



Stoichiometry and food-chain dynamics

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Abstract

Traditional models of chemostat systems looking at interactions between predator, prey and nutrients have used only a single currency, such as energy or nitrogen. In reality, growth of autotrophs and heterotrophs may be limited by various elements, e.g. carbon, nitrogen, phosphorous or iron. In this study we develop a dynamic energy budget model chemostat which has both carbon and nitrogen as currencies, and examine how the dual availability of these elements affects the growth of phytoplankton, trophic transfer to zooplankton, and the resulting stability of the chemostat ecosystem. Both species have two reserve pools to obtain a larger metabolic flexibility with respect to changing external environments. Mineral nitrogen and carbon form the base of the food chain, and they are supplied at a constant rate. In addition, the biota in the chemostat recycle nutrients by means of respiration and excretion, and organic detritus is recycled at a fixed rate. We use numerical bifurcation analysis to assess the model's dynamic behavior. In the model, phytoplankton is nitrogen limited, and nitrogen enrichment can lead to oscillations and multiple stable states. Moreover, we found that recycling has a destabilizing effect on the food chain due to the increased repletion of mineral nutrients. We found that both carbon and nitrogen enrichment stimulate zooplankton growth. Therefore, we conclude that the concept of single-element limitation may not be applicable in an ecosystem context.

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1. Introduction

Food-web models in which a set of ordinary differential equations describe the dynamics of trophic groups are ubiquitous in theoretical ecology. They have been commonly used to study the stability and potential coexistence of species assemblages and predict ecologically realistic phenomena, such as the competitive exclusion principle and the 'paradox of enrichment' (Rosenzweig, 1971; Fussmann et al., 2000), where high nutrient provisions cause an equilibrated food chain to become unstable and oscillations to occur. Furthermore, these models may predict the occurrence of multiple

stable states and associated hysteresis loops, which have been shown to occur in nature as well (Scheffer et al., 1993).

Over the past decades, global change has drawn attention to the understanding of environmental carbon and nutrient cycles. These involve the transfer of matter through the trophic niches within ecosystems. A proper understanding of element cycling involves a modelling strategy in which mass balance of all elements is satisfied, such that the whereabouts of elements can be precisely followed. Traditional models are however simplistic and they do not always correctly handle mass balance (Kooi et al., 1998). Furthermore, they usually focus on a single currency, mostly energy, rather than a spectrum of potentially important elements, such as carbon, nitrogen, phosphorous and iron. In this study

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we aim for a model, which traces the trophic flow of nitrogen and carbon through a simple marine food chain, using a mass-balance formulation.

The co-occurrence of multiple currencies requires rules for merging multiple resources into biomasses. When homeostasis for biota is assumed, biomass has a fixed elemental ratio or stoichiometry, while the availability of substrates may be variable. The classic approach here is to apply ‘Liebig’s law of the minimum’ (Liebig, 1840; Huisman and Weissing, 1999; Loladze et al., 2000; Huisman and Weissing, 2001; Grover, 2003). This law states that the availability of the limiting element determines the rate at which a population grows, exclusively. This implies that at some point in the availability of nutrients, limitation switches from the one nutrient to another. This switching behavior is generally modelled using a minimum operator in the description of the growth rate (Tilman, 1982). Simulation of a minimum model can be done without experiencing any trouble; however, if one is interested in a bifurcation analysis, this approach leads to elements of discontinuity in the Jacobian matrix with respect to parameter values associated with resource availability where limitation switches from one resource to another. To circumvent this problem, so-called synthesizing units (SUs) can be used (Kooijman, 1998). Their dynamics relate to classic enzyme kinetics. The latter map substrate concentrations to product fluxes. In contrast, SUs merge fluxes of substrates, rather than concentrations, into biomass and by-products. The SU production rate is a smooth function of substrate availability and a maximum production rate.

Many models dealing with multiple nutrient limitation assume homeostasis for total biomass for each species (Elser and Urabe, 1999). Although this assumption is convenient for many purposes, the elemental composition of biomass appears to be dependent on the nutritional conditions for many species (Kooijman, 2000; Boersma and Kreutzer, 2002; Villar-Argaiz et al., 2002; Cross et al., 2003). Organisms may store nutrients that are provided in excess quantities, hence their nutritional value to the next trophic level may change. Quota models (Droop, 1983) allow for such deviations of whole-body homeostasis, by dividing biomass into permanent (structural) and non-permanent (reserve) components, each with their own composition. Although both components themselves obey homeostasis, total biomass composition need not be constant as reserve densities may vary over time. The implementation of this biological detail comes at the cost of an extra ODE for each reserve pool in the model, which makes numerical analysis more time consuming. However, current computer power compensates for this drawback. Grover used a quota model on Liebig Law principles to analyze effects of stoichiometry on predator–prey systems.

Muller et al. (2001) abandoned the Liebig approach and used synthesizing units in the context of a dynamic energy budget model (DEB, Kooijman, 2000) to investigate the effects of stoichiometry on the dynamics of a producer–consumer system. DEB provides consistent rules for the uptake and use of substrates and can be applied to all organisms. In DEB, assimilated materials are passed to reserve pools, which are mobilized for metabolic processes such as maintenance and growth. The SUs govern these processes in which multiple types of substrates may figure, and the fate of compounds which are in excess provision for metabolic transformations, i.e. non-limiting substrates, can be conveniently determined. This facilitates the formulation of a mass-balance model, in which storage and recycling are implemented.

Recently, Kuiper et al. (2004) demonstrated that a multiple reserve DEB model, employing SUs, could adequately predict egg-production and metabolic mineral release in the copepod *Acartia tonsa*, while a single reserve model was unable to do so. Essential to this study was the dual role of nitrogenous organic reserves that could be preferentially used as building blocks for egg-production, or for energization of metabolic processes. Here, an SU-complex with rules for preferential use of substrates determines the fate of reserves. This approach substantially increases the metabolic flexibility imposed on the consumer model in a physiologically plausible manner.

We expand on the work of Muller et al. (2001) by developing a DEB model where the producer and consumer both possess particular reserve pools for energy and nutrients, where Muller used a single reserve for the producer and no reserve for the consumer species. The model in this paper considers a simple food chain of copepods and diatoms in a chemostat, a setup which lends itself in principle for experimental testing. The diatom population, modelled after *Thalassiosira weissflogii* uses nitrogen (DIN), carbon (DIC) and light, which are supplied to the chemostat at fixed rates. In turn, the copepod population, *Acartia tonsa*, feeds on diatoms. Dead biomass and fecal pellets are stored in nitrogenous and non-nitrogenous detritus pools, from which they are mineralized. These recycled minerals, plus the minerals excreted by the copepods and the diatoms themselves can be assimilated again by the diatoms. The volume of the chemostat is constant, and all constituents are washed out at a fixed rate. We study the combined effects of resource enrichment and recycling in this setup on the qualitative behavior of the food chain and compare them to predictions of traditional food chains.

We are aware that taking the step from very simple stoichiometric models to biologically detailed ones comes with a few drawbacks. For instance, it becomes increasingly difficult to assess the effect of any particular

model parameter on model dynamics when there are many candidate parameters that can be varied simultaneously. Moreover, one requires more biological knowledge and experimental data to validate a more complex model. On the other hand, traditional simplistic stoichiometric models have been unable to correctly capture element limitation in zooplankton production (Anderson and Hessen, 1995; Muller et al., 2001; Kuiper et al., 2004), while a DEB-based model could (Kuiper et al., 2004). One can question whether simple stoichiometric models are able to adequately describe food web dynamics if their use in population studies is limited. We address this question by comparing results of a stoichiometric multiple-reserve DEB model using synthesizing units with results of models following a traditional approach.

The paper is organized as follows. The next section holds a detailed introduction to the modelling framework, in which we motivate our modelling decisions. In the section thereafter, we present a summary of the chemostat model as used in this study. In the results section, we present a bifurcation analysis of the model, in which we vary the availability of resources. In the discussion, we will compare the model results to classic studies and point out the implications of this study.

2. Modelling framework

2.1. Primary producers

2.1.1. Assimilation

For simplicity's sake, we assume that the producers may only be limited either by light, mineral carbon or mineral nitrogen. While iron has been shown to be a potential limiting factor in phytoplankton (Scharek et al., 1997; Erdner and Anderson, 1999; Erdner et al., 1999), this currency is not included in the basic structure of the model. Iron limitation can be implemented without loss of consistency, but this makes model formulations considerably more complex, thereby compromising the aim of this study. For now, we assume ad libitum availability of iron.

In addition to structural volume, we assume two reserve pools for the diatoms, one consisting of non-nitrogenous organic materials (hydrocarbons) and one consisting of mineral nitrogen. Assimilation of minerals into these reserves follows the biochemical reaction



where N and C stand for inorganic sources of nitrogen and carbon. Autotroph inorganic nitrogen and organic carbon reserves are represented by E_N^A and E_H^A , respectively. The notation is summarized in Table 1.

Table 1
Interpretation of symbols

Symbol	Interpretation
<i>Species</i>	
A	Producer
C	Consumer
<i>Compounds</i>	
C	Mineral carbon
D_H	Carbohydrate detritus
D_P	Protein detritus
E_x^z	Reserves x of species z
H	Carbohydrates
N	Mineral nitrogen
P	Proteins
X^z	Structural mass of species z
<i>Processes</i>	
A	Assimilation
B	Catabolism after maintenance
C	Catabolism
E	Excretion
G	Growth
H	Mortality
I	Ingestion
M	Maintenance
R	Rejection
<i>Other</i>	
f_x^z	Scaled functional response of z feeding on x
$\tilde{f}_{x,y}^z$	Flux of x in process y of species z
k_D	Decomposition rate of organic matter
k_E^z	Reserve mobilization rate of species z
k_H^z	Mortality rate of species z
k_M^z	Maintenance rate of species z
r^z	Structure-specific growth rate of species z
y_{x_1,x_2}^p	Mass coupler $x_2 \rightarrow x_1$ in pathway p
D	Dilution rate
$[E]_x^z$	Reserve density x of species z
L	light
I_x^z	Maximum specific ingestion rate of species z on x
K_x^z	Half-saturation value of species z utilizing x
κ^z	Fraction of unused reserves directed back to reserves of species z
θ_{s_1,s_2}	fraction of SUs in state s_1, s_2
ρ_x^p	SU binding probability of x for pathway p
ϕ_x	C:N ratio of compound x
$\psi_{x,y}^z$	Transformation efficiency of x in process y of species z

Algal acquisition of minerals and energy is a complex process, and we simplify the modelling thereof considerably to maintain a certain degree of simplicity. Firstly, we assume a spatially homogeneous environment, which implies that the model does not allow for light gradients, caused by photon-scattering and self-shading, which occur in natural aquatic ecosystems. However, our focus is on the effects of more metabolic flexibility, and this can best be studied in a spatially

homogeneous environment. This is due to the metabolic memory; in a spatially heterogeneous environment the travelling path of individuals then becomes important. Secondly, we simplified the speciation of non-living resources in the environment to a large extent. As for carbon uptake, we omit the complex carbon chemistry of marine systems, and its impact on diatom production (Morel et al., 2002). Instead, we use a single carbon currency (DIC).

We use a type-II functional response to model the assimilation of inorganic nitrogen. Although light impacts on the enzymatic activity of nitrogen reductase, which is important in the assimilation of nitrogen (Berges and Harrison, 1995), it appears that nitrogen uptake rates can be described by a simple saturating function (Eppley et al., 1969). Carbon assimilation is modelled by a complementary SU, which requires both light and carbon. The formulation of SUs for biochemical reactions can be found in detail in Kooijman (1998). Data from Riebesell et al. (1993) show that, provided that pH is constant and CO₂ is therefore a constant percentage of total inorganic carbon, carbon assimilation can be described with a saturating function of DIC availability. For the mathematical derivation of SU dynamics, we refer to Kooijman (1998). The assimilated fluxes, scaled to structural biomass, are

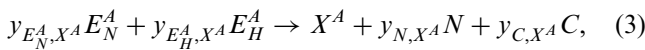
$$j_{N,A}^A = I_N^A f_N^A = I_N^A \frac{N}{N + K_N^A}, \quad (2a)$$

$$j_{H,A}^A = I_C^A f_C^A = I_C^A \left(1 + \frac{K_L^A}{j_L} + \frac{K_C^A}{C} - \frac{1}{\frac{j_L}{K_L^A} + \frac{C}{K_C^A}} \right)^{-1}, \quad (2b)$$

where I_N^A, I_C^A are the maximum structure specific assimilation rates of mineral nitrogen and carbon dioxide, respectively, f_N^A, f_C^A are the corresponding scaled functional responses, in which K_N^A, K_C^A are the half-saturation concentrations of minerals, K_L^A is the half-saturation flux of photons, and j_L is the photon flux.

2.1.2. Growth

We use an extended Droop-model (Droop, 1983) with two reserve pools for the diatom species, by which we assume that costs associated with basal metabolism are negligible. The transformation of reserves into biomass and by-products is described by the following macro-biochemical process:



where E_N^A, E_H^A are the autotroph's nitrogen and carbon reserves, respectively, X^A represents autotroph structural biomass and C and N are minerals excreted into the environment. The coefficients y couple substrates and by-products to structural biomass stoichiometrically.

Their values are determined by using the maximum attainable production efficiencies per substrate and on the C:N ratios of the compounds involved in the transformation. Here,

$$y_{E_N^A, X^A} = \frac{1}{\phi_{X^A} \psi_{N,G}^A}, \quad (4a)$$

$$y_{E_H^A, X^A} = \frac{1}{\psi_{H,G}^A}, \quad (4b)$$

$$y_{N, X^A} = \frac{1 - \psi_{N,G}^A}{\phi_{X^A} \psi_{N,G}^A}, \quad (4c)$$

$$y_{C, X^A} = \frac{1 - \psi_{H,G}^A}{\psi_{H,G}^A}, \quad (4d)$$

where ϕ 's refer to the C:N ratio of the particular compound and ψ 's are production efficiencies on the corresponding substrate.

A fundamental principle of DEB-theory is that reserves are mobilized as a first-order process in reserve density. Hence, reserve dynamics are described by

$$\frac{d}{dt}[E_N^A] = j_{N,A}^A - k_E^A [E_N^A], \quad (5a)$$

$$\frac{d}{dt}[E_H^A] = j_{H,A}^A - k_E^A [E_H^A], \quad (5b)$$

where k_E^A is the turnover rate of reserves. Throughout this paper, bracketed variables indicate that the associated compound is expressed in units per unit of structural biomass. The structure-specific fluxes of mobilized reserves amount to

$$j_{N,C}^A = [E_N^A](k_E^A - r^A), \quad (6a)$$

$$j_{H,C}^A = [E_H^A](k_E^A - r^A), \quad (6b)$$

in which r^A is the structure-specific growth rate $\frac{1}{X^A} \frac{d}{dt} X^A$. The two reserves are merged to form biomass at a complementary synthesizing unit. Biomass-specific growth equals

$$r^A = \left(\frac{y_{E_N^A, X^A}}{j_{N,C}^A} + \frac{y_{E_H^A, X^A}}{j_{H,C}^A} - \frac{y_{E_N^A, X^A} y_{E_H^A, X^A}}{y_{E_N^A, X^A} j_{N,C}^A + y_{E_H^A, X^A} j_{H,C}^A} \right)^{-1}. \quad (7)$$

Note that $j_{N,C}^A$ and $j_{H,C}^A$ now figure in both the left-hand side and right-hand side of Eq. (6), by which the biomass-specific growth rate, r^A , is implicitly defined and must be solved numerically. The growth SU differs from the assimilation SU which merges carbon and photons, in that growth is not bounded by a maximum transformation rate, such as I_C^A in Eq. (2b). Rather, the growth rate is limited by the boundedness of the reserve fluxes, mobilized from the reserve pools.

2.1.3. Excretion

Excreted materials are recycled back into the environment, from which they become available again to the producer population. Metabolic by-products are excreted in mineral form, so that they become directly available again. Organic materials must be decomposed before they are available in mineral form, and they are stored in organic detritus pools.

Growth comes with overhead costs. The evolution of by-products amounts to

$$j_{N,G}^A = y_{N,X^A} r^A, \quad (8a)$$

$$j_{C,G}^A = y_{C,X^A} r^A. \quad (8b)$$

Imbalances between supply rates and growth requirements may result in rejection of the non-limiting substrate at the SU. Excess substrates are only partly excreted and partly returned to their original reserve pools (fraction κ^A). This enables non-limiting reserves to dam up within the algae, which affects the total biomass composition, and the associated nutritional value to the next trophic level. The biomass-specific fluxes of excreted NH_3 and D_H are

$$j_{N,R}^A = (1 - \kappa^A)(j_{E_{N,C}}^A - y_{E_{N,X^A}}^A r^A), \quad (9a)$$

$$j_{D_{H,R}}^A = (1 - \kappa^A)(j_{E_{H,C}}^A - y_{E_{H,X^A}}^A r^A). \quad (9b)$$

The total amount of excreted compounds by the producers is

$$j_{N,E}^A = j_{N,G}^A + j_{N,R}^A, \quad (10a)$$

$$j_{C,E}^A = j_{C,G}^A, \quad (10b)$$

$$j_{D_{H,E}}^A = j_{D_{H,R}}^A. \quad (10c)$$

2.2. Consumers

2.2.1. Assimilation

Food composition for consumers can be expressed in terms of structural volume X^A , nitrogen reserves E_N^A and carbohydrate reserves E_H^A of the diatoms. The producer's structural mass X^A comprises proteins, carbohydrates and unassimilable materials. Homeostasis dictates that each of them has a fixed contribution to structural mass. The consumer species can assimilate the structural proteins directly with efficiency $y_{E_P^C,X^A}$. It is known that low C:N-foods enhance copepod production (Checkley, 1980; Kjørboe, 1989). In the model, the reserve densities largely determine the C:N of diatoms. We assume that the producer's nitrogen reserves can, in conjunction with carbohydrates, also be transformed into protein reserves, thus modelling a positive copepod response to ingesting low C:N diatoms. The associated carbohydrates derive from either the producer's reserves E_H^A or structural components X^A . The biochemical

transformations involved are

$$X^A \rightarrow y_{E_P^C,X^A} E_P^C + y_{H,X^A} H + y_{D_P,X^A} D_P + y_{D_H,X^A} D_H \quad (11a)$$

$$E_H^A \rightarrow H \quad (11b)$$

$$H \rightarrow y_{E_H^C,H}^H E_H^C + y_{C,H}^H C, \quad (11c)$$

$$H + y_{E_{N,E_P}^{NH}} E_N^A \rightarrow y_{E_P^C,H}^{NH} E_P^C + y_{C,H}^{NH} C, \quad (11d)$$

where H is the hydrocarbon precursor formed from autotroph structure and reserves, and D_P and D_H represent nitrogenous and non-nitrogenous detritus formed, respectively. The coefficients y balance the transformations stoichiometrically. We base their values on assimilation efficiencies of carbon and nitrogen, such that

$$y_{E_P^C,X^A} = \psi_{P,A}^C \frac{\phi_P}{\phi_{X^A}}, \quad (12a)$$

$$y_{H,X^A} = \psi_{H,X^A}^C \left(1 - \frac{\phi_P}{\phi_{X^A}}\right), \quad (12b)$$

$$y_{D_P,X^A} = \left(1 - \psi_{P,A}^C\right) \frac{\phi_P}{\phi_{X^A}}, \quad (12c)$$

$$y_{D_H,X^A} = \left(1 - \psi_{H,X^A}^C\right) \left(1 - \frac{\phi_P}{\phi_{X^A}}\right), \quad (12d)$$

$$y_{E_H^C,H}^H = \psi_{H,E,A}^C, \quad (12e)$$

$$y_{C,H}^H = 1 - \psi_{H,E,A}^C, \quad (12f)$$

$$y_{E_{N,E_P}^{NH}} = \frac{\psi_{H,E,A}^C}{\phi_P}, \quad (12g)$$

$$y_{E_P^C,H}^{NH} = \psi_{H,E,A}^C, \quad (12h)$$

$$y_{C,H}^{NH} = 1 - \psi_{H,E,A}^C. \quad (12i)$$

We assume that unassimilable producer structure is egested as pellets, which contribute to the carbohydrate and protein detritus pools, D_H and D_P , respectively. An SU governs transformations (11c,11d), which occur simultaneously, i.e. carbohydrates may be used for production of either carbohydrate or protein reserves, of which the latter occurs in association with the diatoms nitrogen reserves. The SU resembles the production SU of Kuijper et al. (2004) (cf. auxiliary SU as introduced in Kooi et al., 2004). When carbohydrates bind to an empty SU, reaction (11c) takes place and carbohydrate reserves are produced, while reaction (11d), and the associated production of protein reserves, occurs when carbohydrates bind to an SU that is already saturated

with E_N^A . Net assimilation of copepod reserves is

$$j_{P,A}^C = I_{X^A}^C f_{X^A}^C (y_{E_P^C, X^A}^C + y_{E_P^C, H}^{NH} (y_{H, X^A} + [E]_H^A) \theta), \quad (13a)$$

$$j_{H,A}^C = I_{X^A}^C f_{X^A}^C y_{E_H^C, H}^H (y_{H, X^A} + [E]_H^A) (1 - \theta), \quad (13b)$$

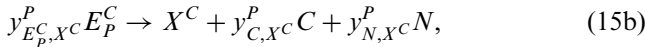
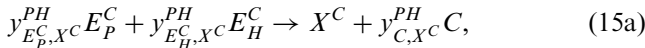
in which $I_{X^A}^C$ is the maximum copepod ingestion rate with respect to diatoms and θ is the fraction of assimilation SUs saturated with diatom nitrogen reserves

$$\theta = \frac{[E]_N^A}{[E]_N^A + \frac{y_{H, X^A} + [E]_H^A}{y_{E_N^A, EC}^{NH}}}. \quad (14)$$

Furthermore, $f_{X^A}^C = \frac{X^A}{K_{C, X^A} + X^A}$, and this models the functional response of copepod feeding on algae.

2.2.2. Maintenance and growth

For maintenance and growth, we employ the model for *Acartia* egg production by Kuijper et al. (2004). Reserves can be transformed into structural biomass in one of two production routes. We will name a P-route, in which proteins are processed exclusively, and a PH-route, where merging of proteins and carbohydrates takes place. The transformations are



in which the stoichiometric couplers are defined in terms of maximum growth efficiencies and C:N ratios of the substrates

$$y_{E_P^C, X^C}^{PH} = \frac{\phi_P}{\phi_{X^C}}, \quad (16a)$$

$$y_{E_H^C, X^C}^{PH} = \frac{1}{\psi_{C, PH}} - \frac{\phi_P}{\phi_{X^C}}, \quad (16b)$$

$$y_{C, X^C}^{PH} = \frac{1 - \psi_{C, PH}}{\psi_{C, PH}}, \quad (16c)$$

$$y_{E_P^C, X^C}^P = \frac{1}{\psi_{C, P}}, \quad (16d)$$

$$y_{C, X^C}^P = \frac{1 - \psi_{C, P}}{\psi_{C, P}}, \quad (16e)$$

$$y_{N, X^C}^P = \frac{1}{\phi_P \psi_{C, P}} - \frac{1}{\phi_{X^C}}. \quad (16f)$$

Analogous to the modelling of *Thalassiosira*, the copepod reserve dynamics are

$$\frac{d}{dt}[E]_P^C = j_{P,A}^C - k_E^C [E]_P^C, \quad (17a)$$

$$\frac{d}{dt}[E]_H^C = j_{H,A}^C - k_E^C [E]_H^C, \quad (17b)$$

and, accordingly, the catabolic fluxes are

$$j_{P,C}^C = [E]_P^C (k_E^C - r^C), \quad (18a)$$

$$j_{H,C}^C = [E]_H^C (k_E^C - r^C). \quad (18b)$$

Maintenance and production require building blocks and energy to meet the associated costs. Protein reserves serve as building blocks, whereas carbohydrates are the preferred substrate for respiration to avoid wasting proteins. However, when the supply of carbohydrates is short, the copepods may respire proteins instead. Costs for maintenance are proportional to structural volume. Biomass-specific costs for maintenance are subtracted from the catabolic flux by an auxiliary SU. For an elaborate derivation of SU dynamics, the reader is referred to Kuijper et al. (2004). Maintenance costs are

$$j_{P,M}^C = k_M^C \frac{\rho_P^P j_{P,C}^C + \frac{y_{E_P^C, X^C}^{PH}}{y_{E_H^C, X^C}^{PH}} \rho_H^PH j_{H,C}^C}{\frac{\rho_P^P}{y_{E_P^C, X^C}^P} j_{P,C}^C + \frac{\rho_H^PH}{y_{E_H^C, X^C}^P} j_{H,C}^C}, \quad (19a)$$

$$j_{H,M}^C = k_M^C \frac{\rho_H^PH j_{H,C}^C}{\frac{\rho_P^P}{y_{E_P^C, X^C}^P} j_{P,C}^C + \frac{\rho_H^PH}{y_{E_H^C, X^C}^P} j_{H,C}^C}, \quad (19b)$$

where k_M^C is the maintenance rate coefficient. The ρ 's stand for the probability of binding a substrate-molecule that is directed to an SU, ρ_P^P is the probability of protein binding to an empty SU and ρ_H^PH is the binding probability of carbohydrates to an available binding site on the SU. The remainder of the catabolic flux after maintenance is paid is the growth-directed flux

$$j_{P,B}^C = j_{P,C}^C - j_{P,M}^C, \quad (20a)$$

$$j_{H,B}^C = j_{H,C}^C - j_{H,M}^C, \quad (20b)$$

and these two fluxes are used for biomass production. The SU which governs the associated transformations resembles the maintenance SU in that it completes exactly the same transformation; however, the production rate is not fixed here; and the growth rate depends on the availability of proteins and carbohydrates (Kuijper et al., submitted). The biomass-specific growth rate amounts to

$$r^C = j_{P,B}^C \frac{y_{E_H^C, X^C}^{PH} \rho_P^P}{\frac{y_{E_P^C, X^C}^{PH}}{\rho_H^PH} j_{P,B}^C + \frac{y_{E_P^C, X^C}^{PH}}{\rho_P^P} j_{H,B}^C} + j_{H,B}^C \frac{y_{E_P^C, X^C}^{PH}}{\rho_H^PH} j_{P,B}^C + \frac{y_{E_H^C, X^C}^{PH}}{\rho_P^P} j_{H,B}^C} \quad (21)$$

with ρ_P^PH as the binding probability of protein reserves on SUs that have already bound carbohydrates. The

associated use of reserves is

$$j_{P,G}^C = j_{P,B}^C \frac{\frac{y_{E,H}^{PH} \rho_P^{PH} j_{P,B}^C}{y_{E,P}^{PH} \rho_H^{PH}} j_{P,B}^C + j_{H,B}^C}{\frac{y_{E,H}^{PH} \rho_P^{PH}}{y_{E,P}^{PH} \rho_H^{PH}} j_{P,B}^C + j_{H,B}^C}, \quad (22a)$$

$$j_{H,G}^C = j_{H,B}^C \frac{\rho_H^{PH} j_{P,B}^C}{\frac{y_{E,H}^{PH} \rho_P^{PH}}{y_{E,P}^{PH} \rho_H^{PH}} j_{H,B}^C + j_{P,B}^C}. \quad (22b)$$

Reserves unable to bind to the growth SU are partly restored into the corresponding reserve pools with fraction κ^C . The fraction $1 - \kappa^C$ is excreted as minerals.

2.2.3. Excretion and defecation

Fecal pellets and the dead biomass contribute to the detritus pools. Egestion of pellets, i.e. unassimilated materials, amounts to

$$j_{D_P,A}^C = I_{X^A}^C f_{X^A}^C (1 - \psi_{P,A}^C) \frac{\phi_P}{\phi_{X^A}}, \quad (23a)$$

$$j_{D_H,A}^C = I_{X^A}^C f_{X^A}^C (1 - \psi_{H,X^A}^C) \left(1 - \frac{\phi_P}{\phi_{X^A}}\right). \quad (23b)$$

The overhead of assimilation quantifies as the difference between ingestion and assimilation (Eq. (13)) and fecal production (Eq. (23)). The associated biomass-specific excretion of minerals is

$$j_{N,A}^C = I_{X^A}^C f_{X^A}^C \left(\frac{1}{\phi_{X^A}} + [E]_N^A \right) - \frac{j_{P,A}^C + j_{D_P,A}^C}{\phi_P}, \quad (24a)$$

$$j_{C,A}^C = I_{X^A}^C f_{X^A}^C (1 + [E]_H^A) - j_{P,A}^C - j_{H,A}^C - j_{D_P,A}^C - j_{D_H,A}^C. \quad (24b)$$

We assume that all metabolic products of the consumer species are in mineral form. The excretion of maintenance products is a weighted sum of the products of the P and the PH-route

$$j_{N,M}^C = \frac{j_{P,M}^C}{\phi_P}, \quad (25a)$$

$$j_{C,M}^C = j_{P,M}^C + j_{H,M}^C. \quad (25b)$$

Growth overhead giving rise to excretion quantifies as

$$j_{N,G}^C = j_{P,B}^C \frac{\frac{y_{N,X^C}^P}{y_{E,P}^{PH} \rho_H^{PH}} \rho_P^P j_{P,B}^C}{\frac{y_{E,H}^{PH} \rho_P^{PH}}{y_{E,P}^{PH} \rho_H^{PH}} j_{P,B}^C + j_{H,B}^C}, \quad (26a)$$

$$j_{C,G}^C = j_{P,B}^C \frac{\frac{y_{C,X^C}^P}{y_{E,P}^{PH} \rho_H^{PH}} \rho_P^P j_{P,B}^C + \frac{y_{C,X^C}^P}{y_{E,H}^{PH} \rho_H^{PH}} \rho_H^{PH} j_{H,B}^C}{\frac{y_{E,H}^{PH} \rho_P^{PH}}{y_{E,P}^{PH} \rho_H^{PH}} j_{H,B}^C + j_{P,B}^C}. \quad (26b)$$

To our knowledge, copepods do not excrete organic substances. Therefore, excretion as a consequence of rejection at the growth SU is also assumed to be in mineral form. It amounts to

$$j_{N,R}^C = \frac{(1 - \kappa^C)(j_{P,B}^C - j_{P,G}^C)}{\phi_P}, \quad (27a)$$

$$j_{C,R}^C = (1 - \kappa^C)(j_{P,B}^C + j_{H,B}^C - j_{P,G}^C - j_{H,G}^C). \quad (27b)$$

The total excretion of consumers amounts to

$$j_{N,E}^C = j_{N,A}^C + j_{N,M}^C + j_{N,G}^C + j_{N,R}^C, \quad (28a)$$

$$j_{C,E}^C = j_{C,A}^C + j_{C,M}^C + j_{C,G}^C + j_{C,R}^C. \quad (28b)$$

2.2.4. Death

For simplicity, we assume that the consumers have a constant death rate. Death results in the production of detritus species. Biomass-specific contributions to the detritus pools amount to

$$j_{D_P,H}^C = k_H^C \left(\frac{\phi_P}{\phi_{X^C}} + [E]_P^C \right), \quad (29a)$$

$$j_{D_H,H}^C = k_H^C \left(1 - \frac{\phi_P}{\phi_{X^C}} + [E]_H^C \right). \quad (29b)$$

2.3. Decomposition and recycling

Excreted minerals are in the form of utilizable nutrients for the producer species. However, organic materials must be decomposed first. For reasons of simplicity, we have chosen to model the biodegradation of detritus as a first-order process.

2.4. Model summary

The structure of the complete model is

$$\begin{aligned} \frac{d}{dt} N &= (j_{N,E}^A - j_{N,A}^A) X^A + j_{N,E}^C X^C \\ &\quad + k_D \frac{D_P}{\phi_P} + D(X_{r,N} - N), \end{aligned} \quad (30a)$$

$$\begin{aligned} \frac{d}{dt} C &= (j_{C,E}^A - j_{H,A}^A) X^A + j_{C,E}^C X^C \\ &\quad + k_D(D_H + D_P) + D(X_{r,C} - C), \end{aligned} \quad (30b)$$

$$\frac{d}{dt} [E]_N^A = j_{N,A}^A + \kappa^A(j_{N,C}^A - y_{E,N}^A r^A) - k_E^A [E]_N^A, \quad (30c)$$

$$\frac{d}{dt} [E]_H^A = j_{H,A}^A + \kappa^A(j_{H,C}^A - y_{E,H}^A r^A) - k_E^A [E]_H^A, \quad (30d)$$

$$\frac{d}{dt} X^A = (r^A - D) X^A - I_{X^A}^C f_{X^A}^C X^C, \quad (30e)$$

$$\frac{d}{dt} [E]_P^C = j_{P,A}^C + \kappa^C(j_{P,B}^C - j_{P,G}^C) - k_E^C [E]_P^C, \quad (30f)$$

$$\frac{d}{dt} [E]_H^C = j_{H,A}^C + \kappa^C(j_{H,B}^C - j_{H,G}^C) - k_E^C [E]_H^C, \quad (30g)$$

Table 2
Parameter values

Parameter	Value	Units	Reference
k_E^A	0.36	h^{-1}	Zonneveld et al. (1997)
k_E^C	0.1	h^{-1}	Kuiper et al. (2004)
k_H^C	0.008	h^{-1}	Takahashi and Ohno (1996)
k_M^C	0.0041	h^{-1}	Kuiper et al. (2004)
k_D	0.005	h^{-1}	Fujii et al. (2002)
I_C^A	0.01	h^{-1}	Riebesell et al. (1993)
I_N^A	0.01	h^{-1}	Davidson and Gurney (1999)
$I_{X^A}^C$	0.06	h^{-1}	Kjørboe (1989)
K_C^A	750.0	μM	After (Riebesell et al. (1993), Burkhardt et al. (2001))
K_L^A	210	$\mu\text{mol m}^{-2} \text{s}^{-1}$	Zonneveld et al. (1997)
K_N^A	2.5	μM	Eppley et al. (1969)
K_{C,X^A}	20.0	μM	fitted after (Kjørboe et al. (1985))
κ^A	0.98	—	Kooijman (pers. comm.)
κ^C	0.5	—	Kuiper et al. (2004)
ρ_H^{PH}	0.66	—	Kuiper et al. (2004)
ρ_P^P	0.66	—	Kuiper et al. (2004)
ρ_P^{PH}	0.95	—	Kuiper et al. (2004)
ϕ_P	3.7	##	Vollenweider (1985)
ϕ_{X^A}	10.0	##	Strzepek and Price (2000)
ϕ_{X^C}	5.9	##	Kjørboe et al. (1985)
$\psi_{H,E,A}^C$	0.881	—	Anderson (1994)
$\psi_{H,G}^A$	0.8	—	—
$\psi_{H,X,A}^C$	0.553	—	Anderson (1994)
$\psi_{N,G}^A$	0.8	—	—
$\psi_{P,A}^C$	0.688	—	Anderson (1994)

$$\frac{d}{dt} X^C = (r^C - D - k_H^C) X^C, \quad (30h)$$

$$\frac{d}{dt} D_P = (j_{D_P,H}^C + j_{D_P,A}^C) X^C - (k_D + D) D_P, \quad (30i)$$

$$\frac{d}{dt} D_H = j_{D_H,E}^A X^A + (j_{D_H,H}^C + j_{D_H,A}^C) X^C - (k_D + D) D_H. \quad (30j)$$

The currencies for structural biomasses are X^A and X^C ; however, carbonous reserves also contribute to the C -molar volume of biomass. Total C -molar biomasses are

$$\mathcal{A} = X^A(1 + [E]_H^A), \quad (31a)$$

$$\mathcal{C} = X^C(1 + [E]_H^C + [E]_P^C). \quad (31b)$$

Table 1 lists the model notation, and Table 2 holds referenced parameter values as used in the model.

3. Model dynamics

In this section we analyze the model's long-term behavior. We will concentrate on the influence of the nutritional conditions, on the role of increased metabolic flexibility with respect to variable nutritional conditions, and on effects of recycling. To facilitate

the analysis, we follow a stepwise approach in which we deal with subsections of the model before we analyze the complete model as given in Eq. (30j). We start with the analysis of the resource–producer system, in which the consumer level is absent. We continue with the analysis of a producer–consumer system, in which both the composition of the producer species and the supply rate of producers act as input parameters, i.e. in this analysis, the dynamics of the diatoms are not modelled explicitly. In this way, the model effectively becomes a static model, comparable to that of Anderson and Hessen (1995) and Kuiper et al. (2004). We conclude this section with the analysis of the resource–producer–consumer system. To study the effect of recycling, we will compare results to analyses, in which we omitted the recycling of nutrients.

As default environmental conditions for the system to run, we chose an inorganic carbon ($X_{r,C}$) and nitrogen ($X_{r,N}$) supply concentration of 2 mM and 10 μM , respectively. These are realistic values for the upper layers of those marine waters where nitrogen is likely to be the limiting factor. Both minerals are supplied at a fixed throughput rate of $D = 0.001 \text{ h}^{-1}$. The default light flux (j_L) is set constant to $600 \mu\text{mol m}^{-2} \text{s}^{-1}$, at which light is abundant. This simplification has been done to facilitate the model analysis. The default recycling rate

for organic matter, k_D , was set to 0.005 h^{-1} (Fujii et al., 2002).

3.1. The resource–producer system

Fig. 1 contains the analysis of the resource–producer system. This system is a subsection of system 30, where the consumer is absent ($X^C = 0$). The diatom biomass is plotted against resource density for the resources light, inorganic carbon and inorganic nitrogen. Recycling effectively complements the resource supply, so that biomasses are lower when this process is excluded from the model (Fig. 1, lower row). For the same reason, the reserve densities of non-limiting reserves are also higher when recycling takes place. The qualitative behavior of the model does not depend on recycling.

The effect of light is shown in the left graphs of Fig. 1. When light intensity is too low, the producer population cannot survive. There appears to be a threshold intensity at which the population suddenly reaches a considerable biomass. Although the sharp angle in the curves (Fig. 1, left panel) might suggest a switch in survivability, light dependency is continuous. When light intensity is increased further, the total producer biomass increases, although the structural biomass is seemingly unaffected by light enhancement. Increased light intensity facilitates carbohydrate assimilation through higher photosynthesis rates. However, excess carbohydrate reserves cannot be used for production when nitrogen is scarce, so that they will effectively dam up.

Carbon dependency is shown in the center diagrams of Fig. 1. Carbon limitation occurs at supplies roughly between 100 and $500 \mu\text{M}$, below which the producers cannot survive and above which further enrichment has

no effect on the structural biomass density of the producers. This result is similar to the predictions of Liebig’s law. When carbon is limiting, the associated reserve density is small, as carbon is then efficiently used for growth. However, further carbon enhancement causes carbohydrate reserve accumulation and the associated growth of total biomass.

The diagrams on the right-hand side of Fig. 1 show the effect of nitrogen on diatom production. Over the whole plotting range of $X_{r,N}$ nitrogen is the limiting nutrient. The relative contribution of structural biomass to total biomass decreases with increasing nitrogen provision. This is due to a decrease in carbohydrates reserve density. The reduction of carbohydrate accumulation with increasing $X_{r,N}$ can be attributed to the lesser extent to which nitrogen is the limiting factor.

3.2. The producer–consumer system

In the analysis, the effect of the diatom’s composition on the copepod’s growth is investigated. For this reason we left out the explicit modelling of producer dynamics. Inert producers are supplied to the chemostat, where consumers feed on them. This corresponds to an experimental setup where a two-stage chemostat is used (Boraas, 1983) and compares to the theoretical approach followed by Anderson and Hessen (1995) and Kuijper et al. (2004). Here, algae are grown under controlled conditions in one vessel and then supplied to a second vessel, in which grazers are present, at a fixed rate. In the associated model, the density of diatoms in the supply to the second chemostat, as well as their composition in terms of reserve densities act as model parameters.

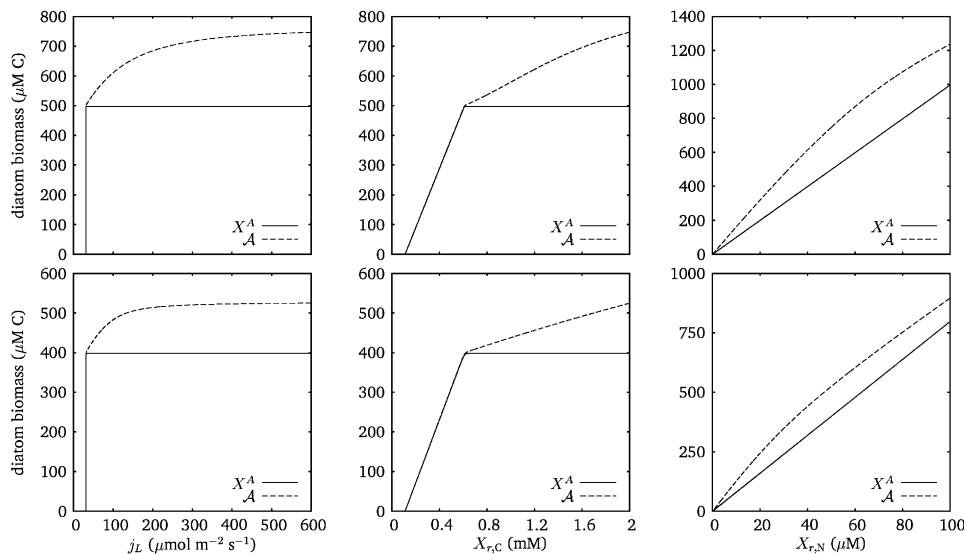


Fig. 1. Algal total biomass ($\mathcal{A}$, dashed line) and structural biomass (X_A) as a function of light intensity (left), inorganic carbon supply (center), or nitrogen supply (right) when excreted compounds are recycled (upper row) or not (lower row). When kept constant, $X_{r,N} = 50 \mu\text{M}$, $X_{r,C} = 2 \text{ mM}$ and the photon flux is $600 \mu\text{mol m}^{-2} \text{s}^{-1}$. Biomasses, as well as the densities of the non-limiting reserve are higher when recycling is included in the model.

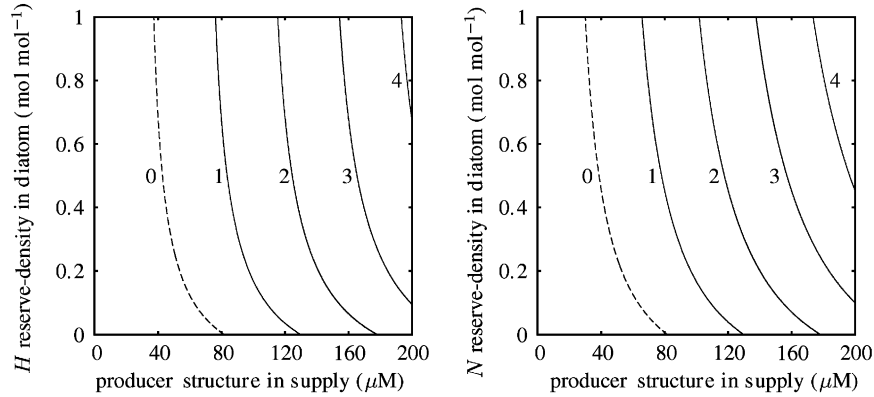


Fig. 2. Contourplots of the consumer's structural mass at variable algal structure concentrations and reserve densities are $[E]_H^A$ (left) and $[E]_N^A$ (right). Contours are in μM carbon in consumer structure. The density of the alternative reserve is kept at zero, which corresponds to severe limitation of the associated nutrient. The contourline marked zero indicates the invasion boundary of the consumer species. High producer reserve densities facilitate consumer persistence. This effect is stronger for nitrogen than for carbohydrate reserves..

Fig. 2 gives contourlines of consumer densities when producer supply rates and either of their reserve densities are varied. It is to be expected that the density of the reserve associated with the limiting nutrient will be generally low. Therefore, the density of the reserve that does not appear on the vertical axis is kept at zero, thereby simulating limitation of the corresponding nutrient. The contourline marked zero indicates the survival boundary of the consumer species. Higher diatom reserve densities facilitate invasion of the copepod, more so for nitrogen reserves than for carbohydrate reserves.

Fig. 3 shows the effect of balancing the producers reserve densities. Here, the total reserve density is kept constant at 0.5 (in molar ratio to biomass). The graph gives contourlines of copepod densities, and the zero-contourline indicates the consumer survival boundary. The figure shows that a relatively even distribution of producer nitrogen and carbohydrate reserves promotes consumer survivability ($E_N^A/(E_N^A + E_H^A) \approx 0.6$). Producers are generally low in reserves that limit their production and high in reserves that are non-limiting. As a consequence, an even distribution in reserve densities is only achievable when the producer species experiences proper nutrition. It appears that grazers profit from a proper nutrition of the primary producers.

Consumer biomass densities as a function of supplied producer structure are presented in Fig. 4. Here, five scenarios are compared, in which diatoms of different compositions, in terms of reserve densities, are supplied to the copepods in the chemostat. The diagrams show that the composition of the producers significantly affects the consumer density. When producer reserves are both high, the consumers can persist at a lower supply of food, and their population size is largest. Nitrogen-limited diatoms (N^-, H^+) lead to lower structural copepod biomasses than carbon-limited ones (N^+, H^-). When both producer reserves are evenly

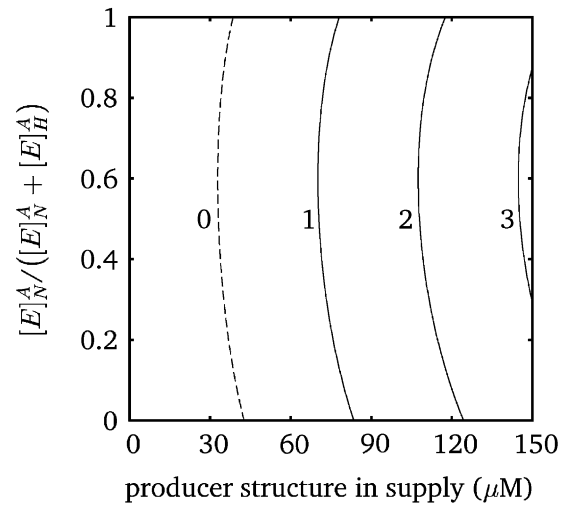


Fig. 3. Contourplots of the consumer's structural mass when the structure-specific density of total producer reserves is held constant at 0.5, while the quantity of producer structure (x-axis) and the composition of its reserves (y-axis) are varied. Contours are in μM carbon in consumer structure. A properly balanced composition of net producer biomass facilitates survival of the consumer species.

abundant, (N^+, H^+), consumer biomasses are higher than when producers are limited by either resource, which again suggests that copepods may benefit from a well-balanced nutrition of the lower trophic level. The model predicts that the total biomass of copepods, living on nitrogen limited algae, exceeds that of copepods, living on carbon limited ones. This can be attributed to the damming up of carbohydrates in the copepods themselves.

3.3. The resource–producer–consumer system

Here we analyze the complete food chain, where both the diatom and the copepod species are modelled explicitly. The result so far predicts that under ambient

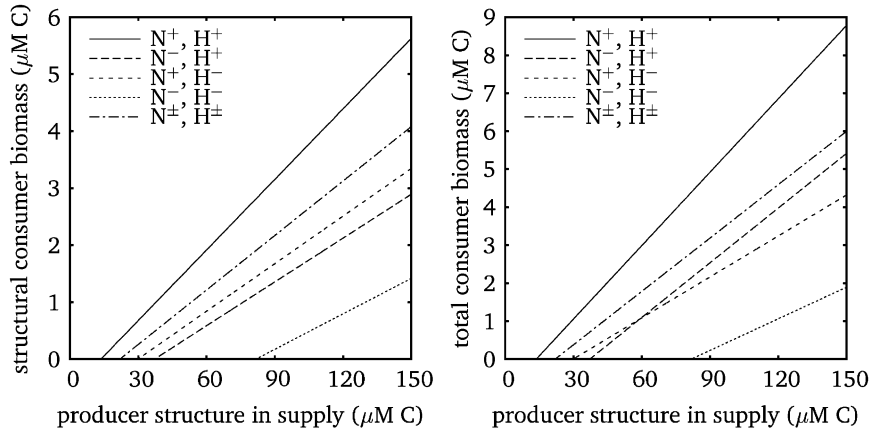


Fig. 4. Biomass densities of consumers (left: structural only, right: structural + reserves) when producers of different nutritional quality are supplied. N^+, H^+ : E_N^A, E_H^A fixed at 1; N^-, H^+ : $E_N^A = 0$ and $E_H^A = 1$; N^+, H^- : $E_N^A = 1$ and $E_H^A = 0$; N^-, H^- : E_N^A, E_H^A fixed at 0; $N^\pm, H^\pm$: E_N^A, E_H^A fixed at 0.5. The producers benefit when both producer reserves are abundant (N^+, H^+). The absence of both reserves results in a significant growth reduction (N^-, H^-). The ($N^\pm, H^\pm$)-curve is always above the (N^-, H^+) and (N^+, H^-)-curves, which indicates that a proper balance in the presence of the producers reserves facilitates growth. The (N^+, H^-)-scenario results in higher structural biomasses than the reversed situation, (N^-, H^+). However, the total biomass of the (N^-, H^+)-scenario increases faster with increasing food supply. This can be attributed to the damming up of non-limiting hydrocarbon reserves.

conditions, nitrogen is the model's limiting factor for diatom growth. Therefore, we concentrate mainly on nitrogen supply as input parameter.

Fig. 5 contains a one-parameter bifurcation analysis of the food web, when the concentration of the nitrogen supply, $X_{r,N}$, is varied. The upper graphs concern the biomass densities of producers and consumers in the absence of recycling. All excreted and decomposed organic matter is lost from the system, which is a common feature of traditional models (Rosenzweig, 1971; Oksanen et al., 1981; McCann and Hastings, 1997; Kuijper et al., 2003). In the graphs in the middle panel, the recycling rate, k_D , is held at the ambient value of 0.005 h^{-1} , and the bottom row contains graphs of the food chain when recycling of organic matter is infinitely fast. The vertical lines indicate values for $X_{r,N}$ where the qualitative behavior of the system changes, i.e. bifurcation points. Table 3 gives the nomenclature of the bifurcations involved. The transcritical bifurcation indicates the invasion boundary of the copepods.

When nitrogen enrichment is increased beyond the vertical line indicating the Hopf bifurcation, the stable equilibrium of coexisting producers and consumers breaks down, and limit cycles originate. The amplitudes (maxima and minima) are indicated in the bifurcation diagrams, dashed curves represent unstable states and solid curves are stable states. The model's behavior at high nitrogen inflow resembles Rosenzweig's 'paradox of enrichment' (Rosenzweig, 1971) in that it leads to destabilization of the system. However, this phenomenon is usually associated with the occurrence of a supercritical Hopf bifurcation. Our model predicts that in the absence of recycling, or when the recycling rate is sufficiently low, the system's destabilization is caused by

a subcritical Hopf bifurcation. Here, an unstable limit cycle originates, which forms a separation between two stable states, a limit cycle and a steady state. The ubiquitousness of multiple stable states in complex systems has been pointed out by Scheffer et al. (2001), and our model demonstrates that it is possible even in a simple short food chain.

There is a range of nitrogen provisions at which the producer and consumer can coexist in equilibrium. The exploitation ecosystem hypothesis (EEH) predicts that over this range the producer species should have a constant population density (Oksanen et al., 1981). This result is, however, debated, as primary producer biomass has been shown to increase with nutrient enrichment (Hansson, 1992; Brett and Goldman, 1997). Our model predicts an increasing mass of the primary producer with increasing nitrogen availability. Grover (2003) links such an increase to the resource replenishment associated with recycling by the consumer species. Indeed, the slope of the producer population is steeper when recycling is implemented. However, in the absence of recycling, the slope is still positive (left upper graph), so that the effect cannot be attributed to nutrient recycling exclusively, and must be attributed to the metabolic flexibility of the consumer species.

From Fig. 5 it appears that the occurrence of multiple stable states depends on the recycling rate of organic detritus. Fig. 6 presents a two-dimensional bifurcation curve in which the nitrogen supply $X_{r,N}$ and the decomposition rate k_D are varied simultaneously. The position of the Hopf bifurcation decreases with increasing $X_{r,N}$. This implies that the stable regions of the system become smaller with increasing k_D , and thus, increased recycling rates may destabilize the food chain.

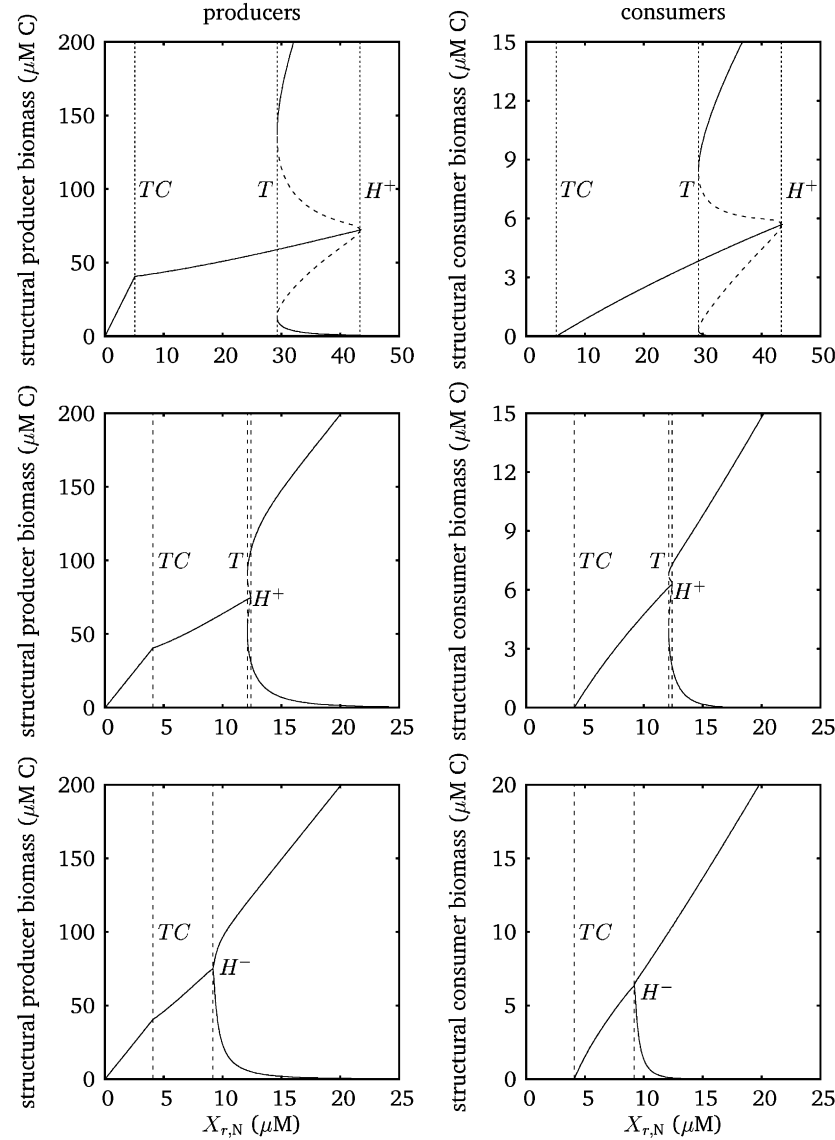


Fig. 5. Biomass densities of producers (left) and consumers (right) as a function of nitrogen provision when recycling is absent (upper row), ambient (middle row) or infinitely fast (lower row). The consumer's invasion boundary is marked TC . At a supercritical Hopf bifurcation (H^-), the stable steady state becomes unstable and a stable limit cycle originates. However, at a subcritical Hopf bifurcation (H^+), an unstable limit cycle originates, which marks the separation between a stable limit cycle and a stable steady state. The region in which these two stable states co-occur is bounded by the subcritical Hopf and the saddle node bifurcation (T).

Table 3
Bifurcations

Symbol	Type	Interpretation
H^-	Supercritical Hopf	Stable equilibrium becomes unstable a stable limit cycle and an unstable equilibrium originate
H^+	Subcritical Hopf	Unstable equilibrium becomes stable an unstable limit cycle originates
T	Saddle node	Stable and unstable limit cycle coincide and disappear
TC	Transcritical	Unstable and stable equilibrium coincide and exchange stability properties

The dashed curve indicates the position of the saddle node, or tangential, bifurcation. The distance between the two bifurcation curves gives the region where multiple

stable states exist. At the point where the saddle node and the Hopf bifurcations intersect, the Hopf bifurcation switches from supercritical (lower part) to sub-

critical (upper part). This point is called a Bautin point and above it, the system's behavior follows the classical paradox of enrichment.

Fig. 7 contains the one-parameter bifurcation diagrams of the food chain when the inorganic carbon supply, $X_{r,C}$ (left), and the light intensity, j_L (right panel), are varied under otherwise ambient conditions. When the light flux or the carbon supply is low (i.e. far beneath ambient conditions) the system oscillates in a region bounded by two supercritical Hopf bifurcations. When light figures as bifurcation parameter (right panel), the invasion boundary of the copepod almost coincides with the Hopf bifurcation, although close inspection revealed that the two bifurcation points do not intersect. The cycling behavior is caused by the relatively high supply of nitrogen in this region of the

parameter space. The paradox of enrichment is usually associated to absolute values of nutrient concentrations. In contrast, our results suggest that food-chain destabilization may also follow from imbalances in the relative supply of particular resources. From Fig. 1 it can be observed that the diatoms are limited by light ($j_L \lesssim 30$) or carbon ($X_{r,C} \lesssim 500$) in only a small region of the analyzed parameter space. However, Fig. 7 shows that the copepod population continues to increase with increasing light and carbon supplies. This implies that the limitation of the lowest trophic levels does not necessarily restrict the production of higher trophic niches.

We conclude our analyses by studying the effect of varying resources supplies simultaneously. Fig. 8 shows the two-dimensional bifurcation diagrams from which the pairwise effect of nitrogen and carbon (left), nitrogen and light (center), and carbon and light (right) can be studied. The unchanged resource supply is fixed at the default value. The solid curves mark the invasion boundary of the copepod species, which can invade the regions to the right of this curve. When nitrogen and carbon or nitrogen and light are varied simultaneously, the food web persists in steady state in the region between the transcritical and the Hopf bifurcation. This region generally becomes larger with increasing carbon and light. This supports the hypothesis that a proper balance in the provision of nutrients may facilitate food-web persistence. However, the range of $X_{r,N}$, where the steady state is stable is largest at very low carbon inputs. In that region, the potential for nitrogen to destabilize the food chain is small, whereas a small enhancement in carbon provision will make the system cross the Hopf bifurcation and become unstable. When carbon and light are varied simultaneously there is a region confined by two supercritical Hopf bifurcations, in which the food chain is unstable. To the right of this region, the food chain is stable, but this region becomes

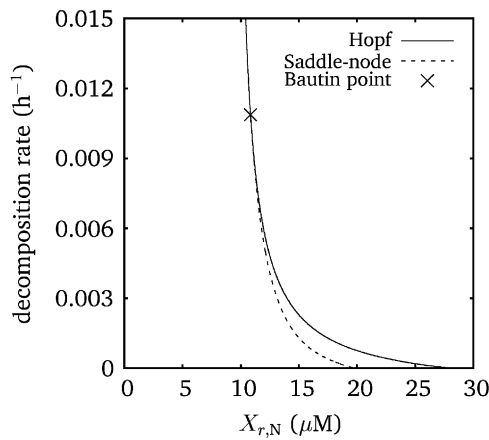


Fig. 6. Two-dimensional bifurcation diagram which demonstrates the influence of the recycling rate of organic detritus in conjunction with nitrogen enrichment. At the Bautin point, the Hopf bifurcation changes from subcritical (low k_D) into supercritical (higher k_D). In the region bounded by the subcritical Hopf curve and the saddle-node curve, there exist multiple stable states. These are a stable steady state and a limit cycle.

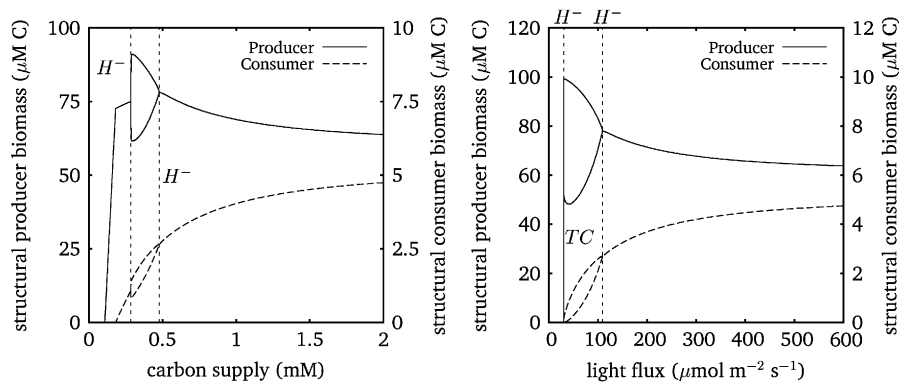


Fig. 7. Biomass densities as a function of inorganic carbon provision (left) and light (right). Solid lines denote the diatom population size, whereas dashed lines are used for the copepod population. The two supercritical Hopf bifurcations mark the region where oscillations occur, in this case at low resource inputs. When light is used as bifurcation parameter, the Hopf and transcritical bifurcation almost coincide. Due to limited space, the transcritical bifurcation point for the invasion of the consumer is omitted in the left diagram.

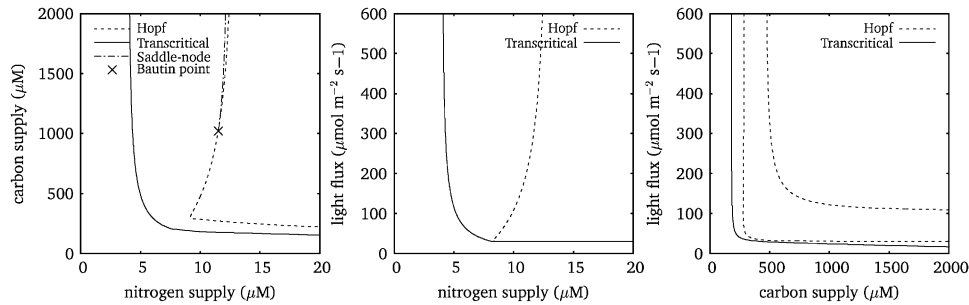


Fig. 8. Two-dimensional bifurcation diagrams illustrating coupled effects of resource provision (left: inorganic carbon against nitrogen, center: light against nitrogen, right: light against carbon). When crossing a solid curve, representing a transcritical bifurcation, from left to right, the consumer species can invade and persist in equilibrium. Regular dashed curves mark a supercritical Hopf bifurcation, while the irregular dashed curve in the left panel marks a saddle-node bifurcation, originating at the Bautin point. In the region held between the saddle node and the Hopf curve, multiple stable states can occur. In the region to the right of this Hopf curve the system's attractor is oscillatory. In the center panel there are three regions. To the right of the transcritical bifurcation, the copepods can persist, but when the Hopf bifurcation is crossed to the right, the system's equilibrium becomes unstable and oscillations occur. In the right panel, oscillations occur in the region bounded by the two Hopf bifurcations. To the right of this region, the system is in equilibrium.

smaller when $X_{r,N}$ is increased. This is not shown in the diagram, but it follows from the $X_{r,N}$ - j_L and the $X_{r,N}$ - $X_{r,C}$ plots, where nitrogen enrichment in the vicinity of a Hopf bifurcation promotes food-chain destabilization.

4. Discussion

We investigated the effect of resource availability in combination with metabolic flexibility on the dynamic properties of a marine microbial food chain, in which we modelled stoichiometry explicitly. Furthermore, we assessed the effect of recycling by decomposition and excretion of non-limiting nutrients and metabolic products by living biota. We used the SU construct for modelling stoichiometric requirements as an alternative for classic Liebig models. Although the model holds more biological detail than traditional stoichiometric food-chain models, it produces, to a large extent, similar results. This finding can be used as a validation of simple models in most cases.

SUs have a range, rather than a point, over which limitation changes gradually from one nutrient to another. This range may be very small, in which case results of an SU-model resemble results of Liebig's minimum law. Indicated by the kink in the associated curve (Fig. 1), switching from carbon to nitrogen limitation in the resource-producer system is very similar to Liebig limitation. However, numerical bifurcation analysis did not cause any problems, as it may in minimum models.

Liebig's law does not dictate what happens to non-limiting resources. We used a mass-balance model, where it is inevitable to explicitly model the fate of any compound. SUs mathematically translate substrate fluxes into product fluxes and rejected fluxes. The rejected fluxes comprise non-limiting elements, of which the fate can be addressed conveniently to model mass

balance, which is a necessity for assessing effects of stoichiometry in food webs (Loladze et al., 2000; Grover, 2002).

The model predicts that, under default conditions, nitrogen and not energy, limits diatom production, although our model does not include other nutrients such as iron or phosphorous. Moreover, while our focus was on the effect of an increased metabolic flexibility, we modelled potentially limiting nutrients in a very simplistic manner and neglected effects of carbon speciation into HCO_3 and CO_2 , as well as the effect of self-shading, which may influence light versus element limitation. This may explain why there is a very small parameter range for light inputs where this resource is limiting the resource-producer system. Nevertheless, our findings with respect to nitrogen limitation are in agreement with Graziano et al. (1996) and Tomasky et al. (1999). Carbon enrichment results in carbohydrate accumulation in the diatom, but the structural biomass remains unaffected in the absence of copepods. A detailed representation of inorganic carbon dynamics and light gradients was beyond the scope of this paper, but may be included in future work. This omission causes limitations in the applicability of the model.

When copepods are present in the system, their structural density increases with both the inorganic carbon (Fig. 7) and nitrogen supply (Fig. 5) to the system. Copepods thus benefit from enhancement of minerals, which they cannot assimilate themselves. The effect of nitrogen enrichment on copepod production can be understood, as it stimulates diatom growth, which in turn, will have an effect on the copepod population size. However, while carbon is non-limiting to the diatoms, carbon enrichment also effectively promotes the copepod population growth (see Fig. 7). This effect can be attributed to the change in diatom biomass composition following carbon enrichment, i.e.

the accumulation of carbohydrate reserves in diatoms. This leads to a change in their nutritional value to copepods. Here, the effect of multiple reserves for the description of population dynamics becomes clear. As both carbon and nitrogen stimulate the growth of the copepod population, it seems that these animals are not limited by either element. Non-linearities in the description of trophic interactions make it difficult to predict how enrichment with nutrients that are non-limiting to the lowest trophic level will affect the dynamics of larger systems. Our results demonstrate that nutrient limitation as applied to single organisms might not be applicable to whole ecosystem functioning. Metabolic flexibility leads to efficient use of limiting resources and allows for sloppier use of non-limiting ones. As each trophic level has its own mode of resource acquisition and use, it is to be expected that whole ecosystems will generally comprise multiple limitations.

In our results, copepods influence the dynamics of the diatom population, a property commonly featured in stoichiometric models (Elser and Urabe, 1999; Loladze et al., 2000). EEH predicts that grazing effectively nullifies the effects of nutrient enrichment on the producer population size (Oksanen et al., 1981; Oksanen and Oksanen, 2000). However, our model predicts that in the presence of grazers, nitrogen enrichment stimulates the diatom population, while light and carbon enrichment cause a decline in the producer's population size. Deviations from the EEH may be caused by storage strategies of herbivores (Grover, 2003). According to Grover, the sequestration of resources by a consumer species may cause a reduction in primary production when the associated nutrient is enriched. In our model, diatoms have a high C:N when nitrogen is limiting, due to the damming up of carbohydrates. When copepods ingest carbon-rich diatoms, they will use nitrogen more efficiently, as transformation (15a) will then prevail over transformation (15b). Consequently, less DIN is formed and excreted as by-product of a biomass synthesis process, which corresponds to lower recycling. Enrichment with nitrogen causes exactly the opposite effect. The C:N of diatoms then becomes lower and copepods will be less efficient with respect to this mineral, thereby recycling it more efficiently and promoting algal growth. Our results are therefore in line with Grover's observations.

We found that nitrogen enrichment can destabilize the food chain (Fig. 5), which is in agreement with the classic results of Rosenzweig (1971). The classic result concerns the crossing of a supercritical Hopf bifurcation, so that the stable internal equilibrium becomes unstable and a stable limit cycle comes into existence (Oksanen et al., 1981; Rosenzweig, 1973; Abrams and Roth, 1994). The same happens in our model when the recycling rate of organic matter is sufficiently high.

However, many of the classical studies do not take into account the recycling of any nutrient. Another important difference between our study and classic studies on nutrient enrichment is the use of SUs for the description of biomass production, rather than Holling's disc equation. Muller found a richer repertoire of dynamic behaviors for simple food-chain models due to the use of SUs (Muller et al., 2001). In the absence of recycling, our model predicts the existence of a subcritical, instead of a supercritical Hopf bifurcation, an effect that can be attributed to the use of SUs. At a subcritical Hopf bifurcation point, a stable equilibrium becomes unstable and an unstable limit cycle occurs, forming the separatrix between the stable steady state and an alternative stable state. When the recycling of organic matter is set at a biologically plausible value of 0.005 h^{-1} (Fujii et al., 2002), the multiple stable states still exist, although the parameter range at which they occur is narrow. Scheffer et al. (2001) have shown that multiple stable states are common in nature. In correspondence to the results of Muller et al. (2001), our results suggest that they might also occur in food webs as simple as a resource–producer–consumer system.

In addition to high nitrogen input, low carbon input or light availability can also destabilize the food chain in our model. This suggests that destabilization can also be caused by imbalances in the availability of essential resources, as was also found by Loladze et al. in a simple stoichiometric model. This result corresponds to the finding of Muller and co-workers (2001) that a high level of nutrients reduces persistence of the consumer. Indeed, when nitrogen levels are high, the model is more stable when light and carbon are also high. This can be observed in Fig. 8, where the range of values at which a stable internal equilibrium exists becomes larger with increasing light and carbon. In real aquatic systems, nitrogen enrichment can cause algal blooms (Paerl, 1997), which, in turn, reduce light penetration in the water. The combined effects of reduced light and enhanced nitrogen may promote the destabilization of aquatic ecosystems, which corresponds to the findings of Lima et al. (2002).

Recycling appears to be a destabilizing factor in the model. With higher decomposition rates, equilibria destabilize at lower nitrogen provisions. This result goes well with the findings of Kooi et al. (2002). However, a word of caution is needed here. Decomposition in nature is a complex process in which different organic materials are decomposed at different rates. Furthermore, the role of bacteria in the breakdown of dissolved organic matter is significant. As our main interest was in the application of SUs for the modelling of ecological stoichiometry, we simplified the decomposition process to a large extent, i.e. we assigned only two detritus components and we chose not to explicitly model decomposer species.

5. Conclusions

We designed an aquatic food-chain model, capable of assessing effects of organismal metabolic flexibility with respect to ecological stoichiometry, modelled according to the Dynamic Energy Budget theory using synthesizing units.

With the parameters used in the analysis, the model predicted that the lowest trophic level is limited by nitrogen. The model confirmed the paradox of enrichment, although the repertoire of dynamic behaviors is augmented with the presence of multiple stable states for biologically plausible decomposition rates. Our results show realistic responses of population densities in response to nutrient enrichment. However, the model incorporates nutrients in a simplistic manner, and in forthcoming work, a more detailed description of nutrient chemistry is recommended.

While working well for single species, we found that the concept of single element limitation may not be applicable when used in an ecosystem context, because the consumer population benefits both from carbon and nitrogen enrichment. The model demonstrates that not only nutrient enrichment but also an improper balance in the availability of essential resources may destabilize the food chain.

The model shows that accumulation of non-limiting resources on one trophic level may affect population densities of other trophic levels. It is therefore to be expected that on the ecosystem level, where multiple trophic levels coexist, multiple resource limitations may occur simultaneously.

Finally, our results suggest that recycling, which replenishes minerals, thereby enriching the nutritional state of the system, will generally be a destabilizing factor in food-web dynamics. We conclude that our approach allows for bringing more ecological detail in food-chain models, while still being numerically tractable.

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