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Grazing-induced production of DMS can stabilize food-web dynamics and promote the formation of phytoplankton blooms in a multitrophic plankton model

Nicola D. Lewis · Mark N. Breckels · Steve D. Archer · Andrew Morozov · Jonathan W. Pitchford · Michael Steinke · Edward A. Codling

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Abstract Volatile infochemicals including climatically relevant dimethylsulphide (DMS) have been suggested to play important roles in the structuring and functioning of marine food webs. Experimenting with complex natural plankton communities or several trophic levels in laboratory microcosms is challenging and, as a result, empirical data confirming the role of DMS in trophic interactions is lacking. Models are a suitable tool to provide insight into such complex interactions. Here we consider a model of the interactions between three trophic levels of plankton: phytoplankton, grazing microzooplankton and predatory mesozooplankton. We show that the inclusion of a grazing-induced DMS production term has a stabilizing effect on the system dynamics under the assumption that DMS acts as an info-chemical and increases the rate of mesozooplankton predation on grazing microzooplankton. We further demonstrate how this feedback between trophic levels can potentially lead to the formation of a phytoplankton bloom. The model provides a suitable framework for further study into the possible role of DMS in the ecology of marine food webs beyond its recognised role as a climate-cooling gas.

Keywords Multitrophic interactions · Dimethylsulphide · Plankton blooms · Mathematical modelling · Population dynamics

Introduction

Dimethylsulphide (DMS) is a biogenic trace gas derived from the algal secondary metabolite dimethylsulphoniopropionate (DMSP). DMS has been proposed to play a role in climate regulation by contributing to the formation of aerosols and cloud condensation nuclei (CCN) in the atmosphere (Charlson et al. 1987), although uncertainty remains regarding the sensitivity of CCN formation to changes in DMS concentrations and how climate change may alter DMS emissions (Ayers and Cainey 2007).

In marine systems "*chemically mediated interactions strongly affect population structure, community*

N. D. Lewis · E. A. Codling (✉)
Department of Mathematical Sciences, University of Essex, Wivenhoe Park, Colchester CO4 3SQ, UK
e-mail: ecodling@essex.ac.uk

N. D. Lewis · M. N. Breckels · M. Steinke · E. A. Codling
Department of Biological Sciences, University of Essex, Wivenhoe Park, Colchester CO4 3SQ, UK

M. N. Breckels · S. D. Archer
Plymouth Marine Laboratory, Prospect Place, Plymouth PL1 3DH, UK

A. Morozov
Department of Mathematics, University of Leicester, Leicester LE1 7RH, UK

J. W. Pitchford
Department of Mathematics, University of York, York YO10 5DD, UK

organization, and ecosystem function" (Hay 2009). In many cases, the infochemicals that elicit responses within a population are poorly characterized (Pohnert et al. 2007) but DMSP and DMS are known to affect the behavior of marine organisms. Examples include the utility of airborne DMS as directional foraging cues for seabirds (e.g., Nevitt et al. 1995) and marine mammals (Kowalewsky et al. 2006), which use the olfactory landscape to locate patches with high biological productivity (Nevitt 2000). Similarly, there have been numerous examples of behavioral changes in copepods in response to chemical stimulation by prey-related cues (e.g., Buskey 1984; Gill and Poulet 1988). In particular, DMS has been shown to elicit a behavioral response in the copepod *Temora longicornis* (Steinke et al. 2006) suggesting that copepods may use DMS when searching for prey.

Microzooplankton protists are considered to form an important trophic link between phytoplankton and copepods (Sherr and Sherr 1988) and grazing by microzooplankton rapidly accelerates the cleavage of phytoplankton DMSP into DMS in both laboratory (Wolfe and Steinke 1996) and field studies (e.g., Archer et al. 2001). In aquatic environments the physical properties of the viscous medium allow for the spatial persistence of chemical gradients and the reliable transmission of chemical cues. Consequently, chemosensory systems have evolved in many aquatic taxa allowing the exploitation of a broad range of ecological niches (Vos et al. 2006; Pohnert et al. 2007).

Copepods are important in the regulation of phytoplankton and microzooplankton populations in pelagic ecosystems (Yang et al. 2009; Fileman et al. 2010). Grazing studies suggest that copepods, when provided with a choice, may selectively feed on heterotrophic protists rather than small phytoplankton (Hansen et al. 1993; Tang et al. 2001). For example, heterotrophic dinoflagellates are thought to act as the 'middle men' in pelagic food webs and are important for the necessary 'trophic upgrading' of nutritionally poor phytoplankton (Klein Breteler et al. 1999). Hence, it has been suggested that copepod predation on microzooplankton could facilitate *Phaeocystis* blooming by relieving microzooplankton grazing pressure (Hansen et al. 1993). The ability to detect and react to DMS suggests that this trace gas may act as an infochemical cue used by copepods to find individual prey in an otherwise nutritionally sparse three-dimensional environment, or to assist with locating prey-rich patches. Hence DMS can in principle promote multitrophic interactions between phytoplankton, microzooplankton and copepods (Steinke et al. 2002a).

Here we present a simple exploratory food chain model that attempts to capture the key interactions between small phytoplankton, microzooplankton and copepods under the effect of a DMS infochemical cue produced through microzooplankton grazing. We show that the production of DMS in the model releases grazing pressure on the phytoplankton and can lead to a stabilizing of the food-web dynamics and/or allow the phytoplankton to reach densities equivalent to the formation of a phytoplankton bloom. As far as we know, this work presents the first attempt to model the role of DMS in the multitrophic interactions between phytoplankton, microzooplankton and copepods.

Methods

We present a simple population-level (meso-scale) food chain model with an additional chemical component. Small DMS-producing phytoplankton that can grow to high abundance such as *Phaeocystis* sp. or *Emiliania huxleyi* represent the first trophic level. These are grazed by microzooplankton (second trophic level), which are in turn consumed by mesozooplankton such as copepods. Although some copepod species feed on small phytoplankton, studies on the grazing rates of *Calanus helgolandicus* and *C. finmarchicus* have shown that *E. huxleyi* is a suboptimal food source on which these copepods feed inefficiently (Nejstgaard et al. 1995; Levasseur et al. 1996). Furthermore, microzooplankton grazing has been shown to account for around 90% of the loss of particulate DMSP during a northern North Sea phytoplankton bloom (Archer et al. 2002), indicating the importance of microzooplankton grazers in regulating small DMSP producing phytoplankton. Hence, one of the key assumptions in our initial model is that microzooplankton provide the essential trophic link between phytoplankton and copepods. In principle, a more complex model could be developed to also include a direct link between copepods and phytoplankton but this is beyond the scope of this paper where we concentrate on a simple exploratory model.

We make two further important simplifying assumptions about the time scales and ecological processes in the model:

(i) We assume that any changes in the population density of copepods are negligible over the short time-scale under consideration (i.e., a time-scale in the order of a few days).
(ii) We assume that DMS acts as an infochemical in the system; DMS is released when phytoplankton are consumed by microzooplankton, causing an instantaneous proportional increase in the microzooplankton mortality rate due to increased grazing by copepods.

The model is given by:

$$\frac{dP}{dt} = rP\left(1 - \frac{P}{K}\right) - \frac{aPM}{1 + bP} \tag{1}$$

$$\frac{dM}{dt} = \frac{\gamma aPM}{1 + bP} - mM - \frac{\lambda aPM^2}{1 + bP} \tag{2}$$

where P and M are the densities of phytoplankton and microzooplankton in this closed homogeneous system. The derivation of this model is omitted here, but further mathematical details can be found in the Appendix. A key point to highlight is that although we do not directly include a copepod term in the above equations, the effect of copepod predation is accounted for in the mortality terms in Eq. 2.

In the model, phytoplankton are assumed to grow logistically with intrinsic rate of growth r and carrying capacity K, where the carrying capacity corresponds to nutrient limitation and self shading (representing the simplest realistic model for growth in a resource-limited environment). The microzooplankton graze on phytoplankton according to a type II functional response (Holling 1959) where the rate of grazing saturates at high densities of phytoplankton (again, the simplest biologically realistic functional form for this model) and convert phytoplankton biomass to microzooplankton biomass with efficiency γ. The parameter m corresponds to the total microzooplankton mortality that would occur in the absence of DMS; microzooplankton mortality is assumed to be mainly caused by copepods (here this predation is not mediated by DMS but is assumed to occur through other mechanisms or random encounters) but this term also accounts for a background mortality. This background mortality is assumed to be due to processes such as sinking and additional predation by other zooplankton or by higher trophic levels.

We assume the increased production of DMS leads to an increase in the microzooplankton mortality (encapsulated by the parameter λ) caused exclusively by the infochemical effect of DMS increasing copepod predation. The parameter λ corresponds to an increase in the background concentration of DMS thus allowing copepods to improve the efficiency of their search through chemodetection. However, we can account for various possible model factors within this parameter. For example, an increase in λ could also correspond to an increase in the sensitivity of copepods to DMS (e.g., if a different species of copepod was being considered), or an increase in the net predation by copepods (e.g., if the total number of copepods increased, or if the predation rate increased). Although, it should be noted here that an increase in copepod net predation would also result in a corresponding increase in the parameter m (see "Appendix"). In the subsequent analysis we consider λ as an exploratory parameter that we vary to consider different scenarios (such as those described above) for the possible effects of DMS on the food-chain dynamics. Table 1 summarises the variables and parameters in this model.

It is worth pausing here to discuss the justification and implications of assumptions (i) and (ii). By assuming that our model time-scale is short relative to the copepod dynamics we are effectively taking a 'snap-shot' of the longer-term dynamics of a more complex system. We justify assumption (i) through the argument that over a time scale of several days there will be little change in copepod density (relative to M and P) due to the longer and more complex copepod life histories and the inefficiencies of converting predated microzooplankton into new biomass (e.g., Truscott and Brindley 1994; Melle and Skjoldal 1998; but see "Discussion"). Assumption (ii) means that in our model DMS is rapidly propagated through the system to cause an instantaneous grazing response in the copepods. We know that localised DMS production has been shown to be rapid in experimental studies (e.g., Wolfe and Steinke 1996), while it seems reasonable to assume that localised peaks in DMS will not persist for long relative to the DMS background concentration and the movement/sensory abilities of the predating copepods. These assumptions are used in order to make analytic progress in this exploratory model. Ideally, in future studies it should be possible

Table 1 Variable and parameter definitions and the values used for the model given by Eqs. 1 and 2

Variable/parameter	Definition	Value	Range/reference
P	Phytoplankton density	–	–
M	Microzooplankton density	–	–
r	Phytoplankton intrinsic growth rate	1.5 days^{-1}	0.1–2 $\text{days}^{-1\text{a}}$
K	Phytoplankton carrying capacity	120 $\mu\text{g C l}^{-1}$	100–150 $\mu\text{g C l}^{-1\text{b}}$
a	Clearance rate of microzooplankton at low food densities	0.3 $\mu\text{g C l}^{-1}\ \text{days}^{-1}$	0.1–0.3 $\mu\text{g C l}^{-1}\ \text{days}^{-1\text{c,d}}$
b	Half saturation density	0.05 $\mu\text{g C l}^{-1}$	0.01–0.05 $\mu\text{g C l}^{-1\text{c,d}}$
γ	Microzooplankton grazing efficiency	0.5	0.1–1^{e}
m	Microzooplankton mortality in the absence of DMS	0.3 days^{-1}	0.2–1 days^{-1}
λ	Additional microzooplankton mortality due to the presence of DMS	Control parameter	–

The parameter values used were chosen from parameter ranges found from previous experimental and modelling studies in the literature (Edwards and Brindley 1999[a]; Franks 2001[b]; Saiz and Calbet 2007[c]; Hansen et al. 1990[d]; Edwards et al. 2000[e]). The parameter m includes both natural microzooplankton mortality and copepod feeding on microzooplankton in the absence of DMS, meaning this parameter can take a large range. The parameter λ is a control parameter

to remove these assumptions and consider the dynamics of more complex (and arguably more realistic) systems which would be valid over a wider range of time-scales, but it is likely that in this case analytic progress will be much more difficult.

We note here that any increase in the density of phytoplankton in this model is an indirect result of increased copepod predation on microzooplankton resulting in a top-down trophic cascade. Such an interaction was first argued by Hairston et al. (1960) in the 'Green World hypothesis'. Since then such interactions have been demonstrated and modelled in numerous other systems (e.g., James et al. 2003).

We also note that when DMS is not present in the model or its effects are negligible, i.e., $\lambda \approx 0$, the final term in Eq. 2 is negligible and the system reduces to the standard Rosenzweig–MacArthur or 'Paradox of Enrichment' predator–prey equations (Rosenzweig and MacArthur 1963). Our approach is to consider the role of grazing-induced DMS production as a mathematical perturbation of this simpler system, mirroring methods used to assess the role of mixotrophy in plankton systems (Hammer and Pitchford 2005, 2006). The parameter values used were taken from parameter ranges found in the literature. This gives biologically reasonable results, however, we emphasize that it is the qualitative behaviour of the system that we are interested in and that this study is only meant as an initial exploratory attempt to consider this type of trophic dynamics.

Results

A mathematical understanding of the behaviour of the system described by Eqs. 1 and 2 is obtained by carrying out a phase plane analysis of the model. This is a standard technique used for determining the behaviour of an ecological system and has been employed by many authors (e.g., Hilbert et al. 2000; Kot 2001) and hence we omit the full mathematical details, while highlighting the key biologically relevant results.

For all cases presented here (i.e., all values of λ) the trivial equilibrium points at the origin and at $(K, 0)$ are unstable saddle points, and both phytoplankton and microzooplankton population persist indefinitely.

Analysis of the system given by Eqs. 1 and 2 with $\lambda = 0$ (i.e., where DMS does not mediate any trophic interactions) shows that increasing the value of K, the prey carrying capacity, acts to destabilize the system via a Hopf bifurcation (Rosenzweig and MacArthur 1963; Kot 2001). Previous analyses of the Rosenzweig–MacArthur (1963) equations show that if the predator nullcline lies to the right of the peak of the prey nullcline then the system is stable, and if the predator nullcline lies to the left of the peak of the prey nullcline the system exhibits instability (Kot 2001). In the analysis presented here, for $\lambda = 0$, the microzooplankton nullcline lies to the left of the peak of the phytoplankton nullcline (Fig. 1a) suggesting that the system is unstable in the absence of DMS. In this situation solutions will oscillate over time (the amplitude of these oscillations growing with increasing phytoplankton carrying capacity), not reaching a stable steady state (Fig. 2a).

When the role of DMS is taken into account (i.e., $\lambda > 0$) a phase plane analysis of the system reveals three possible situations. If λ is below a certain threshold value ($\lambda < 0.034$ using the parameter values in Table 1) the net effects of DMS-mediated interactions are negligible and the qualitative behaviour of the system is similar to the case when $\lambda = 0$.

When the net effect of DMS-mediated interactions is low ($0.034 \leq \lambda < 0.043$), the phytoplankton and microzooplankton nullclines intersect once in the phase space, at a point corresponding to low densities of phytoplankton (Fig. 1b). This point can be shown to be a stable focus meaning that solutions that initially oscillate will dampen and tend to a stable steady state. In this situation copepods are inefficient at grazing the microzooplankton which results in high phytoplankton mortality due to microzooplankton grazing. However, the presence of DMS in the system has now acted

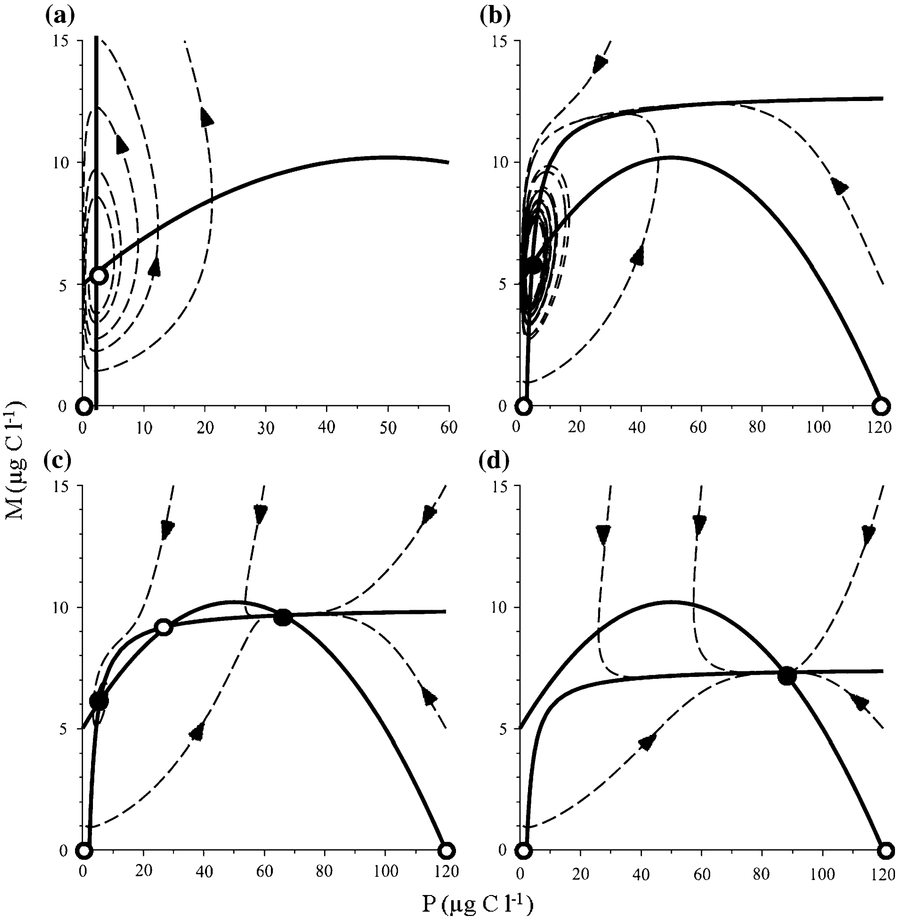

Fig. 1 Nullclines of the system corresponding to different λ (the effect of DMS on the predation of grazers). The *solid lines* show the phytoplankton and microzooplankton nullclines while the *dashed lines* are solution trajectories. The intersections of the nullclines give the equilibrium points of the system; stable equilibria are shown by *closed circles* and unstable equilibria are shown by *open circles*. In all situations the points (0, 0) and (120, 0) are saddle points **a** $\lambda = 0$ (no DMS). The point (2.222, 5.453) is an unstable focus; solution trajectories are drawn to a stable limit cycle around this point (Kot 2001). **b** $\lambda = 0.035$. The point (4.055, 5.810) is a stable focus; trajectories are drawn to this point. **c** $\lambda = 0.045$. The points (5.373, 6.127) and (66.162, 9.664) are stable focus/node respectively (28.100, 9.209) is a saddle point; solutions will tend to either of the stable equilibrium points depending on initial abundances of phytoplankton and microzooplankton. **d** $\lambda = 0.06$. The point (87.305, 7.309) is a stable node; all solution trajectories tend towards this point

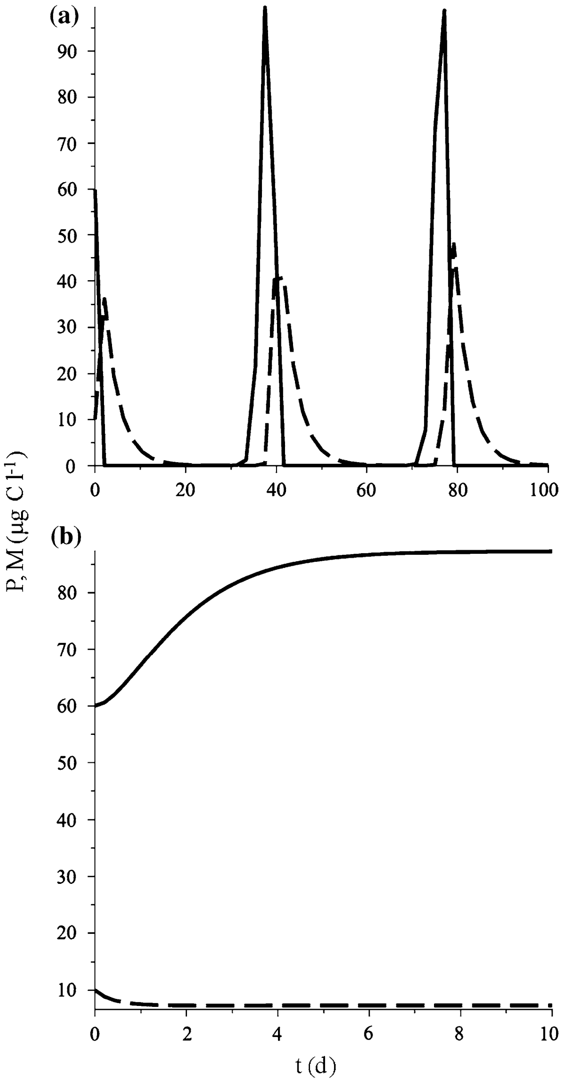

Fig. 2 Time dependent behaviour of the model. The *solid line* shows phytoplankton density over time and the *dashed line* shows microzooplankton density over time. **a** $\lambda = 0$ (no DMS). Solutions oscillate over time not reaching a stable steady state. **b** $\lambda = 0.06$ (high DMS). Solutions tend to a globally stable steady state

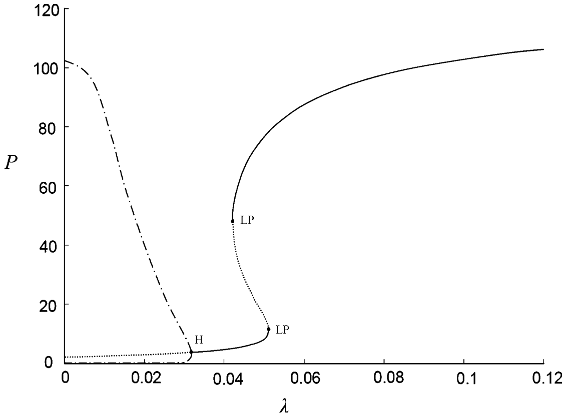

Fig. 3 Bifurcation diagram for variation of λ (effect of DMS on predation of grazers) constructed from the parameter values given in Table 1. The *dotted-solid line* shows where the equilibria occur as the value of λ increases, with the *dotted sections* representing unstable equilibria and the *solid sections* representing stable equilibria. The stationary state is unstable for a negligible DMS effect until the point H (where $\lambda = 0.034$) where a Hopf bifurcation occurs. From this point the system is stable exhibiting multiple equilibria between the limit points LP (where $\lambda = 0.043$) and LP (where $\lambda = 0.052$). The *dot-dashed line* shows the magnitude of the limit cycle for a negligible DMS effect (where $\lambda < 0.034$)

to stabilise what would otherwise be an unstable system (Fig. 3). We note here that this stabilization can take place even when an infinitely large carrying capacity is used in the model.

When the net effect of DMS-mediated interactions is medium ($0.043 \leq \lambda < 0.052$), the phytoplankton and microzooplankton nullclines cross three times, giving three equilibrium points in the phase space. Two of these equilibrium points (closed circles in Fig. 1c) can be shown to be stable equilibria; a stable focus (left closed circle in Fig. 1c) and a stable node (right closed circle in Fig. 1c). The stable focus corresponds to low densities of both phytoplankton and microzooplankton. The stable node corresponds to high densities of phytoplankton at similar microzooplankton densities. These locally stable equilibria are separated in the phase space by a saddle point (open circle in Fig. 1c); solution trajectories that start near this point will diverge towards either of the locally stable equilibria. In other words for this range of λ, the system exhibits bistability; the equilibrium point the solution ultimately reaches will depend on the initial abundance of the phytoplankton and the microzooplankton. Depending on the initial abundances, this may permit the formation of a phytoplankton bloom (right closed circle in Fig. 1c).

When the net effect of DMS-mediated interactions is high ($\lambda \geq 0.052$), the phytoplankton and microzooplankton nullclines intersect once in the phase space (Fig. 1d) at a point corresponding to high densities of phytoplankton. This point can be shown to be a stable node meaning that solution trajectories tend to a stable steady state (Fig. 2b). This occurs when the presence of DMS elicits a strong net feeding response in the copepods, providing a decrease of grazing pressure on phytoplankton and facilitating the formation of a bloom. These results are summarised in the bifurcation diagram presented in Fig. 3.

It should be noted that the solutions given in this analysis are dependent on the parameter values used. In the analysis presented here we have varied only the parameter λ to gain an insight into the potential effect of DMS in multitrophic interactions; varying any of the other parameters may produce other solutions not covered here. However, a qualitatively similar situation to what is observed here is obtained across a large range of the other parameter values. A type III functional response (Holling 1959) was also considered for the microzooplankton grazing term, $f(P)$, but this yielded a qualitatively similar outcome to the second main point highlighted in the above analysis (i.e., for large values of λ, the stable equilibrium point corresponds to phytoplankton bloom formation).

In summary we have set up an exploratory model to consider the potential role of DMS as an info-chemical that mediates interactions between trophic levels in a simple plankton food-chain. After making a number of simplifying assumptions, we are able to make analytic progress and demonstrate the qualitative system dynamics for a range of values of the control parameter λ (which represents the net effect of DMS acting to increase predation on microzooplankton by copepods). The main findings from this initial exploratory model are firstly that when DMS-mediated interactions are not present ($\lambda = 0$), the model system corresponds to the well studied Rosenzweig–MacArthur (1963) equations; the system is unstable with periodic cycles in the density of microzooplankton, M, and phytoplankton, P. Secondly if the net effect of DMS-mediated interactions is large enough ($0.034 \leq \lambda$) then the system changes from an unstable to a stable system through a Hopf bifurcation. Hence the presence of DMS can act to stabilize an otherwise unstable food-web (Fig. 3). Finally if the net effect of DMS-mediated interactions is very large ($\lambda \geq 0.052$) then the system will also have an equilibrium point that corresponds to a plankton bloom. Blooms may also form if $0.043 \leq \lambda < 0.052$, depending on the initial population densities of P and M.

Discussion

We have used an exploratory model to examine the potential effect of DMS liberated following microzooplankton grazing in simple food chain interactions between small phytoplankton, microzooplankton and copepods. Here we have implicitly assumed in our model that an increase in the background concentration of DMS (or alternatively an increase in sensitivity of predators to DMS info-chemical signals) will result in enhanced grazing rates on microzooplankton (encapsulated by the parameter λ). Info-chemicals released following microzooplankton grazing may enhance copepod grazing in a number of different ways and at different temporal and spatial scales. Depth profiles from the ocean have shown that DMS concentrations correspond well to the chlorophyll maxima (Steinke et al. 2002b), so that vertically migrating copepods may be able to use these concentration gradients to locate and remain within ephemeral prey-rich patches. Such dynamic behavior was not the focus of the present study since our model assumes that copepod density remains constant over short timescales but it does support our assumption that copepods may respond to an underlying background concentration of DMS as an info-chemical signal.

In the absence of DMS, Eqs. 1 and 2 reduce to the Rosenzweig–MacArthur (1963) system of equations and standard analysis of this model shows that increasing the value of the prey carrying capacity acts to destabilize what would otherwise be a stable system via a Hopf bifurcation. Creation of a limit cycle results in large oscillations in the system dynamics meaning that both predator and prey may come close to local extinction as their phase plane trajectories are drawn close to the axes (Kot 2001). This is represented by the dot-dashed line in Fig. 3 which shows that oscillations in phytoplankton density are large, and the outer values of the stable limit cycle reach close to zero for very low values of λ. This effect, where the stability of a system is lost through the addition of extra resources, is called the ‘Paradox of enrichment’ (Rosenzweig 1971). We used a value of 120 μg C l^{-1} for the phytoplankton carrying capacity (Franks 2001) which was shown here to result in unstable population dynamics in the absence of DMS (Fig. 1). However, our analysis has shown that increasing λ can initially have a stabilizing effect on this system (Fig. 3). Further increasing λ leads to multiple stable equilibria and finally a stable peak in phytoplankton density. It is worth noting that a number of theoretical studies have identified mechanisms which act to enhance ecosystem stability such as invulnerable or unpalatable prey

(Abrams and Walters 1996; Genkai-Kato and Yamamura 1999), mixotrophy (Hammer and Pitchford 2005), omnivory (McCann and Hastings 1997), intratrophic predation (Pitchford and Brindley 1998), inducible defenses (Vos et al. 2004) and spatial heterogeneity (Morozov et al. 2007). Therefore, the stabilizing effect which we present here is but one of many mechanisms which may act to promote system stability. It should also be noted that different process representations of DMS in the model may result in different model properties or dynamical patterns; however such a claim is true for all models in mathematical ecology. The time scale required for the peak in phytoplankton density to occur was on the order of 4–5 days (Fig. 2b) highlighting the fact that this model applies only over short time scales of a few days.

If DMS-release following microzooplankton grazing enhances their susceptibility to copepod predation, this may provide a 'loophole' in microzooplankton grazing impact leading to the formation of a phytoplankton bloom, as described by Irigoien et al. (2005). Our model assumes that the predominant route for mortality of small phytoplankton is due to microzooplankton grazing, and excludes grazing from copepods. Although grazing behavior is typically highly flexible and grazing by mesozooplankton such as copepods can be responsible for losses of between 10 and 40% of primary productivity across a wide range of marine ecosystems (Calbet 2001), several lines of evidence suggest that some species of copepod select nutritionally superior microzooplankton when provided with a choice. For example, during a 3-trophic level grazing experiment, Hansen et al. (1993) showed that the copepod *T. longicornis* was able to graze on the haptophyte *Phaeocystis globosa* when no alternative prey were available. However, in the presence of the microzooplankton *Oxyrrhis marina* and *Strombidinopsis acuminatum* copepods grazed selectivity on these microzooplankton and net grazing on *P. globosa* was significantly reduced. Furthermore, Nejstgaard et al. (1997) showed that the main impact of copepods on phytoplankton development was induced indirectly by selective feeding on microzooplankton. Incubation experiments at a long-term monitoring station in the Western English Channel showed that the phytoplankton size distribution is an important controlling factor in determining copepod grazing selectivity; where phytoplankton communities are dominated by diatom cells >5 μm the majority of copepods' dietary carbon was obtained from phytoplankton. Conversely, in oligotrophic waters, where the phytoplankton populations are dominated by cells <5 μm, copepods selectively grazed on microzooplankton (Fileman et al. 2007). However, even small phytoplankton such as *E. huxleyi* may become important components in the diets of copepods when present at higher densities (e.g., 1.2×10^7 cells l^{-1}; Nejstgaard et al. 1997). Future modelling studies to investigate the role of DMS in these types of planktonic systems should aim to include phytoplankton functional types and incorporate a trophic link between phytoplankton and copepods that provides for a dynamic density-dependent switch of copepod grazing between prey types depending on size, nutritional quality and abundance.

The spatiotemporal distribution and abundance of phytoplankton is highly heterogeneous in the marine environments (e.g., Cowles et al. 1998) leading to the formation of gradients and disparities in infochemical concentration between areas of high and low biological activity. Morozov et al. (2011) highlighted the importance of vertical heterogeneity in a recent modeling study. By considering attenuation of light and the movement of a zooplanktonic predator through the water column they showed that the addition of vertical heterogeneity to a planktonic predator–prey model acted to stabilize the system even under unlimited supply of nutrients. An important extension to the work presented here would be to add a spatial component to the model that allows copepods exhibiting diel vertical migration to follow gradients of DMS and migrate into the area in their search for microzooplankton prey.

The extent to which DMS, and other such infochemicals, influence trophic interactions in marine food webs remains unresolved. Here we have shown that, in principle, infochemicals such as DMS may play an important role in influencing multitrophic interactions between phytoplankton, microzooplankton and copepods. DMS is ubiquitous in marine environments and important for the global biogeochemical cycling of carbon and sulphur. Only through elucidating the function of DMS in the ecology of marine organisms we will gain the necessary understanding of its production. Modelling studies such as the one presented here will continue to complement and inform experimental efforts to address the function of infochemicals in marine ecosystems.

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Appendix

Here we show the derivation of Eqs. 1–2 and parameters m and λ. We start with a full model with phytoplankton (*P*), microzooplankton (*M*), copepods (*Z*, which we assume is constant due to the fact that we only consider a short time-scale of a few days) and DMS (*C*) are:

$$\frac{dP}{dt} = r(P)P - f(P)M \tag{3}$$

$$\frac{dM}{dt} = \gamma f(P)M - \mu M - \beta ZM(1 + \xi C) \tag{4}$$

$$\frac{dC}{dt} = \eta f(P)M - vC \tag{5}$$

where

$$r(P) = r\left(1 - \frac{P}{K}\right)$$

$$f(P) = \frac{aP}{1 + bP}$$

and

- μ is the background mortality of microzooplankton as described in the Methods section of the main text.
- β and ξ correspond to copepod predation; copepods consume microzooplankton at a linear rate β in the absence of DMS (a linear rate is chosen for simplicity because a type II response leads to similar model results). In the presence of DMS, the overall predation rate is increased by a multiplicative factor of $1 + \xi C$, where the parameter ξ represents how much an increase in levels of DMS leads to an increase in predation by copepods.
- DMS is produced in the system at a rate η proportional to microzooplankton grazing and leaves the system at a rate v (as a result of flux to the atmosphere, bacterial consumption etc.).

C is a fast variable under assumption (ii) from the methods; C will quickly return to the underlying background concentration after any perturbation and hence we assume that $dC/dt \approx 0$. Rearranging Eq. 5 for C under this assumption and substituting back into Eq. 4 gives the following system:

$$\frac{dP}{dt} = r(P)P - f(P)M \tag{6}$$

$$\frac{dM}{dt} = \gamma f(P)M - mM - \lambda f(P)M^2 \tag{7}$$

where $m = (\mu + \beta Z)$ and $\lambda = \frac{\eta \beta Z \xi}{v}$.

Specifying that phytoplankton grow logistically, *r*(*P*), and that microzooplankton follow a type II functional response, *f*(*P*), gives Eqs. 1–2 in the main text.

References

Abrams PA, Walters CJ (1996) Invulnerable prey and the paradox of enrichment. Ecology 77:1125–1133

Archer SD, Stelfox-Widdicombe CE, Burkill PH, Malin G (2001) A dilution approach to quantify the production of dissolved dimethylsulphoniopropionate and dimethylsulphide due to microzooplankton herbivory. Aquat Microb Ecol 23:131–145

Archer SD, Smith GC, Nightingale PD, Widdicombe CE, Tarran GA, Rees AP, Burkill PH (2002) Dynamics of particulate dimethylsulphoniopropionate during a Lagrangian experiment in the northern North Sea. Deep Sea Res Part II Top Stud Oceanogr 49:2979–3000

Ayers GP, Cainey JM (2007) The CLAW hypothesis: a review of the major developments. Environ Chem 4:366–374

Buskey EJ (1984) Swimming pattern as an indicator of the roles of copepod sensory systems in the recognition of food. Mar Biol 79:165–175

Calbet A (2001) Mesozooplankton grazing effect on primary production: a global comparative analysis in marine ecosystems. Limnol Oceanogr 46:1824–1830

Charlson RJ, Lovelock JE, Andreae MO, Warren SG (1987) Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate. Nature 326:655–661

Cowles TJ, Desiderio RA, Carr ME (1998) Small scale planktonic structure: persistence and trophic consequences. J Oceanogr 11:4–9

Edwards AM, Brindley J (1999) Zooplankton mortality and the dynamical behavior of plankton population models. Bull Math Biol 61:303–339

Edwards CA, Batchelder HP, Powell TM (2000) Modeling microzooplankton dynamics within a coastal upwelling system. J Plankton Res 22:1619–1648

Fileman E, Smith T, Harris R (2007) Grazing by *Calanus helgolandicus* and *Para-Pseudocalanus* spp. on phytoplankton and protozooplankton during the spring bloom in the Celtic Sea. J Exp Mar Biol Ecol 348:70–84

Fileman E, Petropavlovsky A, Harris R (2010) Grazing by the copepods *Calanus helgolandicus* and *Acartia clausi* on the protozooplankton community at station L4 in the Western English Channel. J Plankton Res 32:709–724

Franks PJS (2001) Phytoplankton blooms in a fluctuating environment: the roles of plankton response time scales and grazing. J Plankton Res 23:1433–1441

Genkai-Kato M, Yamamura N (1999) Unpalatable prey resolves the paradox of enrichment. Proc R Soc Lond B 266: 1215–1219

Gill CW, Poulet SA (1988) Responses of copepods to dissolved free amino-acids. Mar Ecol Prog Ser 43:269–276

Hairston NG, Smith FE, Slobodkin LB (1960) Community structure, population control, and competition. Am Nat 94:421–425

Hammer AC, Pitchford JW (2005) The role of mixotrophy in plankton bloom dynamics, and the consequences for productivity. ICES L Mar Sci 62:833–840

Hammer AC, Pitchford JW (2006) Mixotrophy, allelopathy and the population dynamics of phagotrophic algae (cryptophytes) in the Darss Zingst Bodden estuary, southern Baltic. Mar Ecol Prog Ser 328:105–115

Hansen B, Tande KS, Berggreen UC (1990) On the trophic fate of *Phaeocystis pouchetii* (Hariot). III. Functional responses in grazing demonstrated on juvenile stages of *Calanus finmarchicus* (Copepoda) fed diatoms and *Phaeocystis*. J Plankton Res 12:1173–1187

Hansen FC, Reckermann M, Klein Breteler WCM, Riegman R (1993) *Phaeocystis* blooming enhanced by copepod predation on protozoa: evidence from incubation experiments. Mar Ecol Prog Ser 102:51–57

Hay ME (2009) Marine chemical ecology: chemical signals and cues structure marine populations, communities, and ecosystems. Annu Rev Mar Sci 1:193–212

Hilbert DW, Roulet N, Moore T (2000) Modelling and analysis of peatlands as dynamical systems. J Ecol 88: 230–242

Holling CS (1959) The components of predation as revealed by a study of small mammal predation on the European pine sawfly. Can Entomol 91:293–320

Irigoien X, Flynn KJ, Harris RP (2005) Plankton blooms: a ‘loophole’ in microzooplankton grazing impact? J Plankton Res 27:313–321

James A, Pitchford JW, Brindley J (2003) The relationship between plankton blooms, the hatching of fish larvae, and recruitment. Ecol Model 160:77–90

Klein Breteler WCM, Schogt N, Baas M, Schouten S, Kraay GW (1999) Trophic upgrading of food quality by protozoans enhancing copepod growth: role of essential lipids. Mar Biol 135:191–198

Kot M (2001) Elements of mathematical ecolgy. Cambridge University Press, Cambridge

Kowalewsky S, Dambach M, Mauck B, Dehnhardt G (2006) High olfactory sensitivity for dimethyl sulphide in harbour seals. Biol Lett 2:106–109

Levasseur M, Michaud S, Egge J, Cantin G, Nejstgaard JC, Sanders R, Fernandez E, Solberg PT, Heimdal B, Gosselin M (1996) Production of DMSP and DMS during a mesocosm study of an *Emiliania huxleyi* bloom: influence of bacteria and *Calanus finmarchicus* grazing. Mar Biol 126:609–618

McCann K, Hastings A (1997) Re-evaluating the omnivory–stability relationship in food webs. Proc R Soc Lond B 264:1249–1254

Melle W, Skjoldal HR (1998) Reproduction and development of *Calanus finmarchicus*, *C. glacialis* and *C. hyperboreus* in the Barents Sea. Mar Ecol Prog Ser 169:211–228

Morozov AY, Petrovskii SV, Nezlin NP (2007) Towards resolving the paradox of enrichment: the impact of zooplankton vertical migrations on plankton systems stability. J Theor Biol 248:501–511

Morozov A, Arashkevich E, Nikishina A, Solovyev K (2011) Nutrient-rich plankton communities stabilized via predator–prey interactions: revisiting the role of vertical heterogeneity. Math Med Biol 28:185–215

Nejstgaard JC, Båmstedt U, Bagøien E, Solberg PT (1995) Algal constraints on copepod grazing growth state, toxicity, cell size, and season as regulating factors. ICES J Mar Sci 52:347–357

Nejstgaard JC, Gismervik I, Solberg PT (1997) Feeding and reproduction by *Calanus finmarchicus*, and microzooplankton grazing during mesocosm blooms of diatoms and the coccolithophore *Emiliania huxleyi*. Mar Ecol Prog Ser 147:197–217

Nevitt GA (2000) Olfactory foraging by *Antarctic procellariiform* seabirds: life at high Reynolds numbers. Biol Bull 198:245–253

Nevitt GA, Veit RR, Kareiva P (1995) Dimethyl sulphide as a foraging cue for Antarctic Procellariiform seabirds. Nature 376:680–682

Pitchford J, Brindley J (1998) Intratrophic predation in simple predator–prey models. Bull Math Biol 60:937–953

Pohnert G, Steinke M, Tollrian R (2007) Chemical cues, defence metabolites and the shaping of pelagic interspecific interactions. Trends Ecol Evol 22:198–204

Rosenzweig ML (1971) Paradox of enrichment: destabilization of exploitation ecosystems in ecological time. Science 171:385–387

Rosenzweig ML, MacArthur RH (1963) Graphical representation and stability conditions of predator–prey interactions. Am Nat 97:209–223

Saiz E, Calbet A (2007) Scaling of feeding in marine calanoid copepods. Limnol Oceanogr 52:668–675

Sherr E, Sherr B (1988) Role of microbes in pelagic food webs. Limnol Oceanogr 33:1225–1227

Steinke M, Malin G, Liss PS (2002a) Trophic interactions in the sea: an ecological role for climate relevant volatiles. J Phycol 38:630–638

Steinke M, Malin G, Archer SD, Burkill PH, Liss PS (2002b) DMS production in a coccolithophorid bloom: evidence for the importance of dinoflagellate DMSP lyases. Aquat Microb Ecol 26:259–270

Steinke M, Stefels J, Stamhuis E (2006) Dimethyl sulphide triggers search behaviour in copepods. Limnol Oceanogr 51:1925–1930

Tang KW, Jakobsen HH, Visser AW (2001) Phaeocystis globosa (Prymnesiophyceae) and the planktonic food web: feeding, growth, and trophic interactions among grazers. Limnol Oceanogr 46:1860–1870

Truscott JE, Brindley J (1994) Ocean plankton populations as excitable media. Bull Math Biol 56:981–998

Vos M, Kooi BW, DeAngelis DL, Mooij WM (2004) Inducible defences and the paradox of enrichment. OIKOS 105:471–480

Vos M, Vet LEM, Wackers FL, Middelburg JJ, van der Putten WH, Mooij WM, Heip CHR, van Donk E (2006) Infochemicals structure marine, terrestrial and freshwater food webs: implications for ecological informatics. Ecol Inform 1:23–32

Wolfe GV, Steinke M (1996) Grazing-activated production of dimethyl sulfide (DMS) by two clones of *Emiliania huxleyi*. Limnol Oceanogr 41:1151–1160

Yang EJ, Kang HK, Yoo S, Hyun JH (2009) Contribution of auto- and heterotrophic protozoa to the diet of copepods in the Ulleung Basin, East Sea/Japan Sea. J Plankton Res 32:647–659