrm{S}}\right)+f_{\mathrm{W}}U_{\mathrm{d}}A_{\mathrm{S}}Z_{\mathrm{W}}\\
&\quad -f_{\mathrm{S}}U_{\mathrm{r}}A_{\mathrm{S}}Z_{\mathrm{S}}-V_{\mathrm{S}}f_{\mathrm{S}}\frac{\mathrm{d}Z_{\mathrm{S}}}{\mathrm{d}t}
\end{aligned}
\quad (34)
$$

Canonical plankton species

The parameter values used in the model are listed in Table 1. To constrain the parameter values, we have used measured size data for *Phaeocystis* spp.[19] and *Euphausia superba*[20] as the 'canonical' species in the NPZD model as these species are common in Antarctic waters. Reynolds[15] observed that 2–20% of phytoplankton mass is made up of fats and oils, hence the lipid fraction of phytoplankton (ξ_{P}) is assumed to be 0.1. The lipid fraction for *Euphausia superba* (ξ_{Z}) is assumed to be 0.045.[20] *Phaeocystis* spp. typically has a volume of ~45 $\mu\mathrm{m}^3$ and, according to the relationship derived by Montagnes et al.[21]:

$$\mathrm{N} = 0.0172V^{1.023} \quad (35)$$

with a nitrogen content (N) of 8.45×10^{-10} mg N cell^{-1}. As $V_{\mathrm{P}} = \gamma_{\mathrm{P}}P$, then γ_{P} converts from milligrams of N per cubic metre to volume of phytoplankton in cubic metres, and $\gamma_{\mathrm{P}} = 5.33 \times 10^{-8}$ has units of cubic metres of P per cubic metre of W per milligram of N. Baird et al.[22] assume $\gamma_{\mathrm{P}} = \gamma_{\mathrm{Z}}$, and as we only model the lipid content of phytoplankton, zooplankton and we further assume that $\gamma_{\mathrm{D}} = \gamma_{\mathrm{P}}$. This is commensurate with the assumption detritus is comprised entirely of organic carbon.[6]

Steady-state of the coupled ecosystem fugacity model

The steady-state of the coupled ecosystem fugacity model is:

$$f_{\mathrm{A}}^{*} = \frac{f_{\mathrm{W}}^{*}D_{\mathrm{AW}}}{D_{\mathrm{AW}}+U_{\mathrm{q}}Q\Phi A_{\mathrm{W}}Z_{\mathrm{x}}+U_{\mathrm{p}}\Phi A_{\mathrm{W}}Z_{\mathrm{x}}} \quad (36)$$

$$f_{\mathrm{W}}^{*} = \frac{\begin{bmatrix} f_{\mathrm{A}}^{*}\left(D_{\mathrm{AW}}+U_{\mathrm{q}}Q\Phi A_{\mathrm{W}}Z_{\mathrm{x}}+U_{\mathrm{p}}\Phi A_{\mathrm{W}}Z_{\mathrm{x}}\right)+f_{\mathrm{S}}^{*}\left(D_{\mathrm{SW}}+U_{\mathrm{r}}A_{\mathrm{S}}Z_{\mathrm{S}}\right)\\ +f_{\mathrm{P}}^{*}D_{\mathrm{PW}}+f_{\mathrm{Z}}^{*}D_{\mathrm{ZW}}+f_{\mathrm{D}}^{*}D_{\mathrm{DW}} \end{bmatrix}}{D_{\mathrm{AW}}+D_{\mathrm{SW}}+D_{\mathrm{PW}}+D_{\mathrm{ZW}}+D_{\mathrm{DW}}+U_{\mathrm{d}}A_{\mathrm{S}}Z_{\mathrm{W}}} \quad (37)$$

$$f_{\mathrm{S}}^{*} = \frac{f_{\mathrm{W}}^{*}\left(D_{\mathrm{SW}}+U_{\mathrm{d}}A_{\mathrm{S}}Z_{\mathrm{W}}\right)}{D_{\mathrm{SW}}+U_{\mathrm{r}}A_{\mathrm{S}}Z_{\mathrm{S}}} \quad (38)$$

$$f_{\mathrm{P}}^{*}=\frac{D_{\mathrm{PW}}f_{\mathrm{W}}^{*}}{D_{\mathrm{PW}}+\rho_{\mathrm{P}}Z_{\mathrm{P}}\left(\mu\frac{N^{*}}{N^{*}+\kappa}P^{*}\right)} \quad (39)$$

$$f_{\mathrm{Z}}^{*}=\frac{D_{\mathrm{ZW}}f_{\mathrm{W}}^{*}+f_{\mathrm{P}}^{*}\rho_{\mathrm{P}}Z_{\mathrm{P}}\varphi P^{*}Z^{*}}{D_{\mathrm{ZW}}+\rho_{\mathrm{Z}}Z_{\mathrm{Z}}\varphi P^{*}Z^{*}} \quad (40)$$

$$f_{\mathrm{D}}^{*}=\frac{D_{\mathrm{DW}}f_{\mathrm{W}}+f_{\mathrm{P}}\rho_{\mathrm{P}}Z_{\mathrm{P}}\sigma_{\mathrm{P}}P+f_{\mathrm{Z}}\rho_{\mathrm{Z}}Z_{\mathrm{Z}}\left(\varphi\psi PZ+\sigma_{\mathrm{Z}}Z\right)}{D_{\mathrm{DW}}+\rho_{\mathrm{D}}Z_{\mathrm{D}}\left(\varphi\psi PZ+\sigma_{\mathrm{P}}P+\sigma_{\mathrm{Z}}Z-\upsilon D\right)} \quad (41)$$

$$P^{*}=\frac{\sigma_{\mathrm{Z}}}{\varphi(1-\psi)} \quad (42)$$

$$Z^{*}=\frac{\mu N^{*}}{\varphi\left(N^{*}+\kappa\right)}-\frac{\sigma_{\mathrm{P}}}{\varphi} \quad (43)$$

$$D^{*}=\frac{\sigma_{\mathrm{P}}\sigma_{\mathrm{Z}}}{\varphi\upsilon\left(1-\psi\right)}+\frac{Z^{*}\sigma_{\mathrm{Z}}}{\upsilon\left(1-\psi\right)} \quad (44)$$

$$N^{*}=\frac{-\beta-\sqrt{\beta^{2}-4\gamma}}{2} \quad (45)$$

where

$$\beta=\kappa-N_{\mathrm{T}}+\left(1+\frac{\sigma_{\mathrm{P}}}{\upsilon}\right)P^{*}+\left(\frac{\mu-\sigma_{\mathrm{P}}}{\varphi}\right)\left(1+\frac{\sigma_{\mathrm{Z}}}{\upsilon}+\frac{\varphi\psi}{\upsilon}P^{*}\right) \quad (46)$$

$$\gamma=\kappa\left[\left(1+\frac{\sigma_{P}}{\upsilon}\right)P^{*}-N_{\mathrm{T}}-\frac{\sigma_{\mathrm{P}}}{\varphi}\left(1+\frac{\sigma_{\mathrm{Z}}}{\upsilon}+\frac{\varphi\psi}{\upsilon}P^{*}\right)\right] \quad (47)$$

$$\gamma=\kappa\left[\left(1+\frac{\sigma_{\mathrm{P}}}{\upsilon}\right)P^{*}-N_{\mathrm{T}}-\frac{\sigma_{\mathrm{P}}}{\varphi}\left(1+\frac{\sigma_{\mathrm{Z}}}{\upsilon}+\frac{\varphi\psi}{\upsilon}P^{*}\right)\right] \quad (48)$$

The steady-state equations reveal that the fugacity model is a fully coupled system in that the fugacities of the biological compartments are influenced by the fugacity of the water, and that the fugacity of the water, and in turn the fugacities of the sediment and air, are influenced by the fugacity of the biological compartments. There is, however, only a one-way coupling between the ecosystem model compartments, the biomass of phytoplankton, zooplankton and detritus, as these compartments affect the fugacities of the other compartments, but the fugacity model does not affect the ecosystem model. Future models could incorporate such a coupling, where the POP burden of a biological compartment could affect the growth, grazing or mortality rates of the population.

References

[1] D. Mackay, L. Reid, Local and distant residence times of contaminants in multi-compartment models. Part I: A review of the theoretical basis. *Environ. Pollut.* **2008**, *156*, 1196. doi:10.1016/j.envpol.2008.04.012

[2] D. Mackay, *Multimedia Environmental Models. The Fugacity Approach, 2nd edn* **2001** (Taylor and Francis: Boca Raton, FL).

[3] D. Mackay, S. Paterson, Evaluating the multimedia fate of organic chemicals: a level III fugacity model. *Environ. Sci. Technol.* **1991**, *25*, 427. doi:10.1021/es00015a008

[4] W. E. Boyce, R. C. DiPrima, *Elementary differential equations and boundary value problems, 6th edn* **1997** (Wiley: New York).

[5] C. L. Moloney, J. G. Field, General allometric equations for rates of nutrient uptake, ingestion and respiration in plankton organisms. *Limnol. Oceanogr.* **1989**, *34*, 1290. doi:10.4319/lo.1989.34.7.1290

[6] A. M. Edwards, Adding detritus to nutrient-phytoplankton-zooplankton model: a dynamical-systems approach. *J. Plankton Res.* **2001**, *23*, 389. doi:10.1093/plankt/23.4.389

[7] F. De Laender, D. Van Oevelen, S. Frantzen, J. J. Middelburg, K. Soetaert, Seasonal PCB bioaccumulation in an Arctic marine ecosystem: a model analysis incorporating lipid dynamics, food-web productivity and migration. *Environ. Sci. Technol.* **2010**, *44*, 356. doi:10.1021/es902625u

[8] R. W. Eppley, Temperature and phytoplankton growth in the sea. *Fish. Bull.* **1972**, *70*, 1063.

[9] T. Platt, C. Gallegos, W. G. Harrison, Photoinhibition of photosynthesis in natural assemblages of marine phytoplankton. *J. Mar. Res.* **1980**, *38*, 687.

[10] D. Marinov, S. Dueri, I. Puillat, R. Carafa, E. Jurado, N. Berrojalbiz, J. Dachs, J.-M. Zaldívar, Integrated modelling of polycyclic aromatic hydrocarbons in the marine environment: coupling of hydrodynamic, fate and transport, bioaccumulation and planktonic food-web models. *Mar. Pollut. Bull.* **2009**, *58*, 1554. doi:10.1016/j.marpolbul.2009.05.009

[11] A. Gabric, G. Ayers, G. Sander, Independent marine and atmospheric model estimates of the sea–air flux of dimethylsulfide in the Southern Ocean. *Geophys. Res. Lett.* **1995**, *22*, 3521. doi:10.1029/95GL02936

[12] A. N. Kolmogorov, Sulla teoria di volterra della lotta per l'esisttenza. *Giorn Instituto Ital Attuari.* **1936**, *7*, 74.

[13] C. A. Ng, K. A. Gray, Tracking bioaccumulation in aquatic organisms: A dynamic model integrating life history characteristics and environmental change. *Ecol. Modell.* **2009**, *220*, 1266. doi:10.1016/j.ecolmodel.2009.02.007

[14] J. A. Arnot, F. A. P. C. Gobas, A food web bioaccumulation model for organic chemicals in aquatic ecosystems. *Environ. Toxicol. Chem.* **2004**, *23*, 2343. doi:10.1897/03-438

[15] C. S. Reynolds, *Ecology of Phytoplankton* **2006** (Cambridge University Press: New York).

[16] J. Dachs, S. J. Eisenreich, J. E. Baker, F.-C. Ko, J. D. Jeremiason, Coupling of phytoplankton uptake and air–water exchange of persistent organic pollutants. *Environ. Sci. Technol.* **1999**, *33*, 3653. doi:10.1021/es990168o

[17] Z. Patwa, R. Christensen, D. C. Lasenby, E. Webster, D. Mackay, An exploration of the role of mysids in benthis–pelagic coupling and biomagnification using a dynamic bioaccumulation model. *Environ. Toxicol. Chem.* **2007**, *26*, 1224. doi:10.1897/06-441R.1

[18] F. Wania, K. Breivik, N. J. Persson, M. S. McLachlan, CoZMo-POP 2 – A fugacity-based dynamic multi-compartmental mass balance model of the fate of persistent organic pollutants. *Environ. Model. Softw.* **2006**, *21*, 868. doi:10.1016/j.envsoft.2005.04.003

[19] H. J. Marchant, F. J. Scott, A. T. Davidson, *Antarctic marine protists* (Eds F. J. Scott, H. J. Marchant) **2005** (Australian Antarctic Division: Hobart).

[20] S. M. Bengtson Nash, A. H. Poulsen, S. Kawaguchi, W. Vetter, M. Schlabach, Persistent organohalogen contaminant burdens in Antarctic krill (Euphausia superba) from the eastern Antarctic sector: a baseline study. *Sci. Total Environ.* **2008**, *407*, 304. doi:10.1016/j.scitotenv.2008.08.034

[21] D. J. S. Montagnes, J. A. Berges, P. J. Harrison, F. J. R. Taylor, Estimating carbon, nitrogen, protein, and chlorophyll a from volume in marine phytoplankton. *Limnol. Oceanogr.* **1994**, *39*, 1044. doi:10.4319/lo.1994.39.5.1044

[22] M. E. Baird, P. R. Oke, I. M. Suthers, J. H. Middleton, A plankton population model with biomechanical descriptions of biological processes in an idealised 2-D ocean basin. *J. Mar. Syst.* **2004**, *50*, 199. doi:10.1016/j.jmarsys.2004.02.002