# Influence de la structure des réseaux trophiques lacustres et des apports de matière organique sur la composition biochimique des compartiments biotiques et sur la biodégradabilité de la matière organique sédimentée

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**Résumé**

Les cycles du carbone et des nutriments des lacs sont en partie contrôlés par la sédimentation, les apports de matières terrestres, les réseaux trophiques et les interactions entre ces compartiments et processus. Les sédiments et les matières terrestres sont des sources de matière organique et de nutriments pour les écosystèmes aquatiques qui peuvent avoir un effet ascendant sur les communautés pélagiques. Les prédateurs de sommets de chaînes exercent quant à eux un contrôle descendant sur le cycle des nutriments aquatiques et sur le processus de sédimentation, *via* la modification des transferts de matière au sein des réseaux trophiques. L'analyse de la composition de la matière organique, notamment les biomarqueurs lipidiques, permet d'étudier les transferts d'énergie au sein des écosystèmes aquatiques. Cette étude a permis de montrer que la structure du réseau trophique, en influençant le contrôle des producteurs primaires par leurs consommateurs, influe sur les compositions élémentaires et biochimique (acides carboxyliques polyinsaturés, stérols, dérivés de la chlorophylle, protéines et sucres) de la matière organique qui sédimente et sur sa biodégradabilité. Cette modification de biodégradabilité influence en retour les biomasses du seston, du zooplancton, ou des poissons. Les matières organiques d'origines différentes (autochtone et allochtone) étudiées ont des effets contrastés sur la composition élémentaire du seston, du zooplancton et des sédiments récemment déposés, mais très peu d'impact sur la composition des biomarqueurs lipidiques de ces compartiments. Les effets ascendants sur la structure des réseaux trophiques pélagiques des apports de matière organique sous forme de sédiment ou de terre se sont avérés assez mineurs comparés à ceux induits par la modification de la structure des réseaux trophiques aquatiques.

**Remerciements**

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Rock’n’roll

**Sommaire**

# Chapitre I

# Synthèse bibliographique

## A. Contexte : cycle du carbone à l'échelle planétaire

Le réchauffement climatique et ses conséquences potentielles sur l'augmentation de la fréquence et de l'ampleur des catastrophes naturelles sont des sujets omniprésents dans la société actuelle. L'émission massive de gaz à effet de serre (GES) dans l'atmosphère par les activités anthropogéniques est considérée comme la cause la plus plausible du réchauffement climatique. Parmi les principaux GES, le dioxyde de carbone ($CO_2$) est celui qui possède le plus faible potentiel de réchauffement global, cependant, il est de loin le plus perturbé par les émissions anthropogéniques puisque sa concentration atmosphérique est passée de 280 ppm avant l'ère industrielle à 380 ppm en 2005 (Houghton, 2007). C'est dans ce contexte que la communauté scientifique mondiale s'attache depuis plusieurs décennies à mieux comprendre le cycle global du carbone.

De manière générale, les études portant sur le cycle du carbone à l'échelle planétaire le schématisent comme résultant d'interactions entre trois « boîtes » distinctes : les compartiments atmosphérique, terrestre et océanique. Le cycle global du carbone est donc considéré comme une succession d'échanges (flux) entre ces compartiments induits par une multitude de phénomènes biotiques et abiotiques. D'un point de vue strictement politique, seul le flux qui va du compartiment terrestre au compartiment atmosphérique est pris en considération. Or dans un modèle en « boîtes » tel qu'est représenté le cycle global du carbone, la moindre modification d'un flux peut avoir d'importantes conséquences sur le cycle entier,d'où les études menées en parallèle par la communauté scientifique sur les trois compartiments et les différents échanges les reliant. Suite aux avancées dans ce domaine de recherche depuis quelques années, les modèles du cycle global du carbone se sont affinés et ont commencé à subdiviser les trois principaux compartiments en sous-compartiments interagissant entre eux (Foley et al., 1996 ; Canadell et al., 2000 ; Cramer et al., 2001 ; Houghton, 2007 ; Figure 1). Les principaux processus connectant les sous-compartiments sont la respiration, la photosynthèse, l'érosion et/ou la sédimentation. Les flux de $CO_2$ vers l'atmosphère induits par les activités anthropiques étant essentiellement dus à la combustion de carbone fossile, ils sont schématisés par un flux partant d'un stock de carbone fossile commun aux compartiments terrestre et océanique. Il est important de souligner que les compartiments terrestre et océanique sont considérés comme n'ayant aucune interaction directe entre eux dans cette génération de modèles. Plus particulièrement, le rôle des écosystèmes aquatiques terrestres (rivières, lacs, réservoirs, mares, eaux souterraines,

marais…) est tout simplement exclu de ces modèles, ou alors inclus de façon non explicite dans les différents flux.

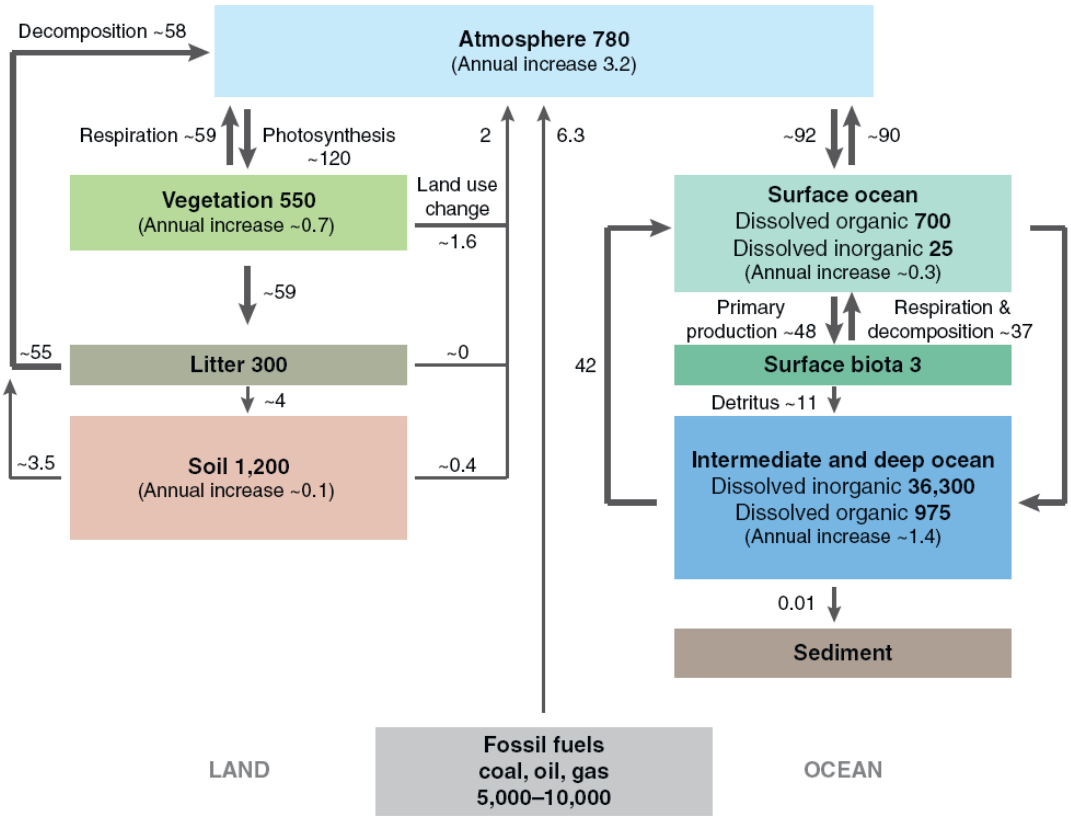



**Figure 1:** Schéma simplifié du cycle global du carbone. Les stocks de carbone sont exprimés en Pg ($10^{15}$ g) de C et les flux en Pg de C par an. Le stock de C des sédiments du compartiment océanique est de 6000 Pg de C. D'après Houghton (2007).

Or, depuis plusieurs décennies, il a été montré que les rivières délivrent des quantités significatives de carbone vers la mer du fait de l'érosion des sols (Duce et Duursma, 1977 ; Handa, 1977 ; Schlesinger et Melack, 1981), démontrant ainsi l'existence d'un flux entre les compartiments terrestre et océanique. Néanmoins, lorsque ces intrants terrestres sont intégrés aux modèles globaux précédemment cités, seuls les apports directs de carbone des cours d'eau vers le compartiment océanique sont pris en compte. Des études récentes ont montré que cette vision simplifiée ne suffit pas à expliquer l'ensemble des échanges dans le cycle global du carbone et que les échanges entre les eaux douces et les compartiments terrestre, océanique et atmosphérique sont bien plus complexes (Cole et al., 2007 ; Tranvik et al., 2009). Ainsi, plusieurs études ont proposé d'intégrer aux modèles globaux de nouvelles interactions entre les écosystèmes aquatiques terrestres et les compartiments océanique et atmosphérique en

prenant notamment en compte les pertes de $CO_2$ vers l'atmosphère et le stockage de carbone *via* la sédimentation (Cole et al., 2007 ; Downing et al., 2008 ; Duarte et al., 2008 ; Tranvik et al., 2009 ; Figure 2). Ces études ont ainsi démontré l'importance que peuvent avoir les lacs dans le cycle du carbone à l'échelle planétaire. Par conséquent, l'étude du fonctionnement général de ces écosystèmes et notamment des processus régulant les flux de carbone se révèle primordiale pour la compréhension de leur rôle à l'échelle de la planète.

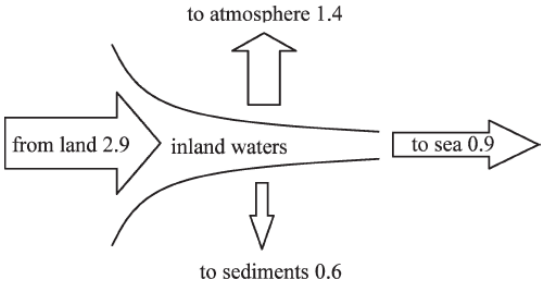



**Figure 2:** Schéma simplifié du rôle des écosystèmes aquatiques terrestres dans le cycle global du carbone proposé par Cole et al. (2007) et révisé par Tranvik et al. (2009). Les flux sont exprimés en Pg de C par an.

## B. Ecosystèmes lacustres

### *1. Cycle du carbone*

Bien que, comparés aux océans, les lacs couvrent un faible pourcentage de la surface de la planète, ils jouent un rôle prépondérant dans le cycle global du carbone puisqu'ils reçoivent et transforment de grandes quantités de carbone provenant du compartiment terrestre, qui est quant à lui un important réservoir de carbone (Battin et al., 2009 ; Tranvik et al., 2009 ; Figure 1). Les principaux processus gouvernant le cycle du carbone dans les écosystèmes lacustres sont la photosynthèse et la production primaire associée, la sédimentation, la minéralisation de la matière organique (MO) et les pertes par exportation vers les cours d'eaux associés à ces écosystèmes (Figure 3).

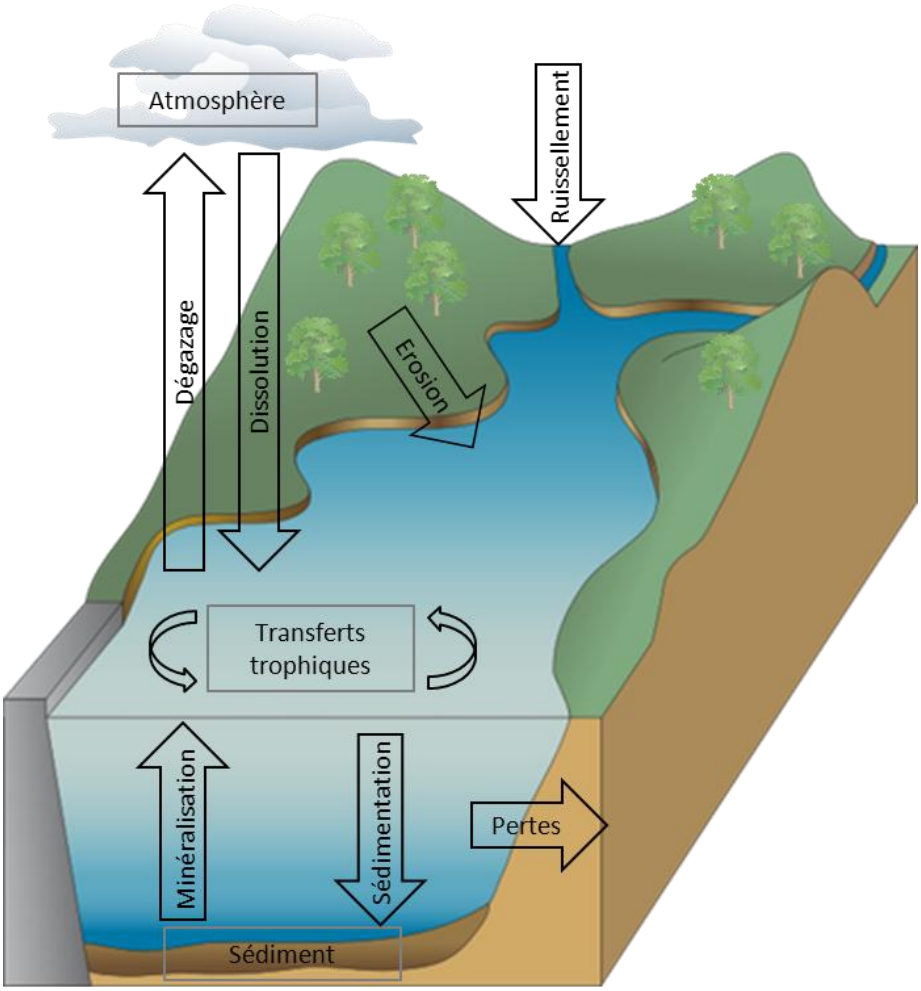



**Figure 3 :** Principaux processus et réservoirs contrôlant le cycle du carbone des lacs. Adapté de Tranvik et al. (2009).

Il est communément admis que la grande majorité des lacs sont hétérotrophes nets, c'est-à-dire qu'ils sont une source de $CO_2$ pour l'atmosphère plutôt qu'un puits du fait de la prédominance de la respiration bactérienne (minéralisation) sur la fixation du $CO_2$ atmosphérique (dissous dans l'eau) par les organismes photosynthétiques (del Giorgio et al., 1997, 1999 ; Cole et al., 2000 ; Duarte & Prairie, 2005 ; Duarte et al., 2008). Cependant, les nombreux facteurs contrôlant les productions respectives des communautés bactériennes et des organismes photosynthétiques (apports de matière organique terrestre dont concentration en substances humiques, lumière disponible, concentration en nutriments, température, prédation …) sont susceptibles de faire varier cet équilibre (voir paragraphes suivants).

Dans les écosystèmes lacustres, le carbone peut être soit d'origine autochtone soit allochtone. Le carbone autochtone est issu de la production de biomasse par les organismes photosynthétiques qui fixent le $CO_2$ dissous dans l'eau. Par ce processus, le carbone passe

d'une forme inorganique ($CO_2$) à une forme organique. Tous les organismes tirant leur énergie de cette source sont considérés comme faisant partie du pool de carbone autochtone.
Le carbone d'origine allochtone est quant à lui, par définition, apporté par une source extérieure au lac. En l'occurrence il s'agit principalement des intrants terrestres dus au lessivage et à l'érosion des sols du bassin versant par les cours d'eau alimentant le lac. Une fois dans le milieu aquatique, ce carbone allochtone sert essentiellement de ressource pour les communautés bactériennes qui vont minéraliser cette MO (Tranvik et al., 1992) afin de subvenir à leur métabolisme, transformant, à l'inverse de la photosynthèse, du carbone organique en carbone inorganique.

Quelque soit l'origine initiale du carbone (autochtone ou allochtone), les communautés phytoplanctoniques et bactériennes sont consommées par leurs prédateurs respectifs, eux même soumis à la prédation par des consommateurs supérieurs. Cet ensemble de chaînes alimentaires représente un mécanisme important dans le cycle du carbone dans la colonne d'eau écosystèmes aquatiques.

Les différents organismes qui constituent la chaîne alimentaire aquatique produisent de la MO dissoute (MOD) ou particulaire (MOP) *via* la production de déchets (exsudats, fèces, cadavre, mues). Selon leurs caractéristiques physiques (densité et forme par exemple), ces déchets vont sédimenter au fond des lacs (Bloesch, 2004). De même, la MOP et une partie de la MOD (qui peut floculer en MOP) provenant de sources allochtones sont sujettes à la sédimentation. La MO des sédiments (MOS) résulte donc d'un mélange de MO autochtone et allochtone. Les sédiments (ou zone benthique) sont le lieu d'une intense minéralisation de la MO par les communautés benthiques. Ces dernières convertissent la MOS en biomasse servant alors de ressource pour les organismes de la colonne d'eau (zone pélagique). De plus, la minéralisation de la MOS est une source de $CO_2$ pour la colonne d'eau. Cependant, une partie de la MOS est réfractaire à la minéralisation et va s'incorporer dans les sédiments à plus ou moins long terme. Les sédiments jouent donc un rôle majeur dans le cycle du carbone des lacs puisqu'ils peuvent être une source et/ou un puits de carbone

Enfin, comme présenté sur la Figure 2, le carbone des écosystèmes lacustres peut également être transféré vers les compartiments terrestre et océanique par l'exportation des matières dissoutes et particulaires à l'exutoire du lac et/ou par l'infiltration d'eau dans les sols.

Le cycle du carbone dans les lacs résulte donc de nombreux processus et des interactions entre compartiments biotiques et abiotiques, processus parmi lesquels la structure

du réseau trophique, la sédimentation et l'origine du carbone peuvent jouer un rôle prépondérant. Malgré leur importance, les interactions entre ces différents compartiments et/ou processus restent encore mal comprises.

### *2. Réseaux trophiques aquatiques*

La diversité des organismes qui peuplent les lacs et les écosystèmes aquatiques en général est très élevée (Lampert et Sommer, 2007). L'un des critères pour classer simplement ces organismes est leur capacité à nager. On parle ainsi de necton pour les espèces capables de se mouvoir par elles-mêmes sous un fort courant. Cette catégorie concerne essentiellement les poissons. Par opposition, le plancton regroupe toutes les espèces en suspension dans l'eau qui ne peuvent résister à de forts courants. Le plancton regroupe (i) le phytoplancton, principalement constitué d'organismes photosynthétiques (algues et cyanobactéries), (ii) le zooplancton, constitué par des organismes hétérotrophes tels que les protozoaires (flagellés et ciliés), les rotifères, les crustacées (cladocères et copépodes) et certaines larves d'insectes, (iii) et le bactérioplancton qui, comme l'indique son nom, regroupe l'ensemble des bactéries aquatiques. Certains organismes aquatiques résident préférentiellement à la surface des sédiments, on parle alors de benthos ou de flore et de faune benthiques.

#### a. Cascade trophique ou contrôle « top-down »

On peut également classer les communautés pélagiques selon leur position dans la chaîne alimentaire aquatique (Carpenter et Kitchell, 1993). Les algues constituant le phytoplancton sont ainsi désignées comme étant des producteurs primaires puisque ce sont les organismes qui vont produire les composés organiques vitaux (acides aminés, sucres, lipides, vitamines…) pour le reste des communautés aquatiques à partir de ressources abiotiques que sont les éléments minéraux, le $CO_2$ atmosphérique et la lumière solaire. Comme les algues n'exercent pas le rôle de prédateur pour d'autres organismes mais qu'elles sont en revanche des proies pour les herbivores (une grande partie du zooplancton mais également certains poissons), le phytoplancton constitue le premier maillon des réseaux trophiques aquatiques. On qualifie ainsi fréquemment les espèces phytoplanctoniques d'espèces basales (Figure 4).

Parmi les bactéries, les hétérotrophes jouent un rôle primordial dans l'écologie et dans les cycles biogéochimiques des systèmes aquatiques puisqu'elles sont capables de minéraliser

la MO (dissoute et particulaire) pour leur métabolisme (Tranvik, 1992 ; Bunte et Simon, 1999 ; Weiss et Simon, 1999). De plus, ce métabolisme bactérien conduit à la production d'une nouvelle biomasse bactérienne qui va intégrer le réseau trophique en étant consommée par ses prédateurs (protozoaires et zooplancton bactérivore). Ainsi, même si le rôle des bactéries et du phytoplancton dans le cycle de la MO est opposé (transformation de carbone organique en carbone inorganique), les bactéries se situent à un niveau trophique proche de celui du phytoplancton, on parle de production secondaire bactérienne (del Giorgio et Cole, 1998 ; Figure 4).

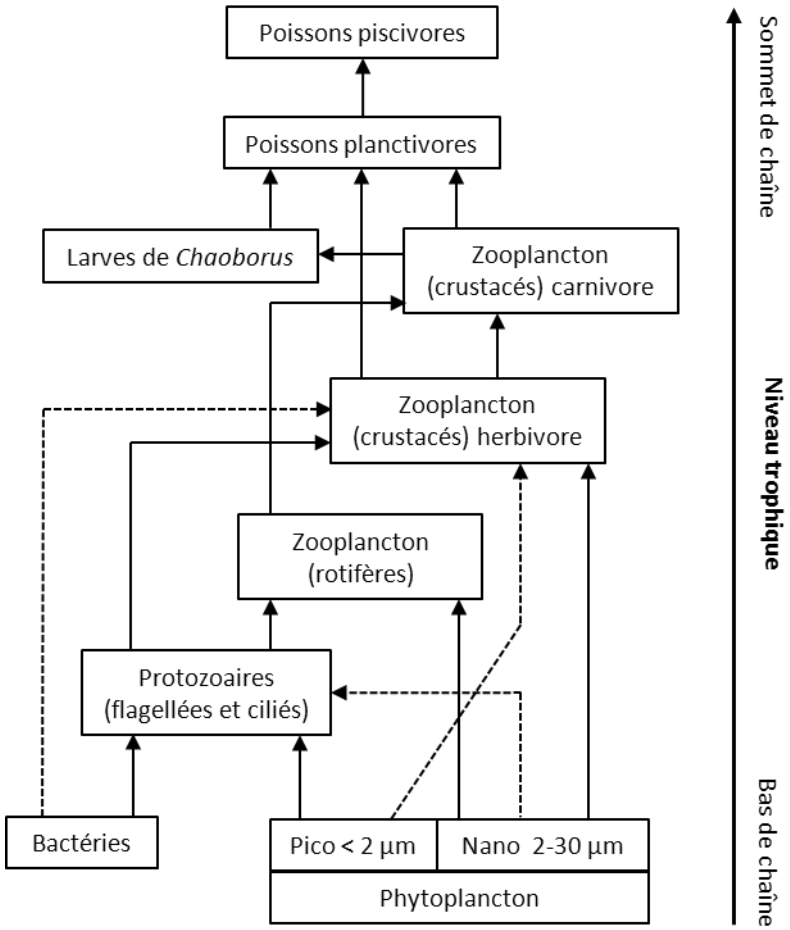



**Figure 4 :** Schéma simplifié d'un réseau trophique aquatique représentant les interactions proie/prédateur des organismes vivants. Les lignes pleines indiquent que la plupart des espèces (proies comme prédateurs) sont impliquées dans le lien trophique en question alors que les lignes pointillées ne concernent que certaines espèces. D'après Lampert et Sommer (2007).

Contrairement au phytoplancton et au bactérioplancton, le zooplancton (rotifères, crustacés, larves d'insectes…) appartient à plusieurs niveaux trophiques puisque les espèces le constituant peuvent être herbivores, bactérivores ou bien zooplanctivores (Gliwicz, 2004; Figure 4). Chez les poissons, on distingue les espèces planctivores qui vont se nourrir essentiellement de zooplancton et dans une moindre mesure de phytoplancton et les espèces piscivores qui se situent en sommet de réseau trophique (on parle de prédateurss de sommets de chaînes ou « top-predators », Lazzaro, 1987). La structure des réseaux trophiques aquatiques dépend fortement de la pression exercée par les consommateurs sur leurs proies et du régime alimentaire des espèces au sommet du réseau trophique considéré. Ainsi, par un effet en cascade, un réseau trophique peut être dominé soit par les producteurs primaires lorsque la population d'herbivores est contrôlée par la prédation, soit par les herbivores lorsque leurs prédateurs respectifs sont eux-mêmes soumis à la prédation par des espèces d'un niveau trophique supérieur (Brett et Goldman, 1996 ; Sommer, 2008), on parle de cascade trophique ou de contrôle descendant (« top-down control »). Cependant, cette cascade trophique n'induit pas forcément des effets visibles sur les biomasses des différents niveaux trophiques. Par exemple, différentes études ont montré que la cascade trophique induite par l'ajout de poissons zooplanctivores conduisait à une augmentation de la biomasse de phytoplancton mais pas nécessairement à une diminution de la biomasse du zooplancton (Bertolo et al., 1999, Danger et al., 2012). Cependant, dans un tel cas de figure, l'introduction des poissons entraîne un changement de la communauté zooplanctonique (Bertolo et al., 19999 ; Duffy, 2002). Deux hypothèses peuvent expliquer ces observations : (i) La prédation sélective des poissons sur les plus grands individus peut induire une diminution de la taille moyenne des individus au sein de chaque population de zooplancton (Lampert et Sommer, 2007), et (ii) la différence de capacité des espèces de zooplancton à échapper à la prédation (vitesse de nage par exemple) peut conduire à une domination de la communauté par les espèces les moins consommées (Danger et al., 2012).

b. Disponibilité des ressources : contrôle « bottom-up » du réseau trophique

La structure des réseaux trophiques aquatiques est également fortement dépendante de la quantité de ressources disponibles pour les consommateurs, on parle alors de contrôle ascendant (« bottom-up », Lindeman, 1942). La biomasse des consommateurs d'un certain niveau trophique est limitée par la disponibilité de leurs proies d'un niveau trophique

inférieur. Donc, si la quantité de ressources disponibles à la base de la chaîne alimentaire augmente, la productivité de tout le réseau devrait également augmenter (Lampert et Sommer, 2007). Comme nous l'avons vu auparavant, le phytoplancton et les bactéries constituent le pool d'organismes à la base de ce réseau (Figure 4), il est donc primordial de comprendre quelles sont les ressources susceptibles de limiter leurs biomasses respectives.

La productivité des organismes photosynthétiques constituant le phytoplancton est principalement limitée par la concentration des nutriments inorganiques (notamment le phosphore et l'azote) dissous dans l'eau (Hecky et Kilham, 1988 ; Elser et al., 2007) ainsi que par la quantité de lumière que reçoivent ces organismes photo-autotrophes (Rhee et Gotham, 1981 ; Padisak, 2004). La disponibilité de ces deux types de ressources indépendantes influence notamment la qualité nutritive du phytoplancton ce qui peut modifier la composition et la dynamique des populations de zooplancton (Sterner et al., 1997a ; Urabe et al., 2002 ; Hall, 2004, 2007 ; Dickman et al., 2006, 2008). La croissance bactérienne est elle aussi limitée par la disponibilité des nutriments (Elser et al., 1995). Cependant, comme la majorité des bactéries sont hétérotrophes, leur métabolisme et leur croissance sont principalement contrôlés par la quantité disponible et surtout par la qualité de la MO (dissoute et particulaire, del Giorgio et Cole., 1998). Les bactéries se nourrissent principalement de la MO dissoute (MOD) provenant des exsudats phytoplanctoniques (Sundh et Bell, 1992) et de la MOD allochtone (Tranvik, 1992).

Comme les prédateurs des communautés phytoplanctoniques et bactériennes sont différents, bactérivores d'un côté et herbivores de l'autre, la cascade trophique va entraîner un changement de diversité à tous les niveaux de la chaîne alimentaire aquatique du fait de la limitation en nutriments. Ainsi, les biomasses phytoplanctoniques et bactériennes à la base des réseaux trophiques lacustres sont fortement dépendantes des concentrations en nutriments dissous, de la lumière disponible, de la quantité et de la qualité et donc de l'origine de la MO. Néanmoins, la plupart des études portant sur ces effets limitants ont été réalisées en contrôlant directement ces paramètres de façon artificielle, dans le but de mimer des conditions particulières rencontrées dans différents écosystèmes aquatiques. Par exemple, la limitation des productions primaires et bactériennes par les nutriments a souvent été étudiée en enrichissant expérimentalement des systèmes aquatiques naturels ou contrôlés avec de l'azote et/ou du phosphore sous forme de nitrate, d'ammonium et/ou de phosphate pour reproduire différents états trophiques (Vrede et al., 1999 ; Elser et al., 2007, et les références y figurant ; Kragh et al., 2008). De même, les effets limitant de la lumière sur la croissance des

organismes photosynthétiques sont souvent étudiés en atténuant artificiellement son intensité (Dickman et al., 2006, 2008 ; Spivak et al., 2007). Enfin, les effets des apports de MO allochtone sur les communautés aquatiques ont été étudiés soit en estimant les contributions relatives des MO d'origine autochtone et allochtone en milieu naturel (Jansson et al., 2000 ; Kritzberg et al, 2005 ; Cole et al., 2011), soit en ensemençant des écosystèmes lacustres naturels ou expérimentaux avec de la MO d'origine diverse, souvent non naturelle, comme des carbonates enrichis en $C^{13}$ (Cole et al., 2002 ; Kritzberg et al., 2004 ; Pace et al., 2004, 2007 ; Carpenter et al., 2005 ; Cole et al., 2006 ; Solomon et al., 2008 ; Weidel et al., 2008), du glucose (Faithfull et al., 2011), du sucre de canne (Kankaala et al., 2010 ), des feuilles d'arbres (Brett et al., 2009), ou de l'amidon de maïs (Bartels et al., 2012).

Si ces approches expérimentales ont permis de mieux comprendre quelles sont les conséquences de ces différents contrôles bottom-up sur le fonctionnement des écosystèmes lacustres, elles n'ont pas pris en compte ou ont fortement simplifié certains compartiments et/ou processus naturels pouvant modifier l'impact ces facteurs. Ainsi, l'impact du compartiment sédiment et de l'érosion des sols des bassins versants sur le fonctionnement des écosystèmes lacustres a été peu étudié (Søndergaard et al., 1992, 2003) alors que sédiments et MO allochtone pourraient jouer un rôle important dans le métabolisme des lacs du fait du stock de MO et de nutriments qu'elles représentent.

### c. Interactions entre contrôles « top-down » et « bottom-up »

Les contrôles descendant et ascendant induit respectivement par la cascade trophique et la disponibilité des ressources sont deux processus qui structurent les communautés des réseaux trophiques aquatiques de façon interdépendante (Lindeman, 1942).
Ces interactions peuvent avoir des effets quantitatifs sur les biomasses des communautés mais également qualitatifs, en modifiant leur diversité (Figure 5).

Ainsi, Brett et Goldman (1996) ont montré que selon le niveau trophique considéré, la réponse des producteurs à la prédation ou à la disponibilité des nutriments est différente. Dans un écosystème marin, Spivak et al. (2007) ont montré que la biomasse d'algue pouvait être modifiée par un effet interactif entre la quantité de lumière disponible, la diversité des herbivores et la présence de prédateurs en sommet de réseau trophique. Cependant, ces interactions n'entraînent pas nécessairement des modifications de la biomasse des producteurs primaires car leurs effets peuvent se compenser (Gruner et al., 2008).

Les effets dus aux interactions entre consommateurs et ressources peuvent aussi induire des modifications de la diversité des communautés aquatiques dans des écosystèmes contrastés (Worm et al., 2002 ; Faithfull et al., 2011).

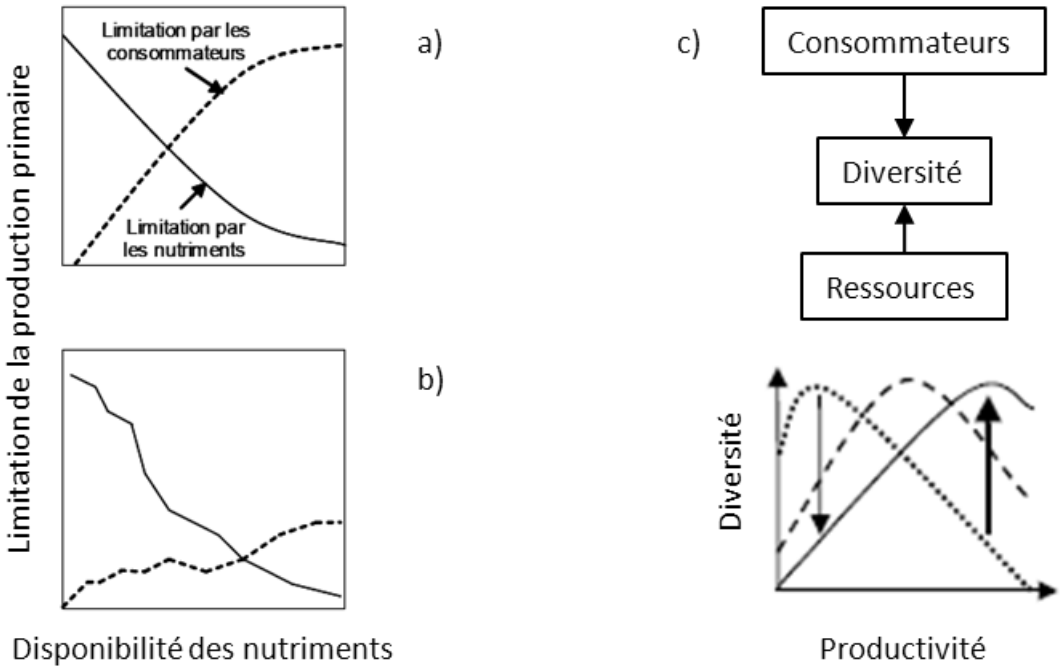



**Figure 5 :** Prédictions et modélisations des effets des interactions entre disponibilité des nutriments et prédation sur la limitation de la biomasse et de la diversité des producteurs primaires. a) Dans un système avec une faible diversité de producteurs (primaires ou secondaires), la limitation de leur biomasse par les nutriments diminue logiquement avec l'augmentation de la disponibilité des nutriments A l'inverse, la limitation par les consommateurs augmente avec la disponibilité des nutriments. b) Dans un système avec une forte diversité de producteurs, la consommation sélective par les herbivores entraîne un changement de la communauté des producteurs mais pas nécessairement de leur biomasse, comme révélé par la limitation des consommateurs qui reste faible le long du gradient de nutriments. c) Selon que la prédation des consommateurs soit faible (pointillés), intermédiaire (tirets) ou grande (trait plein), le maximum du pic de diversité des producteurs est atteint pour des productivités différentes. Pour une faible productivité, l'augmentation de la prédation entraîne une perte de diversité des producteurs (flèche descendante) alors que l'inverse se produit pour une grande productivité (flèche ascendante). a) et b) d'après Darcy-Hall (2006). c) d'après Worm et al. (2002).

### *3. Importance des apports de matières allochtones dans le fonctionnement des écosystèmes lacustres*

#### a. Origine et transport de la MO allochtone vers les milieux aquatiques

Comme cela a été souligné précédemment, les apports de matières allochtones dans les lacs proviennent majoritairement de l'érosion des bassins versants associés. L'érosion des sols est causée entre autres par le vent, les pratiques agricoles et le lessivage par les eaux de pluie et de ruissellement. Le sol érodé est transporté du compartiment terrestre vers les écosystèmes aquatiques *via* le réseau hydrographique (rivières et ruisseaux) du bassin versant.

La quantité et la nature de ces apports dépendent de la région et du bassin versant (type de sol, couvert végétal, nature de la roche, pratiques agricoles ; Lal, 2003). Si du fait de leur origine principalement minérale, les matières allochtones sont majoritairement composées de nutriments inorganiques (principalement carbone, azote et phosphore), elles peuvent également constituer des apports de nutriments organiques (Bloesch, 2004). Une partie du pool de carbone transporté des sols vers les écosystèmes aquatiques se trouve sous forme de matière organique dissoute (MOD) et particulaire (MOP).

Que ce soit en milieu terrestre ou en milieu aquatique, cette MO d'origine terrestre constitue une des sources d'énergie pour les bactéries hétérotrophes (Tranvik, 1992). Cependant, la capacité qu'ont les micro-organismes de minéraliser la MO est différente selon le milieu dans lequel elles se trouvent. En effet, dans les sols, la décomposition de la MO peut être limitée par trois principaux mécanismes (von Lützow et al., 2006): i) le manque d'accessibilité des organismes décomposeurs et de leurs enzymes à cette MO induit par des phénomènes physiques (occlusion dans des agrégats, tailles des pores et des interstices, hydrophobicité, encapsulation dans des macromolécules organique), ii) la stabilisation de la MO par complexation avec des surfaces minérales et/ou des ions métalliques et iii) la récalcitrance relative (de labile à réfractaire) due à par sa composition chimique.

Le passage du milieu terrestre au milieu aquatique peut diminuer l'importance de certains de ces mécanismes de préservation. Tout d'abord, la désagrégation et la dissolution de la MO dans l'eau peuvent significativement diminuer son manque d'accessibilité aux décomposeurs et sa stabilisation par complexation, fournissant ainsi une source de carbone supplémentaire pour les bactéries aquatiques. De plus, la capacité des micro-organismes à minéraliser de la MO réfractaire peut être augmentée lorsque de la MO labile est disponible

pour ces même organismes. Ce phénomène de « priming effect » (PE) a été observé dans les sols (Kuzyakov et al., 2000 ; Fontaine et al., 2007) et dans les milieux aquatiques (Farjalla et al., 2009 ; Guenet et al., 2010). Enfin, certaines molécules ou macromolécules réfractaires à la dégradation bactérienne en milieu terrestre peuvent être plus facilement dégradées dans l'eau. Par exemple, les substances humiques, peu dégradables dans les sols (Piccolo, 1996 ; Qualls et al., 2003), peuvent représenter en milieu aquatique une source d'énergie non négligeable pour les bactéries (Jones, 1992 ; Tranvik, 1992 ; Anesio et al., 2005).

La communauté bactérienne étant, avec le phytoplancton, à la base des réseaux trophiques lacustres, ces apports de MO allochtone sont susceptibles d'être transférés vers toutes les communautés aquatiques *via* les interactions trophiques.

### b. Importance de la MO allochtone comme ressource des réseaux trophiques aquatiques

Récemment, de nombreux auteurs ont étudié l'importance de la MO allochtone dans le métabolisme des lacs en faisant la distinction entre MO autochtone et allochtone composant différents organismes du réseau trophique aquatique par des techniques de marquage isotopique (enrichissement du phytoplancton en $C^{13}$ par des apports de carbonates marqués au $C^{13}$, Cole et al., 2002 ; Kritzberg et al., 2004 ; Pace et al., 2004, 2007 ; Carpenter et al., 2005 ; Cole et al., 2006 ; Solomon et al., 2008 ; Weidel et al., 2008). La contribution de la MOD allochtone par rapport à la MOD autochtone en tant que ressource d'énergie pour la communauté bactérienne peut fortement varier selon les écosystèmes (Carpenter et al., 2005). Ainsi, Pace et al. (2007) ont notamment montré que dans un lac oligotrophe soumis à peu d'apports terrestres, la MO allochtone était une ressource peu importante pour les bactéries comparée à la MO autochtone. De même, dans une étude expérimentale en mésocosmes, Kankaala et al. (2010) ont montré que des apports artificiels de sucre de canne ne stimulent pas nécessairement la biomasse bactérienne. Contrairement à ces résultats, plusieurs auteurs ont montré que la MOD allochtone peut supporter une grande partie la respiration et la biomasse bactérienne dans des lacs soumis à des apports allochtones significatifs et présentant des états trophiques contrastés (Jansson et al., 2000 ; Blomqvist et al., 2001 ; Cole et al., 2002 ; Kritzberg et al., 2004 ; Cole et al., 2006). La MO d'origine allochtone constituant la biomasse bactérienne peut ensuite intégrer les différents maillons de la chaîne alimentaire *via* les transferts trophiques (Carpenter et al., 2005). Ainsi, plusieurs études ont montré que la MO allochtone pouvait constituer une ressource importante pour des consommateurs

appartenant à des niveaux trophiques différents, que ce soient des flagellés bactérivores (Blomqvist et al., 2001), du zooplancton (Pace et al., 2004 ; Perga et al., 2006 ; Faithfull et al., 2011), des larves d'insectes zooplanctivores comme *Chaoborus* (Cole et al., 2006) ou des poissons (Carpenter et al., 2005 ; Weidel et al., 2008). Cependant, le transfert de la MO d'origine allochtone des bactéries vers le reste du réseau trophique n'est pas forcément induit uniquement par l'augmentation de la production bactérienne minéralisant la MOD allochtone (Cole et al., 2002). En effet, la consommation directe de la MOP par le zooplancton est un autre point d'entrée de la MO d'origine allochtone dans le réseau trophique (Brett et al., 2009 ; Cole et al., 2011). Ainsi, les apports de MO terrestre dans les écosystèmes aquatiques stimulent généralement les biomasses des communautés et les transferts d'énergie et de nutriments entre les différents niveaux trophiques, ce qui a pour conséquence de modifier le métabolisme des lacs, en entraînant notamment la domination de la respiration sur la production primaire (Duarte et al., 2005). La MO autochtone originaire de la production primaire constituant l'autre pool d'énergie à la base des réseaux trophiques, la question se pose alors de savoir quels sont les impacts relatifs de ces différentes MO (autochtone *vs* allochtone) dans le fonctionnement des écosystèmes aquatiques.

### c. Compétition entre MO autochtone et allochtone

Pour leurs besoins métaboliques, les bactéries hétérotrophes minéralisent la MOD, qu'elle soit autochtone ou allochtone. Les sources de MOD offrant la plus grande efficacité de conversion de la MO en biomasse bactérienne sont les exsudats du phytoplancton (del Giorgio et Cole, 1998) puisqu'ils sont majoritairement composés de polysaccharides facilement assimilables par les bactéries (Myklestad, 1995). Cependant, dans les écosystèmes où la production primaire est limitée (lacs oligotrophes) ou ceux soumis à de forts apports de MO terrestre, les bactéries utilisent principalement cette dernière pour leur croissance, bien qu'elle soit moins intéressante que la MO autochtone d'un point de vue énergétique (Jansson et al., 2000). Cette 'allochtonie' (utilisation de la MO allochtone) peut donc se transmettre à tout le réseau trophique et ainsi dominer le cycle du carbone dans les écosystèmes aquatiques. Cette compétition entre MO autochtone et MO allochtone peut s'expliquer par deux mécanismes. Tout d'abord, dans les milieux recevant peu d'apports terrestres, les bactéries se développent essentiellement en utilisant la MOD exsudée par le phytoplancton et peuvent par conséquent être limitées par la production primaire, ce qui conduit à la domination de la

production primaire sur la production bactérienne (Jansson et al., 2006). A l'inverse, dans les écosystèmes soumis à des apports significatifs de MOD allochtone, les bactéries ne sont plus limitées par la quantité de carbone disponible et donc leur croissance est indépendante de la production primaire. Dans ces conditions, les nutriments comme l'azote et la phosphore étant limitants pour la communauté bactérienne et pour la communauté des organismes photosynthétiques, ces deux communautés vont entrer en compétition pour cette ressource. Or, comme les bactéries ont plus d'affinité pour l'azote et le phosphore que le phytoplancton (Thingstad et al., 1993 ; Vadstein, 2000), cette compétition pour les nutriments est dominée par les bactéries, avec pour effet potentiel d'augmenter leur biomasse et de diminuer celle du phytoplancton (Blomqvist et al., 2001). De plus, la MOD allochtone peut être essentiellement constituée de substances humiques (Amador et al., 1990), or ces composés ont la propriété d'absorber la lumière et entrent en compétition avec les organismes photosynthétiques pour cette ressource. Ainsi, selon la concentration des substances humiques dans l'écosystème aquatique, la lumière nécessaire aux producteurs primaires pour la photosynthèse va être plus ou moins disponible, pouvant conduire à une diminution de la biomasse de phytoplancton (Jones, 1992 ; Steinberg, 2004). Cependant, même dans des lacs ayant de fortes concentrations en substances humiques, la limitation de la production primaire par le manque de disponibilité de la lumière semble être moins importante que celle due aux nutriments (Jansson et al., 2007).

La cascade trophique simplifiée présentée dans la Figure 4 peut donc être complétée en y intégrant les contributions respectives de la MO autochtone et allochtone ainsi que les interactions entre producteurs primaires et bactéries (Figure 6).

### *4. Les sédiments : zone d'intense recyclage de nutriments et de MO*

#### a. Sédimentation de MO et de nutriments

La MO allochtone n'ayant pas été directement utilisée par les communautés aquatiques dans la zone pélagique sédimente. En plus de ces apports allochtones, les sédiments reçoivent d'importantes quantités de MO autochtone produites par les communautés du réseau trophique, provenant principalement de la sédimentation du phytoplancton de la zone pélagique (Bloesch et Burgi, 1989). En comparaison, les débris issus

des niveaux trophiques supérieurs (cadavres et mues de zooplancton, pelotes fécales…) semblent représenter une faible proportion de la sédimentation totale (Bloesch, 2004).

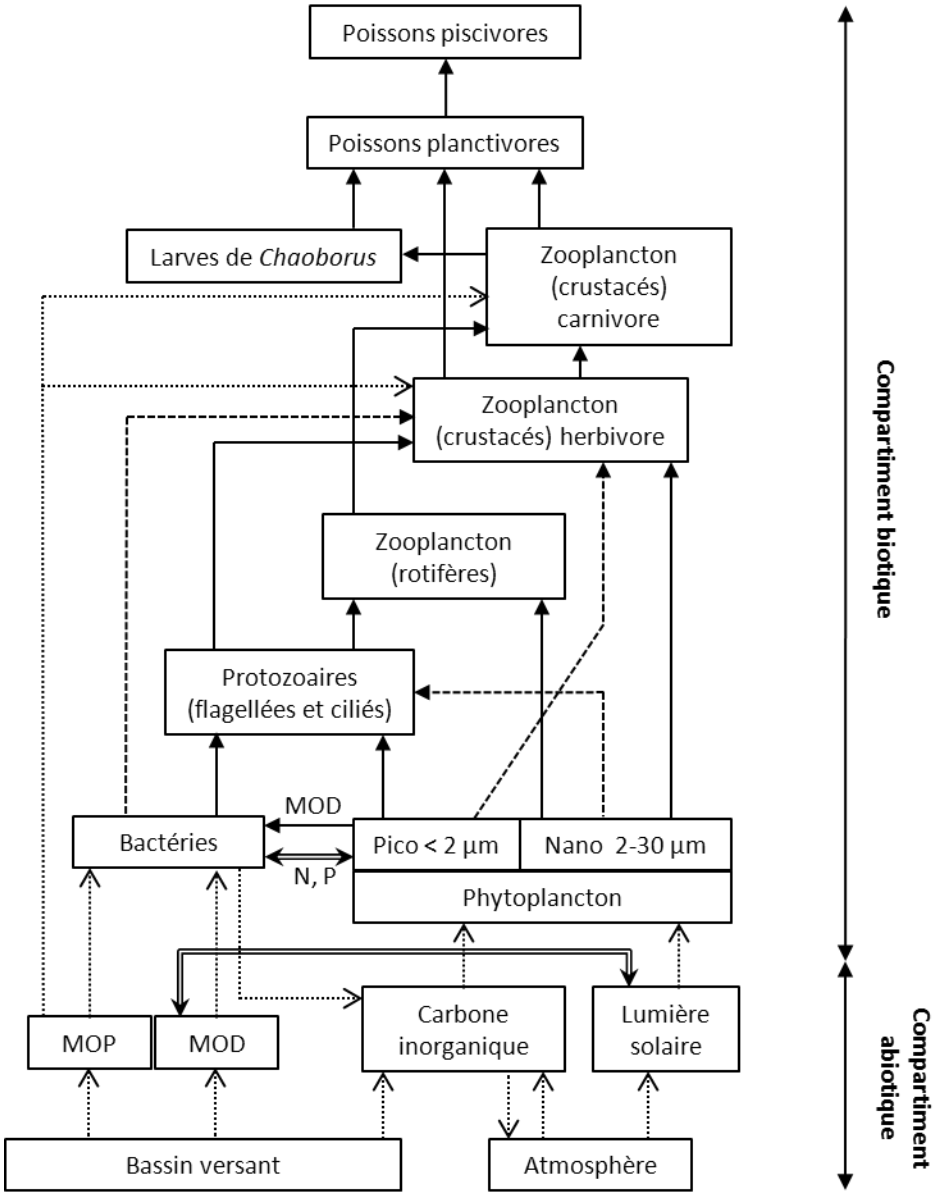



**Figure 6 :** Réseau trophique aquatique simplifié incluant les sources de carbone terrestres et atmosphérique (flèches pointillées) ainsi que les phénomènes de compétitions entre autotrophie et hétérotrophie (doubles flèches). MOD : matière organique dissoute. MOP : Matière organique particulaire. N, P : azote et phosphore, respectivement. Adapté de Lampert et Sommer (2007) et Jansson et al. (2007).

Les sédiments reçoivent également des apports de nutriments particulaires qui n'ont pas été utilisés par le phytoplancton ou le bactérioplancton (bactéries pélagiques) du fait de leur faible temps de résidence dans la colonne d'eau ou de leur préservation sous des formes difficilement assimilables par ces organismes (Forsgren et al., 1996 ; Bloesch, 2004). Ces apports peuvent être particulièrement importants dans des écosystèmes eutrophes soumis à de forts intrants de nutriments liés à l'activité humaine (Søndergaard et al., 2007). De plus, les particules en sédimentation, qui proviennent des communautés pélagiques sont une autre source de nutriments pour les sédiments. Comme la sédimentation de MO et de nutriments dépend des apports allochtones et de la production primaire, les flux de déposition des particules dans les sédiments et leur accumulation varie en fonction des écosystèmes considérés (Tableau 1). En accumulant cette MO et ces nutriments, les sédiments constituent un important réservoir de ressources pour les écosystèmes lacustres. Par l'action de processus biotiques et/ou abiotiques, ce réservoir peut soit accumuler à plus ou moins long terme ces ressources, les rendant peu voire pas disponibles pour les communautés aquatiques, soit jouer le rôle de source de MO et de nutriments pour le réseau trophique aquatique.

| | Lacs oligrotrophes | | Lacs mésotrophes | | Lacs eutrophes | |
|---|---|---|---|---|---|---|
| | Petit lac | Grand lac | Petit lac | Grand lac | Petit lac | Grand lac |
| Production primaire (gC $m^{-2}$ $an^{-1}$) | < 150 | | 150-350 | | > 350-700 | |
| Matières particulaires en suspension : | | | | | | |
| Poids sec (mg $L^{-1}$) | 1,3-2,3 | 10-25 | 2,2 | 2,9-21 | 2,5-3,2 | > 2,5 |
| Carbone organique particulaire (µg $L^{-1}$) | 435-700 | 230 | 500 | 448 | 1150 | 3100 |
| Azote particulaire (µg $L^{-1}$) | 32-53 | 20 | - | 43 | 142 | 536 |
| Phosphore particulaire (µg $L^{-1}$) | 2-6.6 | 4 | 5-12 | 6,3 | 18 | 39-64 |
| Flux de sédimentation : | | | | | | |
| Poids sec (g $m^{-2}$ $jour^{-1}$) | 0,1-1,2 | 7,4-30 | 0,3-2 | 2-6,5 | 2-10 | 5-31 |
| Carbone organique particulaire (mg $m^{-2}$ $jour^{-1}$) | 41-120 | 250 | 160-390 | 268 | 180-920 | 380-1300 |
| Azote particulaire (mg $m^{-2}$ $jour^{-1}$) | 4,8-12 | 9 | 45 | 20 | 45-53 | 131 |
| Phosphore particulaire (mg $m^{-2}$ $jour^{-1}$) | 1,6 | 13 | 6-7 | 5,2 | 6-13 | 26 |
| Taux d'accumulation (mm $an^{-1}$) | 4 | > 20 | 3,5-4 | 4,5-5 | 3,7-10 | 13-31 |

**Tableau 1 :** Production primaire, concentration des particules en suspension, taux de sédimentation et d'accumulation des sédiments dans des lacs de la zone tempérée présentant des statuts trophiques et des tailles différentes. D'après Bloesch (2004).

b. Le sédiment comme source d'azote et de phosphore pour les organismes à la base des réseaux trophiques

Dans les sédiments, l'azote particulaire est minéralisé en ammonium ($NH_4^+$) qui peut être à son tour transformé en nitrates ($NO_3^-$) sous l'action de bactéries nitrifiantes (Forsberg, 1989 ; Rysgaard et al., 1993, Hargreaves, 1998). Ammonium et nitrates sont utilisés comme source d'azote par les bactéries benthiques mais également par les producteurs primaires (benthiques et pélagiques) après avoir diffusé des sédiments vers la zone pélagique.

Le phosphore peut quant à lui être lié à des complexes de MO réfractaires à la minéralisation (Søndergaard et al., 2003) et constituer ainsi une fraction inutilisable par les communautés aquatiques. Il peut également être lié à de la MO labile qui lors de sa minéralisation par les bactéries du sédiment va libérer le phosphore sous forme dissoute (Gächter et al., 1988). De plus, le phosphore peut être lié à d'autres éléments (fer, aluminium, manganèse, calcium, argiles…) sous forme inorganique. Des modifications des conditions d'oxygénation etde pH (Søndergaard, 1988 ; Gomez et al., 1999), des concentrations en nitrates (compétition pour la complexation avec le fer, Jensen et al., 1992) ainsi que les phénomènes de resuspension (courants internes, fouille des poissons benthivores, Søndergaard et al., 1992) peuvent conduire à la libération de ce phosphore lié et le rendre disponible pour les bactéries et les organismes photosynthétiques (voir la review de Søndergaard et al., 2003). Ces aspects ont notamment été étudiés dans l'optique de mieux comprendre le manque d'efficacité des biomanipulations dans les systèmes eutrophes (Jeppesen et al., 2007 ; Søndergaard et al., 2007). Il a en effet été montré que le relargage de phosphore accumulé dans le sédiment vers la colonne d'eau pouvait entraîner une importante augmentation de la biomasse algale dans la zone pélagique puisque ce nutriment n'était plus limitant pour la croissance du phytoplancton. Les sédiments peuvent donc représenter une source non négligeable d'azote et de phosphore qui vont servir de ressources pour les organismes à la base des réseaux trophiques aquatiques (Andersen et Jensen, 1992 ; Martinova, 1993).

c. La MOS comme ressource basale du réseau trophique

La transformation de la MOS par différents processus biotiques et abiotiques dans les couches supérieurs des sédiments se nomme « diagenèse précoce ». La minéralisation de la

MOS par les bactéries hétérotrophes est le principal processus gouvernant la diagenèse précoce et donc le cycle de la MO dans les sédiments (Heinrichs, 1993). Contrairement aux organismes détritivores qui peuvent ingérer directement de la MOP, les bactéries ne peuvent utiliser la MO que sous forme dissoute. Ainsi, la première étape de la dégradation de la MOS par les bactéries des sédiments est l'hydrolyse de la MOP par les exo-enzymes bactériennes. Une fois dissoute, la MO peut être minéralisée en $CO_2$ par les bactéries selon des mécanismes et des cinétiques qui vont différer notamment en fonction de la composition chimique de la MOS (voir paragraphe C.3) et des conditions d'oxygénation du milieu (Wakeham et Canuel, 2006). Dans des conditions aérobies (présence d'oxygène dissous à l'interface eau-sédiment ou dans les premiers millimètres des sédiments), l'accepteur d'électrons offrant le bilan énergétique le plus grand pour la dégradation de la MOD est le dioxygène (respiration oxique). Dans des conditions anaérobiques, les bactéries vont utiliser d'autres accepteurs d'électrons que le dioxygène pour dégrader la MOS : nitrates ($NO_3^-$ : dénitrification), oxyde de manganèse ($MnO_2$ : réduction du manganèse), hydroxyde de fer ($Fe(OH)_3$ : réduction du fer), sulfates ($SO_4^{2-}$ : sulfato-réduction) et carbonates ($CO_2$ dissous, $HCO_3^-$) ou acétate ($CH_3COO^-$ : méthanogenèse) (Froelich et al., 1979). La production de biomasse bactérienne induite par la biodégradation de la MOS peut ensuite servir de ressource basale pour l'ensemble du réseau trophique aquatique. La dégradation de la MOS peut également entraîner le relargage dans l'eau de MOD directement assimilable par le bactérioplancton (Klump et al., 2009).

De plus, les bactéries ne sont pas les seuls organismes des sédiments qui peuvent dégrader la MOS. En effet, la faune benthique (zoobenthos) est constituée d'une multitude d'organismes parmi lesquels figurent les macroinvertébrés. La proportion relative des espèces herbivores, détritivores ou carnivores varie en fonction de l'écosystème considéré mais également au sein d'un même écosystème (par exemple entre zone littorale et profonde). Ainsi le zoobenthos peut être dominé par les espèces détritivores qui se nourrissent de MOP (Jonasson, 2004). Le zoobenthos herbivores se nourrit quant à lui d'algues benthiques qui peuvent être considérées comme appartenant à la MOS. Qu'elles soient herbivores ou détritivores, les communautés de zoobenthos convertissent la MOS en biomasse, tout comme les bactéries benthiques. Cette biomasse est ensuite soumise à la prédation et intègre l'ensemble du réseau trophique *via* les transferts alimentaires. Le zoobenthos peut également jouer le rôle d'ingénieur écologique et avoir des effets positifs indirects sur la minéralisation de la MOS par les bactéries. En effet, certaines espèces de macroinvertébrés benthiques

construisent des tunnels dans les sédiments afin d'échapper à la prédation ou de rechercher des nutriments dans les couches plus profondes des sédiments (Pinder, 1986). La bioturbation, en augmentant la surface de contact entre sédiment et eau, entraîne une augmentation de la diffusion de l'oxygène, et de nutriments dissous, jusque-là piégés dans les sédiments. L'augmentation de la disponibilité en oxygène stimule la dégradation aérobie de la MOS par les bactéries (Mermillod-Blondin et al., 2003 ; Mermillod-Blondin et Rosenberg, 2006). Il est à noter que certains phénomènes physiques induisant la resuspension de sédiments comme les courants internes ou les fouilles de poissons benthivores (Breukelaar et al., 1994) ont des effets positifs sur la minéralisation de la MOS et le recyclage de nutriments encore plus marqués que ceux résultant de la bioturbation par le zoobenthos (Bloesch, 2004).

Les sédiments sont donc le lieu d'importants processus régulant les cycles biogéochimiques de la MO et des nutriments dans les écosystèmes lacustres.

## C. La matière organique aquatique

Comme nous venons de le voir dans les paragraphes précédents, les interactions entre le cycle de la MO et les réseaux trophiques aquatiques sont déterminantes dans le fonctionnement des lacs. Jusqu'ici, la MO n'a été considérée que comme un pool brut de ressources pour les communautés aquatiques. Afin d'affiner la compréhension des différents processus régulant le fonctionnement des lacs, il est nécessaire de considérer la MO comme un ensemble de composés ayant des propriétés et des fonctions différentes dans les écosystèmes aquatiques. La composition chimique à l'échelle moléculaire de la MO peut par exemple renseigner sur son origine et sur son état de dégradation. Différents indicateurs élémentaires et moléculaires sont utilisés pour caractériser l'origine et la qualité de la MO. Seuls les indicateurs utilisés dans le contexte de cette thèse sont présentés ici.

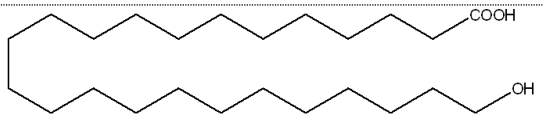
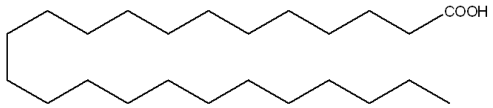
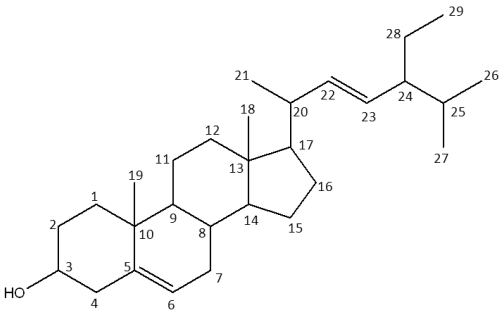
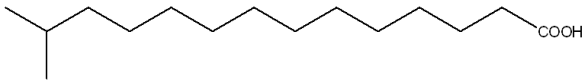
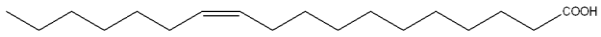
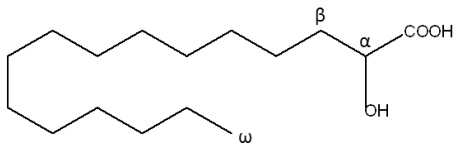
### *1. Utilisation des biomarqueurs pour retracer l'origine de la MO*

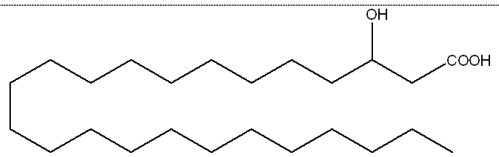
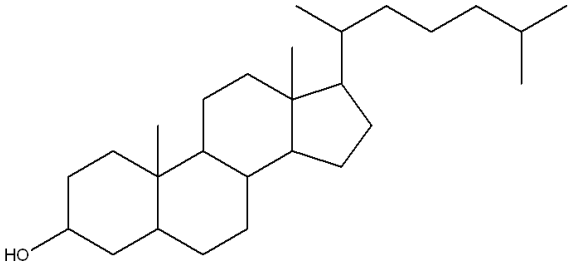
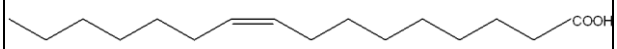
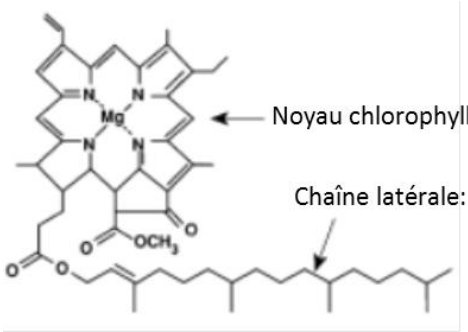
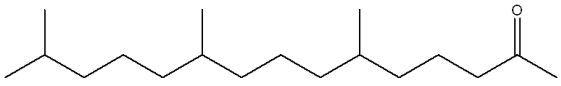
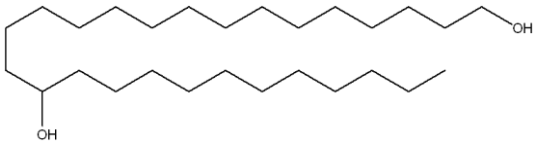
Provenant d'une multitude de sources, la MO des écosystèmes aquatiques regroupe une somme complexe et hétérogène de composés d'origine autochtone et allochtone. Les biomarqueurs chimiques sont des molécules ou des familles de molécules qui sont spécifiques à certains organismes ou groupes d'organismes et de processus conduisant à la synthèse et/ou à la transformation de ces molécules (Hegdes et Prahl, 1993). L'attribution d'un biomarqueur

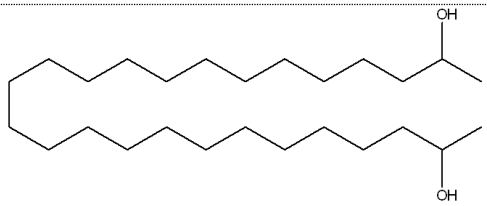
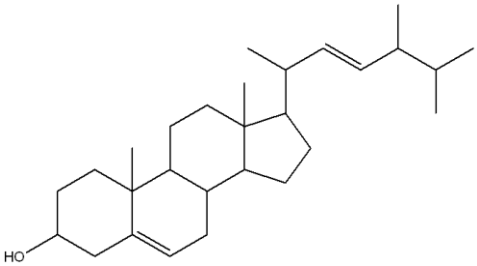
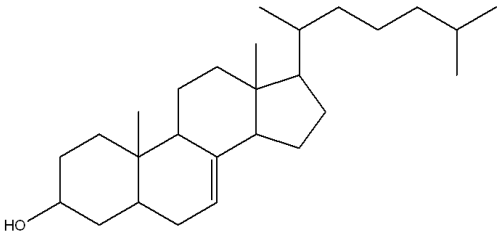
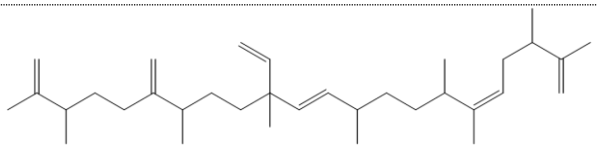
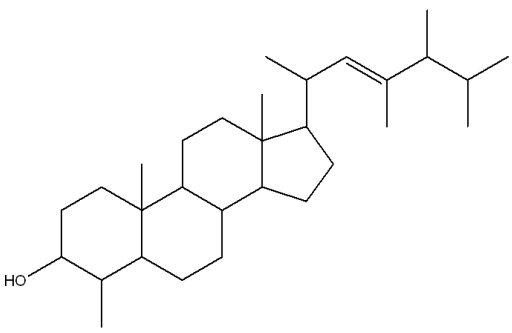
à une source spécifique peut se révéler problématique au vu de la grande diversité d'organismes composant la biosphère. De plus, la présence de biomarqueurs dans un grand nombre d'organismes différents montre que leur spécificité est souvent très limitée. Le rôle de certaines molécules comme biomarqueurs peut également être limité par leur faible résistance aux processus de dégradation chimiques et biologiques auxquelles elles sont soumises dans l'environnement (Wainman, 1999 ; Wakeham et Canuel, 2006). Ces mêmes processus de dégradation peuvent également entraîner des biais dans l'interprétation des contributions relatives des différents organismes sources de la MO étudiée. Enfin, le fait que la composition de la MO de certains organismes change en fonction des conditions environnementales peux compliquer l'attribution de certains biomarqueurs à des sources spécifiques (Siron et al., 1989, Sushchik et al., 2011). Néanmoins, les biomarqueurs chimiques ont souvent été utilisés pour déterminer l'origine et l'état de dégradation de la MO dans différents milieux aquatiques (Cranwell, 1982 ; Saliot et al., 1991 ; Meyers et Ishiwatari, 1993 ; Volkman, 2006).

Dans les organismes, la MO est essentiellement composée de protéines et sucres (Bianchi et Canuel, 2011). Du fait de leur ubiquité dans la biosphère et de leur caractère labile, ces deux classes de molécules organiques ont été relativement peu utilisées comme biomarqueurs de la MO (Dauwe et Middelburg., 1998 ; Lomstein et al, 2006). De plus, ces composés sont plutôt utilisés comme indicateurs de l'état de dégradation de la MO dans les sédiments plutôt que comme biomarqueurs des sources de la MO (Niggeman et Schubert, 2006a).

La MO est également composée de lipides présentant une grande diversité de structures. Cette diversité structurelle les rend particulièrement utiles en tant que biomarqueurs, non seulement pour identifier les sources de la MO (Meyers, 2003), mais également pour étudier sa biodégradabilité dans les sédiments (Cranwell, 1981). Toutefois, certains lipides sont peu spécifiques et doivent être utilisés comme biomarqueurs avec précaution. Seules les molécules utilisées comme biomarqueurs potentiels dans les différents chapitres de cette thèse seront présentées dans les paragraphes suivants. Le Tableau 2 présente les différents biomarqueurs lipidiques utilisés ici ainsi que leurs sources potentielles, leurs spécificités et des exemples de structure des molécules concernées.

| Source | Biomarqueur | Exemple de structure | Spécificité |
|---|---|---|---|
| ***MO allochtone*** : *plantes supérieures* | Ratio OC/N > 20 | | +++ |
| | ω-hydroxy acides : C ≥ 16 |   | +++ |
| | Acides carboxyliques et alcools saturés : C ≥ 20 | 24 :0, acide tétracosanoïque :   | ++ |
| | Stérols : $C_{28}\Delta^5$, $C_{29}\Delta^{5,22}$, $C_{29}\Delta^5$ | $C_{29}\Delta^{5,22}$ , 24-ethyl-cholesta-5,22,dienol:   | -/+ |
| ***Bactéries*** | | | |
| *Biomasse* | Acide carboxyliques saturés impairs, linéaires et branchés : C < 20 | Iso $C_{15:0}$ :   | +++ |
| | Acide vaccénique: 18:1ω7 |   | ++ |
| | α- et β-hydroxy acides linéaires et branchés : C < 20 | α -hydroxy acide en $C_{16}$ :   | ++ |

| | | | |
|---|---|---|---|
| *Activité* | α- et β-hydroxy acides : C ≥ 20 |   | ++ |
| *Dégradation* | Stanols | $C_{27}\Delta^0$,cholestanol:   | + |
| ***Phytoplancton*** | Ratio OC/N entre 4 et 10 | | +++ |
| | Acides carboxyliques insaturés (voir Tableau 3) | Acide palmitoléique (16:1ω7) :   Acide arachidonique (20:4ω6) :   | + |
| | Dérivés phytyles de la chlorophylle | Chlorophylle-a :   6,10,14 trimethylpentadecan-2-one :   | ++ |
| | Diols : 28 ≤ C ≤ 32, second groupe hydroxyle en $C_{14}$ ou $C_{15}$ |   | +++ |

| | | | |
|---|---|---|---|
| | Diols : C < 28, second groupe hydroxyle en α, ω, ou (ω-1) |  | ? |
| *Diatomées* | Stérols : $C_{28}\Delta^{5,22}$, $C_{28}\Delta^{5,24(28)}$ | $C_{28}\Delta^{5,22}$ :  | -/+ |
| *Chlorophycées* | $\Delta^7$-stérols | $C_{27}\Delta^7$ :  | +++ |
| *Botryococcus braunii : race B* | Botryococcènes : $C_nH_{2n-10}$, 30 ≤ n ≤ 37 |  | +++ |
| *Dinoflagellés* | Dinostérol | 4,23,24-trimethyl cholest-22-enol :  | +++ |

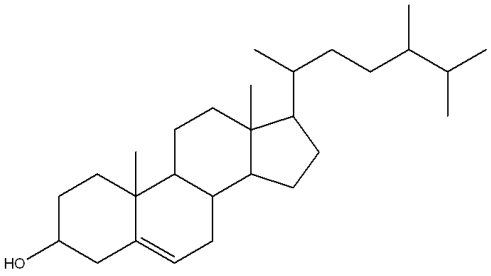
| | | | |
|---|---|---|---|
| ***Zooplancton*** | Cholestérol | $C_{27}\Delta^5$ :  | + |

**Tableau 2 :** Biomarqueurs potentiels permettant de retracer l'origine de la MO dans les écosystèmes aquatiques.

a. Biomarqueurs terrestres

La distinction entre biomarqueurs de MO allochtone et MO autochtone se fait essentiellement grâce aux composés synthétisés par les plantes supérieures. Par exemple, comme les plantes supérieures sont riches en cellulose et pauvres en protéines, leur composition élémentaire à des rapports C/N supérieurs à 20 caractéristiques (Meyers, 1994).

Dans les plantes supérieures, la cutine (pour les parties aériennes) et la subérine (écorce et racines) sont des polymères (polyesters) qui servent de couche protectrice contre les stress environnementaux et les agents pathogènes (Bernards, 2002 ; Heredia, 2003).La cutine est majoritairement constituée de monomères d'acides carboxyliques (ou acides gras) à 16 ou 18 atomes de carbone. Ces acides peuvent comporter un plusieurs groupes hydroxyles (Kolattukudy, 1980, 2001). Le domaine aliphatique de la subérine est principalement constitué d'acides mono- ou dicarboxyliques, d'alcools et de ω-hydroxy acides dont la longueur de chaîne varie de 16 à 32 atomes de carbone (Kolattukudy, 1980, 2001). Ces composés ont été largement utilisés en biogéochimie aquatique comme biomarqueurs des plantes vasculaires terrestres (Cranwell, 1974 ; Meyers, 2003 ; Volkman, 2006).

Cependant, certaines des molécules constituant la cutine et la subérine des plantes supérieures peuvent être présentes dans la MO autochtone. Par exemple, des acides carboxyliques (ou acides carboxyliques) saturés à longue chaîne ont été trouvés dans des micro-algues, bien que dans des proportions faibles (Volkman, 1989).D'autre part, la présence de certains macrophytes peut contribuer de façon significative à la teneur en biomarqueurs de plantes supérieurs (ex : alcanes alcools et acides carboxyliques saturés à longue chaîne carbonée) dans la MO autochtone (Ficken et al., 2000 ; Gao et al., 2011). En

conséquence, certains composés généralement considérés comme biomarqueurs de la MO allochtone doivent être utilisés avec prudence.

L'utilisation de certains stérols comme indicateurs de la contribution allochtone à la MO est limitée par leur manque de spécificité. En effet, même si la composition des stérols des plantes supérieures est dominée par le 24-éthylcholest-5-èn-3β-ol ($C_{29}\Delta^5$), le 24-méthylcholest-5-èn-3β-ol ($C_{28}\Delta^5$) et le 24-éthylcholesta-5,22-diène-3β-ol ($C_{29}\Delta^{5,22}$) et le (Nishimura et Koyama, 1977 ; Rieley et al., 1991), ces mêmes composés ont également été détectés dans de nombreuses micro-algues (Volkman, 1986).

b. Biomarqueurs autochtones

*i. Biomarqueurs bactériens*

Les acides carboxyliques saturés à chaîne courte (< $C_{20}$) ayant un nombre impair d'atomes de carbone sont largement utilisés comme biomarqueurs bactériens (Perry et al., 1979 ; Canuel et Martens, 1993). De même, les acides carboxyliques ramifiés à chaîne courte, particulièrement les acides carboxyliques *iso* et *anteiso* en $C_{15}$ et $C_{17}$, sont des biomarqueurs bactériens classiques (Boon, 1977, Kaneda, 1991). L'acide carboxyliques monoinsaturé 18:1ω7 (acide *cis* vaccénique) est également abondant dans la distribution des lipides des bactéries (O'Leary, 1962). Néanmoins, comme il peut aussi être retrouvé chez certaines espèces du phytoplancton (Perry et al., 1979), son utilisation en tant que biomarqueur de bactéries se fait généralement en utilisant le rapport 18:1ω7 /18:1ω9. En effet, l'abondance de l'acide oléique (18:1ω9), faible dans les bactéries, est forte dans le phytoplancton (Volkman et Johns, 1977 ; Bechtel et Schubert, 2009ab).

Les α- et les β-hydroxy acides sont également utilisés comme biomarqueurs bactériens (Goossens et al., 1986 ; Keinänen et al., 2003 ; Volkman, 2006). Cependant, une distinction peut être faite entre les composés à chaînes courtes qui composent les membranes d'un grand nombre de bactéries et qui sont donc indicateurs d'une biomasse bactérienne (Wilkinson, 1988) et ceux à chaînes longues qui sont plutôt des produits intermédiaires de l'α- et de la β-oxydation des acides carboxyliques et indiquent donc une activité bactérienne (Perry et al., 1979 ; Lattuati et al., 2002 ; Wakeham, 1999 ; Wakeham et al., 2003). Néanmoins, des α- et

les β-hydroxy acides à chaîne courte ont été détectés dans des micro-algues mais dans de faibles proportions (Matsumoto et Nagashima, 1984 ; Matsumoto et al., 1984).

### *ii. Biomarqueurs phytoplanctoniques*

A l'inverse des plantes vasculaires terrestres, les algues, pauvres en cellulose et riche en protéines, ont des rapports C/N compris entre 4 et 10 (Meyers, 1994).

L'utilisation des acides carboxyliques pairs à chaîne courte comme biomarqueurs du phytoplancton est limitée car ils sont également présents dans les bactéries (Stefanova et Disnar, 2000).

De façon générale, aucun acide carboxylique n'est spécifique d'une espèce particulière d'algue et, même en utilisant les contributions relatives de différents acides carboxyliques, il est difficile d'identifier des espèces précises au sein d'une même classe d'algues à l'aide de ces composés (Viso et Marty, 1993 ; Bec et al., 2010). Cependant, en étudiant les contributions relatives de différents acides carboxyliques insaturés variant par la longueur de leur chaîne carbonée, leur nombre de doubles liaisons et la position de ces doubles liaisons sur la chaîne carbonée, il est possible d'attribuer certaines distributions d'acides carboxyliques aux différentes classes d'algues. Par exemple, l'acide palmitoléïque (16:1ω7) est un composé majeur des lipides des diatomées et de certaines cyanobactéries, qui peut représenter jusqu'à 30% des acides carboxyliques (Kates et Volcani, 1966 ; Volkman et al., 1989 ; Ahlgren et al., 1990) mais il peut également contribuer de manière significative aux lipides des dinoflagellées (Ahlgren et al., 1992). L'acide vaccénique (18:1ω7) et l'acide oléique (18:1ω9) peuvent également potentiellement servir de biomarqueurs pour certaines algues comme les cyanobactéries, les algues vertes ou les flagellés (Ahlgren et al., 1992 ; Napolitano, 1999). Dans les écosystèmes aquatiques, les acides carboxyliques polyinsaturés pairs ayant de chaînes carbonées allant de $C_{16}$ à $C_{22}$ sont essentiellement synthétisés par le phytoplancton. Cependant, ces composés sont retrouvés dans tous les organismes aquatiques du fait des transferts au sein des réseaux trophiques (voir paragraphe suivant). Mais les différentes classes d'algues peuvent présenter des distributions caractéristiques de ces composés. Le Tableau 3 présente un résumé des acides mono- et polyinsaturés généralement utilisés comme biomarqueurs potentiels des grandes classes de phytoplancton en se basant sur une liste non exhaustive de références portant sur la distribution des acides carboxyliques des lipides de différentes algues en milieu marin et lacustres.

Les chlorophylles sont les pigments majeurs requis par le phytoplancton pour la photosynthèse. L'hydrolyse induite par le broutage du zooplancton herbivore ou la sénescence des algues ainsi que la photo-oxydation de la chlorophylle-a entraînent la libération de la chaîne phytyl latérale du noyau chlorophyllide-a. Cette chaîne phytyle, appelée phytol (3,7,11,15-tétraméthylhexadéc-2*E*-énol), peut être dégradée en d'autres composés isoprènoïques acycliques tels que l'acide phytanique (acide 3,7,11,15-tétraméthylhexadécanoïqe), la 6,10,14-triméthylpentadécan-2-one ou encore différents isomères de phytadiène (Rontani et Volkman, 2003). Ces molécules qui dérivent de la dégradation de la chlorophylle peuvent ainsi servir de biomarqueurs du phytoplancton.

Certaines familles de composés présentent une grande spécificité pour certaines espèces de micro-algues. Par exemple, la race B de l'algue verte *Botryococcus braunii* (race B)est essentiellement composée d'hydrocarbures branchés ayant des longueurs de chaîne carbonée de $C_{30}$ à $C_{37}$ (ou botryococcènes) qui ne sont retrouvés nulle part ailleurs dans la biosphère (Metzger et Largeau, 1999).

Les alcane diols saturés à longue chaîne peuvent également être utilisés comme biomarqueurs pour certaines classes d'algues en fonction de la position du second groupement hydroxyle sur la chaîne carbonée. Les alcane diols primaires de $C_{28}$ à $C_{32}$ et le second groupement hydroxyle en position 14 ou 15 sont généralement indicateurs de la présence d'eustigmatophytes (Volkman, 1998). D'autres alcane diols primaires ayant des chaînes carbonées allant de $C_{24}$ à $C_{36}$ avec un second groupement hydroxyle en position 11, 12, 13,14 ou 15 ont également été retrouvés dans des sédiments provenant de différents écosystèmes et attribués à la présence de micro-algues (Versteegh et al., 1997). D'autres études ont proposé les diatomées (Damste et al., 2003) ou les cyanobactéries(Morris et Brassell, 1988 ; Xu et al., 2007) comme autres sources potentielles d'alcane diols. Récemment, Allard et al. (2011) ont attribué la présence d'un α,(ω-1) alcane diol en $C_{24}$ et de α,ω alcane diols en $C_{28}$, $C_{30}$ et $C_{32}$ dans le seston et les sédiments récents de mésocosmes lacustres à la contribution du phytoplancton à ces compartiments.

La composition des stérols des micro-algues présente une très grande diversité. Bien que parfois détectés dans des micro-algues (Volkman, 2003), certains stérols, tels que le cholestérol (cholest-5-èn-3β-ol : $C_{27}\Delta^5$) et le 24-éthylcholest-5-èn-3β-ol ($C_{29}\Delta^5$), sont usuellement considérés comme biomarqueur animal pour le cholestérol et comme biomarqueur de plante supérieure pour le $C_{29}\Delta^5$. D'autres stérols comme le 24-méthylcholesta-5,22*E*-dièn-3β-ol ($C_{28}\Delta^{5,22}$) et le 24-méthylcholesta-5,24(28)-dièn-3β-ol

| | **Cyanobactéries** | | **Chlorophycées** | | **Diatomées** | | **Cryptophycées** | | **Dinoflagellés** | |
|---|---|---|---|---|---|---|---|---|---|---|
| Acide carboxyliques | Spef. | Réf. | Spef. | Réf. | Spef. | Réf. | Spef. | Réf. | Spef. | Réf. |
| *16:1ω7* | +** | J | - | J | ++ | K, J | | | - | J |
| *16:3ω4* | | | | | ++ | L | | | | |
| *16:4ω1* | | | | | ++ | L, K, L | | | ++ | J, E |
| *$C_{16}$ polyinsaturés* | | | + | D | ++ | K, J | | | | |
| *18:1ω9* | | | +** | E | | | | | | |
| *18:1ω7* | - | C, E | | | | | | | | |
| *18:2ω6 (LIN)* | +** | J | ++<br>+ | L, J<br>H | - - | J | | | - - | J |
| *18:3ω3 (α-LA)* | +** | E | ++ | L, J, E | | | ++<br>++* | L<br>J, B | | |
| *18:4ω3* | +* | J | +* | J | | | ++ | L | ++<br>+ | K, E<br>L |
| *20:4ω6 (ARA)* | - - | J, C, E, F | - - | J, C, E, F | - | J | | | | |
| *20:5ω3 (EPA)* | - - | J,C, E, F | - - | J, C, E, F | ++ | K, L, H, A | ++ | L | + | L |
| *22:5ω6* | - - | J,C, E, F | - - | J, C, E, F | | | | | | |
| *22:6ω3 (DHA)* | - - | J,C, E, F | - - | J, C, E, F | - -<br>- | L<br>H | ++ | L | ++<br>+ | K, L<br>I |

**Tableau 3 :** Principaux acides carboxyliques insaturés pouvant servir de biomarqueurs potentiels pour différentes classes d'algues. Références: A : Kates et Volcani (1966) ; B : Beach et al. (1970) ; C : Ahlgren et al. (1990) ; D : Cranwell (1990) ; E : Ahlgren et al. (1992) ; F : Murata et al. (1992) ; G : Viso et Marty (1993) ; H : Napolitano (1994) ; I : Napolitano et al. (1995) ; J : Napolitano (1999) ; K : Dalsgaard et al. (2003) ; L : Volkman (2006). Spef. : spécificité du biomarqueur : + = forte abondance relative ; - absence ou faible abondance relative. * : présence dans une seule espèce de la classe d'algue. ** : présence dans plusieurs espèces de la classe d'algue. LIN : acide linoléique. α-LA : acide alpha linoléique. ARA : acide arachidonique. EPA : acide eicosapentaénoïque. DHA : acide docosahexaénoïque

($C_{28}\Delta^{5,24(28)}$) ont été considérés comme indicateurs de la présence de diatomées (Castaneda et Schouten, 2011). Cependant, ces stérols sont également présents dans d'autres classes d'algues, restreignant donc leur utilisation comme biomarqueurs des diatomées (Volkman, 1986). En revanche, certains stérols sont spécifiques d'une classe d'algue, comme les stérols ayant une insaturation en position 7 pour les algues vertes (*Chlorophyceae*, Cranwell, 1982 ; Cranwell et al., 1990), ou les 4-méthyl stérols et plus particulièrement le dinostérol (4α,23,24-triméthyl-5α-cholest-22-èn-3β-ol) pour les dinoflagellés (Boon et al., 1979 ; Volkman, 1998).

### *2. Utilité des biomarqueurs pour l'étude des relations trophiques*

Phytoplancton et bactéries, à la base des réseaux trophiques, sont les principales sources de lipides dans les écosystèmes aquatiques. Ces organismes sont capables de synthétiser *de novo* les lipides nécessaires à leur métabolisme (Müller-Navarra, 2008). Au contraire, les organismes constituant les niveaux trophiques supérieurs ne peuvent dans la plupart des cas pas synthétiser leurs lipides *de novo* et doivent donc subvenir à leurs besoins en lipides en consommant les organismes qui contiennent cette ressource (Dalsgaard et al., 2003). C'est particulièrement le cas pour les acides carboxyliques polyinsaturés ayant une insaturation en position ω 3 ou ω 6 (principalement synthétisés par le phytoplancton) qui sont des composés essentiels pour le zooplancton puisqu'ils jouent un rôle primordial notamment dans la fluidité de leurs membranes, dans leur croissance et leur reproduction (von Elert, 2002, 2004; Wacker et al., 2002 ; Smyntek et al., 2008). Par conséquent, des variations de la quantité de ces composés dans le régime alimentaire du zooplancton peuvent avoir des effets marqués sur son métabolisme (Weers et Gulati, ;1997 ; Masclaux et al., 2009). Ainsi, de nombreuses études en milieux naturels ou en cultures ont démontré que le zooplancton accumule ces acides carboxyliques essentiels à partir de leur régime alimentaire (Brett et Müller-Navarra, 1997 ; Demott et Müller-Navarra, 1997 ; Kainz et al., 2004 ; Hessen et Leu, 2006). Les abondances relatives des acides carboxyliques polyinsaturés dans les lipides des algues sont différentes selon les classes (Tableau 3). Partant de ce constat, l'étude de la composition en acides carboxyliques polyinsaturés du zooplancton peut apporter des informations sur les différentes classes d'algue consommées (Brett et al., 2006). De plus, plusieurs études ont montré (i) que le zooplancton se nourrit de façon sélective en fonction de la qualité nutritionnelle (contenu en acides carboxyliques polyinsaturés en $C_{20}$ et $C_{22}$) des algues à sa disposition (Burns et al., 2011), (ii) que cette prédation sélective est différente

selon les espèces de zooplancton (Ravet et al., 2010 ; Lau et al., 2012) et leur position trophique (Falk-Petersen et al., 1999 ; Persson et Vrede ; 2006), et (iii) que cette prédation sélective peut donc avoir des effets importants sur la dynamique des populations de zooplancton (Müller-Navarra et al., 2000 ; Gladyshev et al., 2006).

D'autres biomarqueurs lipidiques sont utilisés pour étudier le régime alimentaire de différents consommateurs des réseaux trophiques aquatiques. Par exemple, Desvilettes et al. (1997) et Perga et al. (2006) ont démontré que certains acides carboxyliques d'origine bactérienne sont des biomarqueurs utiles pour étudier la consommation de bactéries et de ciliés par le zooplancton. Martin-Creuzburg et von Elert (2004) ont quant à eux montré que le cladocère herbivore *Daphnia galeata* subvenait à ses besoins en cholestérol, stérol essentiel pour la plupart des espèces de zooplancton (Goad et Akihisa, 1997), en transformant certains stérols présents dans les algues qu'il consomme.

Les contributions relatives des MO allochtones et autochtones au régime alimentaire du zooplancton et d'autres consommateurs aquatiques n'ont été que récemment étudiées *via* certains acides carboxyliques utilisés en tant que biomarqueurs (Perga et al., 2006, 2009 ; Lau et al 2008).

### *3. Qualité et biodégradation de la MOS*

L'un des facteurs contrôlant la dégradation de la MOS est sa composition. Les composés étant facilement dégradés par les bactéries aquatiques sont qualifiés de 'labiles' alors ceux difficilement assimilables par ces organismes sont dits 'réfractaires'. La qualité de la MOS dépend donc des contributions relatives de ces deux pools de MO (Rullköter, 2006 ; Wakeham et Canuel, 2006). Enfin, certains biomarqueurs sont caractéristiques de la dégradation de la MO par les différents organismes hétérotrophes (Canuel et Martens, 1993).

Bien qu'étant un indicateur permettant de faire la distinction entre la MO labile provenant du phytoplancton et la MO plus réfractaire provenant des plantes supérieures, le rapport C/N a un intérêt limité dans l'étude de la qualité de la MOS puisqu'il ne donne qu'une information générale sur la composition élémentaire de la MOS (Meyers et Ishiwatari, 1993 ; Meyers, 2003).

Les sucres et les protéines sont essentiels pour les organismes hétérotrophes puisqu'ils représentent respectivement d'importantes sources d'énergie (sous forme d'amidon ou de glycogène) et d'azote (Simon, 1998 ; Bunte et Simon, 1999 ; Weiss et Simon, 1999). Sucres

et protéines sont souvent considérés comme une fraction particulièrement labile de la MO et leur concentration dans les sédiments a souvent été utilisée comme indicatrice de l'état d'altération de la MOS (Cowie et Hedges, 1984 ; Wakeham et al., 1997 ; Dauwe et Middelburg, 1998 ; Panagiotopoulos et al., 2002 ; Meckler et al., 2004 ; Niggeman et al, 2006b).

Les biomarqueurs lipidiques sont également utiles pour étudier la qualité et l'état d'altération de la MOS. Ainsi, parmi les différentes familles de lipides présentes dans des sédiments lacustres, Cranwell (1981) a montré que leur réactivité suivaient l'ordre suivant : Acides carboxyliques insaturés > Alcools > Acides carboxyliques saturés > Alcanes. Plusieurs études ont également montré qu'au sein d'une même famille de lipide, les composés à chaîne carbonée courte se dégradaient plus rapidement que ceux à chaîne longue (Haddad et al., 1992 ; Sun et Wakeham, 1994 ; Canuel et Martens, 1996 ; Grossi et al., 2003 ; Niggeman et Schubert, 2006b).

La biodégradabilité de la MOS a aussi souvent été étudiée en comparant la contribution relative de différente composés considérés comme labiles avec celle des biomarqueurs bactériens qui sont indicateurs de la contribution de la biomasse bactérienne et/ou de l'état de dégradation de la MOS (Canuel et Martens, 1993 ; Canuel et al., 1997 ; Wakeham et al., 1997 ; Bechtel et Schubert, 2009ab).

Les stérols peuvent également être utilisés comme biomarqueurs de la dégradation de la MOS. En effet, la présence de stanols, homologues saturés des stérols, dans les sédiments, a été attribuée à l'hydrogénation des stérols correspondants par les bactéries hétérotrophes (Gaskell et Eglinton, 1975 ; Nishimura, 1977a). Par conséquent, le rapport stanols/stérols est parfois utilisé comme indicateur de l'état de dégradation de la SOM (Wakeham, 1989 ; Rieley et al., 1991, Canuel et Martens, 1993 ; Arzayus et Canuel, 2005 ; Yoshinaga et al., 2008). Cependant, quelques études ont montré que certains stanols présents dans les sédiments pouvaient provenir d'organismes vivants (Nishimura, 1977b ; Nishimura et Koyama, 1977). Cette possibilité pourrait entrainer un biais dans l'utilisation du rapport stanols/stérols comme indicateur de la dégradation de la MOS (Meyers et Ishiwatari, 1993).

Récemment, le 'Chlorin Index' a été utilisé comme indicateur de qualité de la MOS. Cet indicateur est basé sur la biodégradabilité de la chlorophylle et de ses produits de dégradation (Schubert et al., 2005). La comparaison du 'Chlorin Index' avec d'autres indicateurs de la biodégradabilité de la MOS plus fréquemment utilisés à montré sa pertinence (Meckler et al., 2004 ; Niggeman et al., 2006b ; Bechtel et Schubert, 2009a,b). Cependant, cet

indicateur peut se révéler inadéquat pour de la MOS récemment déposée composée de matériel purement autochtone pour lequel la contribution non phytoplanctonique est importante (observations personnelles).

Enfin, les mesures respirométriques constituent une autre approche pour étudier la biodégradabilité de la MOS. La respirométrie consiste à étudier la cinétique de la respiration bactérienne dégradant la MO en mesurant la consommation ($O_2$) ou la production ($CO_2$, $CH_4$) des gaz impliqués dans ce processus (Nay, 1994 ; Lagarde et al., 2005 ; Tremier et al., 2005 ; Maunoury et al., 2007). Dans les écosystèmes aquatiques, ces techniques ont été utilisées *in situ* et *ex situ* pour les écosystèmes marins (Migné et al., 2002 ; Panagiopoulos et al., 2002) et lacustres (Neubauer et al., 2000 ; Goedkoop et al., 2005). L'étude de la dégradation de la MOS en conditions *ex situ* se fait en général par des incubations de sédiments prélevés sur le terrain. Ces incubations ont l'avantage de pouvoir reproduire,dans une certaine mesure, des conditions naturelles tout en contrôlant un certain nombre de paramètres. Toutefois, ces approches ont peu été utilisées pour étudier les effets de l'origine et de la composition de la MOS sur la dégradation bactérienne. Récemment, Guérin et al. (2008) ont notamment montré que la production de méthane et de dioxyde de carbone des sédiments d'un réservoir tropical augmentait avec sa teneur en MO. Goedkoop et al. (1997) ont quant eux observé que l'addition de diatomées en tant que MO labile dans des incubations de sédiment lacustres stimulait la production et la respiration des bactéries benthiques.

## D. Objectifs de la thèse

Le fonctionnement des écosystèmes lacustres est la résultante de nombreux processus biotiques et abiotiques qui interagissent entre eux. Le cycle de la matière organique des lacs semble être fortement dépendant des réseaux trophiques, de la sédimentation, de l'érosion des sols et des interactions entre ces trois compartiments/processus. L'utilisation des biomarqueurs chimiques semble être très utile dans l'étude de ces interactions.

Au cours de cette thèse, nous nous sommes principalement attachés à étudier les effets ascendants induits par les sédiments et les apports de matières terrestres sur les réseaux trophiques aquatiques et le processus de sédimentation. Plus précisément, nous avons voulu apporter des éléments de réponse aux questions suivantes :

- L'origine et la composition de la matière organique ont-elles une influence sur sa biodégradabilité en milieu aquatique ?

- Cette biodégradabilité induit-elle des effets ascendants sur les réseaux trophiques ?
- Les interactions entre effets ascendants et descendants ont-elles des conséquences importantes sur le fonctionnement des écosystèmes lacustres ?

Pour ce faire, nous avons dans un premier temps étudié le processus de biodégradation matières organiques d'origines différentes dans des conditions contrôlées à l'échelle de microcosmes. Dans un second temps, les hypothèses émises à partir des résultats observés en microcosmes ont été testées à l'échelle de mésocosmes. A l'interface entre écologie aquatique et biogéochimie, cette thèse a été l'occasion de combiner différentes approches expérimentales et analytiques inhérentes à ces deux disciplines.

### *1. Influence de la structure des réseaux trophiques aquatiques sur la biodégradabilité des sédiments lacustres.*

*(A partir de l'article Harrault et al., soumis, chapitre 2)*

La minéralisation des sédiments lacustres peut représenter une source non négligeable de matière organique et de nutriments pour ces écosystèmes. La composition biochimique de la matière organique des sédiments est l'un des processus contrôlant sa minéralisation en milieu aquatique et peut dépendre fortement de la structure du réseau trophique.

Des incubations en microcosmes ont donc été réalisées sur des sédiments provenant de mésocosmes soumis à deux réseaux trophiques contrastés (2 niveaux : phytoplancton - zooplancton, 3 niveaux : phytoplancton - zooplancton - poissons planctivores) afin d'étudier l'influence de la structure du réseau trophique sur la biodégradabilité du sédiment. La biodégradation de ces sédiments a été suivie pendant 44 jours en mesurant les quantités de $CO_2$ respirées par une communauté bactérienne. Les résultats ont été discutés en prenant en compte les compositions élémentaires et lipidiques ainsi que les teneurs en protéines et en sucres des sédiments étudiés. Le recyclage des nutriments dans les sédiments des mésocosmes a été étudié en mesurant les pertes de nutriments de ces sédiments pendant 1 an.

### *2. Effets ascendants induits par des sédiments de natures différentes sur les compartiments pélagiques et la sédimentation.*

*(A partir de l'article Harrault et al., en préparation, chapitre 3)*

Les sédiments lacustres représentent un stock substantiel de nutriments et de matière organique dont le relargage dans la colonne d'eau pourrait avoir d'importantes conséquences sur le fonctionnement des écosystèmes aquatiques. Ce relargage pourrait être en partie contrôlé par la biodégradation des sédiments par les micro-organismes. Cette biodégradation pourrait elle-même être contrôlée par la composition biochimique des sédiments.

L'occurrence et l'intensité d'un contrôle ascendant exercé par les sédiments sur les organismes pélagiques d'un réseau trophique à deux niveaux (seston-zooplancton) ont été étudiées en ensemençant des mésocosmes aquatiques avec deux sédiments de natures différentes, l'un étant *a priori* beaucoup plus biodégradable que l'autre. Dans ces mésocosmes, nous avons réalisé un suivi mensuel des biomasses de seston et de zooplancton, et des taux de sédimentation de matières récemment déposées (1 semaine) de février à juin 2010. La composition en carbone et en azote de ces trois compartiments a également été déterminée Les compositions lipidiques du seston, du zooplancton et des sédiments récents prélevés en mai ont également été analysés. Enfin, l'influence du contrôle ascendant exercé par les sédiments lacustres sur la biodégradabilité des sédiments récents a été étudiée en déterminant leurs teneurs en composés potentiellement très labiles.

### *3. Stimulation de la minéralisation de la matière organique d'origine terrestre en milieu aquatique.*

*(A partir de l'article Guenet et al., soumis, chapitre 4)*

Après la production primaire, les apports terrigènes provenant de l'érosion des bassins versants représentent la seconde source de carbone et de nutriments des écosystèmes lacustres. L'origine et la composition de la matière organique allochtone laissent supposer qu'elle est plus réfractaire à la biodégradation que la matière organique autochtone. Cependant, en contexte aquatique la minéralisation de la matière organique des sols pourrait être intensifiée. De plus, la biodégradation de cette matière organique terrestre *a priori* assez réfractaire pourrait être stimulée par la biodégradation de la matière organique autochtone

plus labile. L'occurrence et l'intensité de ce processus de « priming -effect » pourrait dépendre des conditions trophiques de l'écosystème considéré.

La différence de biodégradation des sols entre systèmes terrestres et aquatiques a été étudiée en incubant pendant 44 jours différents sols dans des microcosmes soumis soit à des conditions terrestres soit à des conditions aquatiques (ajout d'eau et inoculum bactérien) en mesurant les flux de $CO_2$ émis lors de la minéralisation de la matière organique. Le « priming -effect » aquatique a été étudié en ajoutant du glucose marqué au $^{13}C$ dans les incubations 'aquatiques' permettant ainsi de faire la distinction entre la minéralisation de la matière organique des sols de celle du glucose. L'ajout de différentes quantités de nutriments inorganiques dans les microcosmes a permis d'observer les effets interactifs entre « priming -effect » et état trophique. Les résultats ont notamment été discutés en fonction des compositions élémentaires et lipidiques ainsi que des teneurs en protéines et en sucres des différents sols.

### *4. Influence de l'érosion des sols et de la structure du réseau trophique des écosystèmes aquatiques sur les organismes pélagiques et la sédimentation.*

*(A partir de l'article Harrault et al., en préparation, chapitre 5)*

La biodégradation de la matière organique des sols pourrait être stimulée, notamment *via* une augmentation de l'activité bactérienne, lorsqu'elle est transportée dans les écosystèmes aquatiques par l'érosion des bassins versants. Cette augmentation de l'activité bactérienne induite par les apports de matière organique allochtone pourrait stimuler le métabolisme de tous les organismes du réseau et donc modifier l'importance de certaines composantes de ce réseau.

L'influence des apports de matière allochtone sur le fonctionnement des écosystèmes aquatique a été simulée par des ajouts mensuels de terre dans des mésocosmes. L'influence de la structure du réseau trophique et ses interactions avec les effets ascendants des ajouts de terre ont été étudiées en ajoutant des poissons planctivores dans une partie des mésocosmes. De mars 2010 à novembre 2011, Nous avons effectué un suivi régulier des biomasses de seston, de zooplancton et de sédiment récemment déposés (1 semaine) ainsi que leurs compositions élémentaires respectives. Les compositions lipidiques du seston, du zooplancton et des sédiments récents prélevés en juin 2010 (avant l'apport des poissons) ont été analysées afin d'étudier les effets ascendants des apports allochtones sur les biomarqueurs lipidiques des

compartiments pélagiques et sur la composition de la matière organique sédimentée. L'influence des effets ascendants (apports allochtones), descendants (structure du réseau trophique) et leurs interactions sur la nature de la sédimentation a été étudiée *via* l'analyse de la composition lipidique des sédiments récents prélevés en juin 2011 (environ un an après l'ajout des poissons). Les teneurs en protéines et en sucres des sédiments récents ont été déterminées pour étudier l'influence des différents processus sur leur biodégradabilité.

# Chapitre II

# Influence de la structure des réseaux trophiques sur la biodégradabilité des sédiments

# Influence of food-web structure on the biodegradability of lake sediment

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**Abstract**

1. Sediment plays a key role in internal nutrient cycling and eutrophication process in lakes. In spite of its major importance, studies focusing on the efficiency of the biomanipulation techniques for improving the control of primary producers rarely examined the effects of changes in food-web structure on the sediment biochemical composition and biodegradability.
2. In a one-year experiment conducted in large replicated mesocosms, we tested how the absence or presence of a zooplanktivorous fish (roach, *Rutilus rutilus*) affected the elemental composition and the potential biodegradability of recently deposited sediment in eutrophic system. The potential biodegradability of these sediment samples was assessed in laboratory microcosms by measuring the production of $CO_2$ during 44–day incubations.
3. The potential biodegradability of recently deposited sediment from fish treatment was 60% higher than that from fishless treatment. This higher biodegradability was corroborated by a higher annual loss of sediment in fish enclosures (36%) than in fishless ones (16%). Annual losses of carbon, nitrogen and organic phosphorous were higher for sediment from fish enclosures.
4. Carbon and nitrogen contents of sediment were higher for fish treatment. In contrast, the sediment C/N ratio, one of the proxies used to estimate sediment biodegradability, did not differ between treatments. No relationship was observed between elemental composition of sediment and its potential biodegradability. This latter appeared to be more probably dependent on the biochemical composition of the sediment, especially on the content of labile compounds such as proteins, sugars and polyunsaturated fatty acids.
5. The use of sterols as biomarkers revealed an important degradation by microorganisms of one-year-old sediment from both fish and fishless treatments.
6. Our results revealed that fish biomanipulations might favour clear water states not only through a stronger top-down control on phytoplankton but also through a lower biodegradability of sediment reducing internal nutrient cycling.

**Introduction**

Eutrophication remains a serious problem for lakes subjected to high external nutrient loading from their watershed, or for lakes maintaining an important internal nutrient loading despite reduction of allochthonous inputs (Søndergaard *et al.*, 2003). Various physico-chemical and biological techniques have been used to reduce the negative effects of eutrophication, with more or less success over time. Sediment removal, chemical fixation of phosphorus, and hypolimnetic oxygenation have been shown to have a positive short-term effect on water clarity, but biomanipulation remains one of the most used restoration techniques to improve water quality and clarity (Jeppesen & Sammalkorpi, 2002; Søndergaard *et al.*, 2002, 2007). Biomanipulation often consists in removing planktivorous fishes or in adding piscivorous fishes in eutrophic ecosystems (Jeppesen *et al.*, 2007). Based on the trophic cascade theory (Carpenter & Kitchell, 1993), this method involves a top-down control through the decrease of predation on invertebrate community, which in turn enhances grazing pressure not only on phytoplankton but also on periphyton (Jones & Sayer, 2003; Danger *et al.*, 2008) and increases water clarity.

Manipulation of food-web structure can also affect quantitatively sedimentation, either directly through changes in phytoplankton biomass (Reynolds & Wiseman, 1982) or resuspension of settled material by benthivorous fish (Roozen *et al.*, 2007), or indirectly through the top-down control exerted by zooplankton grazing on phytoplankton and fish predation on zooplankton (Laroque *et al.*, 1996). In a recent long-term experiment in mesocosms, Danger *et al.* (2012) confirmed this quantitative effect. By manipulating the occurrence of planktivorous fish, they modified the specific composition of zooplankton communities and the phytoplankton biomass (increase of Daphniidae and decrease of phytoplankton biomass in fishless mesocosms). They observed that sedimentation rates were higher in fish enclosures than in fishless ones. They also showed that food-web structure modified the elemental and biochemical compositions of recently deposited sediment (RDS). Indeed, the stoichiometric characteristics of RDS were correlated to those of either seston or zooplankton, depending on food-web structure. In fish-dominated mesocoms, where zooplankton grazing on phytoplankton was low, sediment N/P ratio was positively correlated to seston N/P ratio, suggesting a major contribution of seston to sedimentation. In contrast, in fishless mesocosms, dominated by a high grazing activity, a negative relationship between N/P ratios of sediment and zooplankton was found, suggesting that sedimentation

was mainly derived from zooplankton egesta. Moreover, Danger *et al.* (2012) found higher contents of proteins and sugars in RDS from fish enclosures than in RDS from fishless ones sampled at the end of the experiment. Allard *et al.* (2011) compared the lipid composition of seston, zooplankton, and RDS in fish and fishless mesocosms in the same experiment. They found higher amounts of phytoplankton biomarkers and lower amounts of zooplankton biomarkers in RDS from fish enclosures than in RDS from fishless ones, which confirmed that the respective contributions of seston and zooplankton to RDS depended on food-web structure. Moreover, Allard *et al.* (2011) showed that the abundance of polyunsaturated fatty acids was higher in RDS from fish enclosures than in RDS from fishless ones. As they found different amounts of labile compounds such as polyunsaturated fatty acids (Allard *et al.*, 2011) or proteins and sugars (Danger *et al.*, 2012) between fish treatments, these researchers suggested that biomanipulations might affect the biodegradability of sediment organic matter (SOM). Gullberg *et al.* (1997) had previously studied the fate of sedimented carbon from a diatom pulse in microcosms with different benthic communities. However, to our knowledge, scientists have rarely, if ever, conducted studies focusing on the effects of pelagic food-web structure on sediment biodegradability.

Sediment can act as a potential source of nutrients for pelagic food webs (Reynolds, 1996; Burger *et al.*, 2007), in particular through the biodegradation of SOM by microbial communities (Gächter *et al.*, 1988; Martinova, 1993; Hargreaves, 1998). This nutrient release could strongly affect ecosystem functioning. Biodegradation of SOM strongly depends on its biochemical composition (Hulthe *et al.*, 1998). A series of proxies, based on the biochemical (proteins, sugars, and fatty acids) and elemental compositions (C/N and C/P ratios, TOC) of sediment, have been used to estimate the biodegradability and the degradation dynamics of sediments (Dauwe & Middelburg, 1998; Schubert *et al.*, 2005; Meckler *et al.*, 2004; Niggemann & Schubert, 2006a, b; Bechtel & Schubert, 2009). Besides, respirometric approaches have proved to be useful tools to study sediment biodegradation under controlled conditions (Goedkoop *et al.*, 1997; Pedersen *et al.*, 1999; Guérin *et al.*, 2008). Surprisingly, studies on SOM biodegradability have rarely associated analyses of proxies based on SOM biochemical composition and respirometric experiments. Moreover, for a similar potential degradability of OM, environmental conditions influence its actual degradation. Changes in SOM decay via microbial activity have been attributed to changes in redox conditions in sediment or at the sediment/water interface (Søndergaard *et al.*, 2003; Wakeham & Canuel, 2006). These changes have also involved sediment reworking through physical resuspension

(Sanford, 1992) or activity of benthic macroinvertebrates (Hansen et al., 1998; Mermillod-Blondin *et al.*; 2003, Nogaro *et al.*, 2008). Thus, field analyses are also critically needed for understanding SOM evolution within aquatic ecosystems.

In this study, we tested the hypothesis that the biodegradability of RDS from the experiment of Danger *et al.* (2008, 2012) was higher in fish mesocosms than in fishless ones using two different approaches. First, we conducted *ex situ* respirometric measurements of the potential biodegradability of RDS samples originating from the two treatments, and we analysed the link between this potential biodegradability and RDS elemental composition. Second, we estimated the annual loss of sediment (ALS) in fish and fishless enclosures. This measurement of *in situ* biodegradation of sediment was compared to sterol biomarkers for biodegradation of one-year sediment (OYS). To our knowledge, this experimental study is the first one focusing on food-web biomanipulation effects on sediment biodegradability.

## Methods

### *Study site and experimental design*

The study took place in Lake Créteil (48°46’37’’N, 2°26’47’’E), a small (42-ha), shallow (mean depth 4 m) sand-pit lake, 15 km southeast of Paris (France). At the end of June 2005, eight enclosures of ca. 40 $m^3$ sealed at the bottom were suspended inside a rectangular floating pontoon, with the upper end of each enclosure suspended 25 cm above the lake surface. To minimize seston heterogeneity, mesocosms were randomly and steeply filled with lake water pumped between 1 m and 2 m depth. Lake water was filtered through a 1-mm mesh to avoid contamination by large particles. Each month, 4 L of unfiltered water from the lake were added to each enclosure to allow colonization by any species absent at the beginning of the experiment but occurring in the lake throughout the seasons.

Eutrophic conditions were maintained by weekly enriching enclosures with inorganic fertilizers ($NaNO_3$ and $KH_2PO_4$) corresponding to a N/P molar ratio of 20 : 1 and a phosphorus load of 3 µg P $L^{-1}$ $day^{-1}$.

To obtain two different food-web structures, we applied two contrasting treatments: a treatment with added zooplanktivorous fish (roach, *Rutilus rutilus* L., Cyprinidae; fish treatment; F+), characterised by a predominance of small planktonic herbivores, and a fishless treatment (F-) dominated by large planktonic herbivores. Each treatment was replicated in

four separate enclosures. The initial mean standard length (± SE) of fishes was 42.6 ± 2.7 mm and their mean fresh weight was 0.66 ± 0.15 g. An initial density of one fish $m^{-3}$ was chosen, i.e. 40 fish per enclosure. At the beginning of the experiment, there was no sediment at the bottom of enclosures. Thus, the newly formed sediments within the enclosures were mainly autochthonous and originated from the inputs of the pelagic communities. For further details see Danger *et al.* (2008).

*Sampling and elemental analyses*

Autochthonous sediment was collected during one year (from July 2005 to August 2006) in three sediment traps deployed at the bottom of each enclosure either during 8-15 days (recently deposited sediment, RDS) or during 1 year (one-year sediment, OYS). Traps consisted in classical PVC tubes (5 cm diameter, 30 cm length), suspended at 3.5 m depth. Sediment exportation through sediment resuspension by internal current or fish activity was improbable. Indeed, the height/diameter ratio (H/D ratio > 5) of sediment traps was chosen to minimize physical losses (Bloesch & Burns, 1980). Thus, biodegradation should be the major process explaining the loss of sediment over time. Within each enclosure, the sediments collected from the three tubes were pooled. In order to separate most of the living zooplankton from sediment, samples were placed for 36 h at 4°C in glass funnels closed with tips at the bottom. Living zooplankton was located in the water or just above the surface of sediment, which settled in the narrow part of the pipe. Zooplankton-free sediment was then collected by opening tips at the bottom, and dried in an oven at 65°C for 24 h. Total carbon (Tot-C), organic carbon (OC) and nitrogen (Tot-N) content of short-term sediment samples were determining using a CHN elemental analyser (NA 1500 Series 2; Fisons, Manchester, UK). OC content was determined as total carbon after acidification to remove inorganic carbon (Hedges & Stern, 1984). Organic P (OP) content was determined according to Ormaza-Gonzales & Statham (1996) after oxidation by sodium persulphate.

*Incubations of recently deposited sediment*

The potential biodegradability of RDS was estimated by measuring the $CO_2$ production across the sediment/water interface using laboratory incubations. The method, adapted from Goedkoop *et al.* (1997), consisted in incubations of sediment samples in closed microcosms. Sediments from four sampling dates (November 2005, June, July and August

2006) originating from the experiment of Danger *et al.* (2012) were used for incubations. Incubations were conducted in standardized conditions similar for each microcosm. Oven-dried sediment samples (19-60 mg) were placed into 100-mL glass vessels filled with 80 mL of filtered (GF/F glass fiber filters, nominal cut-off: 0.7 µm) water from natural freshwater (Lake Créteil, France) as bacterial inoculum and culture medium. Dissolved organic carbon (DOC) concentration of lake water was 1.78 mg OC $L^{-1}$ (total organic carbon analyser, TOC-5000A, Shimadzu, Kyoto, Japan). Weiss & Simon (1999) showed that the labile fraction of DOC consumed by bacteria in Lake Constance never exceeded 36% of the total DOC. Applying their results to our microcosms filled with water of Lake Créteil, the amount of potentially biodegradable organic matter (OM) supplied by lake water should not exceed 57 µg OC per microcosm. In contrast, the lowest amount of OC supplied by sediment was 465 µg OC per microcosm. Thus, the contribution of DOC from lake water was assumed to be minor in measured respiration rates.

Vessels containing only lake water were used as control. Microcosms were sealed gas tight with aluminium cap and kept at 20°C in the dark to avoid phytoplankton development. Microcosms were continuously aerated with $CO_2$-free air using an aquarium pump. $CO_2$ from ingoing air was trapped in a 10-M NaOH containing flask, and air was washed in two subsequent deionised water flasks. This aeration ensured the establishment of a $CO_2$ gradient between the sediment and the overlying water, resulting in the enhancement of the efflux of $CO_2$ from the sediment (Goedkoop *et al.*, 1997). Furthermore, aeration could enhance heterotrophic degradation of sediment by aerobic microorganisms. The headspace (20 mL) of each microcosm was connected to NaOH traps (100-mL vials filled with 50 mL of 5 mM NaOH) for $CO_2$ quantification. NaOH traps were sampled and changed at days 1, 2, 4, 8, 22 and 44 of the incubations. After 44 days of incubation, $CO_2$ efflux reached a plateau, therefore incubations were stopped. Trapped $CO_2$ (present as dissolved inorganic carbon) was subsequently measured using a total organic carbon analyser (TOC-5000A, Shimadzu, Kyoto, Japan). Carbon respired from microcosms corresponding to each sampling date was corrected from that of dissolved inorganic carbon measured in the blank. Cumulated $CO_2$ production was determined by addition of respired carbon measured at each sampling date (from day 1 to day 44). Mineralization rates were expressed as mg C g $DW^{-1}$ $d^{-1}$.

*Calculation of annual losses of sediment and nutrients*

The hypothesis of a cascading effect of top consumers on sediment biodegradability was extended from a microcosm scale to a mesocosm scale. The quantity of sediment cumulated during one year, estimated as the sum of the quantities of RDS sampled in sedimentation traps (CRDS), was compared with the stock of remaining sediment in traps deployed in the mesocosms throughout the experiment (one year sediment, OYS). The cumulated mass of recently deposited sediment (CRDS) represented the total quantity of matter sedimented (expressed as g DW $m^{-2}$) over one year. It was estimated from the measured short-term sedimentation rates (expressed as g DW $m^{-2}$ $d^{-1}$). As samplings of RDS were not continuous over time, the sedimentation rate measured at the $i^{th}$ sampling date, $R_i$, was assumed constant over the time interval $[D_{i+1} - D_{i-1}]/2$, ($D_{i-1}$ and $D_{i+1}$ being the previous and the next dates of the $i$th sampling date, respectively). CRDS was thus calculated as the sum of $R_i \times [D_{i+1} - D_{i-1}]/2$ from the 15th July 2005 to the 8th August 2006, corresponding to the exposure time of OYS traps. Annual loss of sediment (ALS) was calculated for each enclosure as the difference between CRDS and OYS (expressed as g DW $m^{-2}$). By subtracting OYS (which was exposed to environmental conditions during one year) from CRDS, we obtained a conservative estimate of sediment losses in the enclosures. Likewise, annual losses of Tot-C (ALC), Tot-N (ALN) and OP (ALOP) were calculated as the difference between CRDS and OYS normalized to their respective elemental content (expressed as g C $m^{-2}$, g N $m^{-2}$ and g P $m^{-2}$, respectively).

*Lipid analysis*

Sterol biomarker analysis was performed on OYS to provide information on the degree of alteration and the origin of the sedimented organic matter. Lipids containing sterols were isolated and analyzed as previously described (Allard et al., 2011). Briefly, sediment samples were extracted at reflux with a dichloromethane/methanol (2/1, v/v) mixture. The lipid fraction was derivatized with a mixture of anhydrous pyridine/N,O Bis(trimethilsilyl)trifluoroacetamide to convert carboxyl and hydroxyl groups to trimethylsilyl (TMS) ester and trimethylsilyl ether groups, respectively. Lipid components (as TMS esters and TMS ethers) were analysed by gas chromatography–mass spectrometry.

*Statistical analyses*

Statistical analyses were performed using R software (www.r-project.org). One–way ANOVAS with time as repeated measure were used to test the effect of food-web structure (F+ *vs* F- treatments) and the evolution of this effect on sediment elemental composition and potential biodegradability. Due to constraints of sediment quantity to perform respirometry experiments, we only analysed the effect of fish occurrence on sediment potential biodegradability with samples obtained during the warm season. Thus, although we took into account an eventual time effect in our statistical analyses, we did not interpret this effect. One-way ANOVAS were performed to test the effect of food-web structure on the ALS and on the lipid composition of OYS. Simple linear regressions were used to study the relationships between sediment elemental composition and respiration measurements. Data were log-transformed when necessary to normalize distributions and homogenize variances. A significant threshold of $p < 0.05$ was chosen for all analyses.

**Results**

*Potential biodegradability and elemental composition of recently deposited sediment*

The potential biodegradability of RDS (measured as $CO_2$ production) from fish treatment was on average 60% higher (0.89 ± 0.12 mg C g DW $^{-1}$ $d^{-1}$) than that from fishless treatment (0.56 ± 0.08 mg C g $DW^{-1}$ $d^{-1}$; $F_{1,16} = 5.16$; $P = 0.037$, $n = 32$; Fig.1). Time and interaction between fish treatment and time had no significant effect on potential biodegradability of RDS ($F_{3,16} = 0.53$, $P = 0.66$ and $F_{3,16} = 1.89$, $P = 0.17$, respectively). Elemental composition of RDS from fish and fishless treatment corresponding to the four sampling dates used for the incubations was reported in Table 1. On average, total carbon (Tot-C) and total nitrogen (Tot-N) contents were higher in RDS from fish enclosures than in RDS from fishless enclosures ($F_{1,16} = 34.34$, $P < 0.0001$, $n = 32$, for Tot-C; $F_{1,16} = 14.17$, $P < 0.005$; $n = 32$; for Tot-N). In contrast, no significant difference was observed between sediments from fish and fishless treatment for OC ($F_{1,16} = 4.23$, $P = 0.059$, $n = 32$) and OP ($F_{1,16} = 2.99$, $P = 0.30$, $n = 32$) contents (Table 1). Time had a significant effect on Tot-C, Tot-N, OC and OP contents ($F_{3,16} = 20.90$, $P < 0.0001$; $F_{3,16} = 16.24$, $P < 0.0001$; $F_{3,16} = 7.33$, $P = 0.0034$ and $F_{3,16} = 17.91$, $P < 0.0001$, respectively, $n = 32$). Although significant,

temporal responses were idiosyncratic at this scale of analysis. No significant effect was observed for the interaction between fish treatment and time on Tot-C, Tot-N, OC and OP contents ($F_{3,16}$ = 0.83, $P$ = 0.49; $F_{3,16}$ = 3.15, $P$ = 0.054; $F_{3,16}$ = 1.46, $P$ = 0.27 and $F_{3,16}$ = 1.44, $P$ = 0.27, respectively). A linear relationship between Tot-C and Tot-N contents of RDS was observed but did not differ between treatments ($R^2$ = 0.89, $P$ < 0.0001 for N effect; $P$ = 0.25 for N × fish treatment interaction; $n$ = 32; Fig. 2). In addition, we did not observe any significant relationships between sediment Tot-C, Tot-N, OC and OP contents and RDS potential biodegradability (Fig. 3).

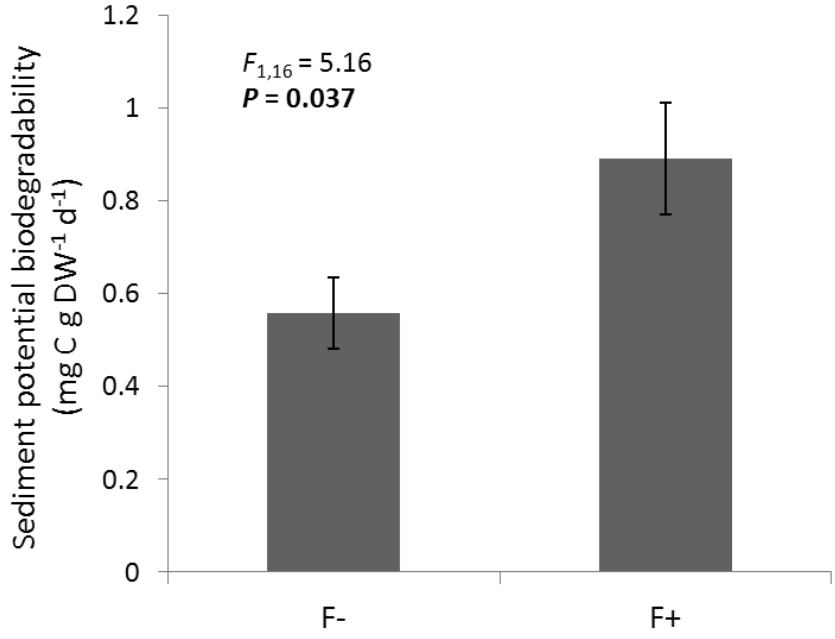


**Figure 1:** Potential biodegradability of recently deposited sediment (mean ± SD; n = 16: 4 replicates × 4 dates per treatment).

| Treatment | Tot-C | Tot-N | OC | OP |
|---|---|---|---|---|
| F- | **21.15 ± 1.03** | **2.14 ± 0.14** | 12.05 ± 1.91 | 0.76 ± 0.10 |
| F+ | **27.20 ± 1.56** | **2.80 ± 0.22** | 17.69 ± 2.47 | 0.78 ± 0.07 |

**Table 1:** Elemental composition (% of DW; mean ± SE; n = 16: 4 replicates × 4 dates per treatments) of recently deposited sediment (RDS) for fishless (F-) and fish (F+) treatments. Mean of each treatment comprises values of the four sampling dates used for incubations**.** Compositions that differed significantly between F- and F+ treatments are in *bold.*

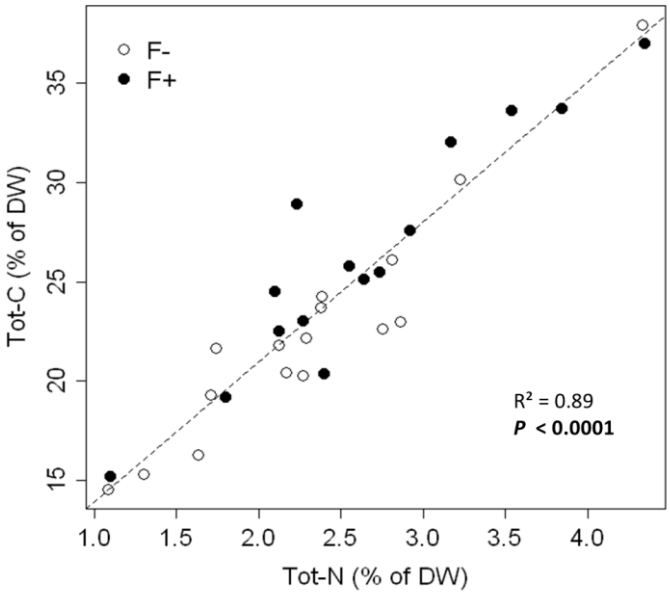


**Figure 2:** Relationship between total carbon and total nitrogen contents (% of DW) of recently deposited sediment (n = 32: 4 replicates × 4 dates × 2 treatments). As no significant interaction of Tot-N content and fish treatment on Tot-C content was observed, the fitted regression line comprises values of both treatments.

The annual loss of sediment (ALS) was estimated as the difference between the CRDS over one year and the one-year-old sediment (OYS) (see materials and methods). CRDS was about 3-fold higher for fish treatment than for fishless treatment (664.9 ± 62.1 and 240.9 ± 15.4 g DW $m^{-2}$ respectively, $F_{1,16}$ = 70.38, $P$ < 0.001; $n$ = 8; Fig. 4a). Mass of OYS was ca. 2-fold higher for fish treatment than for fishless treatment (433.6 ± 66.0 and 199.7 ± 13.7 g DW $m^{-2}$, $F_{1,16}$ = 16.71, $P$ < 0.01; $n$ = 8; Fig. 4a). The ALS was about 6-fold higher for fish treatment than for fishless treatment (231.4 ± 21.8 and 41.2 ± 19.6 g DW $m^{-2}$, $F_{1,16}$ = 42.06, $P$ < 0.001; $n$ = 8; Fig. 4a), representing a relative loss of CRDS over one year of 36 % and 16 % respectively. Relative to its elemental content (Tot-C, Tot-N and OP), OYS represented an annual stock of nutrients still available in sediment after one year of experiment. The Tot-C content of OYS for fish treatment was about 3-fold higher than for fishless treatment (113.5 ± 23.4 and 41.7 ± 3.2 g C $m^{-2}$, $F_{1,16}$ = 12.44, $P$ = 0.012; $n$ = 8; Fig. 4b). The Tot-N and OP contents of OYS did not differ significantly between fish and fishless treatments (10.5 ± 2.6 and 4.4 ± 0.5 g N $m^{-2}$, respectively, $F_{1,16}$ = 5.16, $P$ = 0.064, $n$ = 8, Fig. 4c for Tot-N; 2.3 ± 0.5 and 1.4 ± 0.2 g P $m^{-2}$, respectively, $F_{1,16}$ = 2.89, $P$ = 0.14, $n$ = 8, Fig. 4d for OP). ALC was about 10-fold higher for fish treatment than in fishless treatment (62.8 ± 7.0 and 6.2 ± 4.3 g C

$m^{-2}$, $F_{1,16}$ = 47.17, $P$ < 0.0005; $n$ = 8; Fig. 4b). ALN was about 15-fold higher for fish treatment than in fishless treatment (7.6 ± 0.9 and 0.5 ± 0.4 g N $m^{-2}$, $F_{1,16}$ = 50.72, $P$ < 0.0005; $n$ = 8; Fig. 4c). ALOP was about 8-fold higher for fish treatment than in fishless treatment (2.2 ± 0.3 and 0.3 ± 0.3 g P $m^{-2}$, $F_{1,16}$ = 18.74, $P$ < 0.005; $n$ = 8; Fig. 4d).

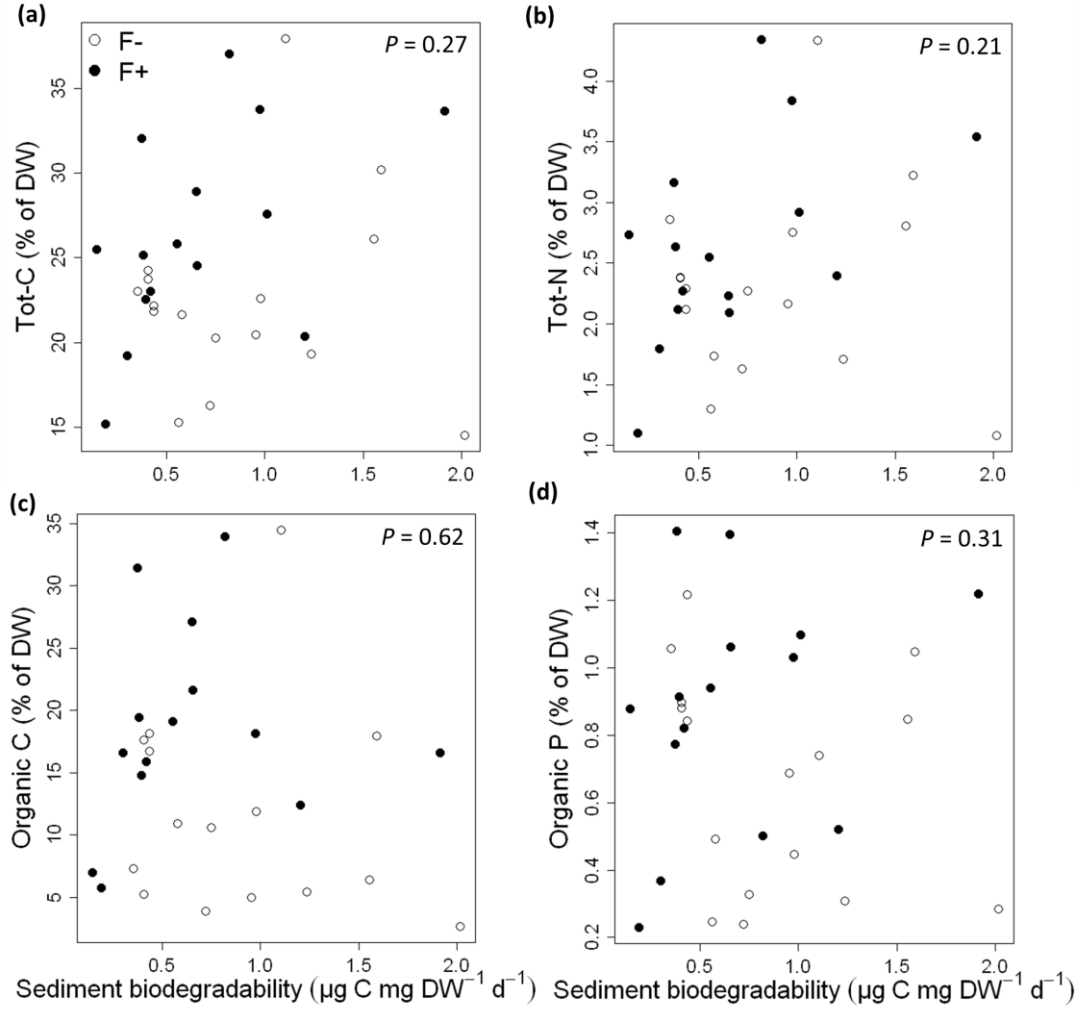


**Figure 3:** Relationship between potential biodegradability and total carbon (a), total nitrogen (b), organic carbon (c) and organic phosphorous (d) contents for recently deposited sediment from fishless (open circles) and fish (full circles) treatments (n = 32: 4 replicates × 4 dates × 2 treatments).

*Annual loss of sediment and nutrients*

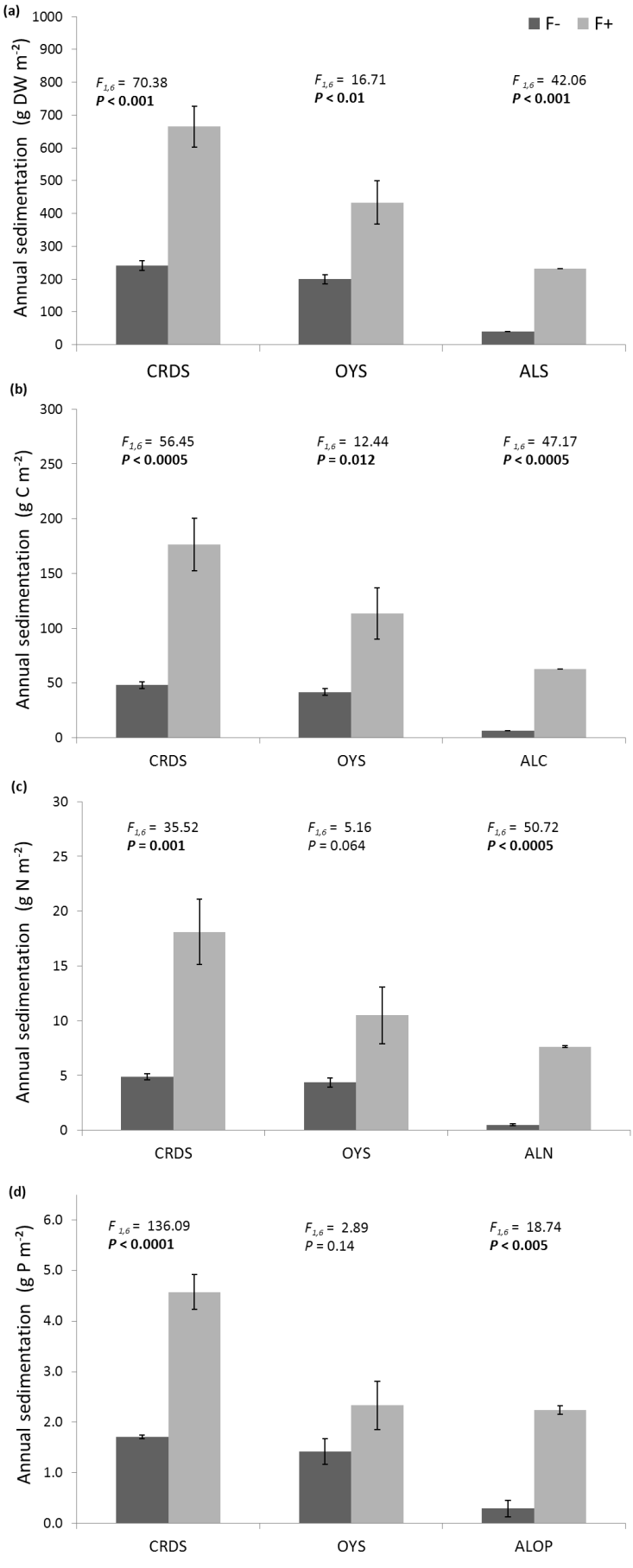


**Figure 4:** Comparison between fish treatments of cumulated mass of recently deposited sediment (CRDS), measured long-term (OYS) mass and annual loss (AL) of sediments (a), total carbon (b), total nitrogen (c) and organic phosphorous (d) after one year of experiment (mean ± SD; n= 4: 4 replicates per treatment). Significant P values are in bold.

*Sterol biomarkers in one-year sediment*

The sterol composition of OYS strongly differed between treatments (Table 2). The sterol distribution of OYS from fishless enclosures was dominated by $\Delta^5$-sterols, cholesterol being the major component. The proportion of $\Delta^7$-sterols was < 3% of total sterols. In contrast, $\Delta^7$-sterols largely dominated the sterol distribution of OYS from fish enclosures. Differences in the relative abundance of $\Delta^5$- and $\Delta^7$-sterols in OYS between treatments were highly significant ($F_{1,16}$ = 191.21, $P < 0.0001$ for $\Delta^5$-sterols; $F_{1,16}$ = 302.79, $P < 0.0001$ for $\Delta^7$-sterols).

Stanols, the saturated analogues of unsaturated sterols, were present in high abundance in OYS from fishless treatment (ca. 30% of total sterols). The relative abundance of stanols in OYS was significantly higher for fishless treatment than for fish treatment (ca. 9% of total sterols, $F_{1,16}$ = 68.62, $P < 0.0005$). The stanols/unsaturated sterols ratio observed in OYS was significantly higher for fishless treatment than for fish treatment ($F_{1,16}$ = 45.89, $P$ = 0.001). In contrast, the stanols/$\Sigma\Delta^5$-sterols ratio did not significantly differ between treatments ($F_{1,16}$ = 1.65, $P$ = 0.001).

**Table 2:** Contribution of sterols (% of total sterols[a]) to recently deposited (RDS) and one-year-old (OYS) sediments from fishless (F-) and fish (F+) treatments (mean ± SE, n = 4). Compositions that differed significantly between treatments are in *bold*.

| | RDS[b] | | OYS | |
|---|---|---|---|---|
| | F- | F+ | F- | F+ |
| Stanols | tr | tr | **30.5 ± 1.6** | **9.0 ± 1.8** |
| Unsaturated Sterols | 100 ± 0 | 100 ± 0 | **65.7 ± 2.5** | **90.5 ± 2.2** |
| Cholesterol | **55.6 ± 11.2** | **4.8 ± 0.4** | **27.3 ± 3.2** | **5.8 ± 0.5** |
| Stanols/Unsaturated Sterols | | | **0.47 ± 0.04** | **0.10 ± 0.02** |
| Stanols/$\Delta^5$-sterols | | | 0.52 ± 0.04 | 0.66 ± 0.11 |
| $\Delta^5$-sterols | **99.2 ± 0.6** | **16.0 ± 1.0** | **59.7 ± 2.5** | **13.5 ± 1.7** |
| $\Delta^7$-sterols | **0.8 ± 0.7** | **76.2 ± 2.2** | **2.6 ± 0.9** | **74.2 ± 4.1** |

[a] Total sterols = unsaturated sterols + stanols.

[b] Data from Allard et al. (2011).

## Discussion

*Relevance of the annual loss of sediment as an estimation of sediment biodegradability*

Considering the short exposure time of RDS in traps to the environmental conditions (from 1 to 2 weeks), we assumed that sediment loss due to degradation by microorganisms during trap deployment could be considered as negligible. This hypothesis was supported by the lipid biomarker analysis performed by Allard *et al.* (2011) on RDS sampled at the end of the experiment. Indeed, they showed that (i) stanols, usually considered as evidence for *in situ* microbial reduction of unsaturated sterols (Gaskell & Eglinton, 1975), were absent in RDS for both treatments and (ii) polyunsaturated fatty acids (PUFAs), which are more sensitive to bacterial degradation than most types of biogenic lipids (Cranwell, 1981), were present in noticeable abundances in the RDS from both treatments. Therefore, it can be assumed that CRDS was a conservative estimate of gross sedimentation during one year. Thus, ALS was used in the present study as a measure of sediment biodegradability.

*Effects of sediment origin on its biodegradability*

The potential biodegradabilities of RDS measured in this study were of the same order of magnitude as those found with lacustrine and artificial sediments under similar experimental conditions by Goedkoop *et al.* (1997, 2005). Both the higher potential biodegradability of RDS and the ALS from fish enclosures than those from fishless enclosures found in the present study support the hypothesis that food-web structure influences the biodegradability of sediment. Indeed, in the same experiment, Danger *et al.* (2012) showed that fish predation on zooplankton indirectly increased phytoplankton biomass through the trophic cascade. Their results were supported by Allard *et al.* (2011) who found a higher contribution of phytoplankton biomarkers (i.e. chlorophyll-derived compounds, long-chain alkanediols and $\Delta^7$-sterols) to the lipid composition of seston from fish enclosures. These authors also showed that the increase in phytoplankton biomass due to fish addition led to a higher contribution of phytoplankton biomarkers to RDS from fish enclosures compared to the contribution of zooplankton biomarkers (mainly cholesterol). In the present study, we showed that the increase in phytoplankton biomass by fish predation on zooplankton led to an increase in the potential biodegradability of RDS and in the ALS. These results are in

agreement with Goedkoop *et al.* (1997) who showed in a similar incubation experiment that addition of diatoms enhanced benthic bacterial activity.

However, it is worth noting that the relative abundances of stanols, biomarkers for microbial biodegradation of sediment (Eyssen *et al.*, 1973), were higher in OYS from fishless treatment than in those from fish treatment. This discrepancy could be explained by the difference in the nature of sterols present in the sediments. Indeed, $\Delta^7$-sterols that dominated the sterol distribution of OYS from fish treatments do not appear to be involved in the process of sterol biodegradation (eg. Eyssen *et al.*, 1973; Robinson *et al.*, 1984). Consequently, $\Delta^7$-sterols could be resistant to biodegradation in gut of animals and in sediments. This is strongly suggested by the stanols/unsaturated sterols ratio, which provides information about sterol degradation state. Indeed, this ratio was lower for fish than for fishless treatment. In contrast, the stanols/$\Delta^5$-sterols ratio did not depend on treatment, suggesting that the lower contribution of stanols to sterol composition of sediment from fish treatment compared to fishless one was likely due to its higher $\Delta^7$-sterols content.

Finally, the similarity of the predominance of $\Delta^7$-sterols between RDS (Allard *et al.*, 2011) and OYS (the present study) of fish treatment suggests that the indirect effect of fish addition on the biomass of phytoplankton and on the biochemical characteristics of settling organic matter were still considerable after one year of sediment accumulation. Indeed, Allard *et al*. (2011) also observed a predominance of $\Delta^7$-sterols over $\Delta^5$-sterols in the sterol composition of RDS from fish enclosures. As $\Delta^7$-sterols are well-known biomarkers of Chlorophyceae (Cranwell, 1982; Volkman, 1986, Cranwell *et al.*, 1990), these authors used them as an indicator of the high contribution of phytoplankton to RDS in fish enclosures. Undoubtedly, cascading effects from the top predators (here planktivorous fish) of aquatic communities have profound and long-lasting consequences on the biochemical composition of sediments, and thus on their biodegradability, through their impact on phytoplankton biomass.

*Relationship between the elemental and biochemical composition of recently deposited sediment and its biodegradability*

The potential biodegradability of RDS was not driven by its elemental composition. Indeed, fish treatment had no effect on OC and OP contents of RDS and on the relationship between Tot-C and Tot-N of RDS while the potential biodegradability of RDS from fish

enclosures was higher than that from fishless ones. These results indicate that the C/N ratio was not a valuable proxy for RDS biodegradability in our experiment, and support the previous suggestions that sediment C/N ratio alone does not allow to assess sediment biodegradability and quality (eg. Meckler *et al.*, 2004). Our results are opposite to the findings of Sander and Kalff (1993), who found a positive linear correlation between the bacterial production in freshwater sediments and their organic matter content. Two factors could explain this discrepancy. First, the positive relationship observed by Sander and Kalff (1993) had been established over a much larger range of sediment OC content. Second, RDS from fish treatment contained higher amounts of labile compounds (i.e. proteins, sugars and PUFAs) than RDS from fishless treatment (Allard *et al.*, 2011; Danger *et al.*, 2012). It has been shown that bacterioplankton growth is essentially supplied by dissolved carbohydrates and by amino acids (Bunte & Simon, 1999; Weiss & Simon, 1999; Rosenstock & Simon, 2001). This strongly suggests that the higher potential biodegradability of RDS from fish treatment derived from its high content of proteins and sugars.

*Potential consequences for eutrophic ecosystems*

The nutrient release from the labile organic pool of sediment to the pelagic compartments is considered as one of the major factors involved in the eutrophication of freshwater ecosystems (Søndergaard *et al.*, 2003). Our results clearly indicate that sediment biodegradability is higher when phytoplankton is poorly controlled by grazers than when zooplankton efficiently controls phytoplankton. Thus, the mineralization of settled organic matter in aquatic ecosystems depends not only on the redox conditions, benthic activity, physical resuspension and/or sorption on mineral matrix as shown by others (Wakeham & Canuel, 2006), but also on food-web structure.

The higher potential remineralization of sediment in alga-dominated systems could lead to an enhanced release of nutrients from sediment to the water column, increasing the internal cycling of organic matter and nutrients. This phenomenon was clearly shown by the higher annual losses of Tot-C, Tot-N and OP estimated in fish treatment. Besides, our results are in agreement with those of Liu *et al.* (2009) who showed that the addition of fresh organic matter in microcosms enhanced phosphorus release from freshwater sediments to overlying water.

On the other hand, the long-term efficiency of biomanipulations for the restoration of turbid, eutrophic ecosystems is thought to be potentially limited by internal nutrient cycling, which might favour the release of these nutrients from sediment over time (Søndergaard *et al.*, 2007). Maintaining during a sufficiently long period a top-down control of phytoplankton biomass through the biomanipulation of fish communities should not only induce a more efficient grazing of phytoplankton (Danger et *al.*, 2009) and periphyton (Danger *et al.*, 2008) by invertebrate herbivores, but also reduce the quantity (Danger *et al.*, 2012) and biodegradability (this study) of sedimented organic matter and the stock of carbon in sediments (stocks of Tot-N and OP followed a similar trend but were not significant), ultimately decreasing internal nutrient cycling. We suggest that this latter mechanism is another process, neglected yet, that might lead to a faster-than expected recovery of clear water state in biomanipulated ecosystems (Jeppesen et al., 2005).

In conclusion, in this experimental study, the modification of food-web structure clearly affected the C and N contents and the biodegradability of RDS. Besides, nutrient cycles (release and storage) in sediment and sediment turnover on the long term (one year) were also affected by biomanipulation. The biodegradability of sediment did not depend upon elemental ratios of organic matter but was more probably linked to its content of labile components, such as proteins, sugars and PUFAs. The distribution of sterols in RDS and OYS afforded valuable information on sediment biodegradation. Finally, our results stress the need for further studies combining ecological and biochemical approaches for a better understanding of the functioning of aquatic ecosystems.

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# Chapitre III

# Effet ascendant et influence de la biodégradabilité des sédiments sur les compartiments pélagiques et la sédimentation

# Bottom-up effects of lake bottom sediment on pelagic compartments: a mesocosm study

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**Abstract**

Sediment plays a key role in organic matter and internal nutrient cycling in lakes. The phosphorus content of sediment is notably responsible for the decrease of the long-term efficiency of biomanipulation in eutrophic ecosystems. The role of sediment as a source of organic matter and its potential bottom-up effects on aquatic food web has been rarely studied. Particularly, the influence of the biochemical composition of sediment organic matter on pelagic compartments remained largely unknown. In a five-months experiment conducted in large replicated mesocosms, we studied how the absence or the presence of different bottom sediments affected the biomass, the elemental and the lipid composition of seston and zooplankton. The influence of sediment treatments on sedimentation rates, elemental and biochemical compositions and potential biodegradability of short-term sediment was also tested. The first sediment ($S_1$) used for this study had very low contents of organic carbon, nitrogen, proteins, sugars, mono- and polyunsaturated fatty acids compared to the second sediment ($S_2$) used, suggesting a higher potential biodegradability of $S_2$. Probably due to its poor content in labile compounds, the presence of $S_1$ at the bottom of mesocosms did not induce changes in the biomass of seston and zooplankton and few changes in the stoichiometry of these compartments compared to the mesocosms without sediment ($S_0$). The $S_2$ treatment induced an increase in both seston and zooplankton biomass. Seston from these mesocosms had a higher N content and a lower C/N ratio than those from $S_0$ and $S_1$ treatments. However, no sediment treatments affected the lipid composition of seston and zooplankton. Moreover, neither $S_1$ nor $S_2$ induced change in sedimentation rates, elemental and lipid composition and potential biodegradability of short-term sediment. This mesocosm experiment demonstrated that differences in the quality of lake bottom sediment can lead to contrasted modifications of pelagic communities. But, these bottom-up effects of sediment occurred only with a sediment rarely found in nature. Thus, our results might explain the efficiency of biomanipulations for improving water quality of eutrophic lakes despite potential nutrient release from sediment. Finally, our results tend to confirm the ecological significance of mesocosms to study processes occurring at a larger scale.

**Introduction**

Since the last decades, the role of sediment in the biological and biogeochemical processes in lacustrine ecosystems has received an increasing attention. Lipid composition of sedimented organic matter (SOM) has been widely used to assess, via specific biomarkers, the sources of ancient and recent sediments. The majority of these studies have focused on the role that SOM plays as a paleolimnological proxy (Meyers & Ishiwatari, 1993; Meyers, 2003; Castaneda & Schouten, 2011). Numerous authors have also studied the relationship between recent SOM and organic matter (OM) originating from the pelagic communities or from terrestrial inputs (Cranwell, 1982; Cardoso & Eglinton, 1983; Canuel & Martens, 1993; Bechtel, 2009a, b). Lipids biomarkers, mainly fatty acids (FAs), have been often used to study the transfers of energy and nutrients between primary producers, herbivores and other consumers within aquatic food webs (Prahl et al., 1984; Müller-Navarra et al., 2000; Masclaux et al., 2009; Gladyshev et al., 2010) and to characterise inter-specific differences (Volkman et al., 1988; Cranwell et al., 1990). Another aim of the sediment geochemistry is the study of the carbon balance in lacustrine ecosystems and of its contribution to the global carbon cycle (Alin & Johnson, 2007; Cole et al., 2007). The net heterotrophy of lakes ($CO_2$ source for atmosphere) is the most commonly observed carbon fate in concerned studies (del Giorgio et al., 1997; Cole et al., 2000). Nevertheless, it has been shown that this balance can be influenced by food-web structure and nutrient concentrations, which modify sedimentation (Flanagan, 2006). Several recent studies in mesocosms, in both marine (Canuel et al., 2007; Spivak et al., 2007) and freshwater (Allard et al., 2011; Danger et al., 2012) ecosystems, have shown that the biochemical composition (eg. organic carbon, protein, sugar and lipid contents) of recently deposited sediments (RDS) strongly depends on food-web structure.

Once sedimented, OM is subject to transformation by benthic macroinvertebrates (Mermillod-Blondin et al., 2003; Nogaro et al., 2008) and degradation by microorganisms (Cranwell, 1984; Gächter et al., 1988, Martinova et al., 1993; Hargreaves et al., 1998). This degradation depends on several parameters such as dissolved oxygen concentration at the sediment-water interface, bounding on mineral matrixes (Wakeham & Canuel, 2006), physical resuspension (Sanford, 2008), or OM composition (Hulthe et al., 1998). The latter has been largely used to provide information on the degradation state and the biodegradability of the sediment thanks to the large range of lability covered by the diverse components of OM (Cranwell, 1981; Dauwe & Middelburg, 1998; Meckler et al., 2004; Arzayus & Canuel, 2005;

Schubert et al., 2005). Recently, Harrault et al. (Chapter 2) showed in a study coupling mesocosm and microcosm approaches that the top-down control exerted by herbivores and/or top predators on primary producers has a strong effect on the biodegradability of recently sedimented OM as well. These authors showed that the short-term sediment in the phytoplankton-dominated systems was potentially more biodegradable than the short-term sediment in the zooplankton-dominated ones. They suggested that these results were probably due to the different biochemical compositions of the SOM. In strong accordance with this hypothesis, Allard et al. (2011) and Danger et al. (2012) measured higher contents of proteins, sugars and polyunsaturated fatty acids (PUFAs) of the SOM from the phytoplankton-dominated systems compared to those from the zooplankton-dominated ones in this experiment.

During its degradation, the sediment can release dissolved organic matter (DOM) and nutrients to the water column (Reynolds, 1996; Klump et al., 2009) that will support both bacterial and primary productions (del Giorgio & Cole, 1998). As phytoplankton and bacteria are the basal resources for aquatic food webs, release of OM and nutrients from sediment might strongly impact food-web communities.

While the predators from higher trophic levels exert a top-down control on primary producers through the well-known trophic cascade (Carpenter & Kitchell, 1993), the abiotic environmental parameters can exert as well a bottom-up control on these organisms though the availability of resources for the food web. In aquatic environments, the bottom-up forcing on primary producers has been mainly studied in relation to nutrient concentration (Spivak et al., 2011; or see Elser et al., 2007, for a meta-analysis). In natural lakes, Kritzberg et al. (2006) and Berdjeb et al. (2011), showed, respectively, that the temporal dynamics of bacterioplankton communities were strongly dependent on the nutrient concentrations and DOM origin and amount. In eutrophic ecosystems, the long-term efficiency of biomanipulations is probably limited by the nutrient load of sediment. Indeed, the nutrients accumulated in the sediment during periods of highly external discharge can be released from the sediment to the water column even after the reduction of allochthonous inputs (Sondergaard et al., 2007). This differential release leads to an increase of the biomass of autotrophic organisms that are less limited by nutrients (Sondergaard et al., 2003). In a mesocosm study conducted in a marine environment, Spivak et al. (2007) showed that the light availability also increased the biomass of eelgrass and algae, and the contribution to SOM of the FAs biomarkers derived from these sources. Besides, it has been shown that the

bottom-up effect exerted by resource availability (i) modify the stoichiometry of primary producers (C/N/P ratios, Dickman et al., 2006), and (ii) affect several processes such as herbivore growth, nutrient cycling and carbon sequestration (Urabe et al., 2002; Cebrian & Lartigue, 2004; Hessen et al., 2004).

In this paper, we report results of a lake mesocosm study examining how origin and potential biodegradability of sediment influence the composition of pelagic compartments and recently deposited matter. Two sediments, differing in their origin, carbon content and biochemical composition, were added at the bottom of mesocosms containing phytoplankton and zooplankton, as potential sources of organic matter and nutrients for these pelagic compartments. The biomass and the elemental composition of the pelagic compartments, the sedimentation rate, the elemental composition and the sugar and protein contents of short-term sediments were compared. The lipid composition of the biotic compartments was determined, with a particular focus on FAs and sterols. Lipid analysis was used to determine the extent of the bottom-up effect of sediment forcing on the biochemical composition of seston, zooplankton and short-term sediment. According to the results found by Spivak et al. (2007) and Harrault et al. (Chapter 2), we hypothesise that: (i) a positive bottom-up forcing will increase the biomass of seston (direct effect) and the biomass of zooplankton (indirect effect), and that (ii) this effect will be different among sediment treatments, depending on the elemental and lipid compositions and on the sugar and protein contents of the initial sediments. To our knowledge, this bottom-up forcing of lake sediments on pelagic compartments has never been studied in controlled conditions.

## Materials and methods

### *Study site and experimental design*

This study took place in Lake Créteil (48°46’37’’N, 2°26’47’’E), a small (42 ha), shallow (mean depth 4 m) sandpit lake 15 km southeast of Paris, France (for more information on this lake, see Lacroix & Lescher-Moutoué, 1995; Bertolo et al., 1999; Danger et al., 2008). Twenty-four translucent polyethylene enclosures, sealed at the bottom, were suspended above the lake surface on a floating pontoon. The volume of each enclosure was ca. 13.5 $m^3$ (2 × 1.5 × 4.5 m depth). At the end of November 2009, enclosures were randomly filled in successive steps with pumped lake water to minimize initial heterogeneity between

enclosures. To study the bottom-up effects of sediment on pelagic compartments and short-term sediment, two contrasted sediments were set down at the bottom of the enclosures. Enclosures without added sediment were used as a control ($S_0$). Each treatment was replicated eight times. The first sediment ($S_1$) was collected randomly in Lake Créteil with a Uwitec bottom sampler and consisted of a dark grey sandy material. The second sediment ($S_2$) was collected in enclosures used for a previous study (Danger et al., 2008) and consisted mainly of autochthonous material, with the exception of wind-driven atmospheric particles. Once collected, sediment (ca. 600 L each) was pooled into 200-L tanks for homogenisation. Before sediment addition into enclosures, the supernatant was removed from the collection tanks. Trays (2 × 1.5 m), filled with ca. 70 L of homogenized sediment (ca. 2.4 cm depth layer), were lowered very slowly at the bottom of each enclosure to minimize sediment resuspension and subsequent dissolution of nutrients and OM. Empty trays were put in the control enclosures. To allow sedimentation of suspended material in $S_1$ and $S_2$ enclosures, we started samplings only at the end of January 2010. Aliquot of $S_1$ and $S_2$ were freeze-dried and stored in the dark at room temperature until analyses.

***Seston and zooplankton sampling***

Seston biomass and elemental composition were determined monthly. Water was sampled monthly from February to June 2010 at different depths and locations with a 2-L sampling bottle (Uwitec) in each enclosure. Water samples were filtered through a 50-µm nylon filter to remove zooplankton, and then filtered through a pre-weighted Whatman GF/F glass-fiber filter (nominal cut-off: 0.7 µm). Filters were dried overnight at 60°C and weighted to determine seston biomass. Dry filters were stored in the dark at room temperature until elemental and lipid analyses. Zooplankton biomass was determined monthly by sampling 60 L of water at different depths and locations in each enclosure with a 12-L sampling bottle equipped with a 50-µm filter. Zooplankton was gathered in GF/F-filtered water for several hours to allow evacuation of gut content. Zooplankton was concentrated on a 50-µm filter, washed with deionized water to remove particles (bacteria, phytoplankton, detritus) and dissolved matter bound to their shell, placed on a pre-weighted Whatman GF/A glass-fiber filter (nominal cut-off: 1.6 µm), and dried overnight at 60°C. Dry zooplankton was grinded and stored in the dark at room temperature until elemental and lipid analyses.

***Particles and zooplankton counting***

An aliquot of 50-µm-filtered water was preserved in 4% formaldehyde. Particles ranging from 2 to 50 µm were counted with a Multisizer 4 Coulter Counter (Beckman Coulter) with a 100-µm probe. Zooplankton composition was determined in February and May by sampling 60 L of water at different depths and locations in three enclosures of each treatment with a 12-L sampling bottle equipped with a 50-µm filter. Zooplankton was preserved in 4% formaldehyde. Zooplankton were identified and counted under a stereo-microscope on subsamples at different dilutions in Dollfuss chambers. Copepods were separated into cyclopoids, calanoids and nauplii. Cladocera were separated into *Daphnia*, *Ceriodaphnia*, and Chydoridae. Rotifers were counted globally.

***Sampling of short-term sediment***

Due to insufficient sedimentation rates during winter (Danger et al., 2012), short-term sediments were only sampled in May and June 2010. Sedimentation rates were determined using six sediment traps deployed in each enclosure. Traps consisted of 5 cm diameter and 30-cm long PVC tubes, suspended at 4 m depth, close to the centre of the enclosures to limit potential contamination by biofilm particles falling down from enclosure walls. During the periods of lake stratification, traps were typically in the non-turbulent hypolimnion. Suspended 0.5 m above the bottom of the enclosures, sediment traps were preserved for bottom sediment resuspension. Traps were deployed for 7- to 9-day intervals. Material collected from the six traps was pooled in a collection flask and allowed to sediment overnight at 4°C. The supernatant and zooplankton therein was removed. Sediment was freeze-dried, weighted, grinded and stored in the dark at room temperature until analyses. Sedimentation rates were calculated as the mass of dry matter divided by the duration of trap deployment and the total surface of the six traps, and expressed in g $m^{-2}$ $day^{-1}$.

***Elemental composition of seston, zooplankton, initial and short-term sediment***

Carbon and nitrogen contents of dried samples were determined using a CHN elementary analyzer (FlashEA 1112 series, Thermo Fisher Scientific) with acetanilide as standard. Initial and short-term sediment organic carbon contents (OC) were determined after

removal of inorganic carbon (IC) from sediment by successive additions of 1 M HCl (Hedges & Stern, 1984).

***Sugar protein and orthophosphate colorimetric assays***

Freeze-dried sediments were extracted with $H_2O$ at 100°C for 2 h. The mixture was filtered through a Whatman GF/F glass-fiber filter, and the filtrate was freeze-dried. The freeze-dried aqueous extract was dissolved in a known volume of $H_2O$ and assayed for sugars and proteins. Sugar contents were determined using the phenol–sulfuric acid colorimetric method with glucose as standard (Dubois et al., 1956). Absorbances were measured at 490 nm. The protein contents were determined using the colorimetric method of Lowry with bovine serum albumin as standard. Absorbances were measured at 650 nm (Lowry et al., 1951). Sugars and proteins contents were expressed as percentage of the sediment dry weight (DW). Orthophosphate concentration was determined for water sampled in May and June by the phosphorus-ammonium molybdate spectrometric method (AFNOR, 2004).

***Lipid analysis***

All chemicals used were of analytical grade.

Apart from initial sediments $S_1$ and $S_2$, analyses of lipids were carried out on three replicates of each treatment for seston, zooplankton and short-term sediment sampled in May. The Whatman GF/F glass-fiber filter with collected seston was extracted with a dichloromethane (DCM)/methanol (MeOH) (2/1, v/v) mixture at room temperature for 18 h. The mixture was filtered through a Whatman GF/F glass-fiber filter and solvent was removed under reduced pressure. Extraction of a GF/F glass-fiber filter in similar conditions was performed as control. Lipid analysis of the extract did not show any contamination from the filter. Extracts were saponified at 80°C for 2 h using 20 mL of 1 M KOH in MeOH. The pH of saponified extract was brought to 2 by addition of 6 M HCl. Lipids were extracted three times with 30 mL DCM. The organic phase was washed with deionized water until neutral pH, dried over $Na_2SO_4$ and DCM removed under reduced pressure. Saponified lipids were treated with ca. 4 M HCl in MeOH (prepared by mixing acetyl chloride with MeOH (1/2.5 v/v) at 80°C for 1h to convert carboxyl groups into their methyl ester derivatives. Esterified extract was then treated with a mixture of anhydrous pyridine/N,O-

Bis(trimethylsilyl)trifluoroacetamide (BSTFA) (10/1, v/v) for 10 min at 60°C to convert hydroxyl groups into trimethylsilyl (TMS) ether groups. Lipid components (as methyl esters and TMS ethers) were analysed by gas chromatography mass spectrometry (GC–MS) with an Agilent 6890 gas chromatograph coupled to an Agilent 5973N mass spectrometer with electron ionization at 70 eV. Separation was achieved using a fused silica column coated with RTX5SilMS (30 m, i.d. 0.25 mm, film thickness 0.5 µm) with helium as carrier gas. The GC oven was programmed from 100 to 320°C at 4°C $min^{-1}$. Compound identifications were based on interpretation of the mass spectra. Unsaturated fatty acids were identified by comparison of retention times with standards (Larodan, Malmö, Sweden) using fused silica column coated with DB23 (60 m, i.d. 0.25 mm, film thickness 0.25 µm) with helium as carrier gas. The GC oven was programmed from 100 to 170°C at 6.5°C $min^{-1}$, then to 215°C at 2.75°C $min^{-1}$ and to 230°C at 40°C $min^{-1}$. Individual component contributions were determined by comparison of the peak areas from GC–MS traces. This method allowed a comparison of the relative abundance of each compound between the different samples analyzed, but does not allow the quantification of individual compounds of the total lipids. Dried zooplankton samples were extracted, and the lipid fraction analyzed as described for seston. The amounts of extracted lipids were too low to allow an accurate weight determination.

Freeze-dried sugar- and protein-free sediment samples were extracted with a chloroform ($CHCl_3$)/MeOH (2/1, v/v) mixture for 2 h at 80°C. Lipid extracts were saponified, derivatized and analysed as described for seston.

***Statistical analyses***

Statistical analyses were performed using R software (www.r-project.org). Two –way ANOVAs with time as repeated measure were used to test the individual and the combined effect of sediment treatment ($S_0$, $S_1$ and $S_2$) and time on the biomass of seston and zooplankton, size distribution of particles, zooplankton composition, sedimentation rates, elemental compositions of seston, zooplankton and short-term sediment, and orthophosphate concentration of water. Effects of sediment treatment on lipid biomarkers were tested with one-way ANOVAs. Post-hoc Tukey's tests were performed to compare one treatment to another. Data were log transformed when necessary to homogenize distributions and variances.

## Results

### *Initial sediments*

*Elemental composition and sugar and protein contents*

The elemental composition and content of sugars and proteins of the initial sediments $S_1$ and $S_2$ were reported in Table 1. The C, OC and N contents of $S_1$ were respectively four-fold, ten-fold and twenty-fold lower than those of $S_2$. The C/N and OC/N ratios of $S_1$ were higher than those of $S_2$. The content of $H_2O$ extracted compounds of $S_1$ was about ten-fold lower than that of $S_2$. Particularly, sugar and protein contents of $S_1$ were lower than those of $S_2$.

*Lipid composition*

The lipid compositions of $S_1$ and $S_2$ were reported in Table 2. Lipid fraction of both $S_1$ and $S_2$ comprised six main compound classes: fatty acids (FAs), alkanols (OHs), sterols, hydroxy acids (OH-FAs), chlorophyll-derived compounds (CHLOs) and alkanediols (OH-OHs).

**Table 1:** Elemental and biochemical compositions (% of dry weight) of initial sediments (n = 1).

| | C | OC | N | OC/N | Hydrophilic compounds | Sugars | Proteins | Lipids |
|---|---|---|---|---|---|---|---|---|
| $S_1$ | 5.7 | 0.9 | 0.1 | 9.0 | 0.5 | 0.1 | tr | 0.1 |
| $S_2$ | 23.1 | 9.7 | 2.4 | 4.0 | 4.5 | 0.7 | 0.2 | 3.0 |

*tr* traces

**Table 2:** Lipid compositions of initial sediments. Total was expressed as % of total lipids. Sub-classes of alkanols and hydroxy acids were expressed as % of total alkanols and hydroxy acids, respectively.

| | FAs | Sterols | OHs | | | OH-FAs | | | CHLOs |
|---|---|---|---|---|---|---|---|---|---|
| | Total | Total | Total | Short-chain | Long-chain | Total | α + β | ω | Total |
| $S_1$ | 36.4 | 16.0 | 26.3 | 5.1 | 94.9 | 8.5 | 71.4 | 26.9 | 4.5 |
| $S_2$ | 48.2 | 19.0 | 13.4 | 1.7 | 98.3 | 2.4 | 100.0 | ND | 9.8 |

FA: fatty acids
OHs: alkanols
OH-FAs: hydroxy acids
CHLOs: chlorophyll-derived compounds

Fatty acids (FAs) dominated the lipid fraction of both $S_1$ and $S_2$. FAs distributions of $S_1$ and $S_2$ were reported in Table 3. This compound class was dominated by saturated fatty acids (SAFAs) in both $S_1$ and $S_2$. SAFAs, ranging from $C_{14}$ to $C_{30}$, exhibited a strong even/odd predominance. For both $S_1$ and $S_2$, the distribution of SAFAs was dominated by 16:0 and long-chain ($\geq C_{20}$) compounds. Even-numbered monounsaturated fatty acids (MUFAs), ranging from $C_{16}$ to $C_{26}$, were found in rather similar proportions of total FAs in $S_1$ and $S_2$. MUFAs consisted essentially of 16:1ω7 18:1ω7 and 18:1ω9 for $S_1$ and of 18:1ω7 and 18:1ω9 for $S_2$. Even-numbered polyunsaturated fatty acids (PUFAs) ranging from $C_{16}$ to $C_{22}$ were found in lower relative abundance in $S_1$ than in $S_2$. In both $S_1$ and $S_2$ PUFAs were dominated by 18:2ω6 (linoleic acid, LIN), 18:3ω3 (α-linolenic acid, ALA), 20:4ω6 (arachidonic acid, ARA) and 20:5ω3 (eicosapentaenoic acid, EPA) homologues. Bacterial fatty acids (BACTs), determined as the sum of saturated $C_{15}$ and $C_{17}$ and branched-chain fatty acids (Wakeham & Beier 1991; Budge & Parrish, 1998), accounted for less than 7% of total FAs for $S_1$ and $S_2$.

Alkanols (OHs) contributed respectively for ca. 26% and 13% to the lipid fraction of $S_1$ and $S_2$ (Table 2). In both $S_1$ and $S_2$, alkanols, ranging from $C_{16}$ to $C_{30}$, exhibited a strong even/odd predominance and were dominated by long-chain homologues ($\geq C_{20}$, ca. 95% and 98% of total OHs for $S_1$ and $S_2$, respectively).

**Table 3:** Fatty acid compositions (% of total fatty acids) of initial sediments $S_1$ and $S_2$ (n = 1).

| **SAFA** | $S_1$ | $S_2$ | **MUFA** | $S_1$ | $S_2$ | **PUFA** | $S_1$ | $S_2$ | **BACT** | $S_1$ | $S_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 14:0 | 1.3 | 0.8 | 16:1ω7 | 5.1 | 1.7 | 16:3ω3 | ND | 0.4 | 14:0 br | 0.0 | 0.2 |
| 16:0 | 12.5 | 10.9 | | | | | | | | | |
| 18:0 | 8.4 | 3.2 | 18:1ω9 | 4.8 | 9.5 | 18:3ω6 | 0.0 | 0.3 | 15:0[a] | 2.9 | 2.0 |
| 20:0 | 3.2 | 1.0 | 18:1ω7 | 3.0 | 2.8 | 18:4ω3 | 0.0 | 0.3 | 16:0 br | 0.4 | 0.4 |
| 21:0 | 0.7 | 0.2 | 18:1ωx | 0.0 | 0.7 | 18:2ω6 (LIN) | 1.0 | 1.6 | 17:0[a] | 3.2 | 1.3 |
| 22:0 | 5.4 | 6.1 | 20:1ω9 | 0.9 | 1.2 | 18:3ω3 (ALA) | 1.6 | 7.8 | | | |
| 23:0 | 1.8 | 0.5 | 22:1ωx | 0.0 | 0.2 | 20:4ω6 (ARA) | 0.9 | 0.3 | | | |
| 24:0 | 12.6 | 9.7 | 24:1ωx | 0.0 | 0.5 | 20:5ω3 (EPA) | 1.4 | 0.9 | | | |
| 25:0 | 1.6 | 0.7 | 26:1ωx | 0.0 | 0.8 | 22:5ω6 | tr | 0.1 | | | |
| 26:0 | 10.7 | 17.1 | | | | 22:6ω3 (DHA) | tr | 0.1 | | | |
| 27:0 | 1.2 | 0.9 | | | | | | | | | |
| 28:0 | 11.4 | 12.3 | | | | | | | | | |
| 29:0 | 0.5 | 0.0 | | | | | | | | | |
| 30:0 | 2.9 | 1.5 | | | | | | | | | |
| Σshort-chain | 22.1 | 14.7 | | | | Σshort-chain | 2.6 | 11.2 | | | |
| Σlong-chain | 52.1 | 50.1 | | | | Σlong-chain | 2.3 | 1.4 | | | |
| Subtotal | 74.2 | 64.9 | Subtotal | 13.9 | 17.6 | Subtotal | 4.9 | 12.6 | Subtotal | 6.6 | 3.9 |

x: unknown position of double bounds
[a] Sum of branched and linear FAs

Sterols accounted for 16.0% and 19.0% to the lipid fraction of $S_1$ and $S_2$, respectively (Table 2). The sterol distributions of $S_1$ and $S_2$ were quite different (Table 4). In $S_1$, sterols were largely dominated by $\Delta^5$-sterols with cholesterol ($C_{27}\Delta^5$) as the major component. In $S_2$, $\Delta^5$- and $\Delta^7$-sterols accounted for ca. 30% and 25%, respectively. $\Delta^5$-sterols were dominated by cholesterol and $\Delta^7$-sterols were dominated by 24-ethyl-cholesta-7,22-dienol ($C_{29}\Delta^{7,22}$). Stanols, the saturated homologues of sterols, were present in high relative abundances in both $S_1$ and $S_2$. In both $S_1$ and $S_2$ stanols were dominated by cholestanol ($C_{27}\Delta^0$). An unidentified sterol ($C_{29}\Delta^{x,y}$) was present in high relative abundance in $S_2$ (Table 4).

Hydroxy acids (OH-FAs) were present in higher relative abundances in $S_1$ than in $S_2$ (Table 2). In $S_1$, the relative contribution of α- and β-OH-FAs total OH-FAs largely dominated that of ω-OH-FAs. ω-OH-FAs were not detected in $S_2$.

Chlorophyll-derived compounds (CHLOs) consisted of isomeric phytadienes, phytanic acid and/or other isoprenoid compounds usually considered to arise from the biodegradation of the phytyl side-chain of chlorophyll (Rontani & Volkman, 2003). CHLOs were about two-fold lower in $S_1$ than in $S_2$ (Table 2).

**Table 4**: Sterol compositions (% of total sterols) of initial sediments $S_1$ and $S_2$ (n = 1).

| Sterols [a] | $C_{27}\Delta^5$ | $C_{27}\Delta^0$ | $C_{28}\Delta^{5,22}$ | $C_{28}\Delta^5$ | $C_{28}\Delta^7$ | $C_{28}\Delta^0$ | $C_{29}\Delta^{5,22}$ | $C_{29}\Delta^{7,22}$ | $C_{29}\Delta^5$ | $C_{29}\Delta^7$ | $C_{29}\Delta^0$ | $C_{29}\Delta^{x,y}$ [b] | $\Sigma\Delta^5$ | $\Sigma\Delta^7$ | stanols |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $S_1$ | 31.2 | 28.9 | 3.8 | 10.7 | ND | 5.5 | 7.2 | ND | 8.3 | ND | 4.4 | tr | 61.2 | ND | 38.8 |
| $S_2$ | 11.4 | 20.0 | 2.5 | 7.3 | 7.8. | 3.1 | ND | 14.0 | 8.9 | 2.7 | 5.1 | 17.1 | 30.1 | 41.7 | 28.2 |

[a] $C_{27}\Delta^5$ : cholesterol; $C_{27}\Delta^0$ : cholestanol; $C_{28}\Delta^{5,22}$ : 24-methylcholesta-5,22-dienol; $C_{28}\Delta^5$: 24-methylcholest-5-enol; $C_{28}\Delta^7$: 24-methylcholest-7-enol; $C_{28}\Delta^0$: 24-methylcholestanol; $C_{29}\Delta^{5,22}$ : 24-ethylcholesta-5,22-dienol; $C_{29}\Delta^{7,22}$ : 24-ethylcholesta-7,22-dienol; $C_{29}\Delta^5$ : 24-ethylcholest-5-enol ; $C_{29}\Delta^7$: 24-ethylcholesta-7-enol; $C_{29}\Delta^0$: 24-ethylcholestanol

[b] unidentified sterol. Mass spectrometric characteristics: the unidentified sterol has a molecular weight of 484 indicating the presence of two unsaturations in a $C_{29}$ sterol. The retention time of this sterol is similar to that of $C_{29}\Delta^{5,22}$ and lower than that of $C_{29}\Delta^{7,22}$. The mass spectrum of this sterol exhibits peaks at m/z 484 ($M^{\cdot+}$), 469 $(M - CH_3)^+$, 394 $(M - HOTMS)^+$, 379 $(M - CH_3 - HOTMS)^+$, 345 (assumed to be $(M - SC)^+$; SC being the side chain of sterol), 255 (assumed to be $(M - SC - HOTMS)^+$), 229 (assumed to involve the loss of side chain together with C-16, C-17 and HOTMS; (Goad and Akihisa, 1997). The peaks at m/z 345, 255 and 229 suggest that one of the unsaturations is located in side chain. The absence of strong peak at m/z 129 indicates that the unidentified sterol is not a $\Delta^5$-sterol (Goad and Akihisa, 1997).

**Table 5**: Biomass (mg $L^{-1}$), elemental and biochemical compositions (% of dry weight) of seston, zooplankton (sampled from February to June). Sedimentation rates (g DW $m^{-2}$ $d^{-1}$), elemental and biochemical compositions (% of dry weight) of short-term sediments (sampled in May and in June). Mean ± SD. Significant effects are in bold.

| | Treatment | | | RM-ANOVA (*P* values) | | |
|---|---|---|---|---|---|---|
| | $S_0$ | $S_1$ | $S_2$ | Sediment | Time | Sediment × Time |
| *Seston* | | | | | | |
| Biomass | 1.18 ± 0.63 | 1.40 ± 1.03 | 2.14 ± 1.49 | **0.0049** | < **0.0001** | 0.11 |
| C | 30.3 ± 8.6 | 29.3 ± 8.8 | 32.2 ± 8.6 | 0.27 | **0.0008** | 0.76 |
| N | 4.6 ± 1.9 | 4.7 ± 1.4 | 5.5 ± 1.5 | **0.031** | 0.80 | 0.18 |
| C/N ratio | 6.6 ± 1.1 | 6.2 ± 1.0 | 5.9 ± 1.3 | **0.0025** | < **0.0001** | < **0.0001** |
| *Zooplankton* | | | | | | |
| Biomass | 0.27 ± 0.16 | 0.29 ± 0.19 | 0.51 ± 0.34 | **0.0016** | < **0.0001** | **0.0024** |
| C | 42.8 ± 8.8 | 42.7 ± 4.6 | 44.3 ± 4.2 | 0.52 | **0.0088** | 0.84 |
| N | 7.9 ± 2.6 | 8.9 ± 2.0 | 8.0 ± 1.7 | 0.66 | < **0.0001** | 0.23 |
| C/N ratio | 5.4 ± 2.1 | 5.3 ± 1.4 | 5.3 ± 1.2 | 0.94 | < **0.0001** | 0.064 |
| *Short-term sediment* | | | | | | |
| Sedimentation rate | 0.77 ± 0.40 | 1.42 ± 0.96 | 1.17 ± 0.53 | 0.13 | 0.093 | 0.65 |
| C | 24.8 ± 2.7 | 15.5 ± 3.7 | 26.9 ± 2.6 | **0.0001** | **0.028** | 0.10 |
| N | 2.8 ± 0.7 | 1.5 ± 0.5 | 3.3 ± 0.4 | < **0.0001** | 0.97 | 0.65 |
| C/N ratio | 9.1 ± 2.4 | 10.3 ± 1.8 | 8.0 ± 1.1 | **0.0021** | 0.17 | 0.95 |

| | | | | | | |
|---|---|---|---|---|---|---|
| OC [a] | 23.9 ± 2.6 | 14.4 ± 5.8 | 27.3 ± 2.2 | **0.016** | - | - |
| OC/N [a] | 8.9 ± 1.1 | 9.6 ± 5.8 | 8.0 ± 0.8 | **0.0022** | - | - |
| Hydrophilic compounds [a] | 23.1 ± 4.7 | 9.8 ± 6.3 | 21.8 ± 3.3 | 0.15 | - | - |
| Sugars [a] | 3.3 ± 0.3 | 2.7 ± 1.2 | 3.2 ± 0.8 | 0.36 | - | - |
| Proteins [a] | 2.2 ± 0.3 | 1.8 ± 0.6 | 3.2 ± 0.9 | 0.78 | - | - |
| Lipids [a] | 2.8 ± 2.3 | 0.9 ± 0.4 | 2.8 ± 1.4 | 0.21 | - | - |

[a] analyses were performed only on sediments sampled in May

***Orthophosphate concentration of water***

Sediment treatment had a significant effect on orthophosphate concentration of water (n = 48, P = 0.014). Orthophosphate concentration from $S_0$ and $S_1$ enclosures did not differ significantly (3.1 ± 5.3 and 3.8 ± 5.5 µg $L^{-1}$, respectively, n = 32, *P* = 0.96). Orthophosphate concentration from $S_2$ enclosures (11.3 ± 10.3 µg $L^{-1}$) was significantly higher than those from $S_0$ (n = 32, *P* = 0.010) and $S_1$ (n = 32, *P* = 0.022) enclosures.

***Seston***

The term "seston" refers to particulate matter between 0.7 and 50 µm diameters.

*Biomass, particle size and elemental compositions*

Biomass and elemental compositions of seston from the different treatments were reported in Table 5.

Sediment treatments had a significant effect on seston biomass (n = 120: 24 enclosures × 5 sampling dates, Table 5, Fig. 1a). On average, seston biomass from $S_0$ and $S_1$ treatments did not differ significantly (n = 80, *P* = 0.56). Seston biomass from $S_2$ treatment was significantly higher than those of seston from $S_0$ (n = 80, *P* = 0.0013) and $S_1$ (n = 80, *P* = 0.031) treatments. Time had a strong significant effect on seston biomass (Table 5, Fig. 1a). This significant trend was indicative of a seston biomass higher during Winter than during Spring (2.60 ± 1.38 and 0.96 ± 0.59, respectively, n = 120, Fig. 1a). No interaction effect between sediment treatments and time on seston biomass was observed.

Seston was always dominated by small particles. On average, 90, 75 and 50% of particles were smaller than 3.5 ± 0.6 µm, 75 % smaller than 6.1 ± 1.5 µm, and 90 % smaller than 12.2 ± 3.3 µm. Sediment treatments had no effect on particle concentration (29850 ± 14211 particles $mL^{-1}$, n = 120, *P* = 0.18) and size distribution (*P* = 0.36 for 50% of particles, *P* = 0.73 for 75% of particles and *P* = 0.43 for 90% of particles). The C content of seston from $S_0$, $S_1$ and $S_2$ treatments did not differ significantly (Table 5). The C content of seston sampled in April was higher than that of seston sampled in February and in March but did not differ from that of seston sampled in May and in June (Fig. 2a). The N content of seston from $S_0$ treatment did not differ from that of seston from $S_1$ treatment but was lower than that of

seston from $S_2$ treatment (Table 5). Time has no significant effect on the N content of the seston (Fig. 2b). The C/N ratio of seston from $S_0$ treatment was higher than that of seston from $S_1$ and $S_2$ treatments (Table 5). The C/N ratio of seston sampled in February was lower than that of seston sampled in March, April, May and June (Fig. 2c). Sediment treatment effect on the C/N ratio of seston was only observed in February and in March, as revealed by the significant effect of the interaction between sediment treatment and time (Table 5).

*Lipid composition.*

Seston from the different treatments was sampled in May 2010. The lipid distribution of these samples was reported in Table 6. Sediment treatments had no significant effect on the relative amounts of the different lipid classes of seston. FAs largely dominated the lipid distribution of seston, followed by alkanols. Sterols, hydroxy acids and chlorophyll-derived compounds were present in lower relative abundances.

*Fatty acids*

Sediment treatments had no effect on the FA distribution of seston (Table 7). For all treatments SAFAs largely dominated the FA distribution (ca. 74% of total FAs) with 16:0 and 18:0 as the major components. MUFAs accounted for ca. 12% of total FAs with 18:1ω9, 16:1ω7 and 18:1ω7 as the major constituents. PUFAs accounted for ca. 4% of total FAs. Long-chain PUFAs ($\geq C_{20}$) were present in very low relative abundances. Bacterial FAs accounted for ca. 10% of total FAs.

*Sterols*

As in the case of FAs, sterol distribution of seston did not depend on sediment treatments (Table 8). For all treatments, 24-ethyl-cholest-5-enol ($C_{29}\Delta^5$) dominated the sterol distribution (ca. 57% of total sterols) followed by cholesterol ($C_{27}\Delta^5$) accounting for ca. 23% of total sterols. 24-methyl-cholest-5-enol ($C_{28}\Delta^5$) and 24-ethyl-cholesta-5,22-dienol ($C_{29}\Delta^{5,22}$) were detected in lower relative abundances.

**Figure 1**: Seasonal variations of (a) seston and (b) zooplankton biomass and (c) sedimentation rates (mean ± SE). White, grey and black bars represent the control treatment ($S_0$), $S_1$ and $S_2$ treatment respectively. Significant effects are represented by different letters.

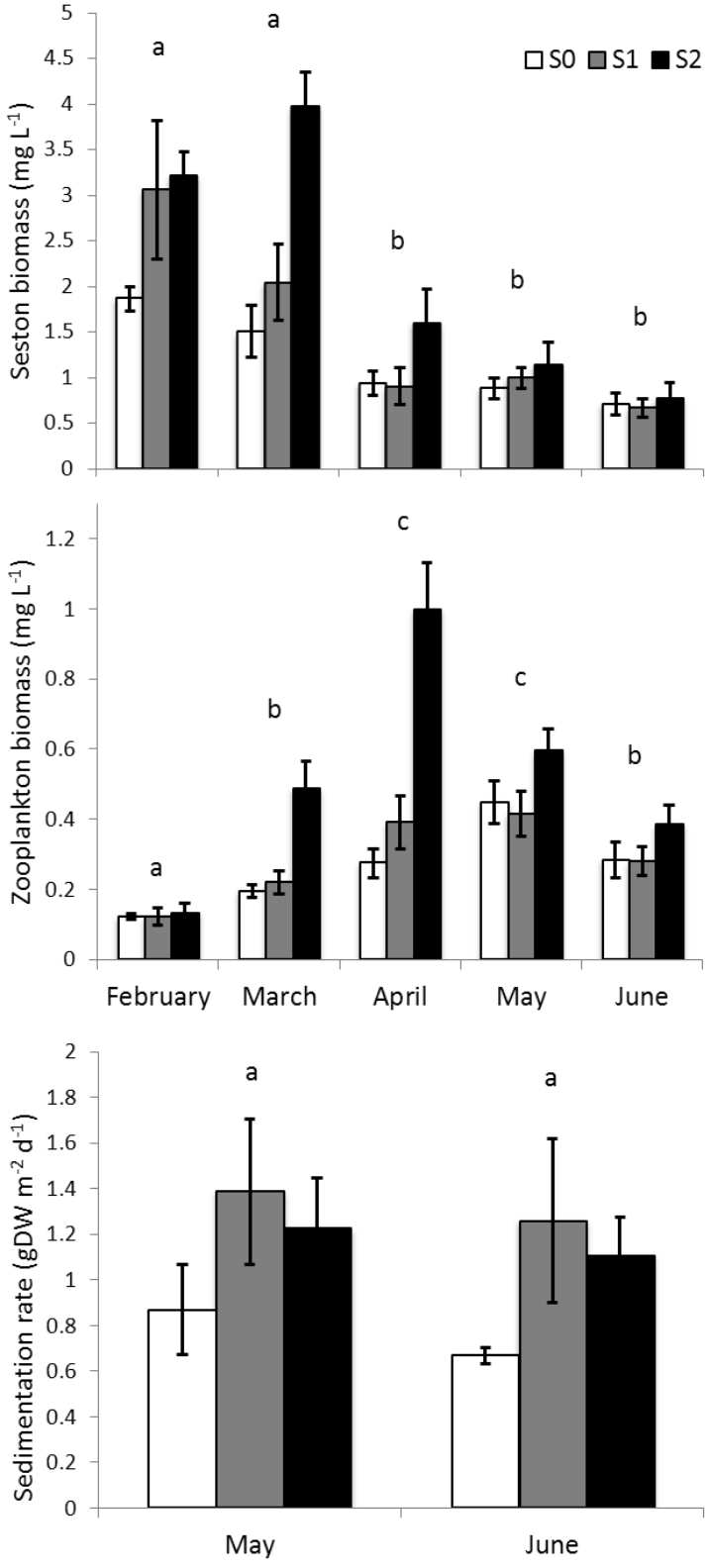


**Figure 2**: Seasonal variations of carbon (a) and nitrogen (b) contents and C/N ratio (c) of the seston (mean ± SE). White, grey and black bars represent the control treatment ($S_0$), $S_1$ and $S_2$ treatment respectively. Significant effects are represented by different letters.

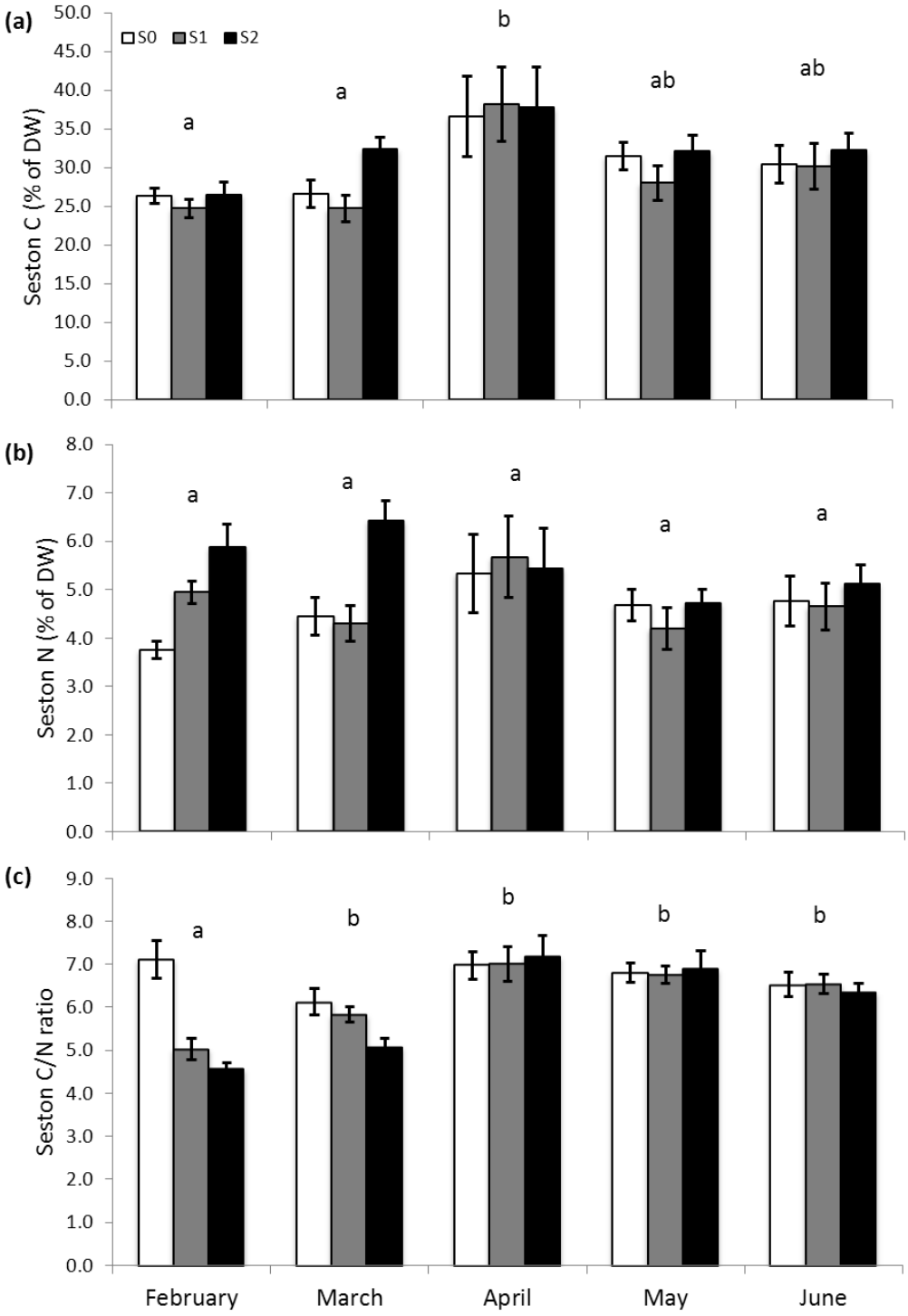


**Table 6**: Lipid compositions (% of total lipids) of seston, zooplankton and short-term sediment sampled in May 2010 (mean ± SD; n = 3). Bold values indicate significant differences between seston, zooplankton and/or short-term sediment. Statistical analyses were performed on the mean of the three sediment treatments for each compartment (n= 9 for seston, zooplankton and short-term sediment). Abbreviations are the same as in Table 2.

| | Seston | | | | Zooplankton | | | | Short-term sediment | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $S_0$ | $S_1$ | $S_2$ | Mean | $S_0$ | $S_1$ | $S_2$ | Mean | $S_0$ | $S_1$ | $S_2$ | Mean |
| FAs | 77.5 ± 7.6 | 74.6 ± 14.8 | 74.2 ± 7.8 | **75.4 ± 9.3** | 89.1 ± 5.6 | 84.9 ± 10.3 | 87.8 ± 6.6 | **87.3 ± 7.0** | 77.2 ± 9.0 | 72.2 ± 7.6 | 75.5 ± 8.7 | **75.0 ± 7.7** |
| OHs | 12.7 ± 3.6 | 15.5 ± 10.9 | 15.3 ± 7.3 | **14.5 ± 6.9** | 2.5 ± 0.9 | 6.1± 4.6 | 3.0 ± 0.9 | **3.9 ± 2.9** | 10.1 ± 3.5 | 13.9 ± 3.6 | 8.1 ± 3.3 | **10.5 ± 3.7** |
| Sterols | 5.5 ± 3.4 | 5.0 ± 1.8 | 5.2 ± 0.9 | 5.2 ± 2.0 | 5.7 ± 4.6 | 6.1 ± 5.2 | 6.3 ± 6.0 | 6.0 ± 4.6 | 6.5 ± 4.2 | 6.9 ± 4.3 | 6.0 ± 3.7 | 6.8 ± 4.1 |
| OH-FAs | 3.6 ± 0.5 | 4.3 ± 2.2 | 4.7 ± 0.3 | **4.2 ± 1.2** | 1.2 ± 0.4 | 1.7 ± 0.9 | 1.1 ± 0.4 | **1.3 ± 0.6** | 4.1 ± 0.7 | 4.3 ± 1.4 | 5.4 ± 1.2 | **4.6 ± 1.1** |
| CHLOs | 0.5 ± 0.2 | 0.4 ± 0.2 | 0.4 ± 0.0 | **0.5 ± 0.1** | 1.4 ± 0.4 | 0.9 ± 0.9 | 1.7 ± 0.9 | **1.3 ± 0.8** | **1.8 ± 0.7** | **2.0 ± 0.5** | **4.7 ± 1.6** | **2.8 ± 1.7** |

**Table 7**: Fatty acid compositions (% of total FAs) of seston, zooplankton and short-term sediment sampled in May 2010 (mean ± SD; n = 3). Bold values indicate significant differences between seston, zooplankton and/or short-term sediment. Statistical analyses were performed on the mean of the three sediment treatments for each compartment (n = 9 for seston, zooplankton and short-term sediment). Statistical analyses were performed on the subtotal of the different classes of fatty acids.

| Fatty acids | Seston | | | | Zooplankton | | | | Short-term sediment | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $S_0$ | $S_1$ | $S_2$ | Mean | $S_0$ | $S_1$ | $S_2$ | Mean | $S_0$ | $S_1$ | $S_2$ | Mean |
| SAFA | | | | | | | | | | | | |
| 12:0 | 0.4 ± 0.2 | 0.4 ± 0.1 | 0.4 ± 0.1 | 0.4 ± 0.1 | 0.3 ± 0.1 | 0.2 ± 0.1 | 0.2 ± 0.0 | 0.2 ± 0.1 | 0.3 ± 0.1 | 0.2 ± 0.1 | 0.4 ± 0.2 | 0.3 ± 0.1 |
| 14:0 | 4.1 ± 1.8 | 5.3 ± 2.5 | 3.2 ± 0.4 | 4.2 ± 1.8 | 6.0 ± 5.1 | 7.2 ± 5.3 | 3.6 ± 1.4 | 5.6 ± 4.1 | 2.4 ± 0.6 | 3.1 ± 1.5 | 3.0 ± 1.7 | 2.9 ± 1.2 |
| 16:0 | 41.6 ± 3.3 | 40.6 ± 3.6 | 40.7 ± 2.7 | 41.0 ± 2.8 | 32.1 ± 1.3 | 34.6 ± 2.0 | 36.7 ± 2.5 | 34.5 ± 2.6 | 35.6 ± 1.7 | 33.5 ± 4.0 | 34.0 ± 2.3 | 34.4 ± 2.6 |
| 18:0 | 17.5 ± 0.4 | 17.1 ± 4.0 | 19.3 ± 2.5 | 18.0 ± 2.6 | 8.7 ± 0.7 | 11.3 ± 1.3 | 9.3 ± 0.8 | 9.8 ± 1.5 | 11.6 ± 1.2 | 12.0 ± 0.9 | 9.6 ± 1.6 | 11.1 ± 1.6 |
| 20:0 | 1.6 ± 0.1 | 1.6 ± 0.4 | 1.9 ± 0.2 | 1.7 ± 0.3 | 0.5 ± 0.1 | 0.8 ± 0.2 | 0.5 ± 0.1 | 0.6 ± 0.2 | 0.9 ± 0.8 | 1.6 ± 0.1 | 1.0 ± 0.2 | 1.2 ± 0.5 |
| 21:0 | 0.5 ± 0.1 | 0.6 ± 0.2 | 0.6 ± 0.0 | 0.6 ± 0.1 | 0.1 ± 0.0 | 0.1 ± 0.1 | 0.1 ± 0.0 | 0.1 ± 0.1 | 0.2 ± 0.2 | 0.3 ± 0.0 | 0.2 ± 0.1 | 0.3 ± 0.1 |
| 22:0 | 3.1 ± 0.0 | 3.6 ± 1.8 | 4.0 ± 0.2 | 3.6 ± 1.0 | 0.8 ± 0.3 | 1.4 ± 0.5 | 0.7 ± 0.1 | 0.9 ± 0.4 | 1.5 ± 1.5 | 3.2 ± 1.1 | 1.6 ± 1.1 | 2.1 ± 1.3 |
| 23:0 | 0.7 ± 0.0 | 0.9 ± 0.5 | 0.9 ± 0.1 | 0.8 ± 0.3 | 0.2 ± 0.0 | 0.3 ± 0.1 | 0.1 ± 0.0 | 0.2 ± 0.1 | 0.3 ± 0.3 | 0.4 ± 0.2 | 0.3 ± 0.2 | 0.3 ± 0.2 |
| 24:0 | 1.2 ± 0.2 | 1.5 ± 1.0 | 1.6 ± 0.3 | 1.4 ± 0.6 | 0.3 ± 0.1 | 0.5 ± 0.4 | 0.2 ± 0.1 | 0.3 ± 0.2 | 0.9 ± 0.9 | 1.2 ± 0.6 | 0.8 ± 0.4 | 0.9 ± 0.6 |
| 25:0 | 0.3 ± 0.1 | 0.5 ± 0.4 | 0.5 ± 0.2 | 0.4 ± 0.2 | 0.1 ± 0.0 | 0.1 ± 0.1 | 0.1 ± 0.0 | 0.1 ± 0.1 | 0.2 ± 0.2 | 0.2 ± 0.1 | 0.1 ± 0.1 | 0.2 ± 0.1 |
| 26:0 | 0.3 ± 0.2 | 0.4 ± 0.4 | 0.4 ± 0.2 | 0.4 ± 0.3 | 0.1 ± 0.1 | 0.2 ± 0.2 | 0.1 ± 0.1 | 0.1 ± 0.1 | 0.5 ± 0.7 | 0.6 ± 0.5 | 0.5 ± 0.4 | 0.5 ± 0.5 |
| 27:0 | 0.1 ± 0.0 | 0.1 ± 0.1 | 0.1 ± 0.1 | 0.1 ± 0.1 | 0.0 ± 0.0 | 0.1 ± 0.0 | 0.0 ± 0.0 | 0.0 ± 0.0 | 0.1 ± 0.1 | 0.1 ± 0.1 | 0.1 ± 0.1 | 0.1 ± 0.1 |
| 28:0 | 0.5 ± 0.4 | 0.7 ± 0.8 | 0.9 ± 0.7 | 0.7 ± 0.6 | 0.1 ± 0.1 | 0.3 ± 0.3 | 0.1 ± 0.1 | 0.2 ± 0.2 | 1.2 ± 1.1 | 0.2 ± 0.1 | 0.4 ± 0.4 | 0.6 ± 0.7 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 30:0 | 0.5 ± 0.6 | 0.7 ± 0.9 | 0.7 ± 0.8 | 0.6 ± 0.7 | 0.1 ± 0.1 | 0.3 ± 0.4 | 0.1 ± 0.1 | 0.2 ± 0.2 | 1.3 ± 1.4 | 0.5 ± 0.8 | 1.8 ± 3.0 | 1.2 ± 1.8 |
| 32:0 | 0.2 ± 0.1 | 0.2 ± 0.2 | 0.3 ± 0.3 | 0.2 ± 0.2 | 0.0 ± 0.0 | 0.1 ± 0.1 | 0.0 ± 0.0 | 0.1 ± 0.1 | 0.1 ± 0.1 | 0.2 ± 0.2 | 0.1 ± 0.1 | 0.1 ± 0.2 |
| Subtotal | 72.6 ± 3.8 | 74.3 ± 9.5 | 75.6 ± 2.5 | **74.2 ± 5.4** | 49.3 ± 2.8 | 57.3 ± 7.0 | 51.8 ± 2.4 | **52.8 ± 5.3** | 57.2 ± 2.0 | 57.5 ± 2.2 | 54.1 ± 4.5 | **56.2 ± 3.2** |
| Σshort-chain | 63.6 ± 5.0 | 63.4 ± 3.8 | 63.7 ± 5.0 | **63.5 ± 4.0** | 47.1 ± 3.3 | 53.2 ± 8.5 | 49.8 ± 3.1 | **50.0 ± 5.5** | 49.9 ± 2.8 | 48.8 ± 6.4 | 47.1 ± 3.9 | **48.6 ± 4.2** |
| Σlong-chain | 9.0 ± 1.6 | 10.9 ± 6.6 | 12.0 ± 2.7 | **10.6 ± 3.9** | 2.2 ± 0.8 | 4.1 ± 2.2 | 2.0 ± 0.7 | **2.8 ± 1.6** | 7.3 ± 4.4 | 8.8 ± 4.2 | 7.0 ± 5.8 | **7.7 ± 4.3** |
| MUFA | | | | | | | | | | | | |
| 15:1ωx | 0.5 ± 0.2 | 0.4 ± 0.2 | 0.3 ± 0.2 | 0.4 ± 0.2 | 0.2 ± 0.1 | 0.4 ± 0.3 | 0.5 ± 0.1. | 0.4 ± 0.2 | 0.2 ± 0.1 | 0.4 ± 0.1 | 0.6 ± 0.5 | 0.4 ± 0.3 |
| 16:1ω7 | 3.6 ± 1.3 | 4.1 ± 2.9 | 3.3 ± 0.8 | 3.7 ± 1.3 | 4.1 ± 0.6 | 3.9 ± 1.5 | 5.2 ± 2.4 | 4.4 ± 1.6 | 4.4 ± 0.3 | 4.8 ± 1.9 | 5.1 ± 1.7 | 4.8 ± 1.3 |
| 16:1ωx | 0.2 ± 0.3 | 0.1 ± 0.1 | 0.3 ± 0.2 | 0.2 ± 0.2 | 0.4 ± 0.1 | 1.0 ± 0.5 | 1.2 ± 0.4 | 0.8 ± 0.4 | 1.5 ± 0.3 | 1.5 ± 0.6 | 2.5 ± 0.5 | 1.8 ± 0.6 |
| 17:1ωx | 0.3 ± 0.5 | 0.1 ± 0.1 | 0.0 ± 0.0 | 0.1 ± 0.3 | 0.4 ± 0.1 | 0.3 ± 0.2 | 0.4 ± 0.3 | 0.4 ± 0.2 | 0.6 ± 0.2 | 0.6 ± 0.2 | 1.2 ± 0.6 | 0.8 ± 0.5 |
| 18:1ω9 | 6.4 ± 1.6 | 2.3 ± 1.6 | 5.2 ± 0.7 | 4.6 ± 2.2 | 10.0 ± 2.8 | 9.8 ± 2.1 | 9.4 ± 2.0 | 9.8 ± 2.0 | 8.1 ± 0.9 | 10.6 ± 0.9 | 8.5 ± 0.7 | 9.1 ± 1.3 |
| 18:1ω7 | 2.2 ± 2.0 | 0.9 ± 0.7 | 1.5 ± 1.3 | 1.5 ± 1.4 | 5.2 ± 1.5 | 4.0 ± 2.4 | 6.2 ± 2.5 | 5.2 ± 2.1 | 6.5 ± 0.8 | 4.3 ± 1.3 | 4.2 ± 0.6 | 5.0 ± 1.4 |
| 18:1ωx | 0.3 ± 0.4 | 1.7 ± 2.8 | 0.6 ± 1.1 | 0.9 ± 1.7 | 0.1 ± 0.0 | 0.1 ± 0.1 | 0.1 ± 0.1 | 0.1 ± 0.1 | 0.4 ± 0.1 | 0.4 ± 0.1 | 2.9 ± 1.8 | 1.2 ± 1.6 |
| 20:1ωx | 0.2 ± 0.1 | 0.3 ± 0.2 | 0.2 ± 0.0 | 0.2 ± 0.1 | 0.4 ± 0.0 | 0.3 ± 0.0 | 0.3 ± 0.0 | 0.3 ± 0.0 | 0.3 ± 0.0 | 0.5 ± 0.3 | 0.4 ± 0.1 | 0.4 ± 0.2 |
| 20:1ω9 | 0.1 ± 0.1 | 0.0 ± 0.1 | 0.2 ± 0.0 | 0.1 ± 0.1 | 0.1 ± 0.0 | 0.0 ± 0.0 | 0.1 ± 0.0 | 0.1 ± 0.0 | 0.1 ± 0.1 | 0.1 ± 0.1 | 0.1± 0.0 | 0.1 ± 0.1 |
| 22:1ωx | 0.1 ± 0.2 | 0.2 ± 0.4 | 0.0 ± 0.1 | 0.1 ± 0.2 | 0.0 ± 0.1 | 0.0 ± 0.1 | 0.0 ± 0.1 | 0.0 ±0.1 | 0.7 ± 0.9 | 0.3 ± 0.3 | 0.1 ± 0.1 | 0.3 ± 0.5 |
| Subtotal | 13.9 ± 3.2 | 10.2 ± 7.3 | 11.8 ± 1.8 | **11.9 ± 4.4** | 21.1 ± 4.4 | 19.9 ± 5.7 | 23.5 ± 7.0 | **21.5 ± 5.3** | 22.9 ± 1.5 | 23.5 ± 0.4 | 25.6 ± 3.2 | **24.0 ± 2.2** |
| PUFA | | | | | | | | | | | | |
| 16:xω3 | 0.1 ± 0.1 | 0.2 ± 0.2 | ND | 0.1 ± 0.1 | 0.2 ± 0.1 | 0.1 ± 0.0 | 0.2 ± 0.1 | 0.2 ± 0.1 | 0.4 ± 0.1 | 0.3 ± 0.1 | 0.3 ± 0.0 | 0.3 ± 0.1 |
| 16:3ω3 | 0.1 ± 0.1 | 0.1 ± 0.1 | ND | 0.0 ± 0.1 | 0.3 ± 0.1 | 0.2 ± 0.1 | 0.5 ± 0.0 | 0.3 ± 0.2 | 0.3 ± 0.0 | 0.4 ± 0.2 | 0.7 ± 0.2 | 0.5 ± 0.2 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 16:2ωx | 0.0 ± 0.1 | 0.1 ± 0.1 | ND | 0.0 ± 0.1 | 0.1 ± 0.0 | 0.2 ± 0.0 | 0.1 ± 0.1 | 0.1 ± 0.1 | ND | ND | ND | ND |
| 18:3ω6 | ND | ND | ND | ND | 0.3 ± 0.1 | 0.1 ± 0.0 | 0.2 ± 0.1 | 0.2 ± 0.1 | 0.2 ± 0.0 | 0.2 ± 0.1 | 0.1 ± 0.0 | 0.2 ± 0.0 |
| 18:2ω3 | 0.5 ± 0.2 | 0.3 ± 0.2 | 0.1 ± 0.2 | 0.3 ± 0.2 | 1.9 ± 0.6 | 1.0 ± 0.4 | 1.5 ± 1.1 | 1.5 ± 0.7 | 0.8 ± 0.2 | 0.5 ± 0.2 | 0.4 ± 0.1 | 0.6 ± 0.3 |
| 18:2ω6 (LIN) | 1.5 ± 1.0 | 0.9 ± 0.6 | 0.8 ± 0.2 | 1.1 ± 0.6 | 6.1 ± 1.7 | 5.4 ± 1.0 | 2.9 ± 0.7 | 4.8 ± 1.8 | 5.7 ± 0.9 | 4.6 ± 1.5 | 3.4 ± 0.2 | 4.6 ± 1.4 |
| 18:3ω3 (ALA) | 1.7 ± 1.2 | 2.9 ± 3.5 | 1.4 ± 0.8 | 2.0 ± 2.0 | 7.6 ± 2.5 | 4.6 ± 1.2 | 6.7 ± 1.7 | 6.3 ± 2.1 | 3.5 ± 0.4 | 3.7 ± 1.8 | 4.1 ± 1.5 | 3.7 ± 1.2 |
| 18:2ωx | 0.3 ± 0.1 | 0.8 ± 0.5 | 0.7 ± 0.4 | 0.6 ± 0.4 | 1.1 ± 1.0 | 0.4 ± 0.3 | 0.7 ± 0.2 | 0.7 ± 0.6 | 0.4 ± 0.1 | 0.4 ± 0.2 | 0.4 ± 0.1 | 0.4 ± 0.1 |
| 20:4ω6 (ARA) | 0.1 ± 0.1 | ND | 0.0 ± 0.1 | 0.0 ± 0.1 | 1.4 ± 0.3 | 1.1 ± 0.1 | 0.6 ± 0.1 | 1.0 ± 0.4 | 0.2 ± 0.1 | 0.2 ± 0.1 | 0.2 ± 0.1 | 0.2 ± 0.1 |
| 20:5ω3 (EPA) | 0.0 ± 0.1 | ND | 0.0 ± 0.0 | 0.0 ± 0.0 | 2.4 ± 0.7 | 1.6 ± 0.6 | 2.1 ± 1.1 | 2.0 ± 0.8 | 0.2 ± 0.1 | 0.4 ± 0.1 | 0.3 ± 0.1 | 0.3 ± 0.1 |
| 20:2ωx | ND | ND | ND | ND | 0.6 ± 0.1 | 0.4 ± 0.1 | 0.2 ± 0.1 | 0.4 ± 0.2 | ND | ND | 0.1 ± 0.1 | 0.0 ± 0.1 |
| 20:3ω3 | ND | ND | ND | ND | 0.2 ± 0.1 | 0.1 ± 0.1 | 0.3 ± 0.0 | 0.2 ± 0.1 | 0.1 ± 0.1 | 0.1 ± 0.1 | 0.1 ± 0.1 | 0.1 ± 0.1 |
| 20:3ωx | ND | ND | ND | ND | 0.2 ± 0.0 | 0.1 ± 0.1 | 0.1 ± 0.1 | 0.1 ± 0.1 | 0.0 ± 0.0 | 0.1 ± 0.1 | 0.1 ± 0.1 | 0.1 ± 0.1 |
| 22:5ω6 | ND | ND | ND | ND | 0.3 ± 0.1 | 0.2 ± 0.1 | 0.2 ± 0.1 | 0.2 ± 0.1 | 0.0 ± 0.0 | 0.0 ± 0.0 | 0.0 ± 0.0 | 0.0 ± 0.0 |
| 22:6ω3 (DHA) | ND | ND | ND | ND | 1.3 ± 0.4 | 0.8 ± 0.5 | 1.0 ± 0.7 | 1.0 ± 0.5 | 0.1 ± 0.1 | 0.0 ± 0.1 | 0.1 ± 0.0 | 0.1 ± 0.1 |
| 22:5ω3 | ND | ND | ND | ND | 0.2 ± 0.1 | 0.2 ± 0.1 | 0.1 ± 0.0 | 0.2 ± 0.1 | ND | ND | ND | ND |
| Subtotal | 4.2 ± 2.2 | 5.3 ± 4.7 | 3.1 ± 1.1 | **4.2 ± 2.8** | 24.1 ± 3.1 | 16.6 ± 2.0 | 17.3 ± 5.5 | **19.4 ± 4.9** | 12.0 ± 1.4 | 10.9 ± 4.1 | 10.2 ± 1.6 | **11.1 ± 2.5** |
| Σshort-chain | 4.1 ± 2.0 | 5.3 ± 4.7 | 3.0 ± 1.0 | **4.1 ± 2.8** | 17.6 ± 2.3 | 12.1 ± 0.9 | 12.7 ± 3.3 | **14.1 ± 3.3** | 11.3 ± 1.5 | 10.0 ± 3.8 | 9.3 ± 1.9 | **10.2 ± 2.4** |
| Σlong-chain | 0.1 ± 0.2 | 0.0 ± 0.0 | 0.1 ± 0.1 | **0.1 ± 0.1** | 6.5 ± 0.9 | 4.6 ± 1.3 | 4.5 ± 2.2 | **5.2 ± 1.7** | 0.8 ± 0.1 | 0.9 ± 0.3 | 0.9 ± 0.3 | **0.9 ± 0.2** |
| BACT | | | | | | | | | | | | |
| 14:0 br | 0.2 ± 0.1 | 0.1 ± 0.0 | 0.3 ± 0.1 | 0.2 ± 0.1 | 0.2 ± 0.1 | 0.2 ± 0.0 | 0.2 ± 0.1 | 0.2 ± 0.1 | 0.3 ± 0.1 | 0.3 ± 0.1 | 0.3 ± 0.2 | 0.3 ± 0.1 |
| 15:0 br [a] | 1.9 ± 0.6 | 2.3 ± 1.4 | 1.8 ± 0.2 | 2.0 ± 0.8 | 1.8 ± 0.2 | 1.5 ± 0.2 | 2.2 ± 0.3 | 1.8 ± 0.4 | 2.0 ± 0.3 | 2.3 ± 1.3 | 4.0 ± 1.8 | 2.8 ± 1.5 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 15:0 | 2.0 ± 0.6 | 2.0 ± 0.1 | 1.9 ± 0.2 | 2.0 ± 0.3 | 0.9 ± 0.1 | 1.3 ± 0.7 | 1.2 ± 0.2 | 1.2 ± 0.4 | 1.4 ± 0.3 | 1.5 ± 0.4 | 1.9 ± 0.6 | 1.6 ± 0.5 |
| 16:0 br | 0.2 ± 0.0 | 0.2 ± 0.2 | 0.2 ± 0.2 | 0.2 ± 0.1 | 0.3 ± 0.1 | 0.2 ± 0.2 | 0.3 ± 0.1 | 0.3 ± 0.1 | 0.5 ± 0.0 | 0.3 ± 0.1 | 0.5 ± 0.1 | 0.4 ± 0.1 |
| 17:0 br [a] | 1.0 ± 0.2 | 1.1 ± 0.4 | 1.0 ± 0.4 | 1.1 ± 0.3 | 0.7 ± 0.1 | 0.8 ± 0.3 | 1.2 ± 0.7 | 0.9 ± 0.5 | 1.5 ± 0.9 | 1.2 ± 0.0 | 1.2 ± 0.2 | 1.3 ± 0.5 |
| 17:0 | 3.4 ± 0.1 | 4.2 ± 0.4 | 3.8 ± 0.1 | 3.8 ± 0.3 | 1.6 ± 0.1 | 2.0 ± 0.7 | 2.1 ± 0.7 | 1.9 ± 0.6 | 2.1 ± 1.0 | 2.1 ± 0.2 | 1.8 ± 0.0 | 2.0 ± 0.5 |
| 19:0 | 0.4 ± 0.2 | 0.3 ± 0.0 | 0.4 ± 0.1 | 0.4 ± 0.1 | 0.1 ± 0.0 | 0.1 ± 0.1 | 0.1 ± 0.0 | 0.1 ± 0.0 | 0.2 ± 0.0 | 0.3 ± 0.2 | 0.3 ± 0.1 | 0.2 ± 0.1 |
| Subtotal | 9.3 ± 1.2 | 10.3 ± 2.7 | 9.5 ± 0.1 | **9.7 ± 1.5** | 5.5± 0.1 | 6.1 ± 1.5 | 7.5 ± 1.0 | **6.4 ± 1.2** | 7.9 ± 1.1 | 8.1 ± 1.7 | 10.1 ± 2.4 | **8.7± 1.9** |

ND non detected
x: unknown numbers and position of double bonds
[a] occurrence of several isomers

**Table 8:** Sterol compositions (% of total sterols) of seston, zooplankton and short-term sediment sampled in May 2010 (mean ± SD; n = 3). Bold values indicate significant differences between seston, zooplankton and/or short-term sediment. Statistical analyses were performed on the mean of the three sediment treatments for each compartment (n = 9 for seston, zooplankton and short-term sediment). Statistical analyses were performed on cholesterol ($C_{27}\Delta^5$), cholestanol ($C_{27}\Delta^0$) and $C_{29}\Delta^5$.

| Sterols [a] | Seston | | | | Zooplankton | | | | Short-term sediment | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $S_0$ | $S_1$ | $S_2$ | Mean | $S_0$ | $S_1$ | $S_2$ | Mean | $S_0$ | $S_1$ | $S_2$ | Mean |
| $C_{27}\Delta^{5,22}$ | 0.5 ± 0.8 | 0.0 ± 0.0 | 0.9 ± 1.5 | 0.4 ± 0.9 | 1.8 ± 0.5 | 2.1 ± 0.3 | 2.2 ± 0.3 | 2.0 ± 0.4 | 1.6 ± 0.7 | 1.8 ± 1.0 | 2.4 ± 0.3 | 1.9 ± 0.7 |
| $C_{27}\Delta^5$ | 29.7 ± 15.5 | 20.1 ± 1.8 | 20.7 ± 11.5 | **23.5 ± 10.8** | 71.5 ± 10.6 | 59.6 ± 11.6 | 73.2 ± 8.6 | **68.1 ± 11.0** | 35.0 ± 13.2 | 34.1 ± 1.9 | 33.2 ± 4.6 | **34.1 ± 7.1** |
| $C_{27}\Delta^7$ | 0.4 ± 0.5 | 0.2 ± 0.3 | 0.0 ± 0.0 | 0.2 ± 0.3 | 0.0 ± 0.0 | 0.1 ± 0.2 | 0.0 ± 0.0 | 0.0 ± 0.1 | 0.2 ± 0.2 | 1.1 ± 1.3 | 0.3 ± 0.3 | 0.6 ± 0.8 |
| $C_{27}\Delta^0$ | 1.0 ± 0.4 | 0.8 ± 0.9 | 0.9 ± 0.4 | **0.9 ± 0.6** | 1.3 ± 1.1 | 0.7 ± 0.1 | 1.7 ± 0.5 | **1.2 ± 0.8** | 2.0 ± 1.7 | 2.1 ± 0.4 | 2.7 ± 0.5 | **2.3 ± 0.9** |
| $C_{28}\Delta^{5,22}$ | 0.0 ± 0.0 | 1.7 ± 2.9 | 0.0 ± 0.0 | 0.6 ± 1.7 | 0.2 ± 0.3 | 0.3 ± 0.5 | 0.3 ± 0.5 | 0.3 ± 0.4 | 2.1 ± 0.6 | 2.7 ± 0.8 | 2.6 ± 1.0 | 2.4 ± 0.7 |
| $C_{28}\Delta^5$ | 7.9 ± 0.9 | 9.0 ± 1.2 | 9.9 ± 1.8 | 9.0 ± 1.5 | 4.8 ± 0.5 | 5.6 ± 0.4 | 4.0 ± 0.4 | 4.8 ± 0.8 | 8.4 ± 0.4 | 9.3 ± 3.3 | 8.8 ± 2.6 | 8.8 ± 2.1 |
| $C_{29}\Delta^{5,22}$ | 2.2 ± 0.6 | 2.3 ± 0.3 | 2.5 ± 0.6 | 2.3 ± 0.5 | 0.8 ± 0.3 | 1.3 ± 0.4 | 0.9 ± 0.3 | 1.0 ± 0.3 | 3.2 ± 1.0 | 4.4 ± 2.5 | 4.1 ± 1.0 | 3.9 ± 1.5 |
| $C_{29}\Delta^5$ | 54.3 ± 18.4 | 58.6 ± 15.1 | 58.8 ± 20.8 | **57.2 ± 16.0** | 18.9 ± 10.3 | 28.3 ± 13.4 | 17.3 ± 9.5 | **21.5 ± 11.0** | 45.2 ± 18.3 | 42.4 ± 9.5 | 44.1 ± 3.5 | **43.9 ± 9.5** |

[a] $C_{27}\Delta^{5,22}$ : cholesta-5,22-dienol; $C_{27}\Delta^5$ : cholesterol; $C_{27}\Delta^7$ : cholest-7-ol; $C_{27}\Delta^0$ : cholestanol; $C_{28}\Delta^{5,22}$ : 24-methylcholesta-5,22-dienol; $C_{28}\Delta^5$: 24-methylcholest-5-enol; $C_{29}\Delta^{5,22}$ : 24-ethylcholesta-5,22-dienol; $C_{29}\Delta^5$ : 24-ethylcholest-5-enol.

**Zooplankton**

*Biomass, specific and elemental compositions*

Biomass and elemental compositions of zooplankton from the different treatments were reported in Table 5. Sediment treatments had a very significant effect on zooplankton biomass (n = 120, Table 5, Fig. 1b). On average, zooplankton biomass from $S_0$ and $S_1$ treatments did not significantly differ (n = 80, $P$ = 0.99). Zooplankton biomass from $S_2$ treatment was significantly higher than that of zooplankton from $S_0$ (n = 80, $P < 0.0001$) and from $S_1$ treatments (n = 80, $P < 0.0001$). Time had a highly significant effect on zooplankton biomass (Table 5, Fig. 1b). The biomass of zooplankton sampled in February (0.13 ± 0.06 mg $L^{-1}$, n = 24) was significantly lower than that of zooplankton sampled on other sampling dates ($P < 0.0001$ for each comparison). The biomass of zooplankton sampled in March (0.30 ± 0.19 mg $L^{-1}$, n = 24) was lower than that of zooplankton sampled in April (0.54 ± 0.39 mg $L^{-1}$, n = 24, $P$ = 0.005) and in May (0.49 ± 0.19 mg $L^{-1}$, n = 24, $P$ = 0.001) but did not significantly differ from that of zooplankton sampled in June (0.32 ± 0.14 mg $L^{-1}$, n = 24, $P$ = 0.90). A very significant interaction effect between sediment treatments and time on zooplankton biomass was observed (Table 5).

Species composition of zooplankton communities was weakly affected by sediment treatments but varied greatly with time (Table 9). Only the concentration of *Chydoridae*, which are benthic and littoral Cladocera, was significantly higher in the $S_2$ enclosures than in $S_1$ ones (n = 6, $P$ = 0.016). On average, the number of individuals was lower in February than in May, especially for nauplii of copepods (7.3 ± 3.4 and 180.9 ± 77.7 individuals $L^{-1}$, for February and May, respectively). C and N contents and C/N ratio of zooplankton from $S_0$, $S_1$ and $S_2$ treatments did not differ significantly (Table 5). Time had a very significant effect on the C content of zooplankton (Table 5). The C content of zooplankton sampled in March was higher than that sampled in June (Fig. 3a). Time had a highly significant effect on the N content and on the C/N ratio of zooplankton (Table 5). The N content of zooplankton sampled in February was lower than that sampled in the other dates (Fig. 3b), leading to the opposite trend for the C/N ratio of zooplankton (Fig. 3c).

Table 9: Mean specific composition of zooplankton communities (Individual $L^{-1}$) sampled in February and May. Mean ± SD. Significant effects are in bold.

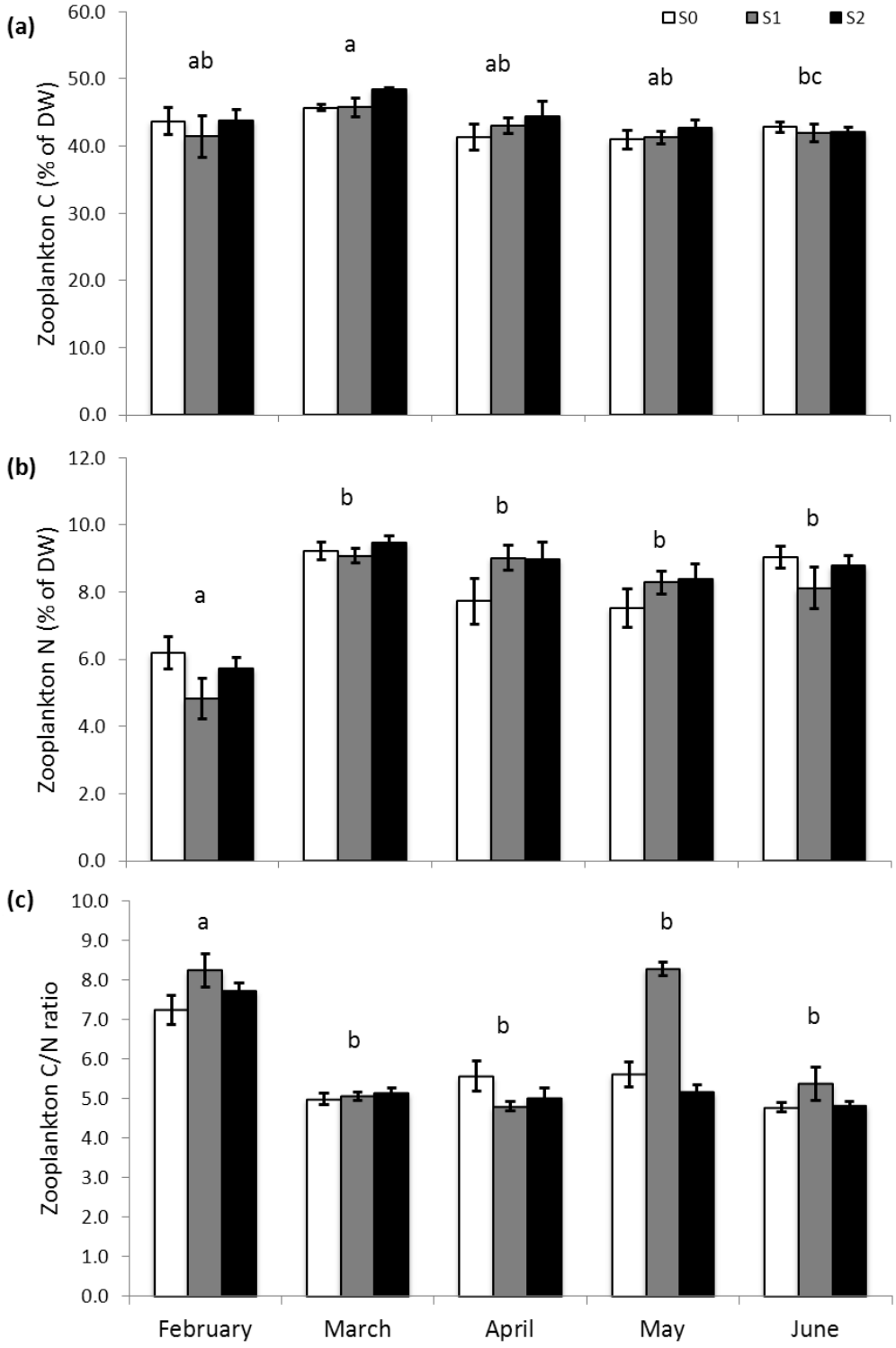
| | Treatment | | | RM-ANOVA (*P* values) | | |
|---|---|---|---|---|---|---|
| | $S_0$ | $S_1$ | $S_2$ | Sediment | Time | Sediment × Time |
| **Rotifers** | 2.8 ± 2.8 | 1.7 ± 1.2 | 7.2 ± 15.4 | 0.86 | 0.23 | **0.002** |
| **Cladocerans** | | | | | | |
| *Daphnia* | 23.4 ± 22.2 | 11.4 ± 13.7 | 3.4 ± 4.2 | 0.11 | **0.066** | **0.24** |
| *Ceriodaphnia* | 1.1 ± 2.2 | 0.1 ± 0.3 | 0.0 ± 0.1 | 0.18 | **0.0008** | **0.0054** |
| *Bosminidae* | 1.3 ± 1.7 | 2.2 ± 3.9 | 2.2 ± 4.4 | 0.95 | **< 0.0001** | 0.94 |
| *Chydoridae* | 5.6 ± 6.2 | 2.8 ± 3.7 | 16.5 ± 23.3 | **0.016** | **< 0.0001** | **< 0.0001** |
| **Copepods** | | | | | | |
| Cyclopids | 13.0 ± 14.0 | 7.5 ± 11.0 | 12.1 ± 12.5 | 0.33 | **< 0.0001** | 0.67 |
| Calanoids | 16.6 ± 10.8 | 10.3 ± 16.5 | 15.7 ± 18.6 | 0.41 | **0.0001** | **0.0008** |
| Nauplii | 111.9 ± 111.5 | 61.0 ± 65.1 | 99.2 ± 124..0 | 0.11 | 0.066 | 0.24 |

*Lipid composition*

Lipid distribution of zooplankton from the different treatments was reported in Table 6.

Sediment treatments had no significant effect on the relative amounts of the different lipid classes of zooplankton. FAs largely dominated the lipid distribution of zooplankton (ca. 87% of total lipids), followed by sterols accounted for ca. 6% of total lipids. Alkanols, hydroxy acids and chlorophyll-derived compounds were present in lower relative abundances (Table 6).

**Figure 3**: Seasonal variations of carbon (a) and nitrogen (b) contents and C/N ratio (c) of the zooplankton (mean ± SE). White, grey and black bars represent the control treatment ($S_0$), $S_1$ and $S_2$ treatment respectively. Significant effects are represented by different letters.



*Fatty acids*

Sediment treatments had no effect on the FA distribution of zooplankton (Table 7). For all treatments SAFAs dominated (ca. 53% of total FAs) with 16:0 and 18:0 as the major components. MUFAs accounted for ca. 21% of total FAs with 18:1ω9, 18:1ω7 and 16:1ω7 as major constituents. PUFAs accounted for ca. 19% of total FAs. Long-chain PUFAs made up 37% of total PUFAs with eicosapentaenoic (EPA, 20:5ω3), arachidonic (ARA, 20:4ω6) and docosahexaenoic (DHA, 22:6ω3) acids as major components. BACTs accounted for ca. 6% of total FAs.

*Sterols*

Sterol distribution of zooplankton did not depend on sediment treatment (Table 8). For all treatments, cholesterol ($C_{27}\Delta^5$) dominated the sterol distribution (ca. 68% of total sterols) followed by 24-ethyl-cholest-5-enol ($C_{29}\Delta^5$) accounting for ca 21%of total sterols. 24-Methyl-cholest-5-enol ($C_{28}\Delta^5$) and 24-ethyl-cholesta-5,22-dienol ($C_{29}\Delta^{5,22}$) were detected in lower relative abundances.).

**Short-term sediment**

*Sedimentation rate, elemental compositions and sugar and protein contents*

Short-term sediments were sampled in May and in June 2010. Sedimentation rates and elemental compositions of short-term sediment from the different treatments were reported in Table 5.

Sediment treatments and time did not significantly affect the sedimentation rates (n = 48 for each variable, Table 5, Fig. 1c), although there was a tendency towards higher sedimentation rates in $S_1$ and $S_2$ treatments.

The C content of short-term sediment from $S_0$ treatment was higher than that of short-term sediment from $S_1$ treatment (n = 32, $P$ = 0.0006) but did not differ significantly from that of short-term sediment from $S_2$ treatment (n = 32, $P$ = 0.43, Table 5). The C content of short-term sediment sampled in May was higher than that of short-term sediment sampled in June but this temporal effect is not highly significant (n = 48, Fig. 4a). The N content of short-term

sediment from $S_0$ treatment was higher than that of short-term sediment from $S_1$ treatment (n = 32, $P < 0.001$) but did not differ from that of short-term sediment from $S_2$ treatment (n = 32, $P = 0.12$, Table 5). Time had no significant effect on the N content of short-term sediment (n = 48, Table 5, Fig. 4b). The C/N ratio of short-term sediment from $S_0$ treatment was lower than that of short-term sediment from $S_1$ treatment (n = 32, $P = 0.038$) but did not differ from that of short-term sediment from $S_2$ treatment (n = 32, $P = 0.37$, Table 5). Time had no significant effect on the C/N ratio of short-term sediment (n = 48, Table 5, Fig. 4c). Sediment treatments had a significant effect on the OC content of short-term sediment sampled in May (n = 24, Table 5). The OC content of short-term sediment from $S_0$ treatment did not differ from that of short-term sediment from $S_1$ treatment (n = 16, $P = 0.53$) but the last was lower than that of short-term sediment from $S_2$ treatment (n = 16, $P = 0.15$). The OC/N ratio of short-term sediments did not differ between treatments (Table 5).

The amount of $H_2O$ extract (n = 9, $P = 0.15$) and sugar (n = 9, $P = 0.36$) and protein (n = 9, $P = 0.78$) contents of short-term sediment did not significantly differ between the different treatments (Table 5).

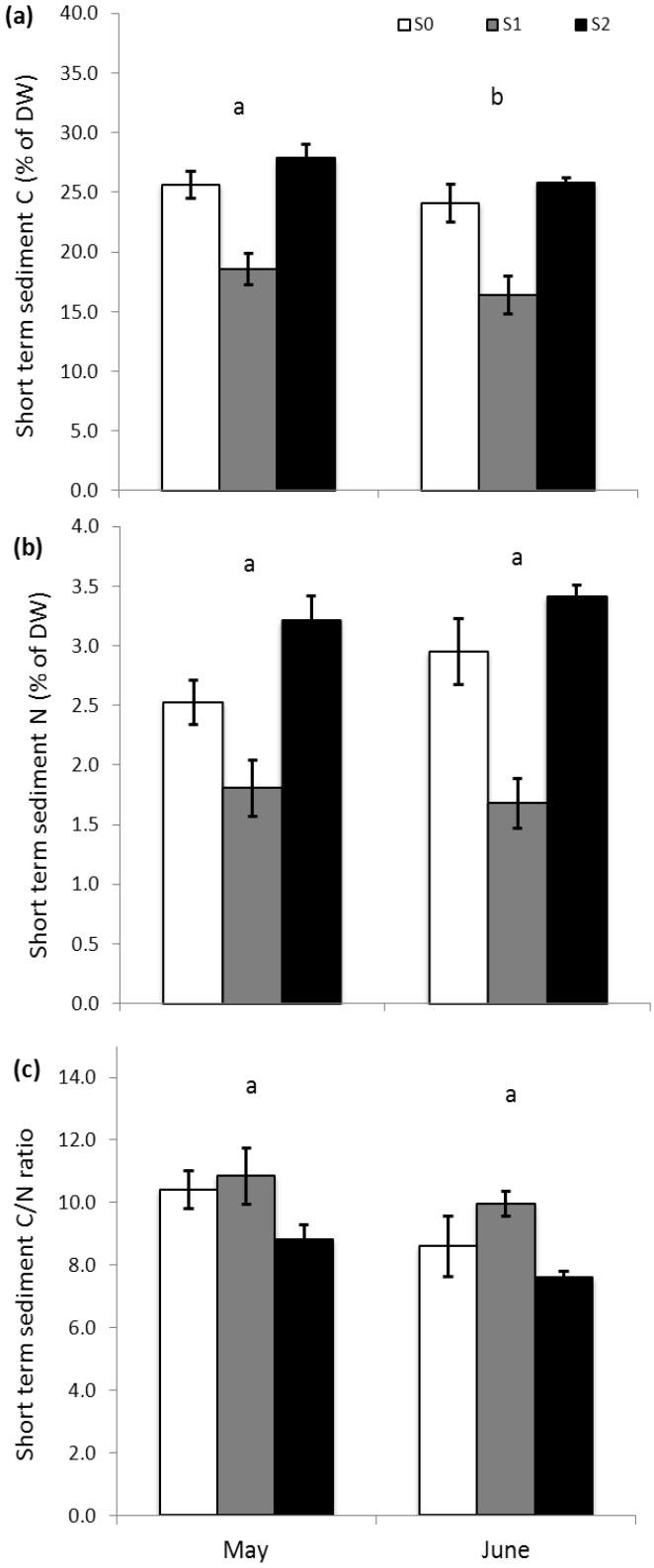
*Lipid composition*

Lipid distribution of short-term sediment from the different treatments was reported in Table 6. Sediment treatments had no significant effect on the relative amounts of the different lipid classes of short-term sediment. FAs largely dominated the lipid distribution of seston (ca. 75%of total lipids), followed by alkanols accounting for ca. 10% of total lipids. Sterols, hydroxy acids and chlorophyll-derived compounds were present in lower relative abundances (Table 6).

*Fatty acids*

Sediment treatments had no effect on the FA distribution of short-term sediment (Table 7). For all treatments SAFAs dominated (ca. 56% of total FAs) with 16:0 and 18:0 as the major constituents. MUFAs accounted for ca. 24 of total FAs with 18:1ω9, 18:1ω7 and 16:1ω7 as major constituents. PUFAs accounted for ca.11% of total FAs. Long-chain PUFAs accounted for ca.8% of total PUFAs. Bacterial FAs accounted for ca. 9% of total FAs.

**Figure 4**: Variations of carbon (a) and nitrogen (b) contents and C/N ratio (c) of the short-term sediment (mean ± SE). White, grey and black bars represent the control treatment ($S_0$), $S_1$ and $S_2$ treatment respectively. Significant effects are represented by different letters.



*Sterols*

Sterol distribution of short-term sediment did not depend on sediment treatments (Table 8). For all treatments, 24-ethyl-cholest-5-enol ($C_{29}\Delta^5$) dominated the sterol distribution (ca. 44%of total sterols) followed by cholesterol ($C_{27}\Delta^5$) accounting for ca.34% of total sterols. 24-Methyl-cholest-5-enol ($C_{28}\Delta^5$) and 24-ethyl-cholesta-5,22-dienol ($C_{29}\Delta^{5,22}$) were detected in lower relative abundances.

**Discussion**

Addition at the bottom of enclosures of sediments $S_1$ and $S_2$, which differed in their origin, composition and potential biodegradability, had several effects on biomass and stoichiometry of pelagic compartments. In contrast, very few differences were observed in the lipid composition of the biotic compartments and in the sugar and protein contents of short-term sediment.

***Differences in origin and quality of initial sediments***

The two initial sediments ($S_1$ and $S_2$) were chosen to simulate contrasted bottom-up treatments in enclosures. It can be assumed that both autochthonous and allochthonous sources contributed to $S_1$, sampled in the lake. Furthermore, this sediment was accumulated and exposed to microbial and benthic reworking over several decades. In contrast, $S_2$ was sampled in closed enclosures largely preserved from allochthonous inputs, and then assumed to be of mostly autochthonous origin. Furthermore, in closed enclosures, sediments were probably more protected from physical reworking induced by internal currents. Physical reworking is one of the main processes responsible for the sediment degradation since it allows supply of dissolved oxygen in the upper part of the sediment, organic matter resuspension and/or liberation of bound compounds from the mineral matrix (Wakeham & Canuel, 2006). Finally, this sediment was relatively young since it was collected in experimental mesocosms installed in 2005 (Danger et al., 2008) and was exposed to degradation over a shorter period than the sediment of the lake.

The differences between the origin and the degradation state of the two sediments are clearly revealed by several differences observed in their elemental and biochemical compositions.

The low OC/N ratio of $S_2$ is in total accordance with its major autochthonous contribution (Martinova, 1993). Although higher than that of $S_2$, the OC/N ratio of $S_1$ appears to be rather low considering the likely autochthonous and allochthonous contributions to this sediment (Martinova, 1993). However, the very low OC and N contents of $S_1$ could have led to a low precision of the estimated OC/N ratio (Meyers, 1997). The high relative abundances of $\Delta^7$-sterols in $S_2$ are in accordance with the high contribution of Chlorophyceae to $S_2$ previously observed by Allard et al. (2011) and Danger et al. (2012). Indeed, these sterols are abundant in many Chlorophyceae (Volkman, 1986), and have been proposed as indicators of these algae (Cranwell, 1982). In contrast, $\Delta^7$-sterols were not detected in $S_1$. $C_{28}$ and $C_{29}$ $\Delta^5$-sterols, present in high amounts in $S_1$, are abundant in algae and in vascular plants as well. So, in the present state of our knowledge, the sterol distribution of $S_1$ cannot allow to discriminate between autochthonous and allochthonous inputs. On the other hand, long-chain ω-hydroxy acids present in $S_1$ could be indicators of allochthonous contribution to $S_1$. Indeed, these compounds are well-known constituents of cutin and/or suberin biopolymers (Kolattukudy, 2001) and they were not detected in $S_2$. The high relative amounts of long-chain alkanols in $S_1$ could also indicate the contribution of higher plant and/or macrophyte inputs (Cranwell, 1982). However, a similar predominance of long-chain alkanols was observed in lipids from $S_2$ for which important allochthonous contributions have been ruled out. Therefore, as in the case of sterol distribution, the alkanol distribution of $S_1$ does not allow to establish unambiguously the contribution of allochthonous sources to $S_1$. Finally, the higher relative abundances in $S_2$ than in $S_1$ of chlorophyll-derived compounds, usually considered as arising from the biodegradation of the phytyl side-chain of chlorophyll (Rontani & Volkman, 2003), corroborate again a higher phytoplanktonic contribution to $S_2$.

The higher relative amounts of bacterial FAs in $S_1$ than in $S_2$ suggest that $S_1$ was in a more advanced degradation state than $S_2$. This is corroborated by higher amounts of α- and β-OH-FAs and stanols in $S_1$ than in $S_2$. Indeed, α- and β-OH-FAs are usually related to microbial input in sediment (Cranwell, 1981; Cardoso & Eglinton, 1983), and stanols, the saturated homologues of sterols, are usually considered as formed through in situ microbial reduction of sterols (Gaskell & Eglinton, 1975).

The qualities of $S_1$ and $S_2$ were also quite different. First, the pool of OM, which represents the total stock of resources potentially used by bacteria, was higher in $S_2$ than in $S_1$. Besides, proteins and sugars, essential for bacterial growth (Bunte & Simon, 1999; Weiss & Simon, 1999; Rosenstock & Simon, 2001), were more abundant in $S_2$ than in $S_1$. Finally, MUFA and PUFA contents, known as the preferentially degraded lipids by bacteria (Cranwell, 1981), were higher in $S_2$ than in $S_1$. Taken together, the differences observed in the amounts of these very labile compounds strongly suggest that $S_2$ was much more biodegradable than $S_1$. The differences in biodegradability between $S_2$ and $S_1$could have potentially led to differences in the release of nutrients and/or essential organic compounds from the sediment to the water column, and therefore could have modified the bottom-up effect on pelagic communities.

***Effects of bottom-up forcing on pelagic compartments***

The differences in quality between the two initial sediments, revealed by their sugar and protein contents and their lipid compositions, led us to hypothesise that the pelagic compartments from $S_2$ treatment could be submitted to a higher bottom-up effect than those from S1 treatment. As a consequence, biomass of pelagic compartments were expected to increase in the order $S_0 < S_1 < S_2$. Biomass of seston and zooplankton from the different treatments corroborated partially this hypothesis. Indeed, no difference in biomass of seston and zooplankton was observed between $S_1$ and $S_0$ treatments. Moreover, biomass of seston from $S_1$ enclosures was similar to that found in a previous mesocosm study where no sediment was added (Danger et al., 2012). $S_1$ contained a very low amount of OM, particularly labile compounds such as proteins, sugars, MUFAs and PUFAs. So, the amount of OM released as DOM available for the pelagic compartments from $S_1$ to the water column was probably low. Besides, the very low N content of $S_1$ strongly suggests that this sediment had a poor nutritional quality for biotic activities. Thus, the capacity of $S_1$ to act as a nutrient source could have been low compared to DOM supplied by the lake water. On the contrary, as hypothesised, biomass of seston and zooplankton from $S_2$ treatment were higher than those from $S_1$ and $S_0$ treatments. As $S_2$ contained much more OM and labile compounds than $S_1$, it could have released enough nutrients to the pelagic compartments to have a noteworthy influence compared to the effect of DOM and nutrients of lake water. This assumption was corroborated by the higher orthophosphate concentration of water from $S_2$ enclosures. Thus,

our results showed that the bottom-up effect of sediment on pelagic biomass strongly depends on the origin and above all, on the quality of the added sediment.

Whatever the treatments, the highest biomass of seston was observed in February and in March while, during this period, biomass and numbers of individuals of zooplankton were the lowest. This seasonal trend, previously observed (Danger et al., 2012), is in total accordance with the fact that the low grazing activity of zooplankton in late winter leads to a weak top-down control on phytoplankton, while the enhanced grazing activity of zooplankton in spring leads to a more important top-down control on phytoplankton (Sarnelle, 1999). Furthermore, the higher biomass of seston and zooplankton of $S_2$ treatment compared to that of $S_1$ and $S_0$ treatments clearly indicates the occurrence of a bottom-up effect resulting from the addition of $S_2$. This bottom-up effect did not modify strongly the structure of the zooplankton community, although inverse trends seemed to occur within Cladocera, with a tendency for the typically pelagic daphniidae to be less abundant and a tendency for the benthic and littoral Chydoridae to attain higher densities in the $S_2$ enclosures. The increase of the abundance of Chydoridae in the $S_2$ enclosures, characterized by their sediment rich in organic matter, is in accordance with the ability of Chydoridae to ingest detritus (de Eyto & Irvine, 2001). We have no robust explanation at this time to explain the inverse patterns between Chydoridae and Daphniidae, but some Chydoridae, such as *Chydorus* sp., which was present in the enclosures, seem to be able to utilise both benthic and open-water food sources (de Eyto & Irvine, 2001). *Chydorus* and *Daphnia* are considered to have complementary feeding niches in terms of size spectra when feeding on seston (Norberg, 2000). However, seston was totally dominated by small particles in the mesocosms, with 90 % of particles that were smaller than 12.2 µm. Thus, we cannot exclude the occurrence of strong competitive interactions in such systems where the dominance of small-sized algae was likely to reduce food resource partitioning for herbivorous zooplankton. Finally, after a strong increase in the beginning of spring, the biomass of zooplankton from $S_2$ treatment slowly decreased in the end of spring. This result is in accordance with our hypothesis that competition might have been important in such experimental systems with no external nutrient supply. Even in the $S_2$ enclosures, bottom-up effect was not important enough to allow a strong increase in the abundance of phytoplankton, which could have become rapidely limiting for zooplankton growth.

The occurrence of a bottom-up effect of $S_2$ treatment is also supported by the elemental composition of seston. Indeed, the higher N content of seston of $S_2$ treatment

compared to $S_0$ and $S_1$ ones suggests that the release of N from the "labile" $S_2$ sediment led to an increase of the N content of seston. As a result, the higher nutritional value of the seston from $S_2$ enclosures, as illustrated by its lower C/N ratio, could have contributed to the higher biomass of zooplankton observed in these enclosures. Interestingly, even in the enclosures without sediment, the C/N ratios of seston were lower than the minimum values determined at the same season in rather similar environmental conditions (Danger et al., 2012). These differences could be explained by the difference in light availability between the two experiments. Indeed, our experimental mesocosms have a 3-fold lower surface than those of Danger et al. (2012) for a similar depth, resulting in a lower exposure to light. According to the light-nutrient hypothesis, a decrease in light availability can induce a decrease in seston C/N ratio (Stramski et al., 2002; Dickman et al., 2006). By contrast, zooplankton C/N ratios determined in this study, did not depend on treatments and were quite similar to those previously obtained under similar experimental conditions (Danger et al., 2012). As species composition of zooplankton was weekly affected by sediment treatments, this result is in agreement with the homeostasis constraints on zooplankton stoichiometry (Hessen, 1990). Indeed, zooplankton species have been shown to have specific elemental compositions (Andersen & Hessen, 1991). For example, the decrease of the zooplankton C/N ratio with time might is in accordance with the increase of copepods within the community (Andersen & Hessen, 1991). Interestingly, changes in seston stoichiometric ratios did not induce similar changes in zooplankton element composition. Danger et al. (2012) showed previously that changes in food-web structure, which had clearly modified elemental composition of zooplankton communities by shifting species dominance, did not have any significant impact on seston stoichiometric ratios. This suggests that stoichiometric changes might not necessarily be transferred up or down along food chains within pelagic food webs.

As stated above, addition of sediment did not significantly influence the lipid composition of seston and zooplankton sampled in May. This indicates that, even in the case of the addition of sediment that resulted in a bottom-up effect on seston stoichiometry and zooplankton biomass (ie. $S_2$), this effect was too low, especially in May, to induce noticeable changes in the lipid composition of pelagic communities at the compartment scale. Inverse results, with changes in biochemical composition despite similar elemental ratios, had been found by Danger et al. (2012). This strengthens the previous conclusions of Allard et al. (2011) and Danger et al. (2012) that both elemental composition and biochemical quality of

organic matter bring useful information for understanding links between changes in food-web structure and functioning of aquatic ecosystems.

The low relative abundances of chlorophyll-derived compounds together with the high relative abundances of cholesterol in seston suggest that components of non-algal origin (zooplankton remains, faecal material) were important contributions to seston. Indeed, cholesterol is commonly considered to be an animal sterol and has been rarely found in high amounts in algae (Volkman, et al. 1998). It is worth noting that $\Delta^7$-sterols were present in very low relative abundances in seston from $S_2$ treatment. These sterols, considered as biomarkers for Chlorophycae (Cranwell, 1982), are abundant in the sterol fraction from $S_2$, indicating a high contribution of Chlorophyceae to this sediment. Then, it appears that migration of Chlorophyceae from $S_2$ to the water column and their subsequent development in the pelagic zone did not occur. This absence of dominance of Chlorophyceae is not necessarily puzzling as phytoplanktonic successions are highly variable in Lake Créteil, depending on both biotic and abiotic forces (Lacroix et al., 1989).

Surprisingly, although gut evacuated, zooplankton contained higher relative amounts of chlorophyll- derived compounds than seston. The presence of algae linked to organic aggregates collected with zooplankton (Simon et al., 2002) could explain the high level of chlorophyll-derived compounds detected in zooplankton samples.

***Effects of bottom-up forcing on short-term sediment***

The higher biomass of both seston and zooplankton observed in $S_2$ enclosures did not induce higher sedimentation rates in these enclosures. This might be due to low production of sinking material from seston and zooplankton in pelagic systems characterized by the absence of fish. Indeed, the values obtained in this study are in agreement with previous studies carried out in zooplankton-dominated systems (Sarnelle, 1999; Danger et al., 2012). These previous studies showed that the sedimentation rates are lower in systems dominated by zooplankton than in systems dominated by phytoplankton. As globally there was a tendency towards higher sedimentation rates in $S_1$ and $S_2$ treatments that in $S_0$ enclosures, this absence of significant effect might also illustrate the difficulty of measuring precisely sedimentation rates in shallow aquatic systems.

In our enclosures, the biomass of seston remained higher than that of zooplankton. Moreover, phytoplankton, which constitutes up to 40% of seston (Hessen, 2003), is known to

sink much more than zooplankton (Sommer, 1984). Thus, changes of the elemental composition of seston that occurred because of sediment treatments were expected to induce similar changes on short-term sediment. This assumption was not supported by the stoichiometric analyses since the elemental composition of short-term sediment from $S_2$ treatment was similar to that of $S_0$ treatment. Surprisingly, in contrast to the pelagic compartments, the elemental composition of short-term sediment from $S_1$ treatment differed from that of short-term sediment from $S_0$ and $S_2$treatments. At the present time, no explanation can be put forward for these results.

Apart from chlorophyll-derived compounds, we did not observe any difference between treatments in the relative amounts of lipid classes of short-term sediment. The higher relative abundances of chlorophyll-derived compounds in short-term sediment from $S_2$ treatment probably indicate a higher contribution of phytoplankton to this sediment. As in the case of pelagic compartments, fatty acid and sterol distributions of short-term sediment did not depend on sediment treatments. The relative abundances of both FAs and sterols of short-term sediment range between those observed for seston and zooplankton. These results suggest that both seston and zooplankton contribute appreciably to short-term sediment. However, the relative contribution of each pelagic compartment to short-term sedimentation is difficult to estimate, although the relative abundances of specific zooplankton biomarkers such as long-chain PUFAs and cholesterol in short-term sediment suggest that the contribution of zooplankton to short sediment was less important than that of phytoplankton.

The amounts of bacterial FAs suggest a rather low contribution of bacteria to short-term sediments. Nevertheless, cholestanol was present in higher relative amounts in short-term sediments than in seston and in zooplankton. This indicates that the degradation of settling organic matter occurs even begins rapidly. However, the relative amounts of unsaturated fatty acids, the most reactive compounds towards biodegradation, were still rather high in short-term sediments. This suggests that microbial reworking remained limited for these very recent sediments.

Lipid biomarkers and bulk parameters such as PUFA, sugar and protein contents have been used to estimate and compare the quality of sediments (Canuel et al., 2007; Allard et al., 2011). In this study, none of these “sediment quality” indicators revealed a bottom-up effect linked to bottom sediment quantity and quality to the quality of the newly short-term sediment.

Finally, the quantity and the quality of settling organic matter in aquatic ecosystems appears to be less affected by bottom-up forces linked to sediment quality than by the top-down forces linked to food-web structure. Indeed, recent studies have shown that the top-down control exerted by planktivorous predators has strong effects on sinking rates, elemental and biochemical compositions, and biodegradability of short-term sediment (Canuel et al., 2007; Allard et al., 2011; Danger et al., 2012).

**Conclusion**

This mesocosm experiment demonstrated that the origin and the quality of lake sediment can lead to modifications of the pelagic communities. This bottom-up forcing mainly affected biomass of pelagic communities and seston stoichiometry but had no effects on the lipid composition of seston and zooplankton. The quantity, the composition and the biodegradability of short-term sediment were not affected by sediment treatments, suggesting that the bottom-up effects associated to sediment presence and quality were close to a classical effect of nutrient addition. Moreover, these bottom-up effects of sediment occurred only with highly biodegradable sediment, rarely found in nature. Microcosms and mesocosms have been frequently criticized for their lack or realism (Carpenter, 1996; Schindler, 1998). Our experimental results suggest that the absence of initial sediment in most mesocosm experiments does not necessarily induces major discrepancies in the functioning of pelagic systems, and tend to confirm the ecological significance of the effects identified by such manipulations (Spivak & Vanni, 2011).

Finally, in comparison to the effects of the trophic cascade on pelagic communities and sedimentation, the bottom-up control exerted by lake bottom sediments appeared to be moderate. This might explain the efficiency of biomanipulations for improving water quality of eutrophicated lakes despite potential internal recycling (Jeppesen et al., 2007).

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# Chapitre IV

# Biodégradation de la matière organique des sols et « priming-effect » aquatiques

# Fast mineralization of eroded land-born C in inland waters

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oligotrophic systems, eutrophic systems.

**Abstract**

1. In the context of global change, soil carbon and in particular carbon from soil erosion are subject to intense debates. A substantial part of eroded soil ends up in aquatic ecosystems and could impact $CO_2$ emissions from these ecosystems.
2. Here, we compared the rates of mineralization of Soil Organic Matter (SOM) sampled from cropland, meadow, forest and bare fallow in an aquatic and in a terrestrial.
3. The aquatic systems were simulated by a mineral medium inoculated with a lake microbial community. We manipulated N and P concentration to simulate oligo-mesotrophic and eutrophic systems. For each nutrient load $^{13}$C-glucose was added to simulate exudation of Labile Organic Matter (LOM) by phytoplankton. The priming effect (PE) resulting from the addition of $^{13}$C-glucose was determined
4. After 45 days of incubation, the mean SOM mineralization was 63% higher in the aquatic than in the terrestrial context. Moreover, after glucose addition, a Priming Effect occurred, increasing by 17% the mean SOM mineralization in water.
5. $CO_2$ emissions originating from SOM mineralization in aquatic systems appears to depend–on the SOM recalcitrance and quality, on the soil aggregate stability–and on the availability of LOM and nutrients.
6. Finally, our results suggest that the most important $CO_2$ fluxes from aquatic ecosystems to atmosphere due to SOM mineralization are produced during the first days after the transport of eroded soil from terrestrial to aquatic ecosystems. This process might be partially controlled by the labile organic matter from primary producers.

## Introduction

The ecosystem capacities to act as carbon sinks or sources are highly dependent upon anthropogenic perturbations of biogeochemical cycles. In this context, improving our knowledge about carbon sources or sinks is of particular interest. Although global stocks of carbon are relatively well known, their dynamics are poorly understood (Houghton, 2007). Soils represent the largest continental stock of Carbon (C) with 1,700 billion tons (Berhe, 2005).The annual rate of soil erosion reaches 36 to 75 billion tons and affects more than 1.1 billions hectares around the Earth (Berhe, 2005). This erosion redistributes between 17 to 40 tons of soil $ha^{-1}$ $year^{-1}$ with 1.5 to 5.0% C-content. Soils may be eroded by wind, tillage, or water runoff. A large part of the eroded soil organic matter (SOM) is transferred into aquatic systems. Whether this SOM is a sink (Smith et al., 2001; Van Oost et al., 2007; Van Oost et al., 2008) or a source of C (Lal, 2003, 2005; Lal et al., 2008) for the atmosphere is still debated.

In a terrestrial context, SOM stability is controlled by three key mechanisms (Lützow et al., 2006). The relative importance and the persistence of these protection mechanisms in aquatic conditions are not well understood. (i) In terrestrial ecosystems, SOM is stabilized by interactions with mineral surfaces and with metal ions. In aquatic ecosystems, such stabilized SOM is buried in the sediment and potentially acts as a sink (Van Oost et al., 2007; Dean & Gorham, 1998). However, resuspension is important in shallow aquatic ecosystems (Hamilton & Mitchell, 1996), potentially reducing the protecting effects on SOM buried in sediment. (ii) SOM may be protected from microbial enzymes by occlusion in soil aggregates. Most continental aquatic ecosystems being shallow (Wetzel, 1975) and disturbed, SOM decomposition might be enhanced in water by physical breakdown of such aggregates (Lal, 2003). (iii) Complex macromolecules may be recalcitrant to mineralization because soil microorganisms are unable to synthesize the enzymes degrading these molecules. However, recent studies underlined the capabilities of soil microorganisms to mineralize recalcitrant organic matter if energy is supplied as Labile Organic Matter (LOM) (Hamer et al., 2004; Fontaine et al., 2007). Such a phenomenon is known as priming effect (PE) (Kuzyakov et al., 2000). A few studies (Farjalla et al., 2009; van Nugteren et al., 2009) suggested that PE exists in aquatic ecosystems. Recently, several arguments were put forward in favor of a major role

of this process in aquatic ecosystems, where LOM is produced in substantial amounts as phytoplankton exudates or labile fractions of plant detritus (Guenet et al., 2010a).

In this study, we first aimed to compare the amount of mineralization of SOM, originating from four contrasted soils, in aquatic and terrestrial context. The occurrence of an aquatic PE was also investigated by adding $^{13}$C-labeled glucose as LOM. Finally, the influence of trophic conditions on SOM mineralization in aquatic context and on aquatic PE was studied by adding two different amounts of mineral nutrients (nitrogen and phosphorus) in microcosms to simulate oligo-mesotrophic and eutrophic conditions. We hypothesized that SOM mineralization rates might be higher in aquatic than in terrestrial systems due to aggregate breakdown. This phenomenon might largely depend on the aggregate stability, particularly in shallow systems where turbulent mixing could play an important role. Moreover, we hypothesized that PE occurs in aquatic systems resulting in an increase in the SOM mineralization.

## Methods

### *Soils*

To broaden our conclusions and to avoid pseudo-replication, we used four very contrasted SOM as replicates. The two first were cambisol (WRB), and were sampled at the Centre de Recherche en Ecologie Expérimentale et Prédictive (CEREEP-Ecotron Iledefrance, ENS, St Pierre Les Nemours, France). One was sampled under deciduous forest dominated by *Quercus robur*, *Quercus petraea* and *Carpinus betulus L.* The second one was sampled under meadow dominated by graminae. The two last soils used were Eutric cambisol (WRB) and were sampled at two long-term experimental sites at the Institut National de la Recherche (Versailles, France). One was sampled at the Closeaux site. We used the control plot, which has always been under C3 plant rotation and under wheat monoculture since 1993. The second one was a bare fallow soil, sampled from the control plots of the "42 plots experiment". The control plot of this long-term experiment is a fallow soil that has been maintained bare and without addition of organic matter or other fertilizer since 1929. The plots were initially weeded manually and herbicides were used to prevent weed growth since 1967. This latter soil, which contains at least 80-year-old SOM, is considered as a model to study the stabilized pool of SOM (Balabane & Plante, 2004; Barre et al., 2010 Guenet et al.,

2010b. The four soil samples were collected in the surface layer (0-20cm), air-dried during 48h and sieved (2mm). The soils were sampled in March 2006 at the INRA site of Versailles and in June 2007 at the CEREEP-Ecotron Ile de France.

*Soil characterization*

C and N contents were measured using a CHN analyzer (NA 1500, AS 128) with acetanilide as standard.

For each soil, hydrophilic and hydrophobic fractions were extracted from a homogenized subsample (60 to 110 mg) using an accelerated solvent extractor (ASE 100, Dionex) at 100°C and $10^7$ Pa. Hydrophilic compounds were first extracted (3 × 5 min) with $H_2O$, concentrated under reduced pressure, freeze-dried and weighted. Hydrophobic fraction was subsequently extracted using ASE at 100°C and $10^7$ Pa with methanol (MeOH , 1×5 min) followed by an extraction (3 × 5 min) with a mixture of dichloromethane (DCM):MeOH (93:7, v/v). MeOH and DCM/MeOH extracts were pooled and dried over $Na_2SO_4$. Solvents were removed under reduced pressure and hydrophobic compounds weighted.

The freeze-dried hydrophilic extracts were dissolved in a known volume of $H_2O$ and assayed for sugars and proteins. Sugar contents were determined by the phenol-sulfuric acid colorimetric method (Dubois et al., 1956) with glucose as standard. The protein contents were determined by the colorimetric method of Lowry (Lowry et al., 1951) with bovine serum albumin (BSA) as standard. Sugars and proteins were respectively expressed as mg of glucose and BSA carbon equivalent per grams of SOM.

*Experimental unit*

Each soil was incubated in 120-ml flasks closed with an airtight septum. The terrestrial context was simulated by incubating 20g of dried soil moistened at 80% of the field capacity. The aquatic context was simulated by incubating 50mg C-soil with pure Fontainebleau sand to normalize the weight, 1 ml of lake water (Créteil, France) filtered through a 0.7 µm GF/F filter to exclude the microorganism predators and 2 ml of mineral media. Osmosed water was added to a final volume of 21mL. These aquatic microcosms were gently agitated in order to simulate water turbulence. Two types of modified COMBO with $NH_4NO_3$ instead of $NaNO_3$ as N source (Kilham et al. 1998) were used as mineral media to simulate the low (9.5 µM of

N and 0.48 µM of P) and the high (95 µM of N and 4.8 µM of P) amount of N and P. These two media corresponded respectively, to a moderate load of nutrients similar to that observed in oligo-mesotrophic ecosystems and to a high nutrient load, similar to that observed in eutrophic ecosystems.

For each terrestrial and aquatic microcosms, the $CO_2$ emission was quantified using micro-GC (Agilent 3000A). The carbon isotope ratios were determined using a gas chromatograph (Hewlett-Packard 5890) coupled to an isotope ratio mass spectrometer (Isochrom III, Micromass-GVI Optima). After each $CO_2$ measurement, all flasks were flushed with reconstituted, moistened and $CO_2$-free air. Incubations were carried out at 20 °C in the dark to avoid input of fresh C through primary production. Samples were incubated for 45 days and measurements were performed at days 2, 8, 15, 22, 29, 36 and 45.

*Priming Effect*

Uniformly $^{13}C$-labeled glucose was obtained from. Sigma-Aldrich (St Louis, USA). The initial $\delta^{13}C$ value was 8,809,023‰. It was diluted (1:20,000) with non-labelled glucose (Sigma-Aldrich, St Louis, USA), in order to respect technical constraints of the isotope ratio mass spectrometer. The final $\delta^{13}C$ value of glucose was -7‰. Controls were performed to verify the stability of the $\delta^{13}C$-$CO_2$ deriving from glucose mineralization by incubating a microbial community in a mineral media with glucose as the sole carbon source.

Priming effect in the aquatic microcosms was studied by adding 1ml of glucose (2.5gC-glucose $L^{-1}$, $\delta^{13}C$=-7‰), corresponding to a final concentration of 50mgC-glucose.$g^{-1}$ C-soil, to the flasks. Controls without glucose were performed. Finally, we simulated one terrestrial system (control without water, glucose and nutrient inputs) and four different freshwater systems (without or with glucose and, low or high amounts of nutrients) per soil.

Priming effect was calculated as follow: $PE= \alpha \times Q_{sample}$

with $Q_{sample}$ is the amount of $CO_2$ in the flask atmosphere with glucose

and $\alpha = (A_{glucose}-A_{sample})/(A_{glucose}-A_{control})$

$A_{glucose}$, $A_{sample}$ and $A_{control}$ represent respectively the isotopic abundance of glucose, of $CO_2$ in the atmosphere of sample and $CO_2$ in the atmosphere of control.

Isotopic abundance derive from the $\delta^{13}C$ as followed: $\delta^{13}C=[(R_{sample}/R_{pdb})-1]*1000$

with $R_{pdb}=0.0112372$

$A_{sample}=R_{sample}/(1+R_{sample})$

*Statistical analysis*

All statistical analyses were performed using R 2.7.1 (R Development Core Team, 2008). We run nested ANOVA, with the type of soil used nested within the aquatic or terrestrial context. Post-hoc Tukey's tests were performed using the multcomp package of R 2.7.1. A significant threshold of $p < 0.05$ was chosen for all analyses.

**Results**

*Soils*

Chemical analyses of soils revealed strong differences in the characteristics of the studied soils (Table 1). Particularly, bare fallow soil contained a very low C content (4.7 mg C $g^{-1}$ soil), whereas the carbon content of forest soil was 4-fold higher than that of bare fallow soil. C/N ratio of the forest soil was 3-fold higher than that of the bare fallow soil. The forest soil was also characterized by a 4-fold higher hydrophobic/hydrophilic compounds ratio than the other soils.

*Aquatic conditions vs. terrestrial conditions*

Without glucose amendment, the cumulated SOM mineralization in the aquatic context was 63% higher than in the terrestrial context at the end of incubation ($P < 0.001$, Fig. 1). Without glucose amendment, neither the amount of SOM mineralized nor the mineralization dynamic was affected by nutrient availability ($P = 0.12$, Fig. 2). Whatever the context and the soil, the dynamic of the rate of SOM mineralization was rather similar (Fig. 2). The rate of SOM mineralization was maximum around the second day and then progressively decreased. With the exeption of meadow soil, incubation of all the samples in water resulted in an increase in the mineralization rate from the first days of the experiment (Fig. 2). For meadow soil, the mineralization was similar in aquatic and terrestrial systems during the first ten days and then, was higher in the aquatic system until the end of the incubation (Fig. 2). Mineralization rates of forest SOM were higher in aquatic microcosms

than in terrestrial ones throughout the incubation period (Fig. 2). By contrast, after 21 days, the mineralization rates of cropland and bare fallow SOM reached a similar level in both aquatic and terrestrial context

**Table 1**: Characteristics of the four soils. C and N contents and C/N ratios are means ± SE (n=3).

| | Bare Fallow | Cropland | Forest | Meadow |
|---|---|---|---|---|
| C content ($mgC.g^{-1}$) | 4.7 ± 0.1 | 11.7 ± 0.1 | 20.0 ± 0.8 | 10.2 ± 0.1 |
| N content ($mgN.g^{-1}$) | 0.54 ± 0.04 | 1.04 ± 0.04 | 0.78 ± 0.06 | 0.84. ± 0.01 |
| C/N | 8.65 ± 0.83 | 11.23 ± 0.41 | 25.34 ± 1.35 | 12.09 ± 0.08 |
| pH | 4.0 | 6.1 | 3.7 | 5.6 |
| Hydrophilic compounds ($mg.g^{-1}$C-SOM) | 177.8 | 129.5 | 145.1 | 193.2 |
| *Proteins* | 5.1 | 15.4 | 42.1 | 35.3 |
| *Sugars* | 18.7 | 23.1 | 37.7 | 37.3 |
| Hydrophobic compounds ($mg.g^{-1}$C-SOM) | 44.4 | 32.6 | 173.8 | 58.8 |
| Hydrophobic/hydrophilic | 0.2 | 0.3 | 1.2 | 0.3 |

*PE in aquatic context*

In the aquatic context, glucose addition increased the cumulated SOM mineralization by ca. 17% (n = 16, $P < 0.002$, Fig. 1), leading to a final 80% increase compared to the terrestrial context ($P < 0.001$). In oligo-mesotrophic conditions, despite the different temporal variations observed between the four soils, the cumulated PE resulted in a ca.12% increase in SOM mineralization at the end of incubation (data not shown). The extent of cumulated PE increased with the load in nutrients and resulted in a final ca. 22% increase in SOM mineralization for eutrophic conditions (data not shown).

At the end of the incubation, whatever the nutrient loads, cumulated PE was positive for all the soils except for the forest one, which exhibited a negative cumulated PE (Fig. 3). In the case of bare fallow, in low nutrient conditions, a negative cumulated PE occurred during about 2 weeks before the positive cumulated PE (Fig.3).

In contrast, whatever the nutrient conditions, a negative cumulated PE occurred for the forest soil nearly throughout the incubation (Fig. 3).

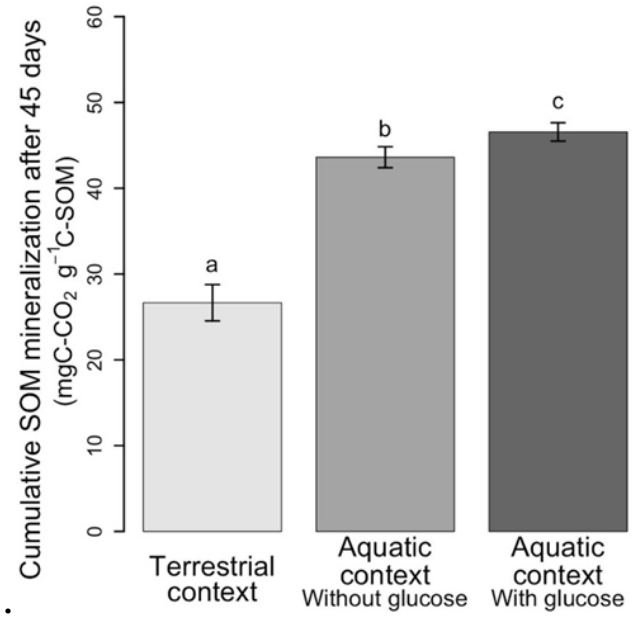


**Figure 1:** Soil organic matter cumulative mineralization after 45 days of incubation for terrestrial and aquatic conditions expressed as mg $C\text{-}CO_2.g^{-1}$ of C-SOM (mean ± S.E.). Standard errors were corrected by the random effect due to the soils. Different letters indicate significant differences.

**Discussion**

Atmospheric carbon is taken up by autotrophic organisms in ecosystems and sequestered in soils and vegetation. A part of this carbon is eroded and either redeposited on land or is transported by streams towards rivers, lakes and seas (Toy et al. 2002). Very high sedimentation rates have been reported, suggesting that inland waters are an important C sink, thus sequestering a part of C from terrestrial origin (Van Oost et al. 2007, Smith et al. 2001). Here, we used four contrasted soils representative of a large range of SOM quality from major ago-ecosystems in Europe (cropland, meadow and forest) and a long-term bare

fallow soil considered as a surrogate of a stabilized SOM. Our results show that the mineralization rates of all the soils studied is much higher in aquatic than in terrestrial context. Furthermore, the mineralization of SOM in aquatic context occurs mainly during the first days of the incubation. This suggests that the transfer of eroded C in water could largely contribute to carbon emission from inland waters to atmosphere and that an important amount of $CO_2$ might be emitted during the very beginning of soil runoff process. Consequently, our results suggest that high sedimentation rates do not necessarily result in high-sequestration of land-born C.

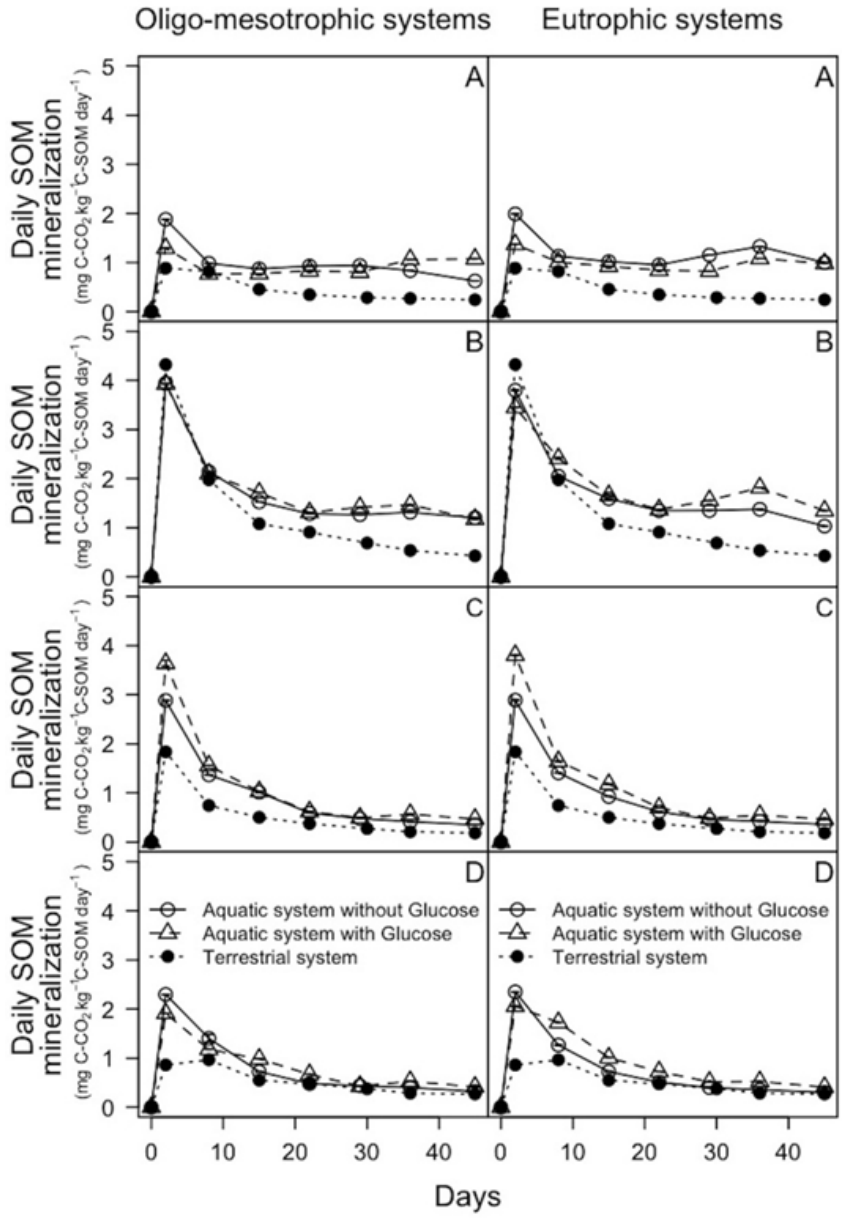


**Figure 2:** Daily soil organic matter mineralization rate for the four studied soils in terrestrial context

(●), in aquatic context without glucose (○) and in aquatic context with glucose (△), expressed as mg $C\text{-}CO_2.g^{-1}$ of C-SOM per day for forest (A), meadow (B), cropland (C) and bare fallow (D).

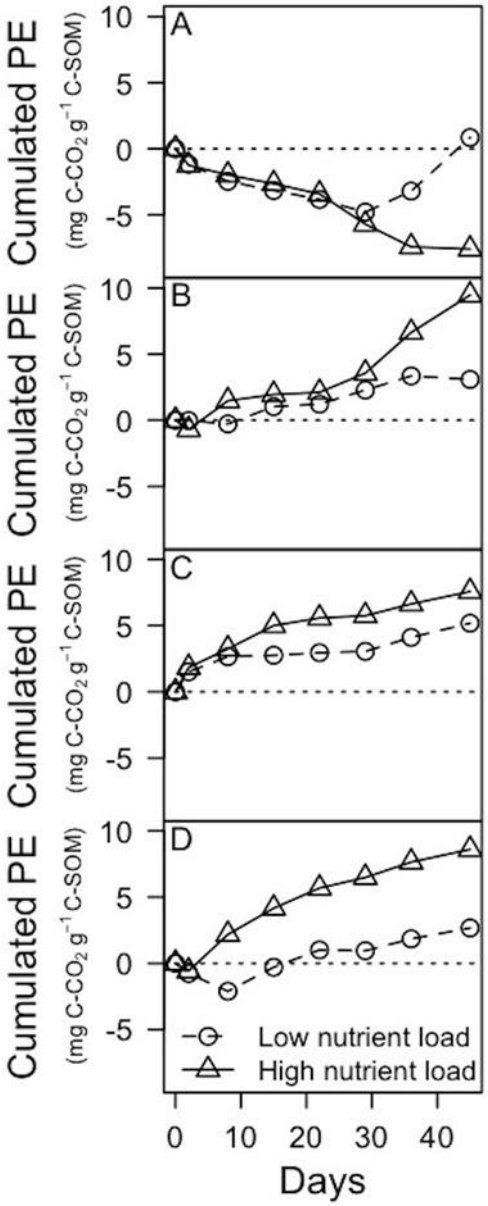


**Figure 3:** Cumulative PE for the four studied soils with low (○) and high nutrient contents (△), expressed as mg $C\text{-}CO_2.g^{-1}$ of C-SOM for forest (A), meadow (B), cropland (C) and bare fallow (D).

In contrast to cropland and bare fallow soils, at the end of the incubation, the mineralization rates of meadow and forest soils are much higher in aquatic than in terrestrial context. Differences in the soil structure could explain the differences observed between the

mineralization rates of the studied soils at the end of the experiment. Indeed, forest and meadow soil structure have not been disturbed by anthropogenic actions since a long time. In contrast, cropland and bare fallow experimental sites were tilled every year, disrupting soil structure and aggregate stability. Furthermore, the weak stability of soil aggregates from the bare fallow soil has been previously demonstrated (Balabane & Plante, 2004).This suggests that the differences observed in the mineralization rate patterns in aquatic context between the four soils are probably due to the differences in the kinetics of the aggregate breakdown and therefore, in the SOM accessibility in water Thus, the delay of C release might depend on the aggregate stability of soil.

This study shows that PE occurs in aquatic systems and depends on both soil and nutrient load.

In low nutrient conditions, despite the great differences in the cumulative PE patterns observed for the studied soils, a positive cumulated PE was observed for all the soils after 45 days of incubation. This result could indicate that, in meso-oligotrophic ecosystems, extra SOM mineralization due to the presence of LOM is a widespread phenomenon that could reduce the C storage due to SOM burying.

For all the soils, the extent of cumulated PE increased with the amounts of nutrients, particularly at the end of the experiment. This suggests that heterotrophic activity was limited by nutrients. However, this result is not in agreement with most experimental (Martin-Olmedo et al. 2002, Fontaine et al., 2004, Blagodatskaya et al. 2007) and theoretical (Fontaine & Barot, 2005) studies carried out in soils. Indeed, these studies more often suggest a decrease in PE intensity as nutrient content increases. These studies attributed this phenomenon to a decrease in the production of the exoenzymes responsible for the SOM degradation (Kuzyakov et al., 2000).

The positive PE observed for meadow, cropland and bare fallow soils can be explained by an increase in the microbial biomass and/or exoenzyme production due to the energy supplied to microorganisms through LOM input (Kuzyakov et al., 2000; Guenet et al., 2010a) and *in fine* in SOM mineralization. The positive cumulated PE observed for the bare fallow soil which is considered as a surrogate of a stabilized pool of SOM suggests that addition of LOM can even increase the mineralization of recalcitrant SOM. The early negative cumulated PE observed for bare fallow soil indicates a preferential substrate utilization of LOM instead of the more recalcitrant SOM (Guenet et al., 2010b). Bare fallow SOM is more recalcitrant than the other ones. Thus the microbial community needs probably more energy to mineralize

this SOM. Furthermore, because this soil has been maintained bare during a long time microbial community has probably shifted to SOM feeding microorganisms which exhibit slow growth rate (so-called K-strategists, Fontaine et al., 2003). These hypothesis could explain the first negative cumulated PE stage for bare fallow soil compared to meadow and cropland ones.

The negative cumulated PE observed for the forest SOM cannot be solely explained by a higher recalcitrance. Indeed, first, bare fallow SOM is likely the most stable SOM and exhibits positive PE. Second, forest soil is richer in easily available organic matter (proteins and sugars) than the other ones. However, a large fraction of the forest SOM was composed by N-free hydrophobic compounds. As a result, the forest soil exhibits much higher C/N than the other ones. In accordance with the preferential substrate utilization hypothesis (Cheng, 1999), this high C/N ratio might have facilitated preferential utilization of LOM because microorganisms should have mineralized more C from SOM to acquire enough N. Another factor, which could also explain this negative PE, is the high concentrations of tannins in forest soils. These compounds are known to complex proteins and deactivate microbial exoenzymes (Kraus et al. 2003).The inactivation of exoenzymes responsible for SOM mineralization could have favored a preferential LOM degradation. Thus, SOM nature is an important determinant of PE in aquatic ecosystems.

We demonstrated in this study that SOM was much more mineralized in aquatic than in terrestrial context. Moreover, we show that PE, commonly observed in terrestrial ecosystems (Kuzyakov et al., 2000) but often ignored in aquatic ecosystems (Guenet et al., 2010a), can also occur in freshwater ecosystems. Thus, mineralization of allochthonous organic matter such as eroded SOM might be strongly enhanced in aquatic ecosystems. Our results are consistent with previous studies, which demonstrated that inputs of allochthonous SOM in lakes generally lead to a dominance of heterotrophy over primary production at the ecosystem scale (del Giorgio et al., 1997; Cole et al., 2000; Duarte & Prairie, 2005). In the context of global change, this phenomenon must be taken into consideration to avoid substantial underestimation of $CO_2$ emissions from aquatic ecosystems to atmosphere due to soil erosion.

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# Chapitre V

# Influence de l’érosion des sols et de la structure des réseaux trophiques aquatiques sur les communautés biotiques et la sédimentation

# Influence of allochtonous carbon inputs and food-web structure on freshwater biotic communities and sedimentation process

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Keywords : allochthonous inputs, trophic cascade, organic matter composition, lipid biomarkers, ecological stoichiometry, nutrient cycling, mesocosms, pelagic compartments, sedimentation

**Abstract**

Soil erosion in freshwaters causes important changes in lake metabolism. The organic matter and the nutrients supplied by soil inputs can subsidize the whole food web from basal organisms to top-predators. Since the last two decades, the role of allochthonous organic matter as a basal resource for aquatic food webs in natural and controlled conditions has received a growing attention. In controlled conditions, these studies used artificial organic matter as a surrogate of allochthonous inputs, but the role of soil organic matter has never been taken into account. Here we studied the impact of soil on the functioning of lake ecosystems by performing monthly additions of soil in freshwater mesocosms. Moreover, the food-web structure was manipulated by addition of omnivorous fish to study the interactions between the bottom-up effects of soil addition and the top-down effects of fish on the biomass, the elemental and the biochemical compositions of pelagic compartments and sediment. Soil inputs had no effect on biomass, stoichiometry and lipid composition of seston and zooplankton but enhanced fish growth at the end of the experiment, and concentrations of daphniidae and calanoids only during the first step of the experiment. Soil treatment had several effects on the stoichiometry and on the lipid composition of short-term sediment. The biodegradability (as protein, sugar and bacterial biomarkers contents) of short-term sediment and sedimentation rates were not affected by soil inputs. Fish addition affected chlorophyll-a concentration of water, seston biomass, sedimentation rates, stoichiometry of seston, zooplankton and short-term sediment, and the lipid composition of short-term sediment. Fish addition did not change the biodegradability of short-term sediment and the percentages of losses of sediment over the whole experiment. Moreover, we did not observe any significant interaction between soil and fish treatments. Our results suggest that the addition of soil as allochthonous inputs to aquatic ecosystem induced a subsidize of the food web on fish, probably due to direct foraging on bottom sediment, and on particular groups of zooplankton, probably through direct consumption of terrestrial DOC and/or POC. Nevertheless, this process did not induce an effect on the biodegradability of short-term sediments. Therefore, allochthonous inputs appeared to have little effects on nutrient cycling. The predominance of the effects of food-web structure over the effects of allochthonous inputs and the absence of interaction between these top-down and bottom-up controls suggest that the impact of the bottom-up forces was small compared to the impact of top-down ones.

**Introduction**

Freshwater ecosystems, especially lakes, are fuelled by two contrasted sources of organic carbon. Within these ecosystems, autochthonous carbon is produced by autotrophic organisms via photosynthesis. By contrast, allochthonous organic carbon–mainly originates from the erosion of the surrounding watershed into lakes (Bloesch, 2004). In freshwaters, bacterial secondary production is supported by dissolved organic carbon (DOC) from both autochthonous sources (phytoplankton exudates and dead autochthonous organic matter) and allochthonous inputs (Sundh & Bell, 1992; Tranvik, 1992). The relative contributions of these two basal resources to supply aquatic food webs strongly depend on the ecosystem studied (Jansson et al., 2000, 2007; Cole et al, 2002; Hanson et al., 2003; Kritzberg et al., 2004; Weidel et al., 2008; Tranvik et al., 2009).

In ecosystems submitted to allochthonous inputs, terrigenous organic matter can be the major subsidy for bacterial production (Kritzberg et al., 2005). As a result, dominance of net heterotrophy (lake release of $CO_2$ to the atmosphere from bacterial respiration) over primary production (uptake of atmospheric $CO_2$) is widespread over world freshwaters (del Giogio et al. 1997, 1999; Cole et al., 2000; Duarte & Prairie, 2005; Duarte et al., 2008). This dominance has been attributed to three major processes. First, allochthonous inputs deliver huge amounts of DOC to freshwaters, increasing bacterial production compared to primary production (Berggren et al., 2010). Second, heterotrophic bacteria fuelled by terrestrial DOC can outcompete phytoplankton for inorganic nutrients since they have higher affinities for nitrogen and phosphorous (Blomqvist et al., 2001; Jansson et al., 2007). Third, allochthonous material often contains high amounts of humic substances and thus chromophoric DOM (CDOM), especially for freshwaters surrounded by forest-dominated watersheds (Steinberg, 2004). In addition to supporting bacterial production (Jones, 1992), CDOM is known to reduce light availability, leading to a decrease in primary production (Steinberg, 2004; Jansson et al., 2007). Therefore, consumption of terrestrially-derived bacterial biomass by bacterial consumers (protozoans, zooplankton) and, subsequently by their predators (insects, fishes, etc.) makes allochthonous inputs a significant subsidy for lake food webs (Pace et al., 2004; Carpenter et al., 2005; Cole et al, 2006; Jansson et al., 2007). Direct ingestion of allochthonous DOC and particulate organic matter (POC) by zooplankton and macroinvertebrates is an alternative pathway allowing the integration of terrestrial inputs

within aquatic food webs (Cole et al., 2011). Thus, allochthonous inputs may constitute an important resource for aquatic food webs and induce a strong bottom-up forcing on lake metabolism (Jansson et al., 2007).

The structure of aquatic communities is also strongly driven by the top-down control exerted by top-predators, in accordance with the trophic cascade theory, which predicts that each trophic level of a food web is inversely related to trophic levels immediately above and below it (Carpenter & Kitchell, 1993; Brett & Goldman, 1996). The general mechanism associated to trophic cascades is that an increase of predators decreases the abundance or alters the traits (size, behaviour) of their prey, thereby releasing the next lower trophic level from predation. Alternatively, a decrease of predators increases the abundance or alters the traits of their prey, thereby increasing the predation on the next lower trophic level. Numerous studies showed the importance of trophic cascades on nutrient dynamics (Vanni & Layne, 1997; Vanni et al., 1997), pelagic communities structure (Bertolo et al., 1999; Sommer, 2008, Berdjeb et al., 2011), stoichiometry in food webs (Danger et al., 2012), and sedimentation process (Bloesch & Burgi, 1989; Allard et al., 2011; Danger et al., 2012).

Studies on the combined effects of allochthonous inputs and changes in top-down control on aquatic food webs are scarce and led to contradictory results. As stated by the subsidy hypothesis (Lindeman, 1942; Polis & Strong, 1996), Leroux & Loreau (2008) predicted theoretically that allochthonous inputs should influence the strength of trophic links. On the other hand, Gruner et al. (2008) showed, in a meta-analysis, that interactions between bottom-up and top-down effects are rather rare and remain weak when they occur. In the same way, Faithfull et al. (2011), studying the interactions between allochthonous inputs (as glucose) and the addition of planktivorous fishes on pelagic communities in freshwater mesocosms, observed an effect only on the rotifer biomass.

Besides being scarce, studies focusing on the combined effects of allochthonous inputs and changes in top-down forces rarely dealt with the effects of these interactions on the sedimentation process despite its key role on the functioning of aquatic ecosystems (Spivak et al., 2007). Indeed, release of DOM and nutrients from bottom sediments can fuel both primary and bacterial productions (Reynolds, 1996; del Giorgio & Cole, 1998; Klump et al., 2009) and thus potentially subsidy the whole food web as a bottom-up forcing similar to allochthonous inputs (see chapter 2). Especially, the magnitude of this process depends on the biodegradability of the sediment, which has been shown to be closely linked to its

biochemical composition (Cranwell, 1981; Hulthe et al., 1998; Wakeham & Canuel, 2006; Canuel et al., 2007; Allard et al., 2011; Danger et al., 2012). Indeed, several compounds such as proteins, sugars, mono- and polyunsaturated fatty acids are known to be easily degradable by bacteria and essential for their growth (Cranwell, 1981; Rosenstock & Simon, 2001). Thus, their absolute and relative amounts in sediments are helpful to determine whether sediment will be subject to a rather low or high degradation.

Moreover, lipid biomarkers have been largely used to determine the relative contributions of autochthonous and allochthonous organic matter to sediments (Cranwell, 1982; Canuel & Martens, 1993; Niggeman & Schubert, 2006; Volkman, 2006; Bechtel, 2009a, b) and trophic interactions between producers and consumers (Brett & Müller-Navarra, 1997; Desvilettes et al., 1997; Müller-Navarra et al., 2000; von Elert et al., 2003; Masclaux et al., 2009). Despite the usefulness of lipid biomarkers for the study of trophic transfers from basal resources to higher trophic levels, they have been rarely used on allochthonous subsidies of aquatic food webs. Perga et al. (2009) used specific fatty acid biomarkers and showed that terrestrial inputs could support fish growth by feeding on zooplankton species that exhibited high amounts of terrestrial biomarkers. As well, Lau et al. (2008) showed with fatty acids biomarkers that a common snail from tropical streams preferentially grazed on autochthonous periphyton rather than allochthonous leaf litter. Moreover, their findings were corroborated by elemental analyses that supported the higher nutritional value of periphyton compared to leaf litter.

Stoichiometry is another tool that has been largely used to study transfers of energy and nutrients within the different trophic levels of aquatic food webs and their contribution to sedimentation (Elser et al., 1995, 2000, 2007; Dickman et al., 2006; Sterner et al., 2008; Danger et al., 2012). Moreover, the organic carbon/nitrogen (OC/N) ratio is a common proxy to determine the rather autochthonous or allochthonous origin of sediments (Martinova, 1993; Meyers & Ishiwatari, 1993; Meyers, 1997, 2003).

In this long-term study (20 months), we assessed the separate and the combined effects of allochthonous inputs and food-web structure on the biomass, the stoichiometry and the lipid composition of seston, zooplankton and short-term (1-week old) sediment. In contrast with other studies that used no*n*-natural carbon sources as allochthonous inputs (Kankaala et al., 2010; Faithfull et al., 2011; Bartels et al., 2012), we monthly added a natural soil into freshwater mesocosms to simulate watershed erosion. Addition or not of an omnivorous fish

(Goldfish, *Carassius auratus*) led to contrasted food-web structures. The content of very labile compounds (proteins and sugars) of short-term sediment was analysed as well to infer potential differences in sediment biodegradability between treatments. According to Jansson et al. (2007) and Weidel et al. (2008), we hypothesise that allochtonous inputs will increase top-predators biomass (zooplankton in fishless mesocosms and Goldfish in fish mesocosms). We expect a trophic cascade induced by fish addition that will increase seston biomass. Trophic cascade could in turn induce differences in the lipid composition of pelagic compartments and the biodegradability of short-term sediment (chapter 2). Finally, we will test the subsidy hypothesis, which states that ecosystems with the highest inputs of allochthonous matter will experience the strongest trophic cascades (see Leroux and Loreau, 2008). We will confront our results to those of Gruner et al. (2008) and Faithfull et al. (2011), which suggested on the contrary weak combined effects of allochthonous inputs and fish addition on food web structure. Last, we will test the occurrence of interaction effects between bottom-up and top-down forces on the composition of short-term sediment, as previously suggested by Spivak et al. (2007).

## Materials and methods

### *Experimental design*

This study took place in Centre de Recherche en Ecologie Expérimentale et Prédictive (CEREEP) located at Saint-Pierre-lès-Nemours, 85 km south from Paris. Twelve galvanized steel circular tanks sealed at the bottom were aligned in a field. Tanks had a volume of ca. 9 $m^3$ (1.5 m height × 2.8 m diameter). The inner surface of tanks was covered with a 1-mm thickness butyl liner for ensuring waterproofing of the systems. Chemically inert sand (Fontainebleau) was added at the bottom of tanks to create a mineral matrix supporting biotic developments. Tanks were randomly filled with tap water in early autumn 2009.

In the first step, watershed erosion (allochthonous inputs) into these shallow aquatic ecosystems was simulated by monthly inputs of dry soil in half of the tanks from March 2010 to June 2010 (soil treatment, S+), while the other tanks did not receive any soil input (S-). We

added monthly 2.5 kg of soil, which accounted for 100 g C $m^{-2}$ $year^{-1}$ of Mass Accumulation Rate (MAR) of bulk sediment (here soil; Dean et al., 1998). The soil was collected in the CEREEP field (sandy/meadow), sieved at 3 mm to remove large stones, grass and roots, air dried and stored in a dark place throughout the whole experiment.

In the second step, cross-treatment between soil inputs and manipulation of the food-web structure was studied. Soil treatment was similar to that of the first step. Food web structure was manipulated by addition of 12 Godfish individuals (*Carassius auratus auratus*, 11.0 ± 1.5 g fresh weight, 8.0 ± 0.4 cm length of caudal, mean ± SD) in half of the tanks submitted to either S- or S+ treatments (S-/F+ and S+/F+ treatments, respectively). The remaining 6 tanks were only submitted to S- or S+ treatments (S-/F- and S+/F- treatments, respectively). Fish were captured in late November 2011 and were weighted and sized (total length).

***Seston and zooplankton sampling***

Seston biomass and elemental composition were determined monthly. Water was sampled from March 2010 to November 2011 at different depths and locations in each tank with a 2-L sampling bottle (Uwitec). Water samples were filtered through 50-µm nylon filters to remove zooplankton, and then filtered on pre-weighted Whatman GF/F glass-fiber filter (nominal cut-off: 0.7 µm). Filters were dried overnight at 60°C and weighted to determine seston biomass. Dry filters were stored in the dark at room temperature until elemental and lipid analyses. Zooplankton biomass were determined monthly by sampling 60 L of water at different depths and locations in each tank with a 12-L sampling bottle equipped with a 50-µm filter. Zooplankton was gathered in GF/F-filtered water for several hours to allow evacuation of gut content. Zooplankton was concentrated through a 50-µm filter, washed with deionized water to remove particles (bacteria, phytoplankton, detritus) and dissolved matter bound to their shell, placed on a pre-weighted Whatman GF/A glass-fiber filter (nominal cut-off: 1.6 µm), and dried overnight at 60°C. Dry zooplankton was ground and stored in the dark at room temperature until elemental and lipid analyses.

***Particles and zooplankton counting***

An aliquot of 50-µm-filtered water was preserved in 4% formaldehyde. Particles ranging from 2 to 50 µm were counted with a Multisizer 4 Coulter Counter (Beckman Coulter) with a 100-µm probe. The specific composition of zooplankton was determined in June 2010 and June 2011 by sampling 60 L of water at different locations in three tanks of each treatment with a 12-L sampling bottle equipped with a 50-µm filter. Zooplankton was preserved in 4% formaldehyde. Zooplankton were identified and counted under a stereo-microscope on subsamples at different dilutions in Dollfuss chambers. Copepods were separated into cyclopoids, calanoids and nauplii. Cladocera were separated into *Daphnia*, *Ceriodaphnia*, and Chydoridae. Rotifers were counted globally.

***Sediment sampling***

Short-term sediments were sampled at the same dates of sampling of seston and zooplankton. Sedimentation rates were determined using sediment traps deployed in each tank. Fifty Traps consisting in PP tubes (17mm diameter × 118 mm long) were filled with little glass balls (ca. 10 mm high) to weight them down. Traps were suspended 10 cm above the bottom of the tanks and hanged far from the edges of the tanks to limit potential contamination by biofilm particles falling down from the mesocosm walls. The aim of this design was to limit contamination of traps by sediment resuspension from the bottom and to maximize the height of the water column to ensure the highest quantity of sedimented material. Traps were deployed for 7- to 9-day intervals and sediments sampled were referred as short-term sediments. Long-term sediments (LTS) were sampled using similar sediment traps that were used for short-term sediment. Long-term traps were deployed over the whole experiment. In tanks submitted to soil treatment (S+), sediment traps were dived only after complete soil sedimentation to avoid direct contamination by allochtonous inputs. Sediments collected from the fifty traps were pooled in a collection flask, allowed to sediment overnight at 4°C. The supernatant and zooplankton therein were removed. Sedimented material was freeze-dried, weighted, ground and stored in dry conditions until subsequent analyses. Sedimentation rates were calculated as the mass of dry matter divided by the duration of trap deployment and the total surface of the fifty traps, and expressed in g $m^{-2}$ $d^{-1}$.

*Calculation of annual losses of sediment and nutrients*

The quantity of sediment cumulated during one year, estimated as the sum of the quantities of short term-sediment sampled in sedimentation traps (CSTS), was compared with the stock of remaining sediment in traps deployed in the mesocosms throughout the experiment (long-term sediment LTS). The cumulated mass of recently deposited sediment (CSTS) represented the total quantity of matter sedimented (expressed as g DW $m^{-2}$) over one year. It was estimated from the measured short-term sedimentation rates (expressed as g DW $m^{-2}$ $d^{-1}$). As samplings of short-term sediment were not continuous over time, the sedimentation rate measured at the $i^{th}$ sampling date, $R_i$, was assumed constant over the time interval $\frac{[D_{i+1} - D_{i-1}]}{2}$, ($D_{i-1}$ and $D_{i+1}$ being the previous and the next dates of the $i$th sampling date, respectively). CSTS was thus calculated as the sum of $R_i \cdot \frac{[D_{i+1} - D_{i-1}]}{2}$ from March 2010 to November 2011, corresponding to the exposure time of LTS traps. Total loss of sediment (TLS) was calculated for each enclosure from the difference between CSTS and LTS (expressed as g DW $m^{-2}$). By subtracting LTS (which was exposed to environmental conditions during one year) from CSTS, we obtained a conservative estimate of sediment losses in the enclosures. TLS was expressed as a percentage of loss relative to CSTS, and was used as a global indicator of sediment biodegradability.

***Elemental composition of seston, zooplankton, soil and short-term sediment***

Carbon and nitrogen contents of dried samples were determined using a CHN elementary analyzer (FlashEA 1112 series, Thermo Fisher Scientific) with acetanilide as standard. Soil and short-term sediment organic carbon contents (OC) were determined after removal of inorganic carbon (IC) from sediment by successive additions of 1M HCl (Hedges & Stern, 1984).

***Sugar and protein colorimetric assays of soil and short-term sediment***

Freeze-dried sediments were extracted with $H_2O$ at 100°C for 2 h. The mixture was filtered through a Whatman GF/F glass-fiber filter, and the filtrate was freeze-dried. The freeze-dried aqueous extract was dissolved in a known volume of $H_2O$ and assayed for sugars and proteins. Sugar contents were determined by the phenol–sulfuric acid colorimetric method with glucose as standard (Dubois et al., 1956). Absorbances were measured at 490 nm. The protein contents were determined by the colorimetric method of Lowry with bovine serum albumin as standard. Absorbances were measured at 650 nm (Lowry et al., 1951). Sugar and protein contents were expressed as mg $g^{-1}$ soil dry weight (mg $g^{-1}$ DW).

***Lipid analysis***

All chemicals used were of analytical grade.

Apart from initial soil, analyses of lipids were carried out on three replicates for each treatment. Seston, zooplankton and short-term sediment sampled in June 2010 were analysed whereas, only short-term sediment sampled in June 2011 was analysed.

The Whatman GF/F glass-fiber filter with collected seston was extracted with a dichloromethane (DCM)/methanol (MeOH) (2/1, v/v) mixture at room temperature for 18 h. The mixture was filtered through a Whatman GF/F glass-fiber filter and solvent was removed under reduced pressure. Extraction of a GF/F glass-fiber filter in similar conditions was performed as control. Lipid analysis of the extract did not show any contamination from the filter. Extracts were saponified at 80°C for 2 h using 20 mL of 1 M KOH in MeOH. The pH of saponified extract was brought to 2 by addition of 6 M HCl. Lipids were extracted three times with 30 mL DCM. The organic phase was washed with deionized water until neutral pH, dried over $Na_2SO_4$ and DCM was removed under reduced pressure. Saponified lipids were treated with ca. 4 M HCl in MeOH (prepared by mixing acetyl chloride with MeOH (1/2.5 v/v) at 80°C for 1h to convert carboxyl groups into their methyl ester derivatives.

Esterified extract was then treated with a mixture of anhydrous pyridine/N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) (10/1, v/v) for 10 min at 60°C to convert hydroxyl groups into trimethylsilyl (TMS) ether groups. Lipid components (as methyl esters and TMS ethers) were analysed by gas chromatography mass spectrometry (GC–MS) with an Agilent 6890 gas chromatograph coupled to an Agilent 5973N mass spectrometer with electron ionization at 70 eV. Separation was achieved using a fused silica column coated with RTX5SilMS (30 m, i.d. 0.25 mm, film thickness 0.5 lm) with helium as carrier gas. The GC oven was programmed from 100 to 320°C at 4°C m*i*$n^{-1}$. Compound identifications were based on the NIST mass spectrum library or interpretation of the mass spectra. Unsaturated fatty acids were identified by comparison of retention times with standards (Larodan, Malmö, Sweden) using fused silica column coated with DB23 (60 m, i.d. 0.25 mm, film thickness 0.25 µm) with helium as carrier gas. The GC oven was programmed from 100 to 170°C at 6.5°C $min^{-1}$, then to 215°C at 2.75°C $min^{-1}$ and to 230°C at 40°C $min^{-1}$. Individual component contributions were determined by comparison of the peak areas from GC–MS traces. This method allowed a comparison of the relative abundance of each compound between the different samples analysed, but does not allow the quantification of individual compounds of the total lipids. Dried zooplankton samples were extracted, and the lipid fraction analysed as described for seston. The amounts of extracted lipids were too low to allow an accurate weight determination.

Freeze-dried sugar- and protei*n*-free sediment samples were extracted with a chloroform ($CHCl_3$)/MeOH (2/1, v/v) mixture for 2 h at 80°C. Lipid extracts were saponified, derivatized and analysed as described for seston.

***Physico-chemical measurements and phosphate colorimetric assays***

pH, specific conductance ($C_{25}$), chromophoric DOM (CDOM), total chlorophyll-a concentrations and light penetration of the water column were measured at each sampling date from July 2010 to November 2011 with a multi-sensor probe CTD-90 (ASD-sensors,

Trappenkamp, Germany). Orthophosphate concentration of water was determined by the phosphorus-ammonium molybdate spectrometric method (AFNOR, 2004).

***Statistical analyses***

Statistical analyses were performed using R software (www.r-project.org). For the first step of the experiment, one–way ANOVAs with time as a repeated measure were used to test the effects of soil treatment (S- and S+) and time on biomass and elemental composition of seston and zooplankton, on taxonomic composition of zooplankton, and on sedimentation rates and elemental composition of short-term sediment. Effects of S+ treatment on fish growth, lipid biomarkers of seston, zooplankton and short-term sediment and protein and sugar contents of short-term sediment sampled in June 2010 were tested with one-way ANOVAs.

For the second step of the experiment, two–way ANOVAs with time as a repeated measure were used to test separate and combined effects of soil and fish (F- and F+) treatments and time on the biomass and elemental composition of seston and zooplankton, on sedimentation rates, CSTS, LTS and TLS, elemental composition of short-term sediment and physical parameters, and orthophosphate concentration of water. Effects of soil and fish treatments on lipid biomarkers of short-term sediment sampled in June 2011 were tested with one-way ANOVAs. Phytoplankton contribution to seston was assessed by simple linear regression between seston biomass and chlorophyll-a measurements.

Data were log transformed when necessary to normalize distributions and homogenize variances. A significant threshold of $p < 0.05$ was chosen for all analyses.

**Results**

The detailed distributions of lipids of seston, zooplankton, short-term sediment sampled in June 2010, and short-term sediment sampled in June 2011 were reported in the appendix associated to this chapter.

***Elemental and biochemical composition of the initial soil***

C, OC and N contents of initial soil were respectively 1.2, 0.5 and 0.1% of DW and OC/N ratio was 5.0 (Table 1). This soil contained 3.8, 0.6, 0.9 and 0.4 mg $g^{-1}$ soil DW hydrophilic compounds, sugars, proteins and lipids, respectively (Table 1).

The lipid composition of the soil was reported in Fig 1. Fatty acids (FAs) dominated the lipid distribution (45.8% of total lipids). Saturated fatty acids (SAFAs) were dominated by long-chain SAFAs (LCSAFAs; $C \geq 20$; 23.5% of total lipids; Fig. 1) ranging from *n*-$C_{20}$ to *n*-$C_{36}$. The series exhibited a stron even over odd predominance with *n*-$C_{22}$, *n*-$C_{24}$ and *n*-$C_{26}$ homologues as the major constituents. Short-chain SAFAs (SCSAFAs; $C < 20$; 7.7% of total lipids) was largely dominated by *n*-$C_{16}$ homologue. Monounsaturated fatty acids (MUFAs; Fig. 1) accounted for 8.6% of total lipids and were dominated by 16:1ω7 and 18:1ω9 homologues. Polyunsaturated fatty acids (PUFAs) accounted for 1.7% of total lipids and were dominated by 18:2ω6 homologue. Bacterial fatty acids (BACTFAs), defined as the sum of short-chain odd numbered and branched FAs accounted for 4.4% of total lipids.

Alkanols, ranging from *n*-$C_{12}$ to *n*-$C_{36}$, accounted for 29.3% of total lipids and exhibited a strong even over odd predominace. Long-chain alkanols largely dominated (28.3% of total lipids), with $C_{26}$ as the major component.

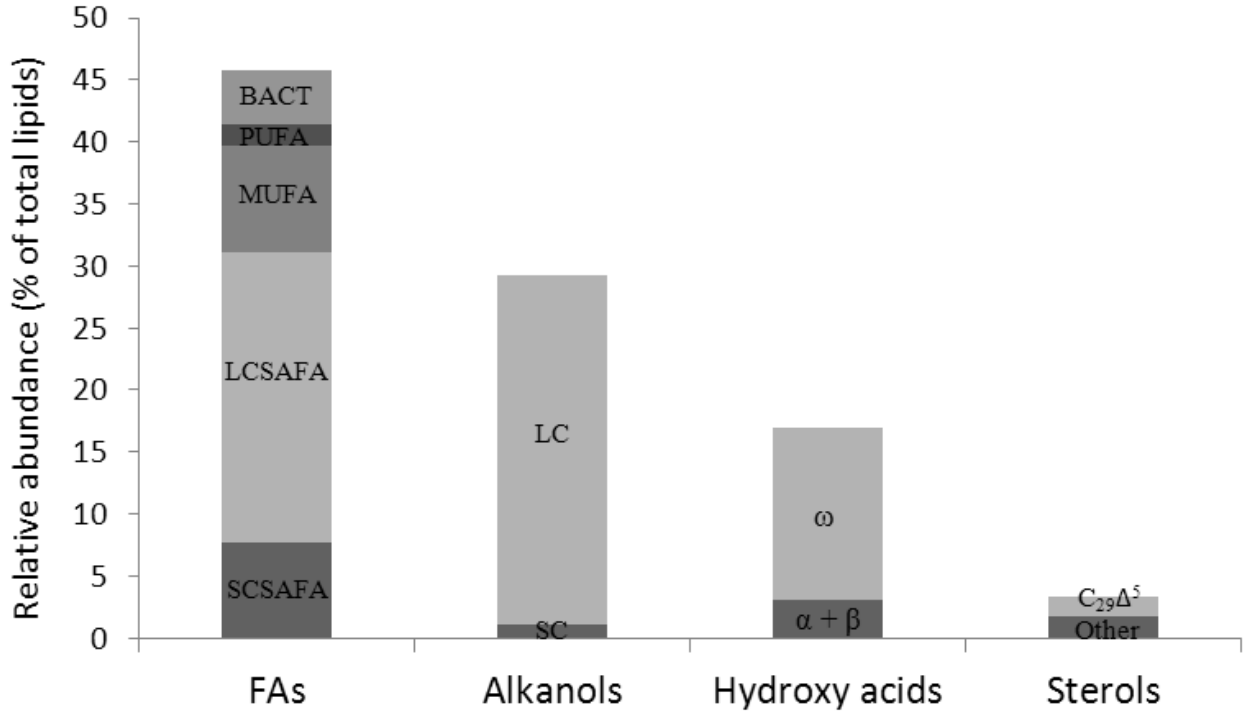
Sterols (3.3% of total lipids; Fig. 1) were largely dominated by 24-ethylcholest-5-enol ($C_{29}\Delta^5$:) which accounted for ca. 46% of total sterols. 24-Methylcholest-5-enol ($C_{28}\Delta^5$; 16.9% of total sterols), 24-ethylcholesta-5,22-dienol ($C_{29}\Delta^{5,22}$; 13.0% of total sterols) and cholesterol ($C_{27}\Delta^5$; 11.6% of total sterols) were present in lower relative amounts.

Hydroxy acids (17.0% of total lipids) were dominated by ω-hydroxy acids (13.9% of total lipids) with $C_{22}$ and $C_{24}$ homologues as the major components (ca. 55% of total hydroxy acids). α- and β-Hydroxy acids accounted for 3.1% of total lipids.

**Table 1:** Elemental (% DW) and biochemical compositions (mg $g^{-1}$ DW) of the initial soil.

| | C | OC | N | OC/N | Hydrophilic compounds | Sugars | Proteins | Lipids |
|---|---|---|---|---|---|---|---|---|
| Soil | 1.2 | 0.5 | 0.1 | 5.0 | 3.8 | 0.6 | 0.9 | 0.4 |

**Figure 1**: Lipid distribution of the soil (% of total lipids). SCSAFA: short-chain (C < 20) saturated fatty acids. LCSAFA: long-chain (C ≥ 20) fatty acids. MUFA: monounsaturated fatty acids. PUFA: polyunsaturated fatty acids. BACTFAS: bacterial fatty acids (sum of short-chain odd numbered and branched SAFAs). SC: short-chain alkanols. LC: long-chain alkanols. α, β: sum of α- and β-hydroxy acids. ω: ω-hydroxy acids. $C_{29}\Delta^5$: 24-ethylcholest-5-enol (sitosterol). Other: remaining sterols.



***First step: soil treatment***

*Seston*

The term "seston" refers to particulate matter between 0.7 and 50 µm diameter.

The biomass and the elemental composition of seston did not differ between S- and S+ treatments (Table 2). Particle concentration and size distribution of particles did not differ between S- and S+ treatments (55155 ± 27778 particles $L^{-1}$ and 66329 ± 34460 particles $L^{-1}$, respectively; n = 36, $P = 0.22$).

Soil treatment had no significant effect on the relative amounts of the different lipid classes of seston sampled in June 2010 (Table 3).

FAs dominated the lipid composition of seston (ca. 68% of total lipids). SAFAs accounted for ca. 78% of total FAs and were largely dominated by *n*-$C_{16}$ and *n*-$C_{18}$ homologues. MUFAs accounted for ca 8% of total FAs and were dominated by 16:1ω7, 18:1ω9 and 18:1ω7 homologues. PUFAs accounted for ca. 2% of total FAs and were dominated by 18:3ω3 homologue. BACTFAS accounted for ca. 12% of total FAs.

Alkanols accounted for ca. 20% of total lipids of seston (Table 3) with *n*-$C_{18}$, *n*-$C_{28}$ and *n*-$C_{30}$ homologues as the major components (ca. 73% of total alkanols). Sterols accounted for ca. 3.5% of total lipids of seston (Table 3). 24-Ethylcholest-5-enol ($C_{29}\Delta^5$) dominated the sterol distribution (ca. 42% of total sterols) followed by cholesterol ($C_{27}\Delta^5$; ca. 26% of total sterols) and 24-methylcholest-5-enol ($C_{28}\Delta^5$; ca. 12% of total sterols).

Hydroxy acids accounted for ca.4.5% of total lipids of seston. α- and β-Hydroxy acids, ranging from $C_{16}$ to $C_{26}$, dominated (ca. 82% of total hydroxy acids). They exhibited a strong even over odd predominance with $C_{24}$ homologue as the major component. ω-Hydroxy acids accounted for ca.12% of total hydroxy acids with $C_{22}$ homologue largely dominating.

A series of botryococcenes, typical triterpenoid hydrocarbons of the B race of the alga *Botryococcus braunii* (Metzger & Largeau, 2005), were observed. They accounted for ca. 3% of total lipids and were largely dominated by $C_{34}$ isomeric botryococcenes.

Chlorophyll-derived compounds, which are biomarkers for alga-derived chlorophyll (Rontani & Volkman, 2003), accounted for ca. 0.5% of total lipids of seston.

*Zooplankton*

The biomass and the elemental composition of zooplankton did not differ between soil treatments. Only the C content of zooplankton from S+ tanks was slightly significantly higher than that of zooplankton from S- tanks (n = 48; $P$ = 0.048; Table 2). Concentrations of daphniidae and calanoids were higher in S+ tanks than in S- ones (Table 4).

Except for FAs and botryococcenes, soil treatment had no effect on the relative amounts of the different lipid classes of zooplankton sampled in June 2010 (Table 3).

FAs dominated the lipid composition of zooplankton from both treatments. The contribution of FAs to the total lipids was higher in zooplankton from S+ treatment than in zooplankton from S- treatment (72.3 ± 6.5 and 50.9 ± 1.3 % of total lipids, respectively; n = 6; $P$ = 0.0051). However, no significant differences were observed between FA compositions of zooplankton from both treatments. SAFAs accounted for ca.51% of total FAs and were dominated by *n*-$C_{16}$ and *n*-$C_{18}$ homologues (ca. 43% of total FAs). MUFAs accounted for ca. 21% of total FAs with 18:1ω9, 18:1ω7 and 16:1ω7 as the major components (ca. 19% of total FAs). PUFAs accounted for ca 18% of total FAs. SCPUFAs (ca. 11% of total FAs) were dominated by 18:3ω3 and 18:2ω6. LCPUFAs (ca. 6% of total FAs) were dominated by 22:6ω3 (docosahexaenoic acid, DHA), 20:5ω3 (eicoapentaenoic acid, EPA) and 20:4ω6 (arachidonic acid, ARA). BACTFAs accounted for ca. 9% of total FAs

Alkanols accounted for ca. 10% of total lipids of zooplankton and were dominated by *n*-$C_{18}$ (ca. 60% of total alkanols), *n*-$C_{28}$ (ca. 11% of total alkanols) and *n*-$C_{30}$ (ca. 8% of total alkanols) homologues.

Sterols accounted for ca. 4.7 % of the total lipids of zooplankton. Cholesterol ($C_{27}\Delta^5$) largely dominated the sterol distribution of zooplankton (ca. 69% of total sterols) followed by 24-ethylcholest-5-enol ($C_{29}\Delta^5$, ca. 14% of total sterols).

**Table 2:** Biomass (mg $L^{-1}$) and elemental composition (% DW) of seston and zooplankton sampled from February to June 2010 (mean ± SD; n = 18). Sedimentation rates (g DW $m^{-2}$ $d^{-1}$), elemental composition (% DW) and biochemical composition (mg $g^{-1}$ DW) of short-term sediment sampled in May and June 2010 (mean ± SD; n = 12). Significant effects are in bold.

| **Step 1** | Soil Treatment | | RM-ANOVA (*P* values) | | |
|---|---|---|---|---|---|
| | S- | S+ | Soil | Time | Soil × Time |
| **Seston** | | | | | |
| *Biomass* | 2.14 ± 1.33 | 1.91 ± 1.31 | 0.74 | **< 0.0001** | 0.98 |
| C | 58.4 ± 33.8 | 60.3 ± 32.7 | 0.67 | **0.0001** | 0.77 |
| N | 9.2 ± 6.9 | 9.4 ± 6.0 | 0.58 | **< 0.0001** | 0.84 |
| C/N | 6.4 ± 1.6 | 6.4 ± 1.1 | 0.70 | **< 0.0001** | 0.83 |
| **Zooplankton** | | | | | |
| Biomass | 0.30 ± 0.39 | 0.27 ± 0.21 | 0.42 | **< 0.0001** | 0.99 |
| C | **19.0 ± 14.3** | **24.4 ± 14.9** | **0.048** | **< 0.0001** | 0.062 |
| N | 3.5 ± 3.1 | 4.3 ± 3.3 | 0.12 | **< 0.0001** | 0.24 |
| C/N | 5.5 ± 3.8 | 5.7 ± 3.4 | 0.99 | **< 0.001** | 0.93 |
| **Short-term sediment** | | | | | |
| Sedimentation rate | 1.88 ± 2.38 | 3.11 ± 3.31 | 0.31 | **< 0.0001** | 0.53 |
| C | **20.3 ± 1.7** | **13.0 ± 2.5** | **< 0.0001** | 0.76 | 0.62 |
| N | **1.7 ± 0.4** | **1.2 ± 0.4** | **0.0084** | 0.10 | 0.69 |
| C/N | 12.1 ± 3.0 | 10.9 ± 2.0 | 0.22 | **0.012** | 0.31 |

| | | | | | |
|---|---|---|---|---|---|
| OC [a] | **10.6 ± 3.3** | **5.9 ± 0.7** | **0.035** | - | - |
| OC/N [a] | 6.2 ± 1.1 | 4.9 ± 0.7 | 0.16 | - | - |
| Hydrophilic compounds [a] | 145.0 ± 25.1 | 97.7 ± 43.7 | 0.20 | - | - |
| Sugars [a] | 24.4 ± 8.1 | 13.4 ± 2.6 | 0.79 | - | - |
| Proteins [a] | 30.8 ± 17.2 | 16.7 ± 9.3 | 0.75 | - | - |
| Lipids [a] | 26.4 ± 12.2 | 15.6 ± 7.7 | 0.30 | - | - |

[a] analyses were performed only on sediments sampled in June 2010; n = 6

.

**Figure 2:** Seasonal variations of (a) seston and (b) zooplankton biomass and (c) sedimentation rates (mean ± SE).

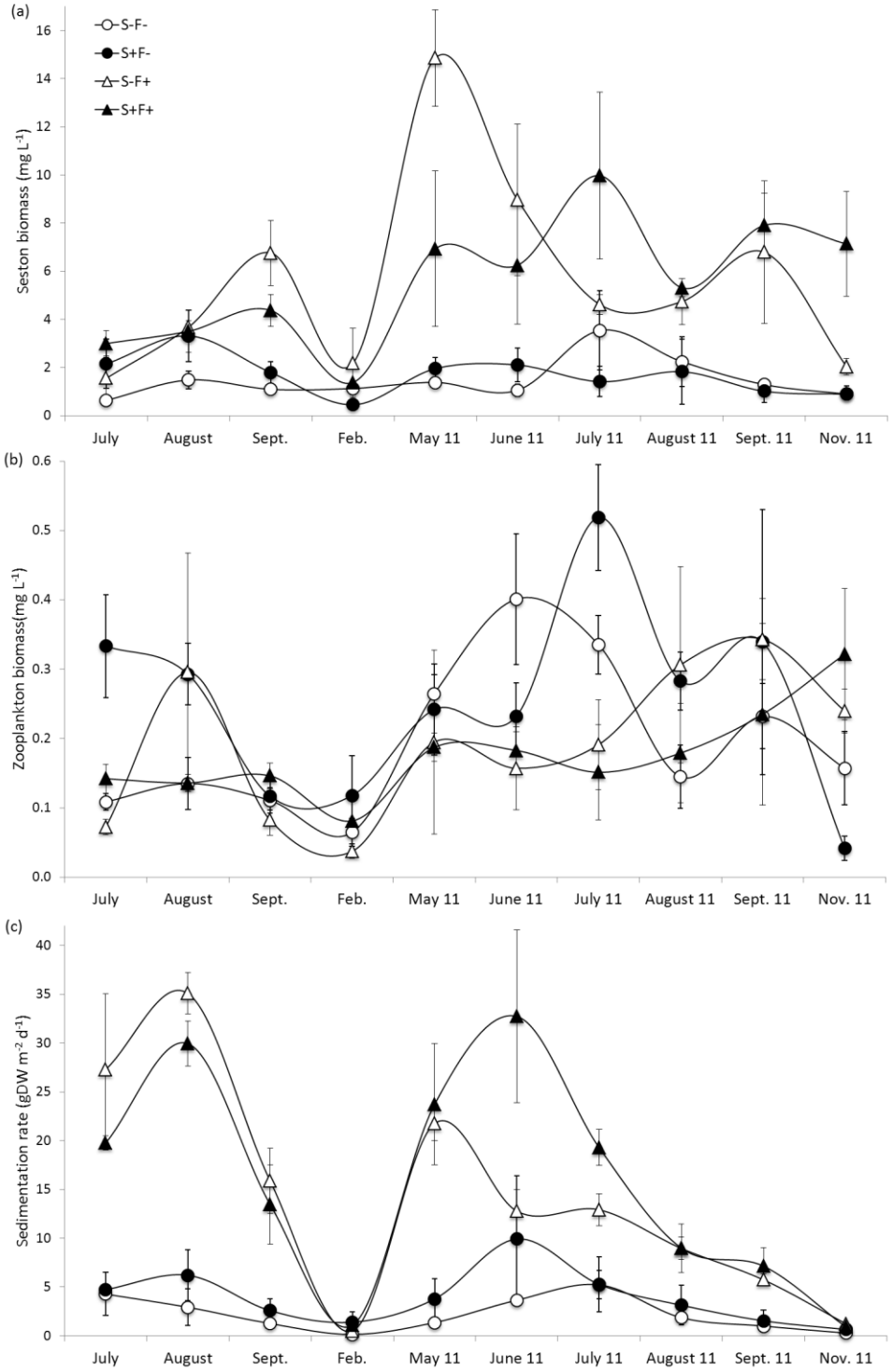


**Table 3:** Lipid composition (% of total lipids) of seston, zooplankton and short-term sediment sampled in June 2010 (mean ± SD; n = 3). Subclasses of FAs, alkanols, sterols and hydroxy acids are expressed as % of their respective class. SCSAFAs and LCSAFAs were expressed as % of total FAs. Significant effects are in bold.

| **June 2010** | Seston | | Zooplankton | | Short-term sediment | |
|---|---|---|---|---|---|---|
| | S- | S+ | S- | S+ | S- | S+ |
| **Fatty acids** | 64.9 ± 7.5 | 70.3 ± 8.7 | **50.9 ± 1.3** | **72.3 ± 6.5** | 89.1 ± 3.1 | 85.0 ± 1.6 |
| Saturated | 77.3 ± 4.8 | 78.6 ± 5.1 | 51.4 ± 4.8 | 51.5 ± 9.4 | 48.9 ± 14.2 | 54.1 ± 2.9 |
| *SCSAFAs* | 60.7 ± 3.9 | 63.2 ± 2.5 | 43.5 ± 2.5 | 46.8 ± 6.7 | 45.7 ± 13.2 | 47.6 ± 1.9 |
| *LCSAFAs* | 16.7 ± 1.9 | 15.4 ± 2.9 | 7.9 ± 2.7 | 4.7 ± 3.0 | 3.2 ± 1.0 | 6.5 ± 2.1 |
| Monounsaturated | 8.1 ± 1.5 | 8.5 ± 4.2 | 19.8 ± 4.8 | 22.8 ± 7.8 | 24.9 ± 6.2 | 28.4 ± 1.5 |
| Polyunsaturated | 1.8 ± 0.8 | 2.4 ± 1.2 | 18.4 ± 2.0 | 17.1 ± 3.9 | 20.7 ± 18.2 | 10.3 ± 2.1 |
| *SCPUFAs* | 1.7 ± 0.8 | 2.2 ± 1.2 | 10.4 ± 0.9 | 12.4 ± 3.5 | 19.9 ± 18.1 | 9.3 ± 2.1 |
| *LCPUFAs* | 0.1 ± 0.0 | 0.1 ± 0.1 | 8.0 ± 1.8 | 4.7 ± 2.4 | 0.8 ± 0.2 | 1.0 ± 0.1 |
| BACTFAs | 12.8 ± 2.8 | 10.5 ± 1.0 | 10.4 ± 0.9 | 8.6 ± 2.1 | 5.4 ± 1.1 | 7.2 ± 1.1 |
| **Alkanols** | 22.3 ± 5.5 | 18.7 ± 8.7 | 9.5 ± 3.0 | 10.9 ± 7.3 | 3.8 ± 1.4 | 5.5 ± 0.6 |
| SC alkanols | 47.2 ± 22.0 | 55.7 ± 22.1 | 65.9 ± 6.0 | 77.3 ± 6.2 | **59.7 ± 6.9** | **41.4 ± 5.2** |
| LC alkanols | 52.8 ± 22.0 | 44.3 ± 22.1 | 34.1 ± 6.0 | 22.7 ± 6.2 | **40.3 ± 6.9** | **58.6 ± 5.2** |
| **Sterols** [(a)] | 3.7 ± 1.1 | 3.3 ± 0.3 | 4.1 ± 0.3 | 5.3 ± 1.7 | 2.1 ± 0.9 | 2.8 ± 0.7 |
| $C_{27}\Delta^5$ | 29.2 ± 7.4 | 23.5 ± 4.7 | 69.6 ± 2.8 | 69.1 ± 11.5 | 52.6 ± 14.2 | 56.6 ± 2.9 |
| $C_{27}\Delta^0$ | 1.7 ± 1.0 | 1.8 ± 0.1 | 1.5 ± 0.4 | 0.9 ± 0.1 | 2.1 ± 0.3 | 2.7 ± 1.3 |
| $C_{29}\Delta^5$ | 37.4 ± 9.9 | 46.3 ± 7.8 | 13.2 ± 1.8 | 14.4 ± 6.3 | 25.5 ± 11.4 | 19.4 ± 3.6 |

| | | | | | | |
|---|---|---|---|---|---|---|
| **Hydroxy acids** | 5.2 ± 1.0 | 4.0 ± 0.5 | 2.5 ± 0.6 | 1.8 ± 0.7 | **1.4 ± 0.5** | **2.6 ± 0.3** |
| a- + β-hydroxy acids | 86.0 ± 3.2 | 87.6 ± 3.3 | 86.9 ± 4.7 | 92.1 ± 3.0 | **93.2 ± 1.4** | **88.1 ± 2.4** |
| ω- hydroxy acids | 14.0 ± 3.2 | 12.4 ± 3.3 | 13.1 ± 4.7 | 7.9 ± 3.0 | **6.8 ± 1.4** | **11.9 ± 2.4** |
| **Botryococcenes** | 3.1 ± 4.0 | 3 .0 ± 3.9 | **31.5 ± 3.6** | **7.9 ± 2.8** | 0.4 ± 0.7 | 0.1 ± 0.1 |
| **Chlorophyll-derived compounds** | 0.5 ± 0.2 | 0.5 ± 0.2 | 1.0 ± 0.3 | 1.1 ± 0.2 | 2.4 ± 1.1 | 2.7 ± 0.4 |

[(a)] $C_{27}\Delta^5$ : cholesterol; $C_{27}\Delta^0$ : cholestanol; $C_{29}\Delta^5$ : 24-ethylcholest-5-enol

**Table 4:** Mean specific composition of zooplankton communities (individual $L^{-1}$) sampled in June 2010. Mean ± SD. Significant effects are in bold

| June 2010 | Treatment | | RM-ANOVA (*P* values) |
|---|---|---|---|
| | S- | S+ | Soil |
| **Copepods** | 121.9 ± 30.5 | 168.1 ± 100.1 | 0.57 |
| Cyclopoids | 18.4 ± 15.3 | 8.1 ± 6.1 | 0.13 |
| Calanoids | 10.1 ± 5.8 | 29.6 ± 17.6 | **0.04** |
| Nauplii | 93.4 ± 21.5 | 130.4 ± 91.8 | 0.69 |
| **Cladocerans** | 4.1 ± 5.4 | 16.7 ± 12.6 | 0.073 |
| *Daphnia* | 0.1 ± 0.2 | 6.5 ± 6.1 | **0.0017** |
| *Ceriodaphnia* | 3.7 ± 5.7 | 9.9 ± 12.7 | 0.35 |
| Chydoridae | 0.4 ± 0.5 | 0.0 ± 0.1 | 0.13 |
| **Rotifers** | 188.1 ± 144.1 | 382.8 ± 519.8 | 0.81 |

Hydroxy acids accounted for ca.2% of total lipids of zooplankton. α- and β-Hydroxy acids strongly dominated the distribution (ca. 88% of total hydroxy acids) with α-$C_{22}$, α-$C_{23}$ and α-$C_{24}$ homologues as the major components. ω-Hydroxy acids (ca. 12% of total hydroxy acids) were largely dominated by $C_{22}$ homologue.

The relative contribution of botryococcenes to total lipids was lower in zooplankton from S+ tanks than in zooplankton from S- tanks (7.9 ± 2.8 and 31.5 ± 3.6 % of total lipids, respectively; n = 6; $P = 0.0008$).

Chlorophyll-derived compounds accounted for ca. 1% of total lipids of zooplankton.

*Short-term sediment*

Short-term sediment was sampled only in May and in June 2010. Only short-term sediment sampled in June 2010 was analysed for lipids and hydrophilic components.

The sedimentation rates did not differ between S- and S+ treatments (Table 2). C, OC and N contents of short-term sediment from S+ tanks were lower than those of short-term sediment from S- tanks (Table 2). However, no effect of soil treatment on C/N and OC/N ratios was observed.

Except for alkanols and hydroxy acids, soil treatment had no effect on the relative amounts of the different lipid classes of short-term sediment sampled in June 2010 (Table 3).

FAs dominated the lipid composition of short-term sediment (ca. 87% of total lipids). SAFAs accounted for ca.51% of total FAs and were largely dominated by *n*-$C_{16}$ homologues. MUFAs accounted for ca. 26% of total FAs and were dominated by 16:1ω7, 18:1ω9and 18:1ω7. PUFAs accounted for ca. 16% of total FAs and were dominated by 18:2ω6 and 18:3ω3. BACTFAS accounted for ca. 6% of total FAs.

Alkanols accounted for ca. 4.5% of total lipids of short-term sediment. The relative abundance of long-chain alkanols was higher in short-term sediment from S+ treatment than in short-term sediment from S- treatment (58.6 ± 5.2 and 40.3 ± 6.9 % of total alkanols, respectively; n = 6; $P = 0.0021$). For both treatments short-chain alkanols were dominated by *n*-$C_{18}$ homologue and long-chain alkanols were dominated by even numbered homologues from *n*-$C_{20}$ to *n*-$C_{30}$.

Sterols accounted for ca. 2.5 % of total lipids of short-term sediment. Cholesterol ($C_{27}\Delta^5$) dominated the sterol distribution of short-term sediment (ca. 55% of total sterols) followed by 24-ethylcholest-5-enol ($C_{29}\Delta^5$, ca. 23% of total sterols).

The relative amount of hydroxy acids was higher in short-term sediment from S+ treatment than in short-term sediment from S- treatment (2.6 ± 0.3 and 1.4 ± 0.5 % of total lipids, respectively; n = 6; $P = 0.035$). For both treatments a strong dominance of α- and β-hydroxy acids was observed (ca. 90% of total hydroxy acids). For both treatments, α- and β-hydroxy acids were dominated by α- and β-$C_{16}$, α- and β-$C_{15}$ and α- and β-$C_{18}$ homologues. The relative abundance of ω-hydroxy acids was higher in short-term sediment from S+ treatment than in short-term sediment from S- treatment (11.9 ± 2.4 and 6.8 ± 1.4 % of total hydroxy acids, respectively; n = 6; $P = 0.013$). For both treatments, $C_{22}$ homologue dominated the distribution of ω-hydroxy acids.

Botryococcenes and chlorophyll-derived compounds accounted respectively for ca. 0.2

and 2.5 % of total lipids of short-term sediment.

***Second step: soil and fish cross-treatment***

Although significant, seasonal variations of physico-chemical measurements, biomass and elemental compositions of seston, zooplankton and, sedimentation rates and elemental composition of short-term sediment were idiosyncratic at this scale of analysis.

*Physico-chemical measurements*

*Soil effects* - Temporal means of physico-chemical measurements were reported in Table 5. Specific conductance and CDOM concentration measured in S+ tanks were on average higher than those measured in S- tanks. Soil treatment had no effect on pH, chlorophyll-a concentration and light penetration.

*Fish effects* - pH and chlorophyll-*a* concentrations measured in fish tanks (F+) were higher than those measured in fishless ones (F-). CDOM concentrations exhibited an opposite trend. Fish treatment had no effect on specific conductance and light penetration (Table 5).

*Soil × fish interaction effects* - The interaction effect between soil and fish treatments was only significant for specific conductance. Differences in specific conductance observed between soil treatments were higher for F+ than for F- treatment (data not shown).

***Orthophosphate concentration of water***

Soil, fish and interaction between soil and fish treatments had no effect on orthophosphate concentration of water (Table 5).

**Table 5:** Seasonal means of physico-chemical parameters and orthophosphate concentration of the water column measured from June 2010 to November 2011 (mean ± SD; n = 60). S- and S+ values are means of both fish treatments. F- and F+ values are means of both soil treatments. RM-ANOVAs were performed on individual treatments (ie. S-F-, S-F+, S+F- and S+F+). Significant effects are in bold.

| | Soil treatment | | Fish treatment | | RM-ANOVA (*P* values) | | |
|---|---|---|---|---|---|---|---|
| | S- | S+ | F- | F+ | Soil | Fish | Soil × Fish |
| pH | 8.6 ± 0.3 | 8.4 ± 0.3 | **8.4 ± 0.3** | **8.6 ± 0.4** | 0.17 | **0.012** | 0.29 |
| $C_{25}$ (µS $cm^{-1}$) | **304.9 ± 25.7** | **343.2 ± 16.5** | 327.1 ± 19.9 | 320.6 ± 36.8 | < **0.0001** | 0.14 | **0.0011** |
| Chromophoric DOM (µg $L^{-1}$) | **64.4 ± 27.9** | **134.0 ± 30.9** | **105.3 ± 45.1** | **92.3 ± 46.9** | < **0.0001** | **0.0008** | 0.057 |
| Chlorophyll-a (µg $L^{-1}$) | 4.8 ± 2.2 | 6.7 ± 3.6 | **4.1 ± 1.6** | **7.7 ± 3.4** | **0.073** | **0.0003** | 0.90 |
| Light penetration (%) | 32.9 ± 8.0 | 32.7 ± 7.6 | 33.0 ± 8.2 | 32.6 ± 7.4 | 0.88 | 0.61 | 0.41 |
| Orthophosphate (µg $L^{-1}$) | 3.1 ± 2.0 | 3.0 ± 2.4 | 2.5 ± 1.8 | 3.7 ± 2.5 | 0.48 | 0.065 | 0.99* |

*Seston*

*Soil effects* - Soil treatment had no effect on biomass and elemental composition of seston (Table 6, Fig. 2a), and on particle concentration and size distribution of particles (data not shown). Significant linear regressions between seston biomass and chlorophyll-a concentration were observed for both S- ($P < 0.001$, $R^2 = 0.39$, n = 43) and S+ ($P = 0.01$, $R^2 = 0.16$, n = 46) treatments. However, linear regressions had similar slopes for both soil treatments (data not shown).

*Fish effects* - Seston biomass was higher in F+ tanks than in F- tanks (Table 6, Fig. 2a). The number of particles ranging from 2 to 50 µm was higher in F+ tanks than in F- tanks (220161 ± 168352 and 101983 ± 106566 particles $L^{-1}$, respectively, n = 120, $P = 0.039$). Fish treatment had no effect on the mean size of 90% of particles (2.8 ± 1.0 µm, n= 120: 12 tanks × 10 sampling dates, $P = 0.4$). C and N contents of seston were higher in the presence of fish whereas, C/N ratio was not affected by fish addition.

*Soil × fish interaction effects* - We did not observe any significant interaction effect between soil and fish treatments on biomass and elemental composition of seston. On average, seston biomass was the lowest in February and in November 2011 for the four treatments (S-, S+, F- and F+). The interaction between soil and fish treatments did not affect particle size (n = 120, $P = 0.15$).

**Table 6**: Biomass (mg $L^{-1}$) and elemental composition (% DW) of seston and zooplankton sampled from July 2010 to November 2011(mean ± SD; n = 60). Sedimentation rates (g DW $m^{-2}$ $d^{-1}$) and elemental composition (% DW) of short-term sediment sampled from July 2010 to November 2011 (mean ± SD; n = 60). S- and S+ values are means of both fish treatments. F- and F+ values are means of both soil treatments. RM-ANOVAs were performed on individual treatments (ie. S-F-, S-F+, S+F- and S+F+). Significant effects are in bold.

| **Step 2** | Soil treatment | | Fish treatment | | RM-ANOVA (*P* values) | | | |
|---|---|---|---|---|---|---|---|---|
| | S- | S+ | F- | F+ | Soil | Fish | Time | Soil × Fish |
| **Seston** | | | | | | | | |
| Biomass | 3.55 ± 3.93 | 3.67 ± 3.40 | **1.59 ± 1.28** | **5.60 ± 4.14** | 0.56 | < **0.0001** | < **0.0001** | 0.74 |
| C | 35.5 ± 16.1 | 35.4 ± 16.9 | **39.1 ± 20.7** | **31.8 ± 9.3** | 0.61 | **0.015** | **0.0002** | 0.15 |
| N | 4.0 ± 2.1 | 3.8 ± 2.2 | **4.4 ± 2.6** | **3.3 ± 1.3** | 0.68 | **0.021** | **0.0001** | 0.89 |
| C/N | 8.9 ± 2.7 | 9.3 ± 2.2 | 8.9 ± 2.6 | 9.6 ± 1.3 | 0.88 | 0.21 | **0.0007** | 0.27 |
| **Zooplankton** | | | | | | | | |
| Biomass | 0.19 ± 0.14 | 0.21 ± 0.15 | 0.22 ± 0.15 | 0.18 ± 0.14 | 0.49 | 0.26 | < **0.0001** | 0.83 |
| C | 43.4 ± 10.0 | 45.9 ± 9.1 | **41.8 ± 5.3** | **47.5 ± 11.9** | 0.11 | **0.016** | < **0.0001** | 0.63 |
| N | 7.4 ± 2.3 | 7.4 ± 2.2 | **8.4 ± 1.7** | **6.4 ± 2.3** | 0.90 | **0.0002** | **0.005** | 0.19 |
| C/N | 5.9 ± 4.6 | 6.2 ± 4.7 | **5.0 ± 2.0** | **7.4 ± 5.6** | 0.46 | **0.0004** | < **0.0001** | 0.47 |
| **Short-term sediment** | | | | | | | | |
| Sedimentation rate | 8.34 ± 10.32 | 9.81 ± 10.91 | **3.11 ± 3.73** | **14.96 ± 11.85** | 0.44 | **0.0006** | < **0.0001** | 0.58 |
| C | **23.1 ± 5.6** | **13.7 ± 5.0** | 18.9 ± 5.6 | 17.9 ± 8.2 | < **0.0001** | 0.053 | < **0.0001** | 0.26 |
| N | **2.1 ± 0.8** | **1.4 ± 0.6** | **2.0 ± 0.8** | **1.5 ± 0.7** | **0.0003** | **0.001** | < **0.0001** | 0.59 |
| OC [(a)] | **17.2 ± 1.7** | **5.9 ± 1.7** | 12.1 ± 5.7 | 11.0 ± 7.3 | < **0.001** | 0.89 | - | 0.51 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| OC/N [(a)] | **8.2 ± 1.1** | **4.2 ± 1.1** | 6.1 ± 1.0 | 7.3 ± 2.1 | **0.031** | 0.94 | - | 0.26 |

[a] analyses were performed only on sediments sampled in June 2010; n = 6

**Table 7**: Mean specific composition of zooplankton communities (individual $L^{-1}$) sampled in June 2011. Mean ± SD. Significant effects are in bold.

| **June 2011** | Soil treatment | | Fish treatment | | ANOVA (*P* values) | | |
|---|---|---|---|---|---|---|---|
| | S- | S+ | F- | F+ | Soil | Fish | Soil × Fish |
| **Copepods** | 44.6 ± 12.2 | 66.3 ± 40.1 | 75.3 ± 30.4 | 35.6 ± 10.0 | 0.25 | 0.025 | 0.23 |
| Cyclopoids | 3.4 ± 2.5 | 1.3 ± 1.1 | 2.5 ± 1.5 | 2.2 ± 2.8 | 0.39 | 0.57 | 0.71 |
| Calanoids | 7.0 ± 5.1 | 7.6 ± 3.0 | 8.1 ± 2.9 | 6.5 ± 5.1 | 0.66 | 0.51 | 0.99 |
| Nauplii | 34.2 ± 13.3 | 57.5 ± 37.2 | 64.7 ± 29.3 | 27.0 ± 10.8 | 0.20 | **0.035** | 0.41 |
| **Cladocerans** | 22.2 ± 17.2 | 31.9 ± 53.1 | 46.3 ± 45.9 | 7.9 ± 9.2 | 0.80 | 0.22 | 0.86 |
| *Daphnia* | 0.0 0.0 | 5.2 ± 5.6 | 1.9 ± 2.4 | 3.3 ± 6.5 | 0.1 | 0.87 | 0.87 |
| *Ceriodaphnia* | 14.0 ± 17.1 | 25.3 ± 50.5 | 39.3 ± 43.6 | 0.0 ± 0.0 | 0.68 | 0.072 | 0.68 |
| Chydoridae | 3.1 ± 4.4 | 1.3 ± 1.9 | 4.1 ± 3.9 | 0.3 ± 0.5 | 0.5 | 0.076 | 0.22 |
| **Rotifers** | 301.0 ± 231.8 | 533.0 ± 361.4 | 422.2 ± 402.3 | 411.9 ± 241.3 | 0.74 | 0.65 | 0.46 |

*Zooplankton*

*Soil effects* - Soil treatment had no effect on biomass, taxonomic and elemental composition of zooplankton (Table 6, Fig. 2b).

*Fish effects* - Fish treatment had no effect on zooplankton biomass (Table 6, Fig. 2b). The concentration of nauplii was lower in fish tanks than in fishless ones (n = 8, $P = 0.029$, Table 7). The genus *Ceriodaphnia* was also totally suppressed in fish enclosures. C content and C/N ratio of zooplankton from F+ tanks were significantly higher than those of zooplankton from F- tanks whereas, N content exhibited the opposite trend. The differences observed in elemental composition of zooplankton were particularly pronounced from July to November 2011 (data not shown).

*Soil × fish interaction effects* - We did not observe any significant interaction effect between soil and fish treatments on biomass and elemental composition of zooplankton. On average, zooplankton biomass was the lowest in February and in November 2011 for the four treatments (S-, S+, F- and F+).

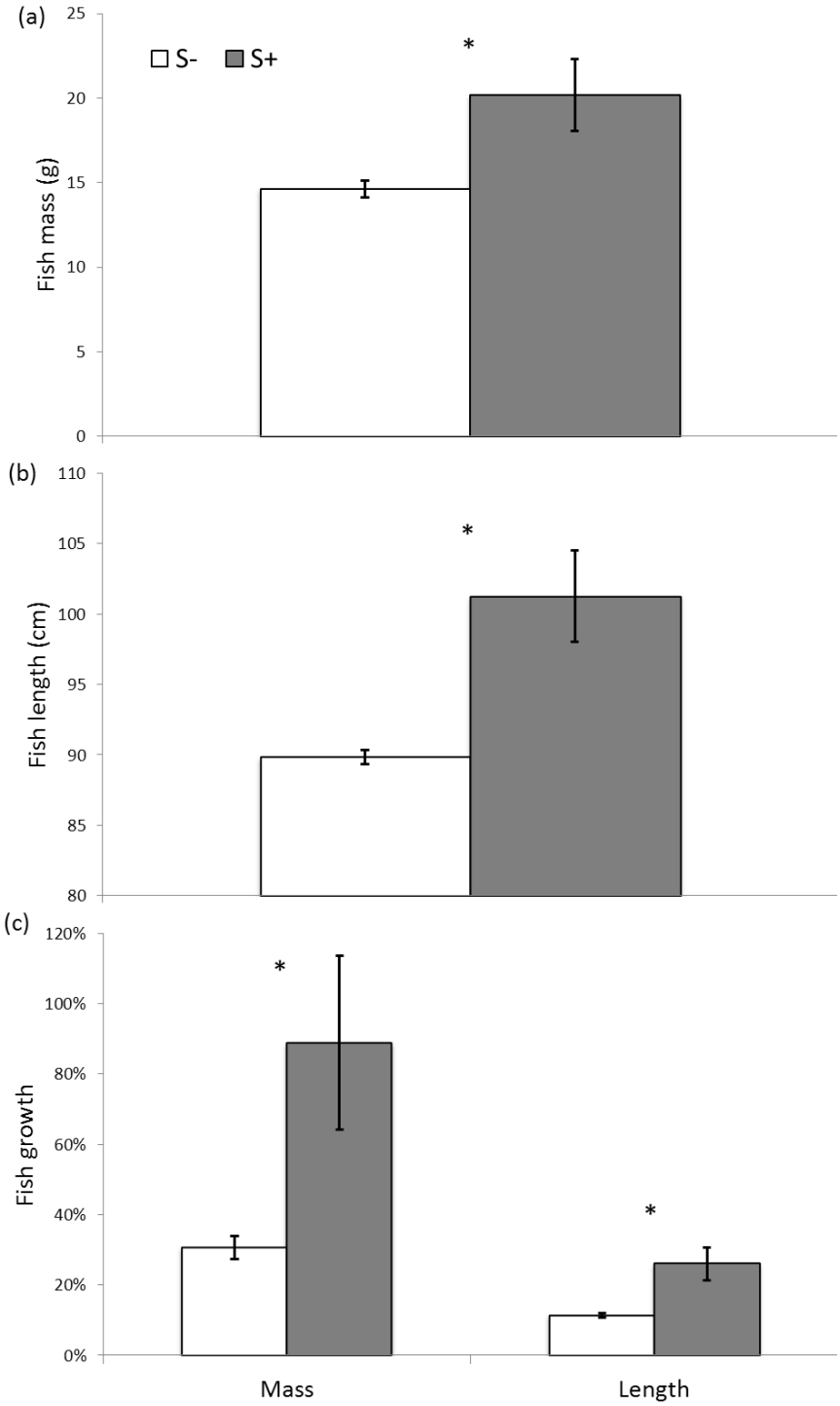
*Fish*

Soil treatment had a significant effect on fish growth. Fish individual from S+ tanks were heavier than those from S- ones (20.2 ± 3.7 and 14.6 ± 0.9 g wet weight, respectively, n = 3, $P = 0.05$, Fig. 3a). The average size of the fish from S+ tanks was larger than that of fish from S- ones (101.3 ± 5.6 and 89.8 ± 0.9 cm length of caudal, respectively, n = 3, $P = 0.022$, Fig. 3b). So, on the basis of mass and length, the growth of fish from S+ treatment was greater than that of fish from S- treatment (89 ± 43 vs 31 ± 6%, n= 3, $P = 0.028$, for the mass and 26 ± 8 *vs* 11 ± 1%, n= 3, $P = 0.015$ for the length, Fig. 3c).

**Table 7**: Mean specific composition of zooplankton communities (individual $L^{-1}$) sampled in June 2011. Mean ± SD. Significant effects are in bold.

| **June 2011** | Soil treatment | | Fish treatment | | ANOVA (*P* values) | | |
|---|---|---|---|---|---|---|---|
| | S- | S+ | F- | F+ | Soil | Fish | Soil × Fish |
| **Copepods** | 44.6 ± 12.2 | 66.3 ± 40.1 | 75.3 ± 30.4 | 35.6 ± 10.0 | 0.25 | 0.025 | 0.23 |
| Cyclopoids | 3.4 ± 2.5 | 1.3 ± 1.1 | 2.5 ± 1.5 | 2.2 ± 2.8 | 0.39 | 0.57 | 0.71 |
| Calanoids | 7.0 ± 5.1 | 7.6 ± 3.0 | 8.1 ± 2.9 | 6.5 ± 5.1 | 0.66 | 0.51 | 0.99 |
| Nauplii | 34.2 ± 13.3 | 57.5 ± 37.2 | 64.7 ± 29.3 | 27.0 ± 10.8 | 0.20 | **0.035** | 0.41 |
| **Cladocerans** | 22.2 ± 17.2 | 31.9 ± 53.1 | 46.3 ± 45.9 | 7.9 ± 9.2 | 0.80 | 0.22 | 0.86 |
| *Daphnia* | 1.0 0.0 | 5.2 ± 5.6 | 1.9 ± 2.4 | 3.3 ± 6.5 | 0.1 | 0.87 | 0.87 |
| *Ceriodaphnia* | 14.0 ± 17.1 | 25.3 ± 50.5 | 39.3 ± 43.6 | 0.0 ± 0.0 | 0.68 | 0.072 | 0.68 |
| Chydoridae | 3.1 ± 4.4 | 1.3 ± 1.9 | 4.1 ± 3.9 | 0.3 ± 0.5 | 0.5 | 0.076 | 0.22 |
| **Rotifers** | 301.0 ± 231.8 | 533.0 ± 361.4 | 422.2 ± 402.3 | 411.9 ± 241.3 | 0.74 | 0.65 | 0.46 |

**Figure 3:** Mass, length and growth of fish caught in November 2011(mean ± SE). Stars indicate significant differences.



*Short-term sediment*

*Soil effects* - Soil treatment had no effect on sedimentation rates at short-term (n = 120, $P = 0.44$), and on total loss of sediment (TLS, 91 ± 2 % for S- and 90 ± 4 % for S+, n = 12, $P = 0.32$) but induced changes in elemental composition of short-term sediment (Table 6). C, N and OC contents and OC/N ratio of short-term sediment from S+ treatment were lower than those of short-term sediment from S- treatment.

Soil treatment had a very small effect on the lipid composition of short-term sediment sampled in June 2011 since only the relative contribution of hydroxy acids (α- and β- *vs* ω-hydroxy acids) was affected by soil treatment (Table 8). The lipid composition of short-term sediment was dominated by FAs (ca. 80% of total lipids). SAFAs, accounting for ca. 50% of total FAs, were largely dominated by short-chain SAFAs (ca. 39% of total FAs) with *n*-$C_{16}$ homologue as the major component. MUFAs accounted for ca 35% of total FAs and were dominated by 18:1ω9, 16:1ω7 and 18:1ω7 (ca. 30% of total FAs). PUFAs accounted for ca. 11% of total FAs and were dominated by short-chain PUFAs (ca. 9% of total FAs). The PUFA distribution was dominated by 18:2ω6 and 18:3ω3. BACTFAs accounted for ca. 4% of total FAs.

Alkanols accounted for ca. 5.3% of total lipids of short-term sediment. The distribution exhibited a strong even over odd predominance. Short-chain alkanols (ca. 39% of total alkanols) were dominated by *n*-$C_{18}$ and *n*-$C_{16}$ homologues and long-chain alkanols (ca. 61% of total alkanols) ranged from *n*-$C_{20}$ to *n*-$C_{28}$.

Sterols accounted for ca. 4.6% of the total lipids of short-term sediment with cholesterol ($C_{27}\Delta^5$) as the major sterol for both treatments (ca. 42% of total sterols). 24-Ethylcholest-5-enol ($C_{29}\Delta^5$), 24-ethylcholesta-5,22-dienol ($C_{29}\Delta^{5,22}$), 24-methylcholesta-5,22-dienol ($C_{28}\Delta^{5,22}$) accounted for ca. 14.3, 10.3, and 5.7 % of total sterols, respectively. Stanols accounted for ca. 4.2% of total sterols and were largely dominated by cholestanol ($C_{27}\Delta^0$).

Hydroxy acids accounted for ca. 2% of total lipids of short-term sediment with a strong dominance of α- and β-hydroxy acids. These latter were dominated by $C_{16}$, $C_{18}$, $C_{22}$, $C_{24}$ and $C_{26}$ homologues. ω-Hydroxy acids were dominated by $C_{22}$ homologue. The relative abundance of ω-hydroxy acids was higher in short-term sediment from S+ treatment than in

short-term sediment from S- one (36.4 ± 19.5 and 10.1 ± 10.1 % of total hydroxy acids, respectively; n = 6; $P = 0.027$).

Chlorophyll-derived compounds accounted for ca. 3% of total lipids of short-term sediment.

A series of long-chain alkanediols was detected in short-term sediment and accounted for 1% of the total lipids. They consisted in $C_{23}$, $C_{25}$ and $C_{27}$ *n*-alkan-1,2-diols and, $C_{24}$ and $C_{26}$ α,(ω-1) *n*-alkanediols (data not shown).

Botryococcenes were not detected in short-term sediment sampled in June 2011.

*Fish effects* - Fish addition had a strong positive effect on sedimentation (Table 6, Fig. 2c). Sedimentation rates from F+ treatment were ca. five-fold higher than those from F- treatment. In February and in November 2011, sedimentation rates were the lowest and no differences were observed between F- and F+ treatments.

The only effect induced by fish treatment on the elemental composition of short-term sediment was the lower N content of short-term sediment from F+ tanks (Table 6). In contrast to soil treatment, fish treatment had several effects on the lipid composition of short-term sediment (Table 8). The main difference observed in the lipid composition between F- and F+ treatments arose from the sterol distribution.

The relative abundance of cholesterol ($C_{27}\Delta^5$) was significantly lower in short-term sediment from F+ treatment than in short-term sediment from F- treatment (ca. 22% vs 63% of total sterols, Table 6). The opposite trend was observed for 24-methylcholesta-5,22-dienol ($C_{28}\Delta^{5,22}$) and 24-ethylcholesta-5,22-dienol ($C_{29}\Delta^{5,22}$). It is worth noting that, in short-term sediment from two of the six tanks with added fish 4-methyl sterols and saturated 4-methyl stanols were detected in high relative amounts (ca. 30% of total sterols).

The relative abundances of long-chain alkanols of short-term sediment from F+ treatment were lower than that of short-term sediment from from F- one (Table 8). However, fish treatment did not influence the distribution of long-chain alkanols.

The contribution of hydroxy acids to the lipids of short-term sediment was higher for F+ treatment than for F- one. However, fish treatment did not influence the relative

abundances of α- and β-, and ω-hydroxy acids.

The relative amounts of long-chain *n*-alkanediols were higher in short-term sediment from F+ treatment than in short-term sediment that from F- one (Table 8). These long-chain *n*-alkanediols consisted predominantly in $C_{23}$, $C_{25}$ and $C_{27}$ *n*-alkan-1,2-diols and $C_{24}$ and $C_{26}$ α(ω-1) *n*-alkanediols.

The contribution of FAs to total lipids of short-term sediment, the relative abundances of SAFAs, MUFAs, PUFAs and BACTFAs and the distribution of each subclass were not affected by fish addition. Fish treatment had no effect on the contribution of chlorophyll-derived compounds to short-term sediment.

*Soil × fish interaction effect* – We did not find any significant interaction effect between soil and fish treatments on the lipid composition of short-term sediment.

*Total loss of sediment*

Soil treatment had no effect on loss of sediment (TLS, 91.2 ± 2.1 % for S- and 89.6 ± 3.8 % for S+, n = 12, $P = 0.32$). Similarly, fish addition had no effect on the total loss of sediment (90.3 ± 4.0 % for F- and 90.5 ± 1.7 % for F+, n = 12, $P = 0.87$). We did not find any significant interaction effect between soil and fish treatments on TLS.

**Table 8:** Lipid-composition (% of total lipids) of short-term sediment sampled in June 2011 (mean ± SD; n = 6). Subclasses of FAs, n-alkanols, sterols and hydroxy acids are expressed as % of their respective class. SCSAFAs and LCSAFAs were expressed as % of total FAs. S- and S+ values are means of both fish treatments. F- and F+ values are means of both soil treatments. RM-ANOVAs were performed on individual treatments (ie. S-F-, S-F+, S+F- and S+F+). Significant effects are in bold.

| **June 2011** | Soil treatment | | Fish treatment | | ANOVA (*P* values) | | |
|---|---|---|---|---|---|---|---|
| | S- | S+ | F- | F+ | Soil | Fish | Soil × Fish |
| **Fatty acids** | 79.6 ± 2.1 | 80.1 ± 5.4 | 81.1 ± 4.8 | 78.6 ± 2.6 | 0.86 | 0.33 | 0.89 |
| Saturated | 51.9 ± 6.2 | 47.3 ± 9.4 | 48.9 ± 9.8 | 50.3 ± 6.6 | 0.38 | 0.78 | 0.42 |
| *SCSAFAs* | 42.2 ± 6.6 | 35.4 ± 6.4 | 37.2 ± 8.2 | 40.4 ± 6.2 | 0.13 | 0.44 | 0.68 |
| *LCSAFAs* | 9.6 ± 4.7 | 11.9 ± 3.8 | 11.7 ± 4.5 | 9.9 ± 4.1 | 0.40 | 0.49 | 0.35 |
| Monounsaturated | 31.4 ± 5.8 | 39.0 ± 10.3 | 34.0 ± 11.7 | 36.4 ± 5.9 | 0.13 | 0.46 | 0.31 |
| Polyunsaturated | 12.2 ± 5.2 | 10.1 ± 3.2 | 13.4 ± 4.3 | 9.0 ± 3.0 | 0.37 | 0.085 | 0.55 |
| *SCPUFAs* | 9.0 ± 3.6 | 8.3 ± 3.3 | 10.3 ± 3.4 | 7.0 ± 2.4 | 0.7 | 0.12 | 0.88 |
| *LCPUFAs* | 3.2 ± 2.1 | 1.8 ± 0.9 | 3.1 ± 2.1 | 2.0 ± 1.0 | 0.2 | 0.29 | 0.45 |
| BACTFAs | 4.5 ± 0.7 | 3.6 ± 0.7 | 3.7 ± 0.9 | 4.4 ± 1.1 | 0.10 | 0.28 | 0.46 |
| **Alkanols** | 4.7 ± 1.3 | 5.9 ± 2.3 | 5.4 ± 2.1 | 5.2 ± 1.8 | 0.34 | 0.87 | 0.81 |
| SC alkanols | 41.2 ± 14.2 | 37.5 ± 13.5 | **28.6 ± 5.8** | **48.3± 11.7** | 0.38 | **0.008** | 0.88 |
| LC alkanols | 58.8 ± 14.2 | 64.3 ± 13.5 | **71.4 ± 5.8** | **51.7 ± 11.7** | 0.38 | **0.008** | 0.88 |
| **Sterols** [(a)] | 4.3 ± 1.2 | 4.9 ± 2.3 | 4.0 ± 0.7 | 5.2 ± 2.4 | 0.59 | 0.32 | 0.84 |
| $C_{27}\Delta^5$ | 43.7 ± 26.5 | 41.3 ± 21.1 | **63.1 ± 7.2** | **21.9 ± 9.0** | 0.61 | < **0.0001** | 0.17 |
| $C_{27}\Delta^0$ | 2.9 ± 1.9 | 4.4 ± 2.1 | 2.5 ± 1.9 | 4.1 ± 2.4 | 0.55 | 0.23 | 0.21 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $C_{28}\Delta^{5,22}$ | 5.7 ± 3.3 | 5.8 ± 4.7 | **3.1 ± 1.8** | **8.4 ± 3.6** | 0.95 | **0.018** | 0.94 |
| $C_{29}\Delta^{5,22}$ | 13.0 ± 12.4 | 7.7 ± 6.1 | **3.4 ± 2.0** | **17.4 ± 9.3** | 0.24 | **0.0092** | 0.99 |
| $C_{29}\Delta^{5}$ | 13.5 ± 2.8 | 15.1 ± 3.1 | 13.2 ± 3.4 | 15.4 ± 2.2 | 0.37 | 0.23 | 0.64 |
| **Hydroxy acids** | 1.7 ± 0.2 | 2.0 ± 0.2 | **1.4 ± 0.5** | **2.3 ± 0.2** | 0.16 | **0.0088** | 0.082 |
| a- + β-hydroxy acids | **89.9 ± 10.1** | **63.6 ± 19.5** | 76.8 ± 23.0 | 77.0 ± 22.9 | **0.027** | 0.99 | 0.51 |
| ω- hydroxy acids | **10.1 ± 10.1** | **36.4 ± 19.5** | 23.3 ± 23.0 | 23.2 ± 22.9 | **0.027** | 0.99 | 0.51 |
| **Chlorophyll-derived compounds** | 3.3 ± 1.3 | 2.7 ± 1.4 | 2.8 ± 1.7 | 3.2 ± 0.9 | 0.46 | 0.62 | 0.67 |
| **LC alkanediols** | 1.0 ± 0.9 | 1.1 ± 1.3 | **0.4 ± 0.4** | **2.1 ± 1.3** | 0.87 | **0.0074** | 0.84 |

[(a)] $C_{27}\Delta^{5}$ : cholesterol; $C_{27}\Delta^{0}$ : cholestanol; $C_{28}\Delta^{5,22}$ : 24-methylcholesta-5,22-dienol; $C_{29}\Delta^{5,22}$ : 24-ethylcholesta-5,22-dienol; $C_{29}\Delta^{5}$ : 24-ethylcholest-5-enol

## Discussion

The addition of soil into tanks had no effect on biomass, stoichiometry and lipid composition of seston and zooplankton. Fish growth was enhanced by soil addition. Soil treatment had several effects on the stoichiometry and on the lipid composition of short-term sediment. However, no effect on protein and sugar contents of short-term sediment and on sedimentation rates was observed. In contrast, fish addition affected chlorophyll-*a* concentration of water, seston biomass, sedimentation rates, stoichiometry of seston, zooplankton and short-term sediment. Lipid composition of short-term sediment was also affected by fish treatment. Finally, interaction effects between soil and fish treatments were not observed.

### *Effects of soil addition*

The influence of soil treatment on the biomass, elemental and lipid compositions of pelagic compartments and on sedimentation rate, elemental and lipid compositions of short-term sediment, was similar for the two steps of the experiment (only soil addition in the first step and, soil and fish additions in the second step).

#### *Seston*

*Effects of allochthonous inputs* - Monthly inputs of soil let us hypothesise that at least a part of these particles could remain in the water column. However, a similar biomass was observed in S+ and S- treatments, and seston biomass values observed in this study were similar to those observed in lake mesocosms that did not received terrestrial inputs (Danger et al., 2012). This suggests that a large part of the added soil had rapidly settled and therefore did not contribute to seston. Furthermore, no difference in the lipid composition was observed between treatments, suggesting that the contribution of lipids originating from soil to seston was likely very minor and that contributions to seston were quite similar for both treatments.

The very low contribution of soil to seston was corroborated by elemental and lipid analyses. First, C and N contents of seston were much higher than those of the added soil. Similarly, the relative abundances of long-chain compounds such as FAs, alkanols and ω-hydroxy acids were much lower in seston than in the soil added. These long-chain compounds are well-known biomarkers of terrestrial (suberin)-derived organic matter (Cranwell, 1974; Kolattukudy et al., 2001). The great differences in their relative abundances observed between seston and soil corroborate the very low contribution, if any, of soil particles to seston. The noticeable contribution of 24-ethylcholest-5-e*n*-3β-ol ($C_{29}\Delta^5$), commonly used as a terrestrial biomarker (Volkman et al., 1986; Canuel et al., 1997; Bechtel & Schubert, 2009ab), could suggest a terrestrial input to seston. However, this sterol has also been found in lipids of many microalgae (Barrett et al., 1995; Volkman, 1998). Furthermore this sterol was also found in similar high relative abundances in seston from S- tanks. Consequently, on the basis of all the present information, terrestrial inputs in seston were likely very minor.

*Autochthonous support of seston* – Similarly to seston biomass, chlorophyll-*a* concentrations in the water column did not depend on soil treatments and corresponded to mesotrophic conditions (Padisak, 2004). Chlorophyll-a concentration has been extensively used for estimating phytoplankton biomass. According to this indicator, phytoplankton contribution to seston did not appear to be dependent on soil treatments. However, the higher CDOM content in S+ tanks might have led to a decrease in photosynthetic activity in these tanks. Indeed, CDOM is known to reduce light availability in aquatic ecosystems (Jansson et al., 2000; 2007; Karlsson et al., 2009). The absence of relationship between CDOM concentrations and phytoplankton biomass, as measured by chlorophyll-*a* concentrations, suggests that the increase in CDOM resulting from soil addition was too low to induce a reduction of photosynthesis (competition for light). Our conclusion is supported by the similar light penetrations observed in mesocosms from both S- and S+ treatments.

Lipid compositions of seston from both treatments are similar. These compositions suggest that both phytoplankton and zooplankton (perhaps as remains or faecal pellets) contributed to seston. Indeed, sterol distribution of seston is dominated by 24-ethylcholest-5-enol ($C_{29}\Delta^5$) which has been found in several microalgae (Volkman, 2003), and cholesterol, commonly considered as an animal sterol. However, it is difficult to estimate the relative contributions of phytoplankton and zooplankton. Indeed, the relative abundance of 24-ethylcholest-5-enol was three-fold higher in seston than in zooplankton, suggesting a high

contribution of phytoplankton. However, on the contrary, the low contribution of chlorophyll-derived compounds, originating from algal chlorophyll-*a* (Rontani & Volkman, 2003) suggests a low contribution of phytoplankton. Similarly, the high relative abundance of cholesterol, which could indicate a high contribution of zooplankton, is contradicted by the low relative amounts of long-chain PUFAS, usually found in relatively high amounts in zooplankton (Persson & Vrede, 2006, Ravet et al., 2010). This discrepancy could be explained by the fact that long-chain PUFAs are degraded more rapidly than other biogenic lipids (Cranwell, 1982). Moreover, long-chain PUFAs have also been found in high abundance in Chryptophyceae and in Diatoms (Volkman 1989, Ahlgren et al. 1992, Dunstan et al. 1994, 2005). Therefore, in the absence at this time of data on the taxonomic composition of phytoplankton, the origin, zooplanktonic or phytoplanktonic, of seston PUFAs cannot be assigned with confidence. The contribution of botryococcenes to the lipid composition of seston indicates the presence of the green alga *Botryococcus braunii* race B in the tanks from both treatments (Metzger et al. 1985a, b; Zhang et al., 2007). These microalgae have been shown to contain quite high amounts of botryococcenes (Metzger et al. 1985a, b; Zhang et al., 2007). So, the low relative abundance of botryococcene in seston could indicate a rather low contribution of *B braunii* race B to seston. Noticeable amounts of BACTFAs found in seston from both treatments suggest that bacteria (free bacterioplankton, biofilms and colony assemblages on particles and/or aggregates) were another potential source for seston. As suggested by Tranvik (1992), the increase in the concentration of CDOM due to soil addition should have led to higher bacterial production in the tanks from S+ treatment. The similar amounts of BACTFAs found in seston from both treatments do not corroborate this assumption. On the contrary, and in agreement with an earlier study (Kankaala et al., 2010), our results suggest that allochthonous inputs did not noticeably subsidize bacterial production within the pelagic zone. The extent of allochtonous C transfer to pelagic bacteria remains controversial, and many studies have shown that allochthonous inputs are major subsidies of carbon and energy for bacteria growth and production (Kritzberg et al., 2004; Lennon & Pfaff, 2005; Cole et al., 2006; Berggren et al., 2010). The absence of effect of soil addition on the pelagic bacterial production in our study could be explained either by a poor quality of added DOM and/or a too low concentration of this DOM (the OC content of soil was 0.5% DW), or by a high sedimentation rate of terrigenous organic matter. The low concentration of allochtonous DOM in water is supported by the fact that, in S+ tanks, CDOM did not compete with chlorophyll-*a* for light availibility, as indicated by the similar contents of chlorophyll-*a*

in both S- and S+ tanks.

*Zooplankton*

Allochthonous inputs had not effect on zooplankton biomass which was of the same order of magnitude as those found in lake enclosure experiments (Danger et al. 2012). However, allochthonous inputs increased the concentration of daphniidae and calanoid copepods. Note that a similar tendency was observed for most groups of zooplankton with the exception of cyclopoids. This result is in accordance with previous studies that showed that allochthony can bring subsidies for both cladocerans and copepods by direct feeding on terrestrial organic carbon (Cole et al., 2011, and references therein). The absence of effect of soil treatment on zooplankton stoichiometry can be due to a balance between the elemental compositions of organisms. For example, Andersen & Hessen, (1991) showed that the C and the N contents of *daphniidae* are lower than those of calanoid copepods. Note also that, in spite of significant changes for some taxa during the first step of the experiment, the general compositions of the communities were not significantly affected by allochthonous inputs during the second step. Globally, rotifers strongly dominated the zooplankton community, and the concentration of Cladocera remained very low during the two steps. Thus, the similar lipid compositions of zooplankton in the two treatments could be explained by the absence of strong effect of soil treatment on the relative importance of major groups within the zooplanktonic community.

Apart from the relative amounts of FAs and botryococcenes, the lipid composition of zooplankton did not depend on soil treatments. The relative amounts of botryococcenes, indicating the presence of *Botryococcus braunii* race B, were higher in zooplankton than in seston samples. This can be explained by the fact that these freshwater microalgae form colonies ranging from 30 µm up to 2 mm diameter and have likely been sampled with zooplankton (sampled on 50 µm filter). *B. braunii* race B contains ca. 30-40% (DW) botryococcenes (Metzger et al., 1985a), while FA content accounts for ca. 10% of the dry biomass with 16:0, 18:1 and 28:1 homologues as the major components (Metzger et al. 1990). Although relative amounts of FAs in zooplankton depended on the soil treatments, the FA distribution did not. Particularly, 28:1 FA has not been detected and, the relative abundances

of 16:0 and 18:1 FA did not depend on the soil treatments. So, the FA contribution of *B. braunii* to FAs of zooplankton could be considered as minor. The observed difference in the relative amounts of FAs between treatments was probably due to the contamination of zooplankton samples with *B. braunii*. However, this contamination did not appear to noticeably impact the distribution of lipid classes of zooplankton samples. The contribution of *B. braunii* and of large non-determined algal filaments to zooplankton biomass (direct observations with a stereo-microscope) obviously resulted in an overestimation of zooplankton biomass and to an underestimation of the phytoplankton contribution to seston. It is worth noting that the relative amounts of botryococcenes are much higher in zooplankton from S- treatment than in zooplankton from S+ treatment. The difference in the abundances of *B. braunii* between S- and S+ treatments suggests that soil inputs resulted in a change in different environmental conditions for some primary producers, leading other faster-growing algae to outcompete with *B. braunii* in S+ tanks. Globally, the lipid compositions of seston and zooplankton from both treatments suggest that allochthonous subsidize for planktonic communities was low compared to the autochthonous one.

*Fishes*

Several studies on whole lake experiments have shown that terrestrial organic matter can significantly support fish metabolism through feeding on benthos, zooplankton and their respective consumers (eg. several species of *Chaoborus* larvae) which are supported by these allochthonous inputs (Carpenter et al., 2005; Cole et al., 2006; Weidel et al., 2008; Perga et al., 2009). Our results, in agreement with these studies, show that mass, length and growth of fish from S+ tanks were higher than those of fish from S- ones. As no significant increase of zooplankton biomass was observed with soil addition in absence of fish, the major pathway for the allochtonous C transfer to fish was probably a benthic one. This is corroborated by our observations on Gastropoda, in particular on the genus *Lymnaea*. Soil addition had a significant positive effect on abundance and size of individuals, clearly indicating that allochthonous inputs subsidized benthic communities (unpublished data).

*Sediment*

*Biomass* - Soil treatment had no effect on the sedimentation rate. However, C, OC and N contents of short-term sediment from S+ tanks were significantly lower than those of short-term sediment from S- ones. This could indicate a soil input to short-term sediment from S+ treatment since C and N contents of seston and zooplankton did not depend on soil treatments. However, the low values of the OC/N ratio suggest a major autochtonous contribution to short-term sediment (Martinova, 1993). This latter result, together with the similar sedimentation rates observed for both treatments, suggest that contribution of the added soil to short-term sediment was probably minor. The minor soil contribution to short-term sediments is also supported by their lipid compositions. Indeed, the relative abundances of MUFAs, PUFAs, cholesterol and chlorophyll-derived compounds in short-term sediments from both treatments were similar and much higher than those found in the added soil.

*Lipid composition* - The lipid composition of short-term sediment sampled in June 2010 and in June 2011 was weakly affected by the soil treatment. The higher relative abundances of long-chain alkanols (in short-term sediment sampled in June 2010) and ω-hydroxy acids (in short-term sediments sampled in June 2010 and in June 2011) observed in short-term sediment from S+ tanks might indicate a higher contribution of terrestrially-derived material. However, the relative abundances of these long-chain compounds were of the same order of magnitude as those found in seston and zooplankton. Furthermore, the relative abundances of these long-chain compounds in seston and zooplankton did not depend on soil treatment. So, even though soil contribution to short-term sediment cannot be completely rule out, it is likely that the long-chain alkanols and ω-hydroxy acids found here had not primarily allochthonous origins. For the first step of the experiment, the contributions of both seston and zooplankton to short-term sediments from S-and S+ treatments were clearly revealed by the lipid composition of the sediments. Particularly, the differences observed between the relative abundances of cholesterol, LCSAFAs and PUFAs in short-term sediment on the one hand, and in the other hand in seston and zooplankton, suggest that short-term sediment from both treatments mainly originated from zooplankton. This result is in agreement with previous results that showed the major contribution of zooplankton to recently deposited sediment in a similar two-level food web (Allard et al. 2011). It is worth noting, that, in contast to seston and to zooplankton, short-term sediments from the first step of the

experiment contained very low amounts of botryococcenes. The low contribution of *B. braunii* to short-term sediments can be explained by the fact that the high lipid content of this alga increases the buoyancy of its colonies (Maxwell et al., 1968).

The similar amounts of bacterial FAs found in short-term sediment from both S- and S+ treatments suggest that bacterial contribution to short-term sediment was not influenced by the addition of soil. Moreover, the relative abundances of α- and β-hydroxy acids, usually related to bacterial input and/or activity (Cranwell, 1982; Wakeham, 1999), and those of cholestanol, the saturated homologue of cholesterol, usually considered as formed through in situ microbial reduction of cholesterol (Gaskell & Eglinton, 1975), did not depend on soil treatment. This suggests that the bacterial reworking of recently sedimented sediment was not affected by soil addition. This assumption is supported by the fact that the relative abundances of lipid biomarkers such as PUFAs and bulk parameters such as sugar and protein contents, which have been used as indicators of the biodegradability of short-term sediment (Canuel et al., 2007; Allard et al., 2011), did not depend on soil treatment. This absence of effect of allochthonous inputs on the biodegradibility of the sedimented organic matter is corroborated by the similar total loss of sediment (TLS) throughout the experiment between soil treatments.

### *Effects of food-web structure*

In contrast to soil inputs, food-web structure had noticeable effects on biomass and elemental composition of seston, zooplankton and short-term sediment and on the lipid composition of short-term sediment.

#### *Biomass and elemental composition of seston and zooplankton*

*Biomass* - The significant increase in both seston biomass and chlorophyll-*a* concentration in the water column with fish addition indicates that phytoplankton biomass was higher in F+ tanks than in F- ones. The higher pH in F+ tanks supports this result. Indeed, the decrease in H+ concentration in the water column of F+ tanks could originate from a higher fixation of dissolved $CO_2$ due to an enhanced photosynthetic activity (Stumm &

Morgan, 1996). This suggests that fish addition resulted in a trophic cascade through predation on zooplankton, subsequently resulting in an increase in phytoplankton biomass (Carpenter, 1993) despite the absence of effect of fish treatment on phosphorus concentration of water and their low values. This trophic cascade did not give rise to a decrease in zooplankton biomass. This is in agreement with previous studies that showed that the consumption of zooplankton by fish does not necessarily result in a decrease of zooplankton biomass (Bertolo et al., 1999; Faithfull et al., 2011; Danger et al., 2012). This phenomenon has been shown to be due to a shift of the zooplanktonic community induced by the species-selective predation by fish, which is corroborated by the lower concentration in the fish tanks of nauplii and by a similar tendency for Cladocera (reduced by more than an order of magnitude in fish tanks).

*Seston stoichiometry* - The presence of planktivorous fish resulted in a decrease in C and N contents of seston. This is in opposition to the results of Danger et. al (2012), who showed that addition of planktivorous fish did not influence the stoichiometry of seston. This discrepancy can be explained by the differences in the experimental design between the two studies. Our mesocosms are shallower than those of Danger et al. (ca. 1.5 *vs* 4.5m; 2012). In these very shallow mesocosms, the benthic foraging of fish probably higher and could have led to a more important resuspension of C- and *N*-poor sedimented material, resulting in lower C and N contents of seston. Moreover, *Carassius* genus, used in our experiment, is more benthivorous than *Rutilus* genus, used in the experiment of Danger et al. (2012). However, the differences in stoichiometry of zooplankton between F- and F+ cannot be explained solely on the basis of the hypothesis of an increase in foraging activity of fish. Indeed, if the N content of zooplankton was lower in F+ tanks, its C content was higher. Two hypotheses can be put forward to explain this discrepancy. First, as suggested by the significant differences in the elemental composition of zooplankton between F- and F+ treatments, fish predation could induce changes in zooplankton community. Indeed, zooplankton species have been shown to have specific elemental compositions (Andersen & Hessen, 1991). Second, fraction of seston particles could have been fed selectively by zooplankton (Gliwicz, 2004). Of course, these two possibilities are not exclusive.

*Short-term sediments*

*Sedimentation rate* - In agreement with several studies carried out in lakes and in mesocosms, planktivorous fishes positively affected sedimentation rates by an indirect increase of algal biomass (Sarnelle, 1999; Vanni et al., 1997; Danger et al., 2012). The seasonal variations of seston and zooplankton biomass (lower in February 2011 and higher from May to July 2011) paralleled those of sedimentation rates. This suggests that seston and zooplankton compartments mainly controlled sedimentation. Note that the higher sedimentation rates observed in fish tanks probably induced in turn a positive feedback on benthic pathways and enhanced the positive effect of allochthonous inputs on the benthic compartments. Indeed, we observed a significant increase of the size of *Lymnaea* individuals in the S+F+ tanks (unpublished data) compared to the other treatments.

*Stoichiometry* - Our previous suggestion is corroborated by the N contents of seston, zooplankton and short-term sediment. Indeed, the contribution of *N*-depleted seston and zooplankton to sedimentation in F+ tanks could have induced a lower N content of short-term sediment from these tanks. On the other hand, the similar C content of short-term sediment from both treatments could be a balance between C contents of seston and zooplankton. Indeed, fish addition results respectively in a decrease in C content of seston and an increase in C content of zooplankton.

*Lipid composition* - The trophic cascade resulting from fish addition is supported by the lipid composition of short-term sediment, particularly by the sterol distribution. Indeed, cholesterol dominates the sterol distribution of short-term sediment from F- tanks. This sterol, although found in some microalgae (Volkman, 2003), is commonly considered as an animal sterol. This suggests that short-term sediment from F- tanks mainly originated from zooplankton. In contrast, the relative abundance of cholesterol was much lower in short-term sediment from F+ tanks. Furthermore, 24-methylcholesta-5,22-dienol ($C_{28}\Delta^{5,22}$) and 24-ethylcholesta-5,22-dienol ($C_{29}\Delta^{5,22}$), found in higher relative abundance in short-term sediment from F+ tanks, have been shown as minor sterols in zooplankton (Prahl et al., 1984, 1985; Harvey et al., 1987; Mühlebach et al., 1999; Allard et al., 2011), while they occur in many microalgae (Volkman, 2003 and references therein). Therefore, in agreement with the trophic casade resulting from the addition of fish, this suggests a higher contribution of phytoplankton to the short-term sediment from F+ tanks. The difference in the extent of zooplanktonic and phytoplanktonic contributions between short-term sediment from F- and F+ treatments is also

supported by the difference in the relative amounts of long-chain alkanediols. Indeed, long-chain alkanediols have been found in several micro-algae (Volkman et al., 1999; Allard & Templier, 2000) and have been suggested as biomarkers for phytoplanktonic contribution to short-term sediment (Allard et al., 2011). The higher contribution of phytoplankton to short-term sediment from F+ tanks appears to be in conflict with the relative abundances of LCPUFAs and chlorophyll-derived compounds, which did not depend on F- and F+ treatments. The similar relative abundances of LCPUFAs in short-term sediments from both treatments could be explained by the presence of a higher biomass of cryptophyceae and/or diatoms in F- tanks. Indeed, these microalgae contain large amount of LCPUFAs (eg. Dunstan et al. 2005; Patil et al. 2007). In the absence of additional information at this time on lipid composition of seston and taxonomic composition of phytoplankton from both treatments, no clear conclusion can be drawn regarding the precise influence of fish addition on the relative contributions of phytoplankton and zooplankton to short-term sediment.

4-Methyl sterols and saturated 4-methyl stanols were found in high amounts in short-term sediment from two of the six mesocosms with added fish. These sterols are generally considered as indicators of dinoflagellate contribution to sediment (Volkman, 2003). This indicates that, at least phytoplankton, did not grow in a homogenous way in our tanks.

*Biodegradability of short-term sediment* - The presence of α- and β-hydroxy acids and cholestanol ($C_{27}\Delta^0$) in short-term-sediment from both F- and F+ treatments suggests that biodegradation of sediment occured even at very short time scales (i.e; 1 week). However, the noticeable presence of highly biodegradable compounds such as MUFAs and PUFAs (Cranwell, 1981) suggests that microbial reworking remained limited for these short-term sediments. The relative abundances of bacterial FAs, α- and β-hydroxy acids and cholestanol did not depend on fish treatments. This suggests that both bacterial contribution and extent of the reworking of short-term sediment were not affected by fish addition. This result is contrary to Canuel et al. (2007) and Allard et al. (2011) who showed that the presence of zooplankton predators enhanced the biodegradability of short-term sediments through a trophic cascade. The absence of effect of planktivorous fish on the biodegradability of short-term sediment and on long-term losses (TLS) in our mesocosms remains unexplained. These results suggest that the addition of planktivorous fish does not necessarily result in an enhanced nutrient recycling from sediment to the water column (Sondergaard et al., 1992, 2003).

**Conclusion**

In this mesocosm study, the addition of soil as allochthonous inputs to aquatic ecosystem subsidized the food web up to certain groups of zooplankton and to fish population. However, the absence of effect of allochthonous inputs on biomass, elemental and lipid compositions of seston and zooplankton suggests that this positive effect of terrigenous inputs did not change greatly the energetic transfers within the planktonic food web, but induced higher resources for fish at the level of the sediment and benthic food chains. Direct fish foraging on benthic layers was corroborated by the elemental composition of seston that suggested an enhanced resuspension of sediment in the presence of fish. Allochthonous inputs and fish did not induce visible effects on the potential biodegradability of sediment. It would be interesting to complement this study by analyses on the evolution of the biochemical composition of sediment on the long term in the different treatments. Moreover, additional analyses such as nutrient concentration of water column and more precise taxonomic determinations of phytoplankton and zooplankton are required to improve our understanding of the effects of allochtonous inputs on the functioning of aquatic ecosystems.

On the other hand, manipulation of the food-web structure through the addition of planktivorous fish exhibited the effects expected from a top-down control induced by the trophic cascade. Biomass of phytoplankton increased due to fish predation on zooplankton. Despite higher biomass of phytoplankton in mesocosms dominated by fish, short- and long-term sediments from fishless and fish treatments exhibited similar biodegradability. The difference in biodegradability of sediment observed between our results and previous studies remains unclear, but suggests that the presence of planktivorous fish does not necessarily enhance the internal nutrient recycling of aquatic ecosystems.

Finally, the predominance of the effects of food web structure over allochthonous inputs and the absence of interaction between these top-down and bottom-up controls suggests that the importance of allochthonous inputs was small compared to changes in top-down control in these ecosystems.

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# Appendice Chapitre V

# Distributions lipidiques du seston, du zooplancton et des sédiments récents

**Figure 1 :** Lipid distribution (% of total lipids, mean ± SD) of seston sampled in June 2010.

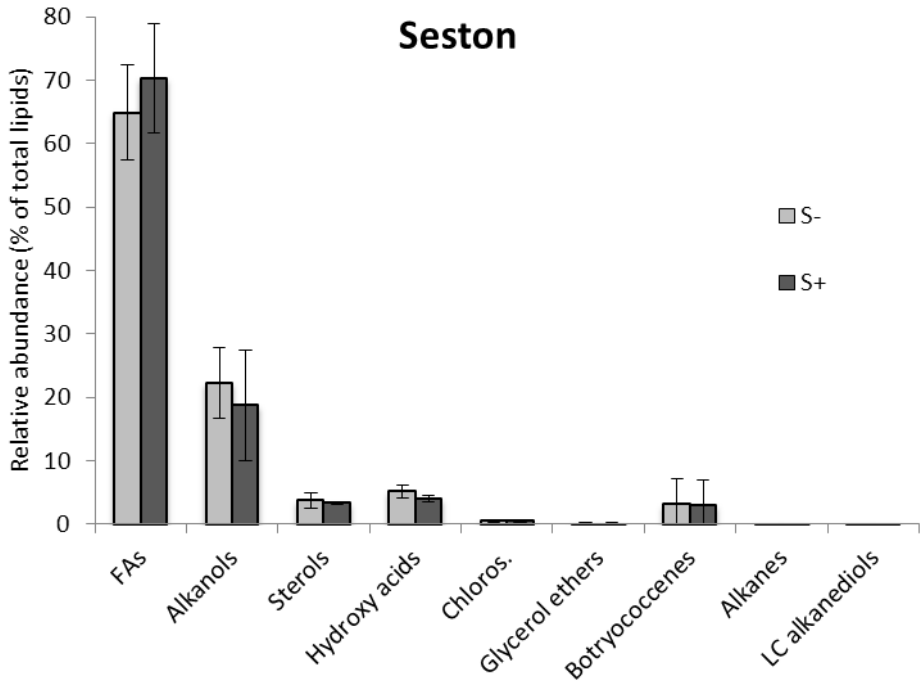



**Figure 2:** Lipid distribution (% of total lipids, mean ± SD) of zooplankton sampled in June 2010.

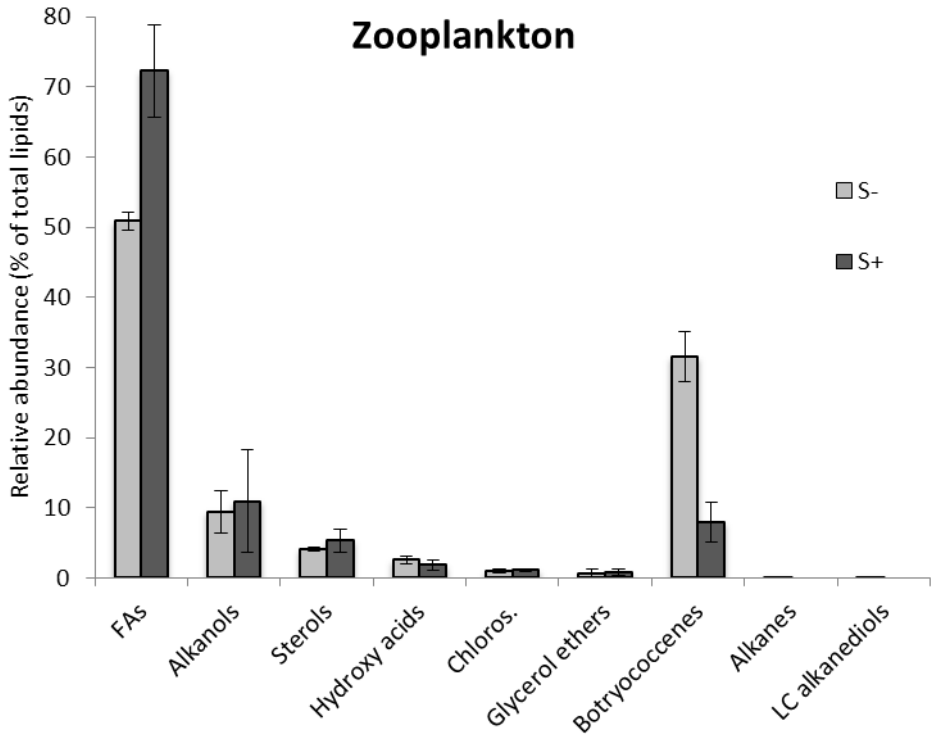


**Figure 3:** Lipid distribution (% of total lipids, mean ± SD) of short-term sediment sampled in June 2010. First graph: full scale. Second graph: zoom.

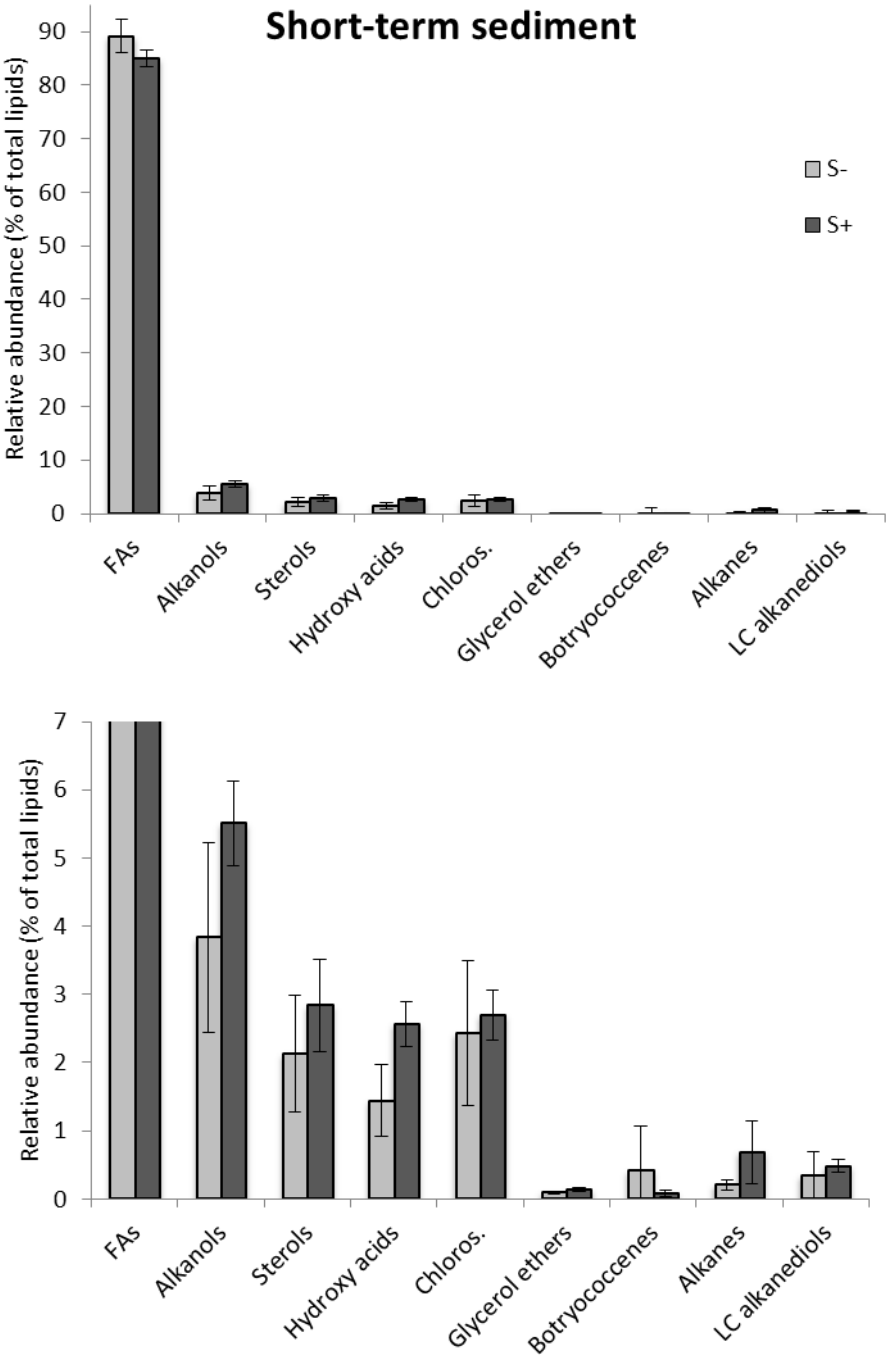


**Figure 4:** Fatty acid distribution (% of total FAs, mean ± SD) of seston, zooplankton and short-term sediment sampled in June 2010.

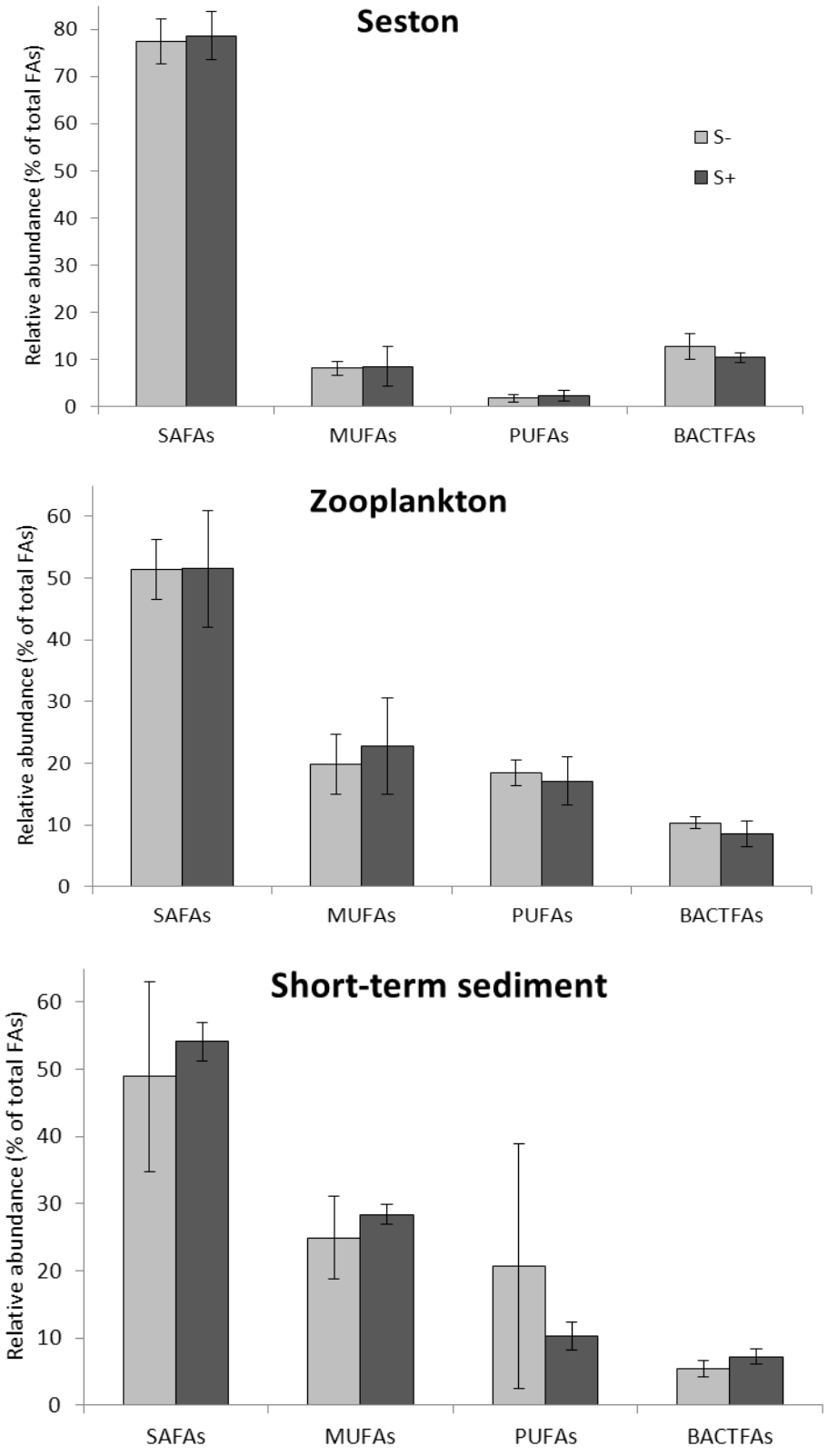


**Figure 5** : Saturated fatty acid distribution (% of total FAs, mean ± SD) of seston sampled in June 2010. First graph: full scale. Second graph: zoom.

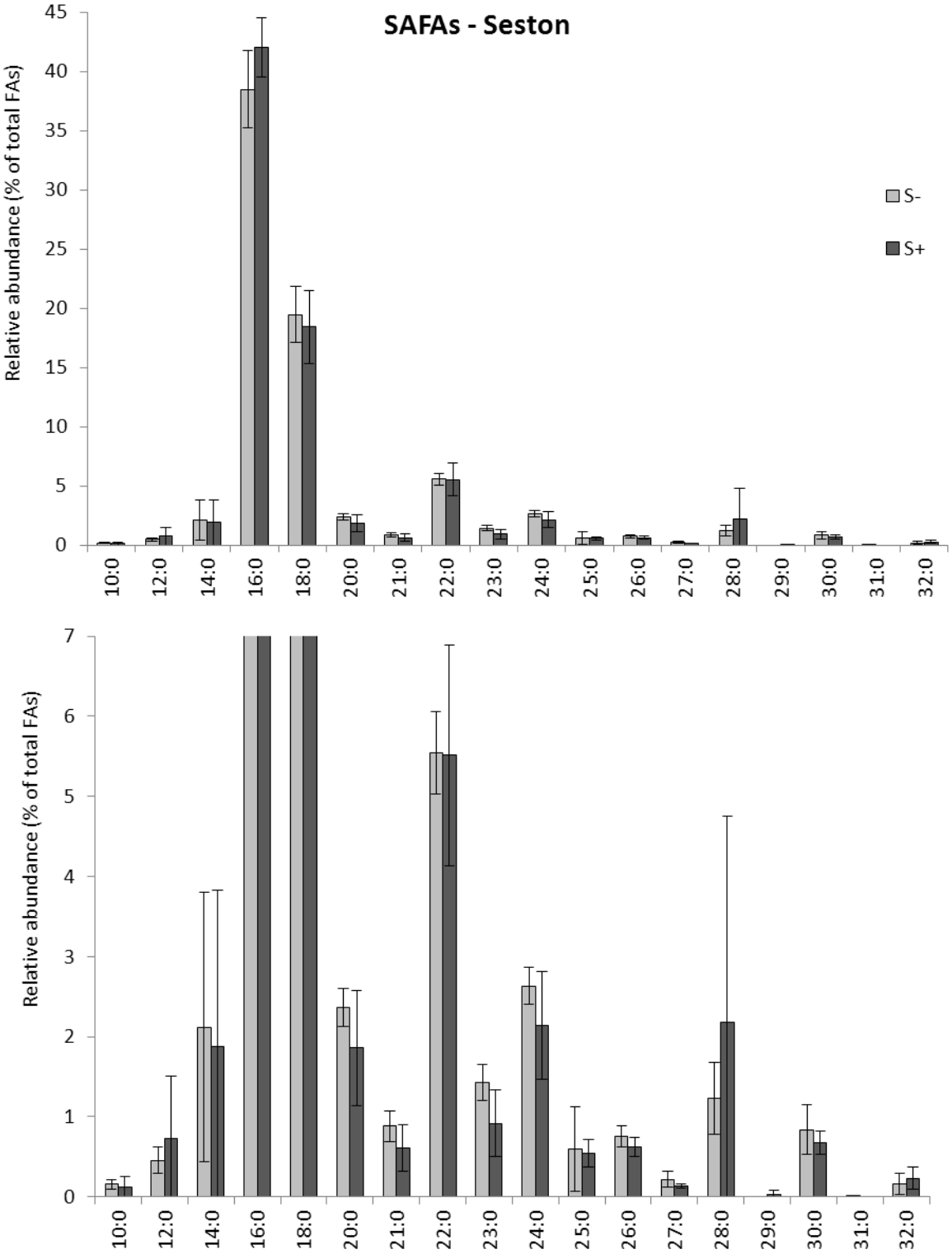


**Figure 6** : Saturated fatty acid distribution (% of total FAs, mean ± SD) of zooplankton sampled in June 2010. First graph: full scale. Second graph: zoom.

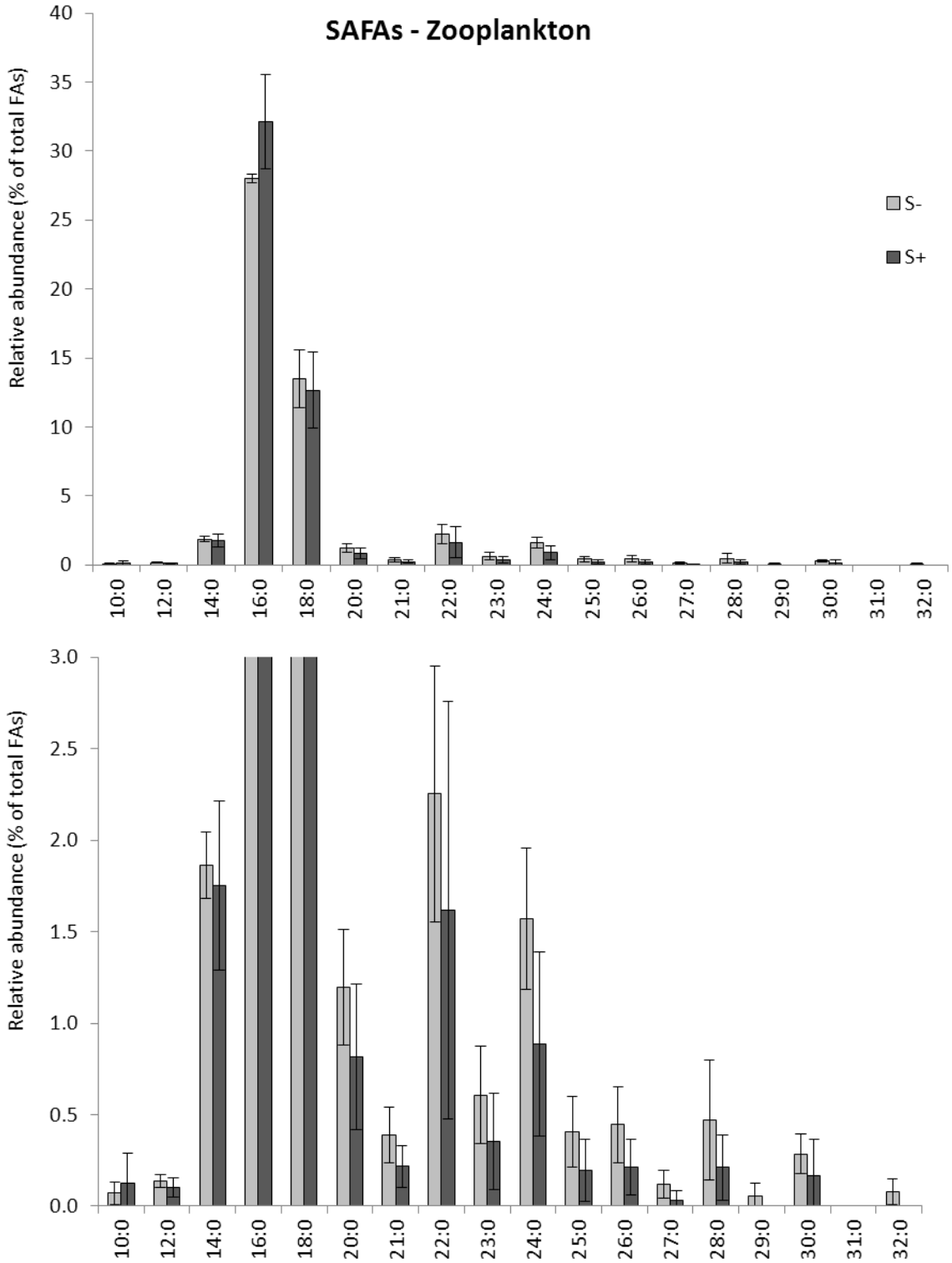


**Figure 7** : Saturated fatty acid distribution (% of total FAs, mean ± SD) of short-term sediment sampled in June 2010. First graph: full scale. Second graph: zoom.

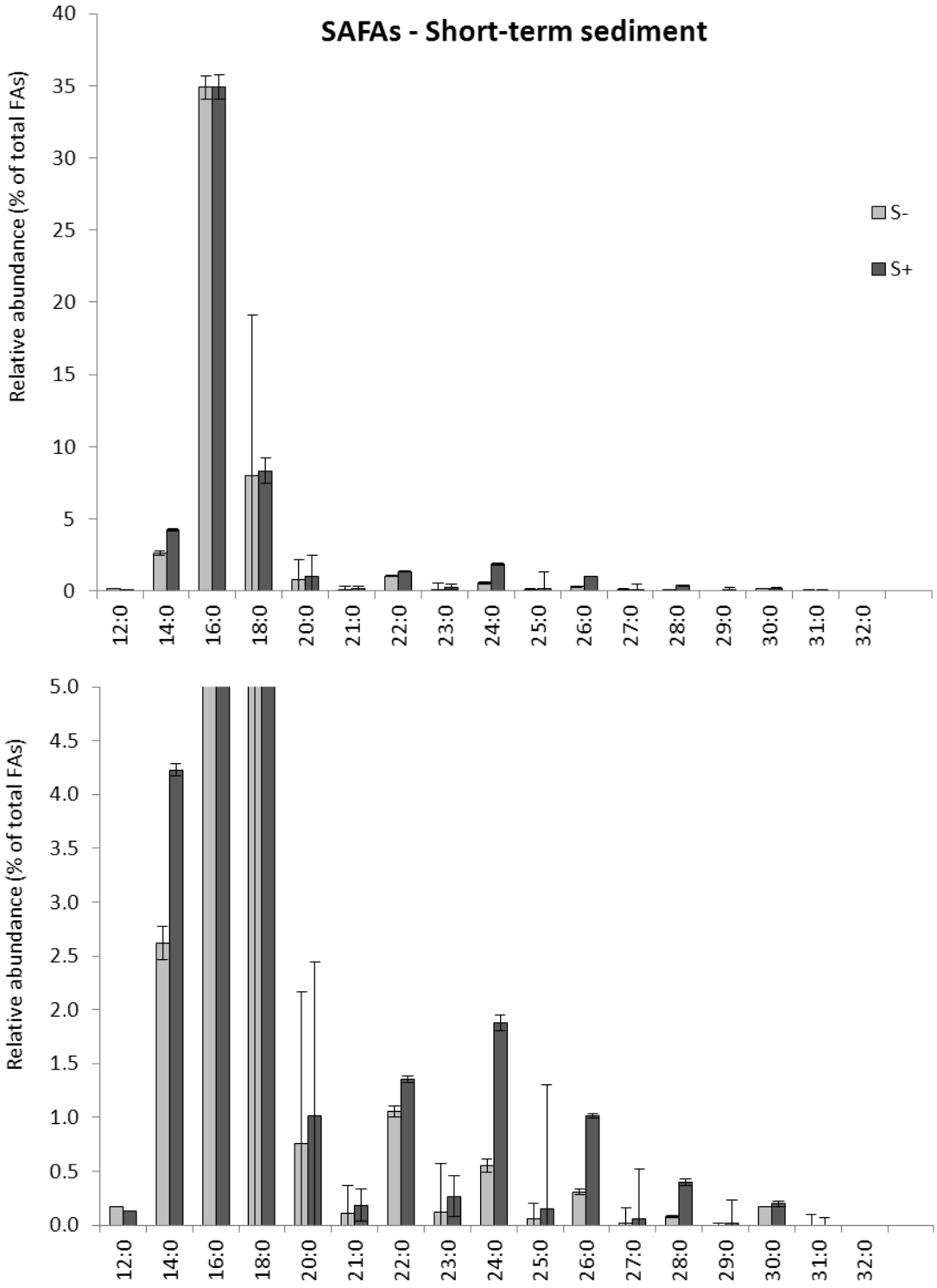


**Figure 8** : Monounsaturated fatty acid distribution (% of total FAs, mean ± SD) of seston, zooplankton and short-term sediment sampled in June 2010.

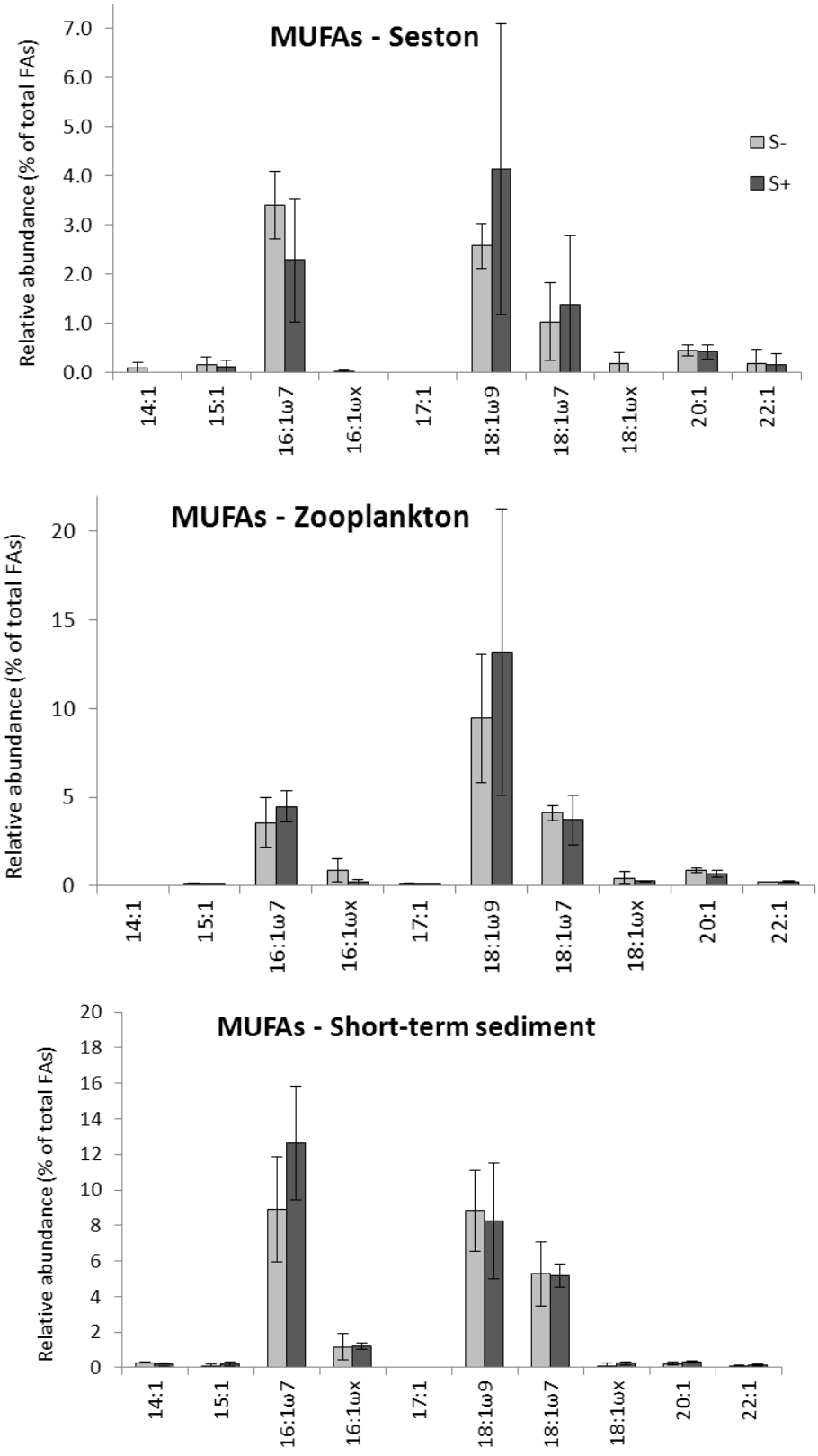


**Figure 9** : Polyunsaturated fatty acid distribution (% of total FAs, mean ± SD) of seston, zooplankton and short-term sediment sampled in June 2010.

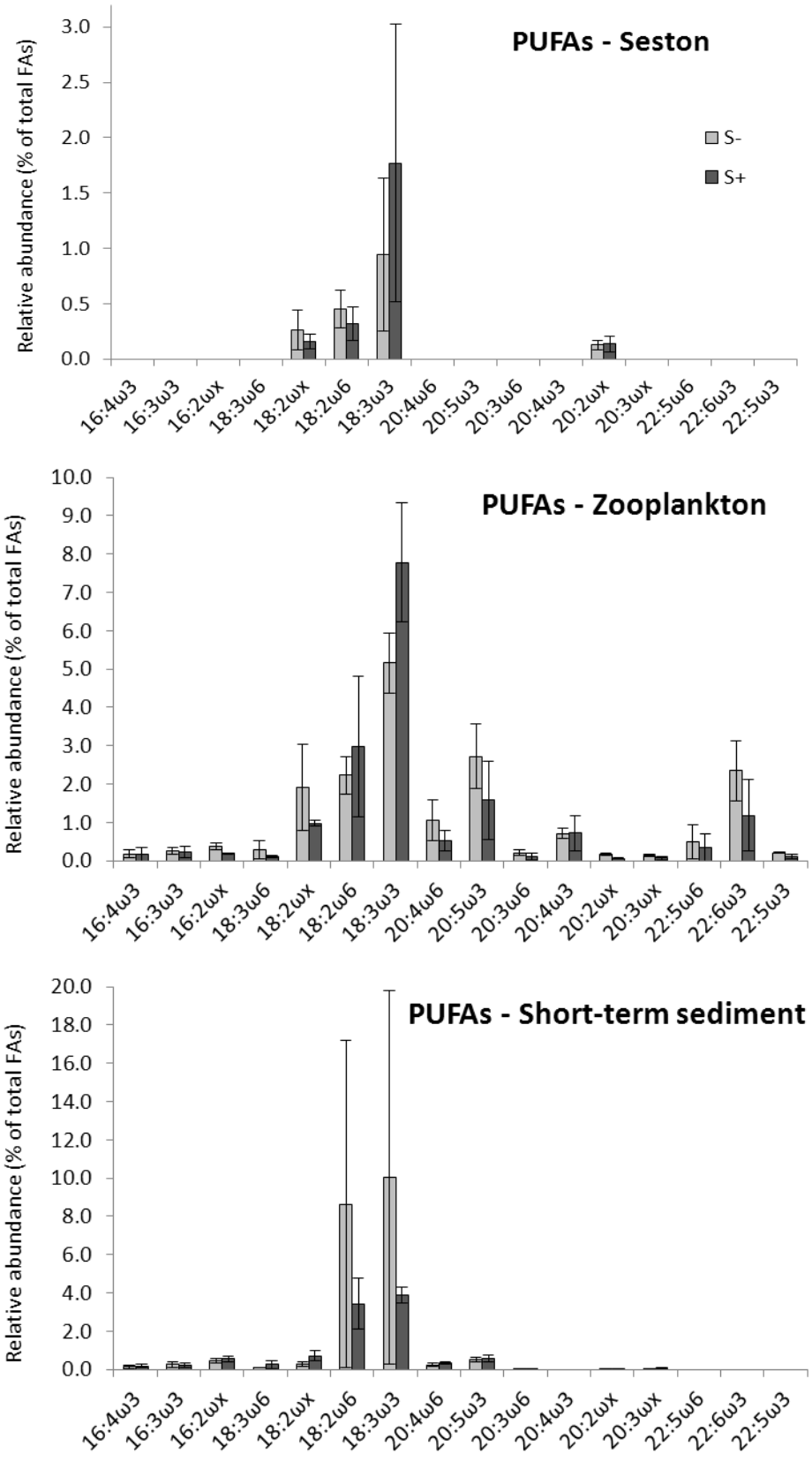


**Figure 10** : Bacterial fatty acid distribution (% of total FAs, mean ± SD) of seston, zooplankton and short-term sediment sampled in June 2010.

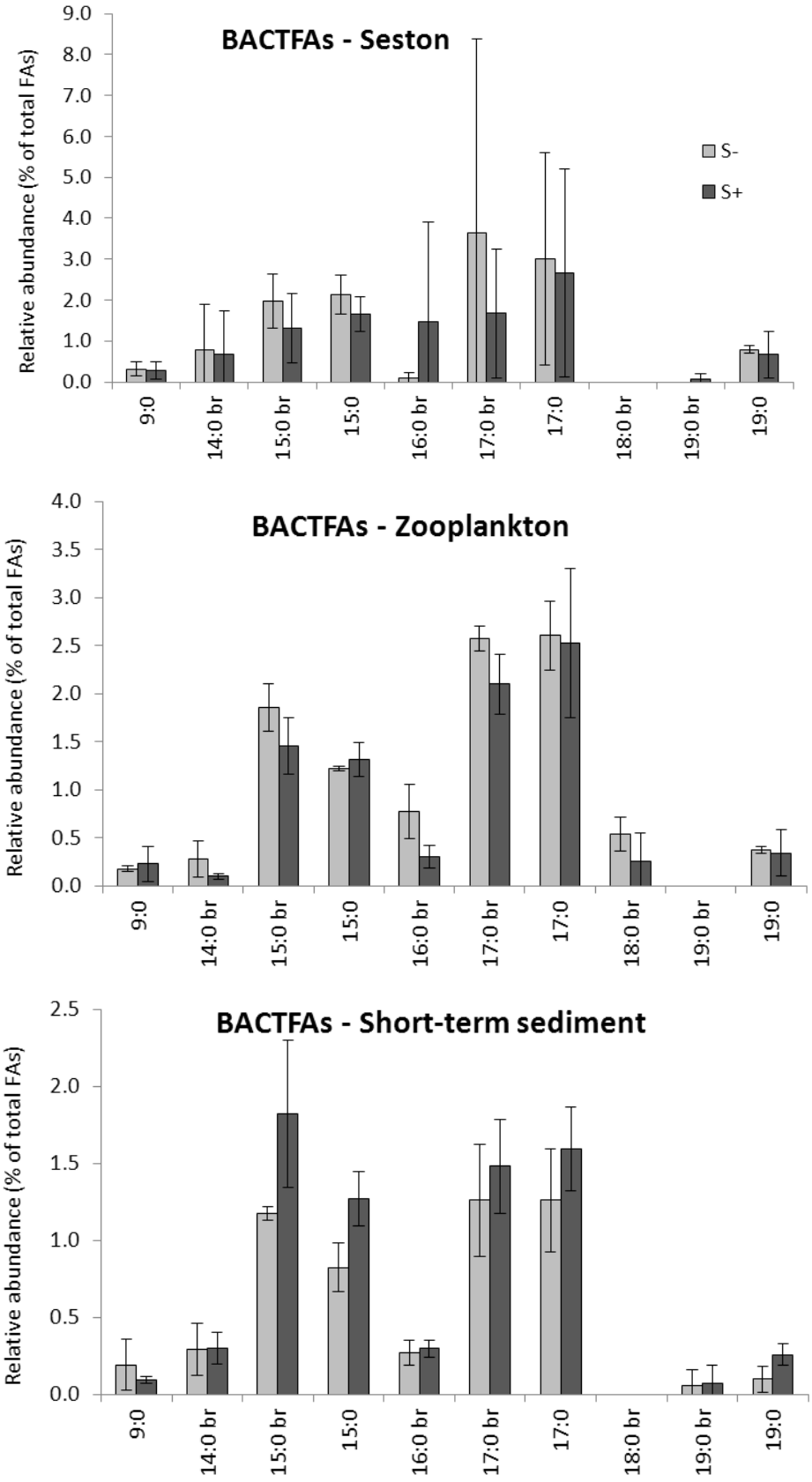


**Figure 11** : Sterol distribution (% of total sterols, mean ± SD) of seston, zooplankton and short-term sediment sampled in June 2010.

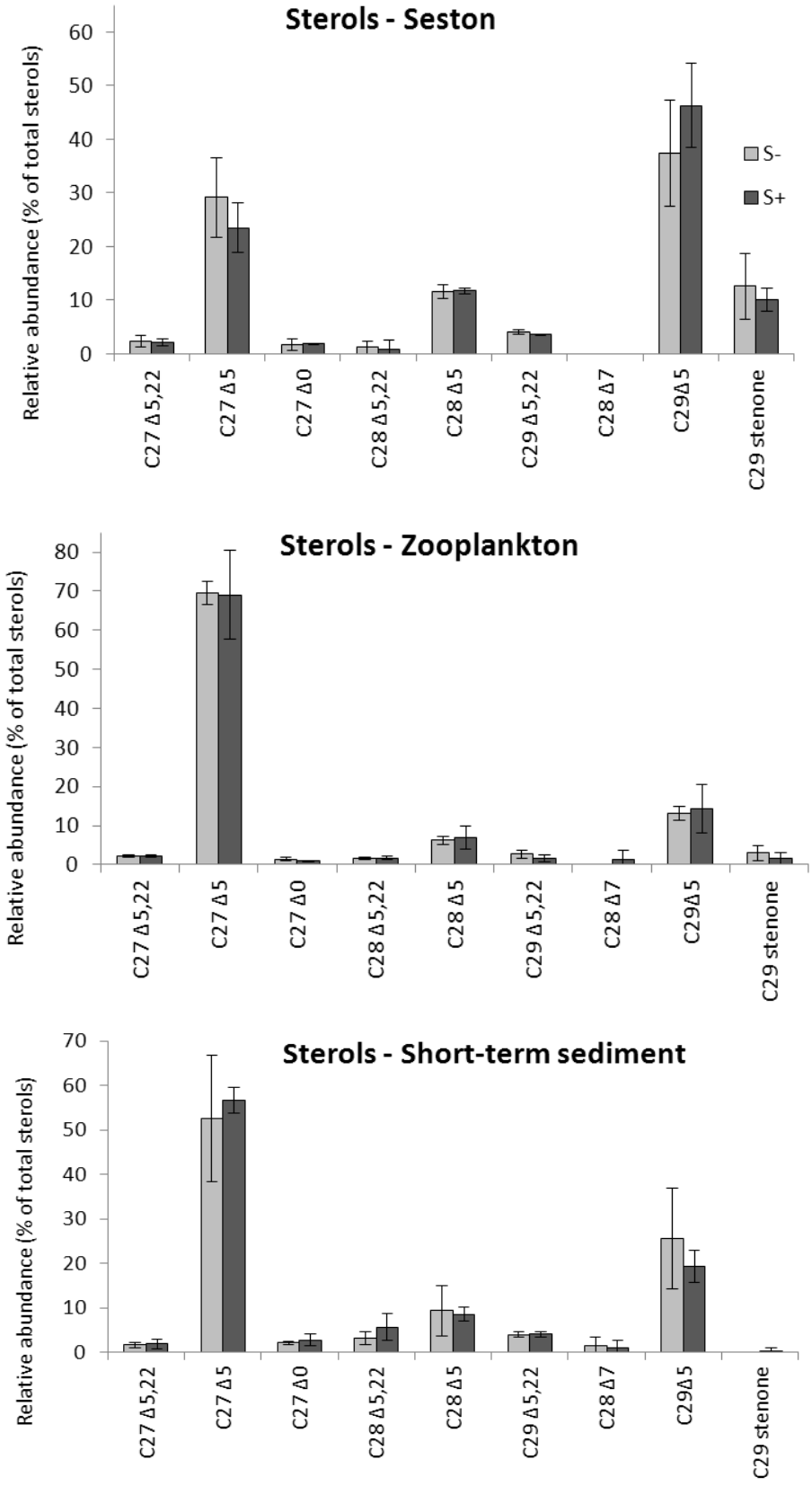


**Figure 12** : Alkanol distribution (% of total alkanols, mean ± SD) of seston sampled in June 2010. First graph: full scale. Second graph: zoom.

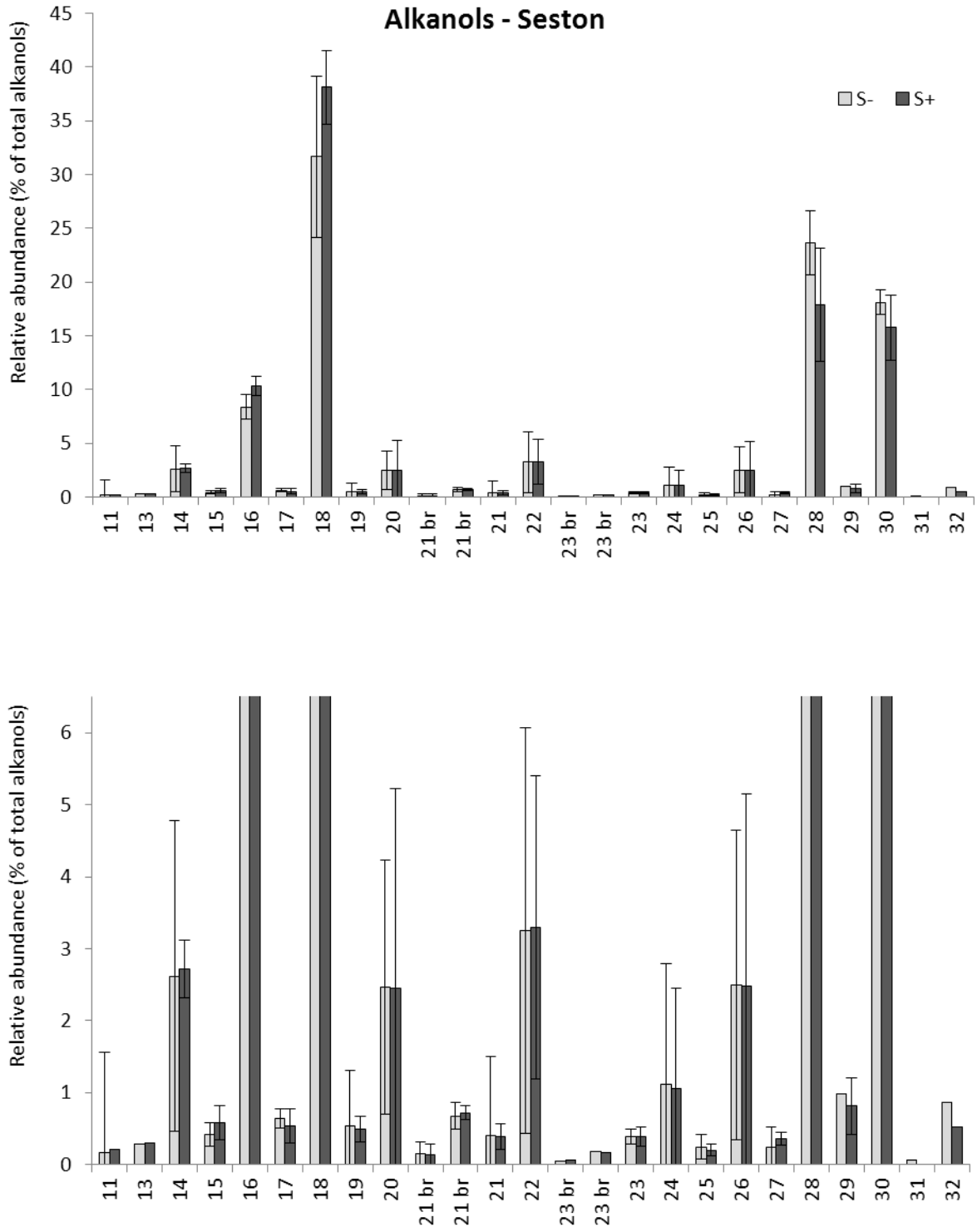


**Figure 13** : Alkanol distribution (% of total alkanols, mean ± SD) of zooplankton sampled in June 2010. First graph: full scale. Second graph: zoom.

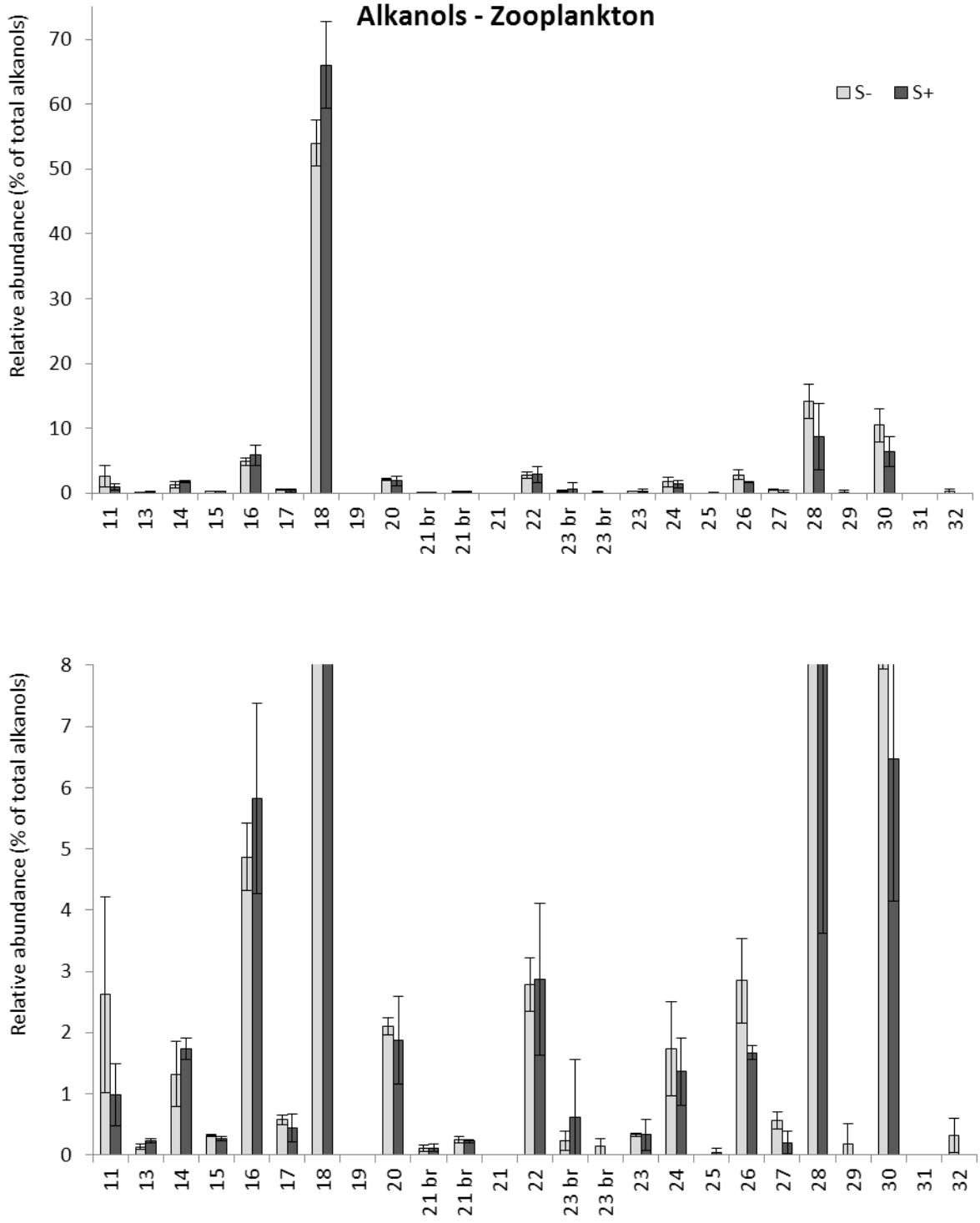


**Figure 14** : Alkanol distribution (% of total alkanols, mean ± SD) of short-term sediment sampled in June 2010. First graph: full scale. Second graph: zoom.

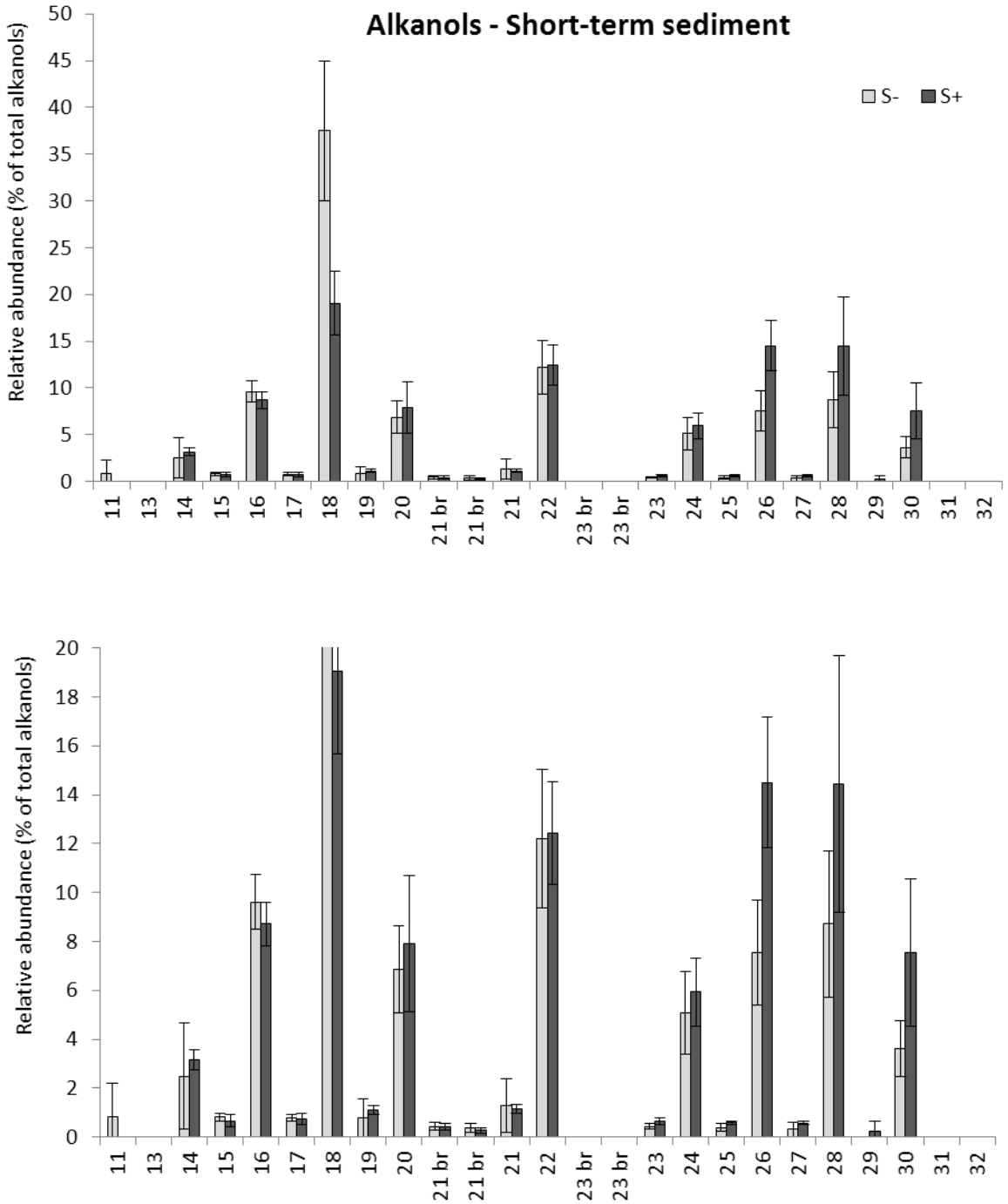
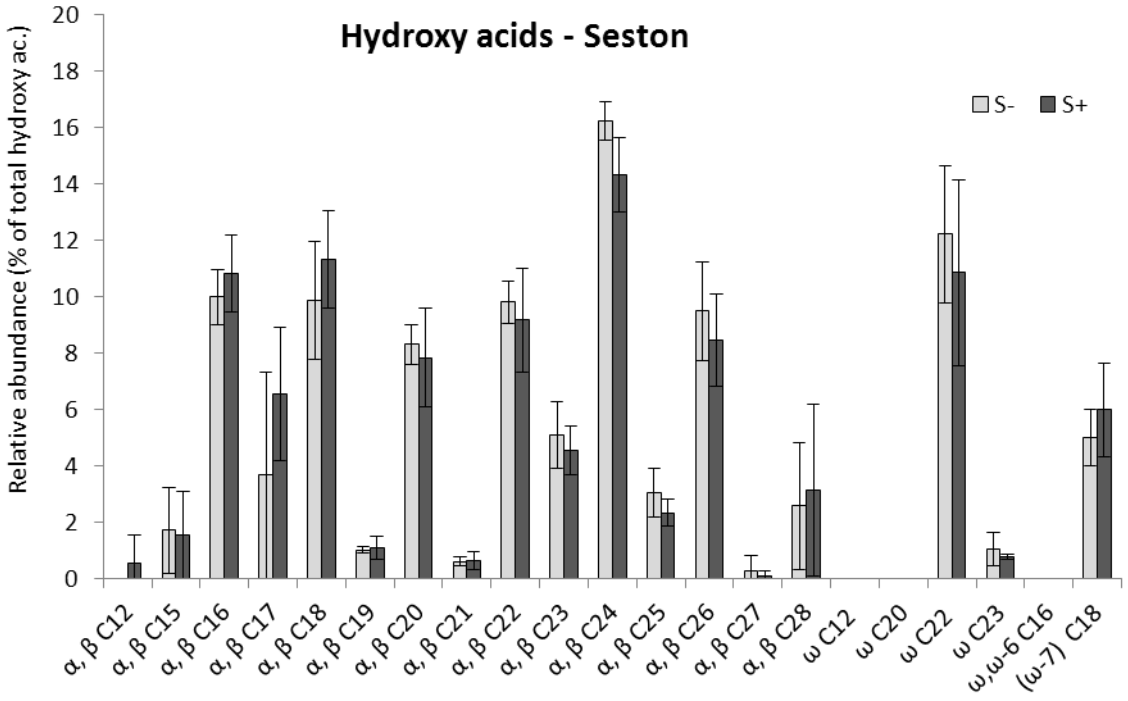


**Figure 15** : Hydroxy acid distribution (% of total hydroxy acids, mean ± SD) of seston sampled in June 2010. First graph: detailed distribution. Second graph: relative distribution of α +β- vs ω-hydroxy acids.



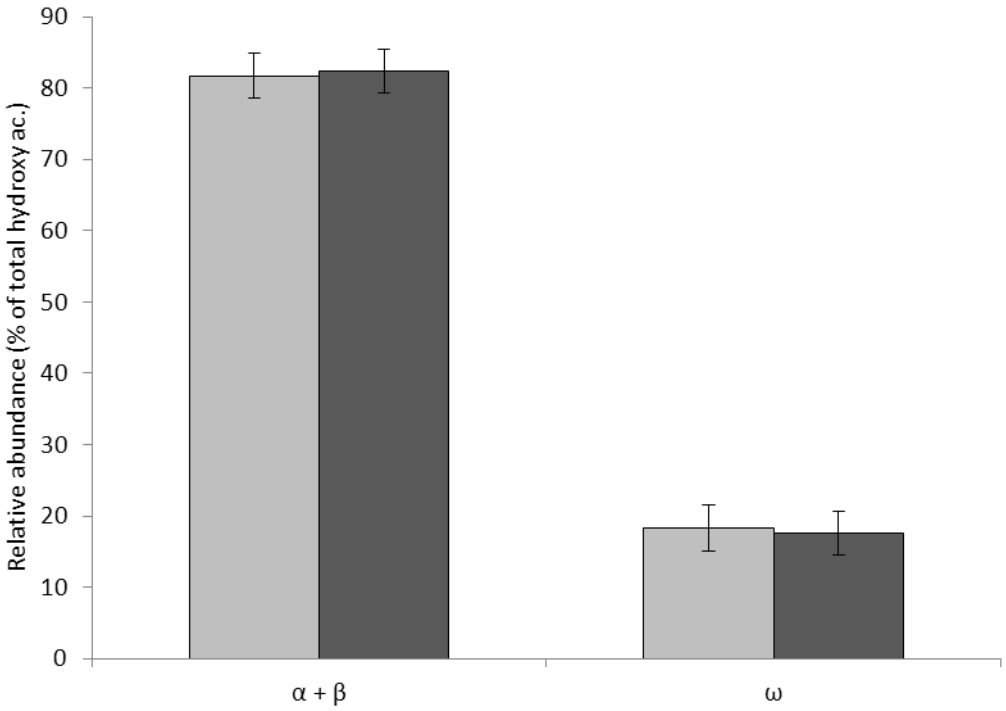



**Figure 16** : Hydroxy acid distribution (% of total hydroxy acids, mean ± SD) of zooplankton sampled in June 2010. First graph: detailed distribution. Second graph: relative distribution of α +β- vs ω-hydroxy acids.

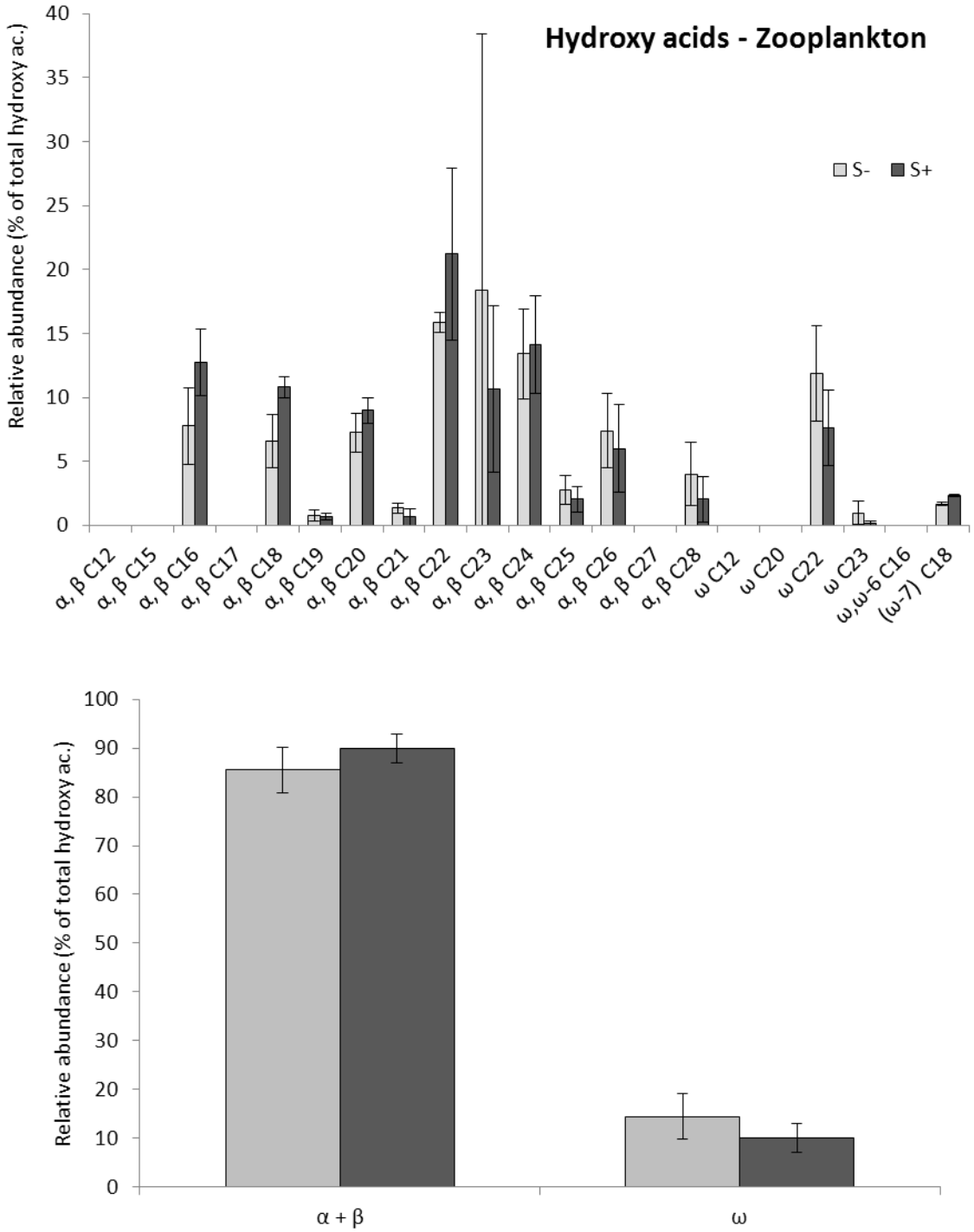


**Figure 17** : Hydroxy acid distribution (% of total hydroxy acids, mean ± SD) of short-term sediment sampled in June 2010. First graph: detailed distribution. Second graph: relative distribution of α +β- vs ω-hydroxy acids.

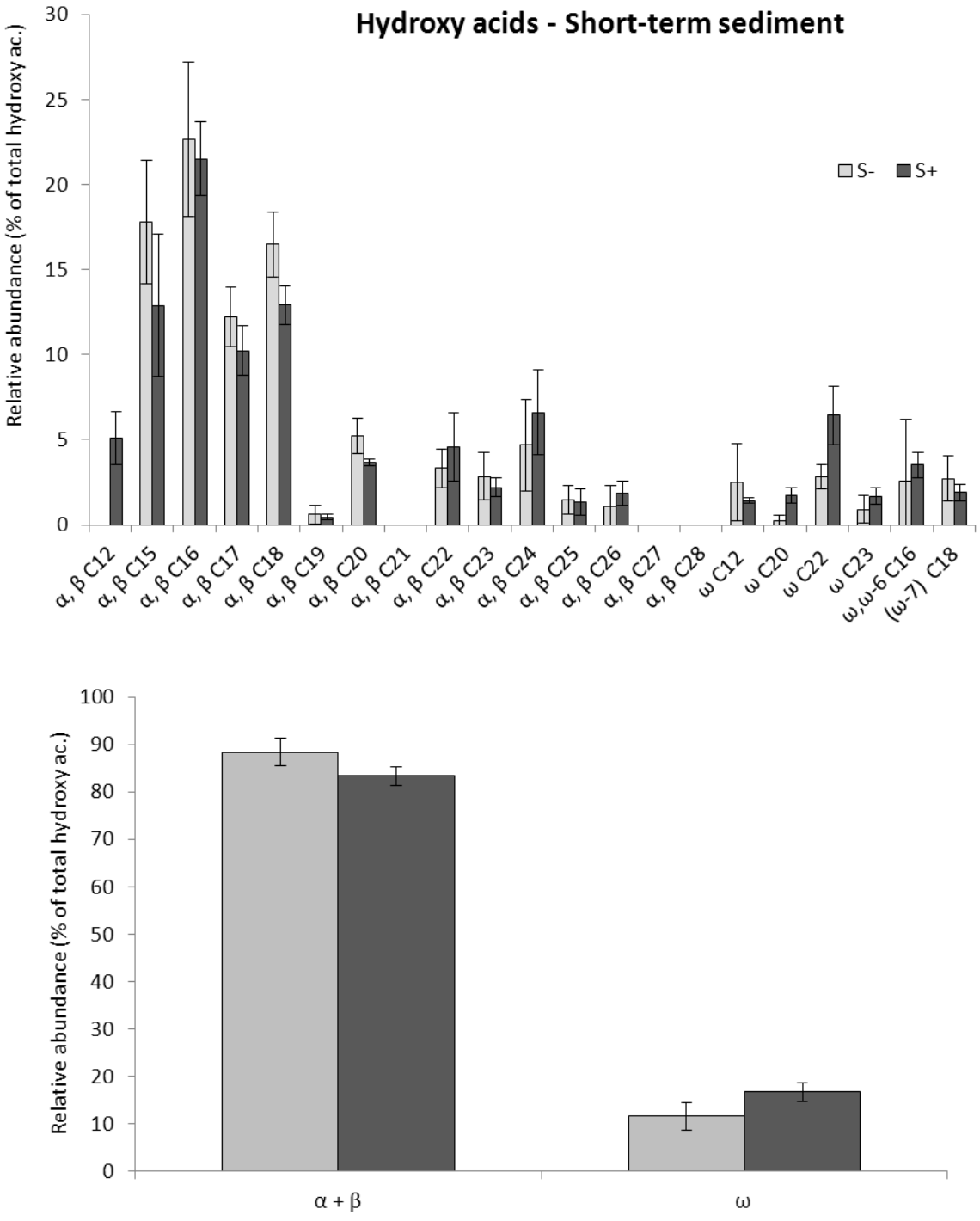


**Figure 18** : Lipid distribution (% of total lipids, mean ± SD) of short-term sediment sampled in June 2011. Without effect of soil treatment, F- and F+ values are means of both soil treatments First graph: full scale. Second graph: zoom.

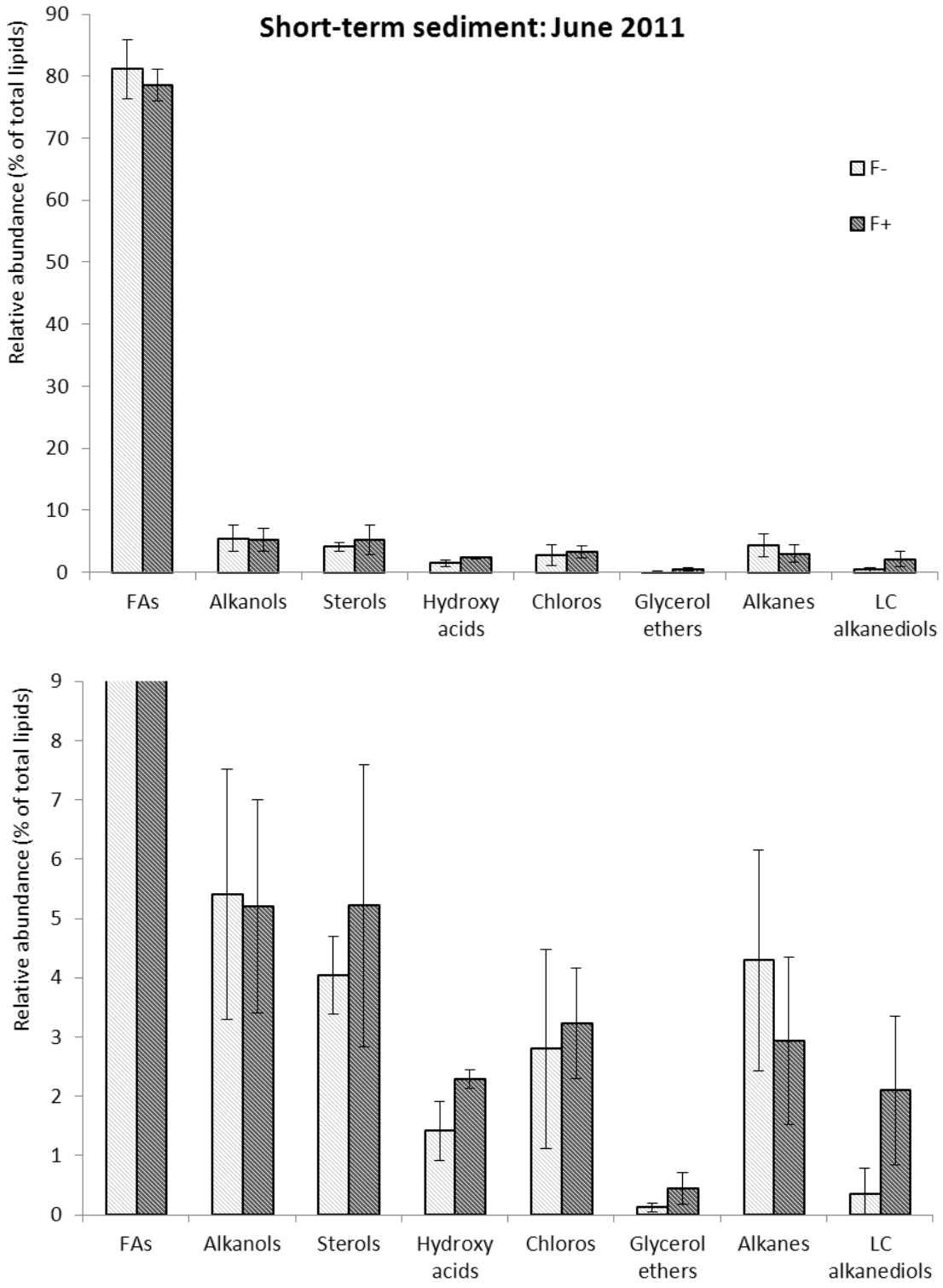


**Figure 19** : Fatty acid distribution (% of total FAs, mean ± SD) of short-term sediment sampled in June 2011. Without effect of both soil and fish treatments, values are means of all treatments

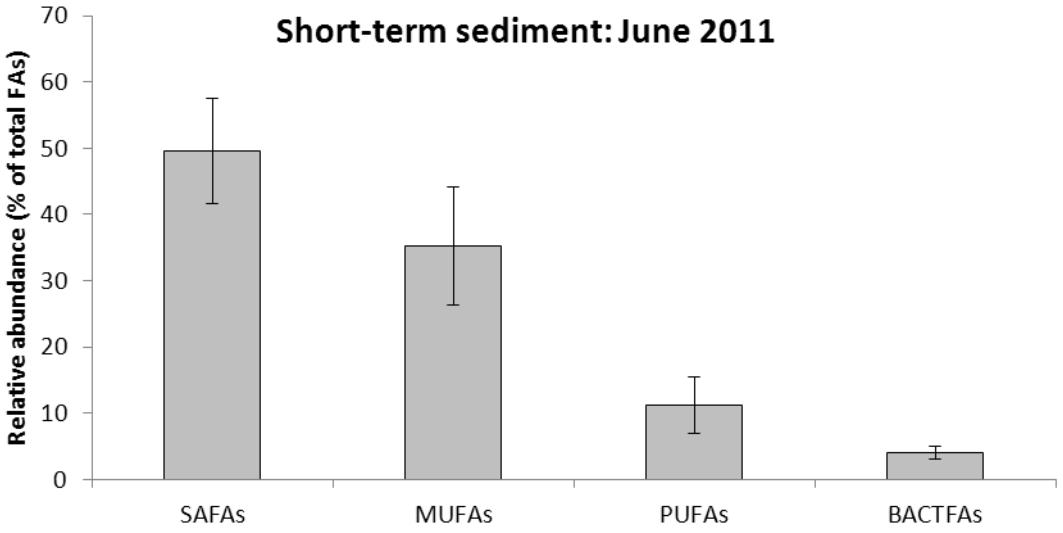



**Figure 20** : Saturated fatty acid distribution (% of total FAs, mean ± SD) of short-term sediment sampled in June 2011. Without effect of both soil and fish treatments, values are means of all treatments

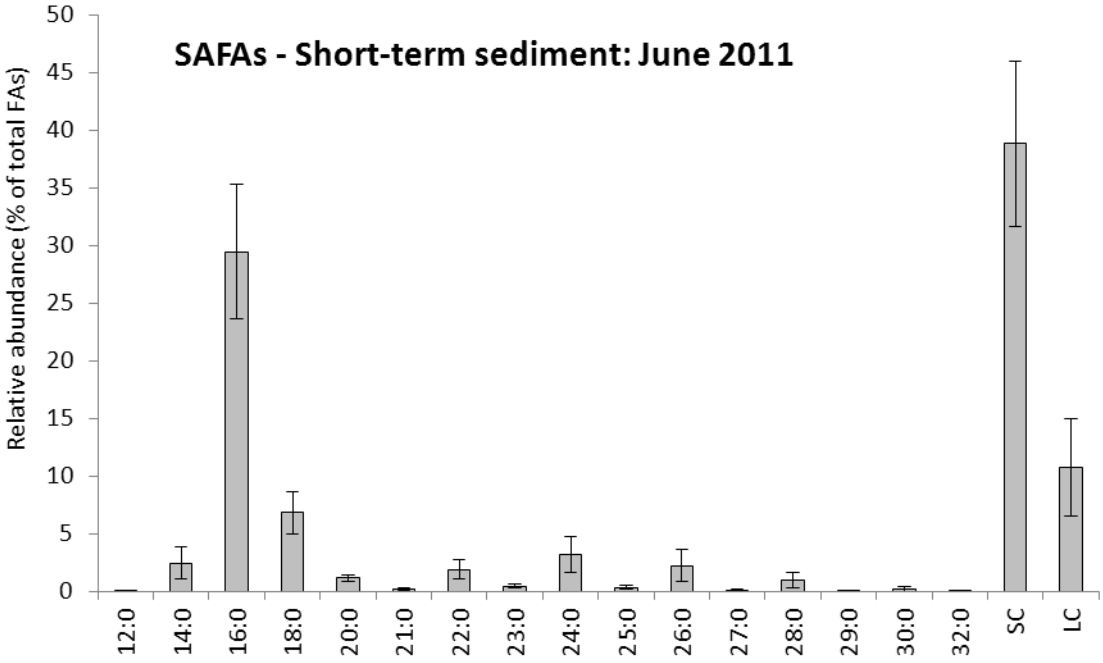


**Figure 21** : Monounsaturated fatty acid distribution (% of total FAs, mean ± SD) of short-term sediment sampled in June 2011. Without effect of both soil and fish treatments, values are means of all treatments.

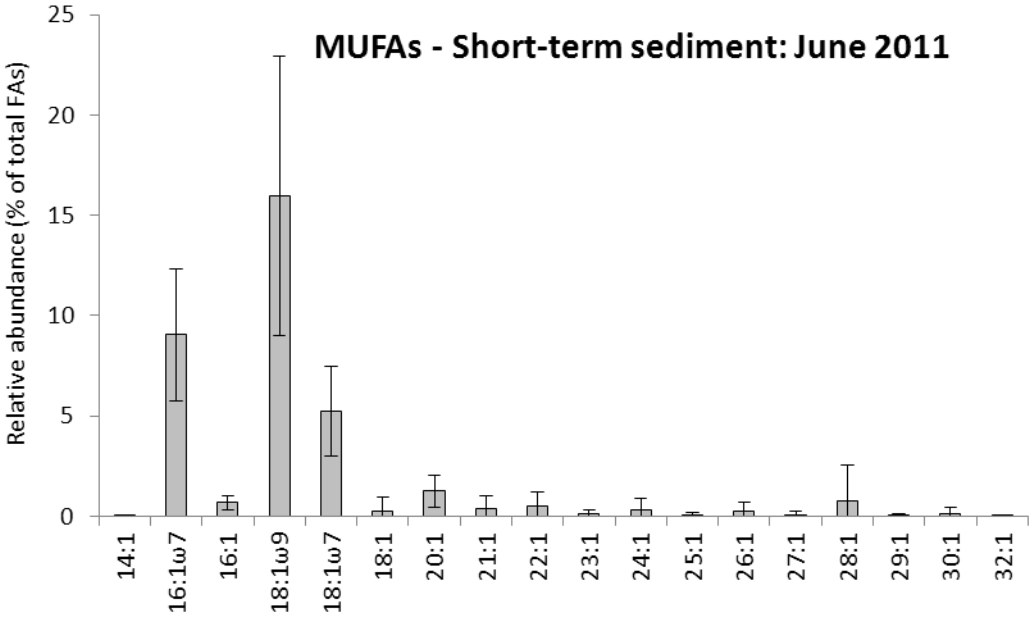



**Figure 22** : Monounsaturated fatty acid distribution (% of total FAs, mean ± SD) of short-term sediment sampled in June 2011. Without effect of both soil and fish treatments, values are means of all treatments.

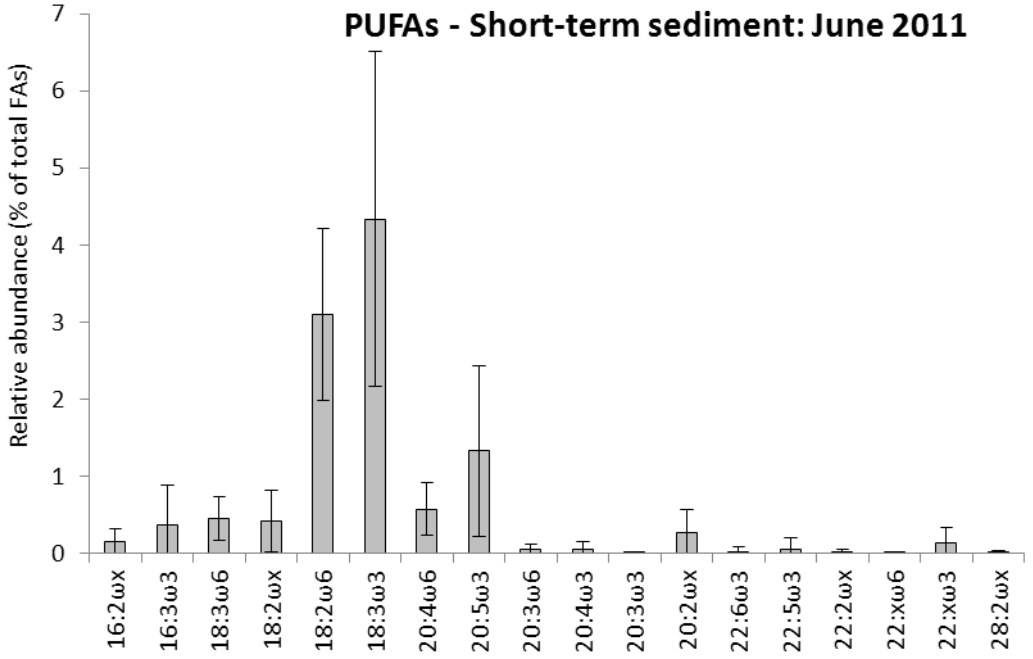


**Figure 23** : Sterol distribution (% of total sterols, mean ± SD) of short-term sediment sampled in June 2011. Without effect of soil treatment, F- and F+ values are means of both soil treatments.

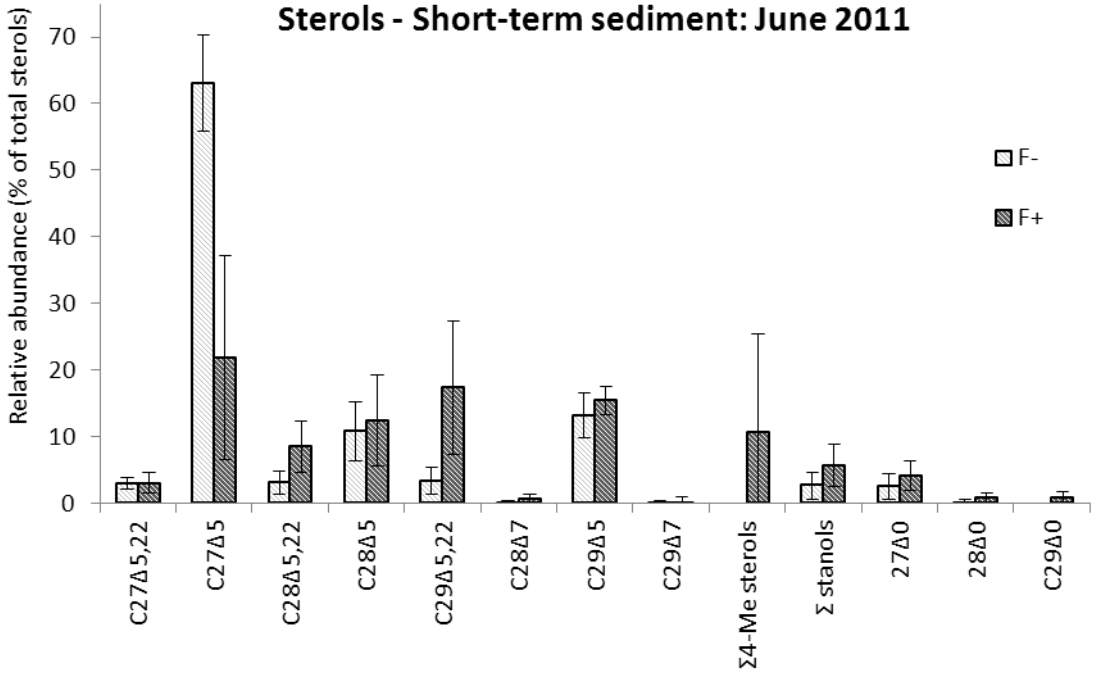



**Figure 24** : Alkanol distribution (% of total alkanols, mean ± SD) of short-term sediment sampled in June 2011. Without effect of soil treatment, F- and F+ values are means of both soil treatments.

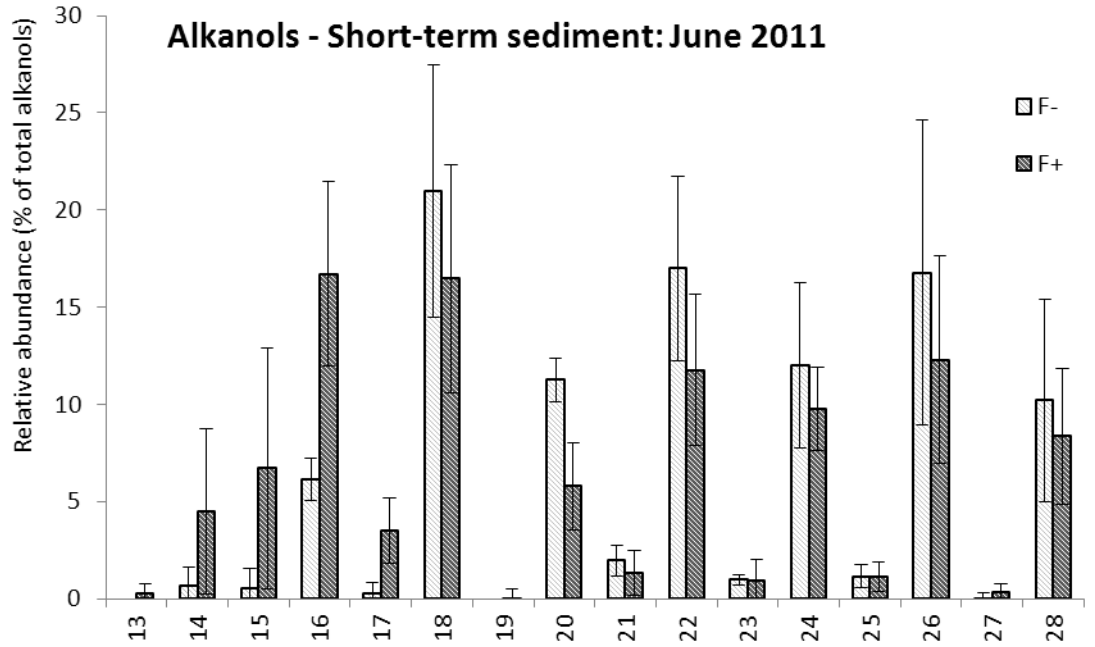
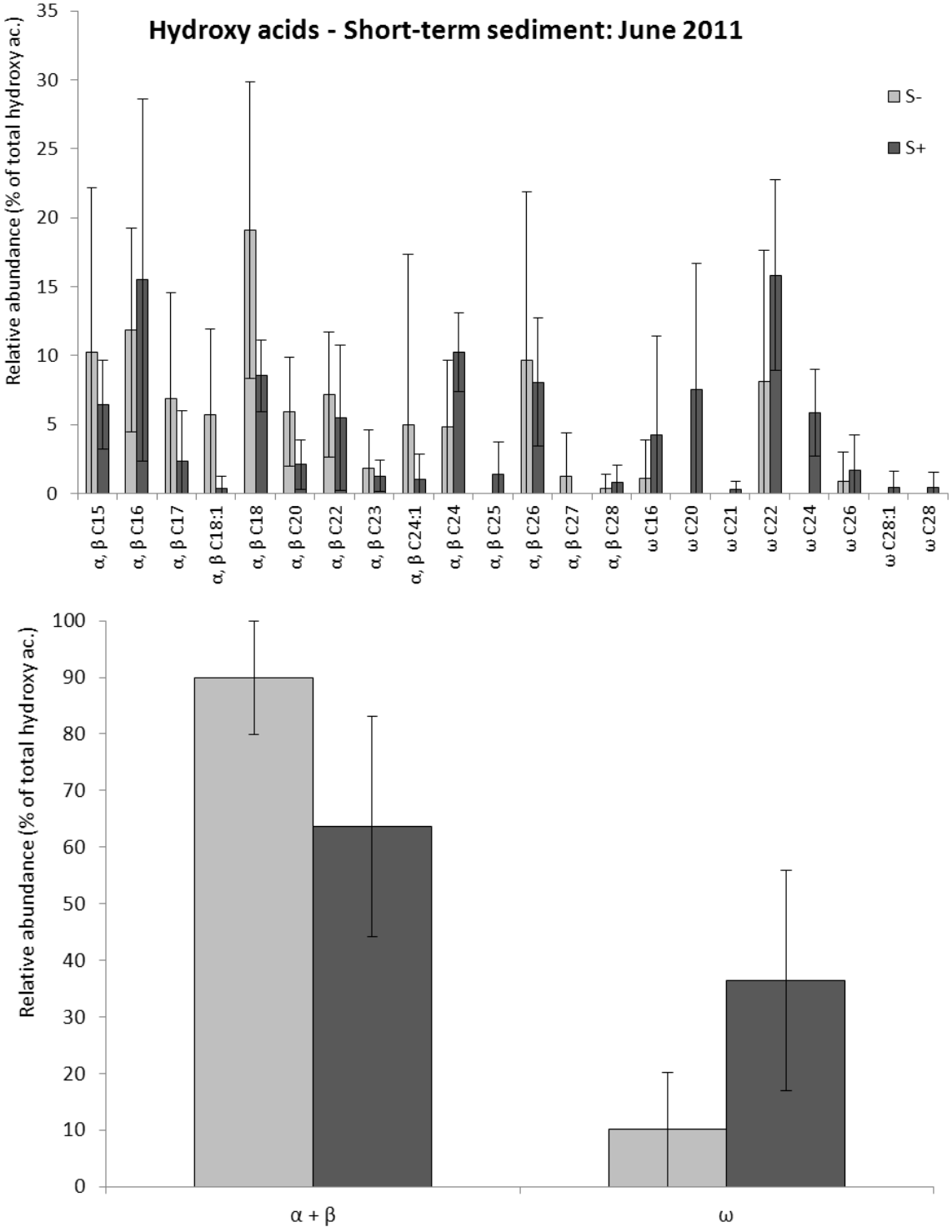


**Figure 25** : Hydroxy acid distribution (% of total hydroxy acids, mean ± SD) of short-term sediment sampled in June 2011. Without effect of fish treatment, S- and S+ values are means of both fish treatments. First graph: detailed distribution. Second graph: relative distribution of α +β- vs ω-hydroxy acids.



# Conclusions et perspectives

**Conclusions et perspectives**

Ce travail de thèse avait deux objectifs principaux : i) étudier l'influence de l'origine et de la composition de la matière organique sur sa biodégradabilité en milieu aquatique dans des conditions contrôlées, et ii) étudier l'influence de différentes matières organiques (autochtone et allochtone), en tant que ressources potentielles d'énergie et de nutriments pour les organismes aquatiques (effet ascendant ou « bottom-up »), sur le fonctionnement des écosystèmes lentiques à une échelle plus réaliste. Dans un premier temps, ces travaux se sont focalisés sur l'étude de la minéralisation de matières organiques autochtones d'origines très différentes à l'échelle du microcosme. Dans un second temps, en s'appuyant sur les conclusions de l'étude précédente et afin de généraliser les résultats obtenus en microcosmes à l'échelle de l'écosystème, l'impact de la biodégradation de la matière organique autochtone et allochtone sur les écosystèmes lacustres a été étudié dans des mésocosmes. Ce changement d'échelle a été effectué pour deux sources de matière organique distinctes : des sédiments lacustres (pour simuler le recyclage interne) et un sol (pour simuler l'érosion des bassins versants).

Des études récentes ont montré que la stœchiométrie (teneur en carbone organique [OC], en azote [N] et rapport OC/N) des compartiments biotiques ne pouvait, à elle seule, rendre compte de l'influence de la structure des réseaux trophiques sur les compartiments pélagiques et sur la biodégradabilité potentielle des sédiments (Allard et al., 2011 ; Danger et al., 2012). Par contre, ces mêmes études ont montré que certains biomarqueurs lipidiques des compartiments pélagiques pouvaient s'avérer des outils assez puissants pour ce type d'étude. Nous avons donc couplé les deux approches, stœchiométrie et biomarqueurs lipidiques, tout au long de cette thèse.

Dans un premier temps (chapitre 2), nous avons montré que la structure du réseau trophique aquatique pouvait fortement influencer la biodégradabilité des sédiments récents et leurs compositions élémentaire et biochimique.

Des mesures de respirométrie ont en effet montré que les sédiments récents provenant de mésocosmes dominés par le phytoplancton (traitement « avec poisson ») avaient une biodégradabilité potentielle 60 % plus élevée que celle des sédiments provenant de mésocosmes dominés par le zooplancton (traitement « sans poisson »). Ce résultat a confirmé l'hypothèse proposée par de précédentes études, à savoir que les sédiments provenant de communautés pélagiques dominées par le phytoplancton, du fait de leurs plus fortes teneurs

en composés très labiles tels que les acides gras polyinsaturés, les protéines et les sucres, étaient potentiellement plus biodégradables que les sédiments provenant de communautés pélagiques dominés par le zooplancton. (Allard et al., 2011 ; Danger et al., 2012).

La perte annuelle des sédiments, plus élevée pour les sédiments issus du traitement « avec poisson », a confirmé la biodégradabilité potentielle plus importante de ces sédiments. En comparant les pertes annuelles *in situ* des sédiments à long terme provenant de mésocosmes soumis aux deux traitements, nous avons en effet montré que les sédiments des enceintes dominées par le phytoplancton étaient soumis à un recyclage des nutriments (carbone organique, azote et phosphore) plus important que les sédiments des enceintes dominées par le zooplancton, confirmant ainsi les résultats obtenus en microcosmes par respirométrie, sur les sédiments à court terme.

La composition biochimique des sédiments à court et long terme laisse supposer que leur biodégradabilité potentielle dépend principalement de leur teneur en composés labiles tels que les acides polyinsaturés, les protéines et les sucres. Dans cette étude, les stérols se sont avérés être des indicateurs aussi bien de l'état de dégradation des sédiments, révélé par exemple par la contribution relative de stanols aux stérols totaux, que de la contribution relative du phytoplancton et du zooplancton aux sédiments provenant des deux traitements, révélée par exemple par les proportions relatives de cholestérol (stérol principalement d'origine animale, Goad et Akihisa, 1997) et de stérols possédant une double liaison en position 7 sur le noyau stérol (stérols rencontrés essentiellement chez les chlorophycées, Cranwell, 1982).

Les différences de biodégradabilité des sédiments et de recyclage des nutriments mises en évidence lors de cette étude pourraient entraîner des modifications dans le fonctionnement des écosystèmes aquatiques. Dans cette étude, la minéralisation de la matière organique autochtone n'a été estimée que de manière globale afin d'avoir une vision générale de l'influence de la structure du réseau trophique sur ce processus. Afin de mieux comprendre ce processus, et notamment quels rôles jouent la composition de la matière organique et la composition de la communauté bactérienne, des incubations similaires pourraient être conduites en suivant l'évolution de différents paramètres comme les teneurs en composés plus ou moins labiles et en biomarqueurs bactériens des sédiments, mais également en effectuant un suivi de la croissance de la communauté bactérienne et de sa composition spécifique (Goedkoop et al, 1997). Cette étude nécessiterait de posséder un nombre suffisant de réplicas afin de pouvoir faire des analyses de façon destructive à différents temps d'incubations. En

couplant analyses biochimiques, respirométrie et techniques de biologie moléculaire, une telle étude permettrait : i) d'identifier quelles sont les molécules les plus labiles ainsi que leur cinétique de dégradation dans des sédiments récemment déposés, ii) d'étudier les modifications de la croissance et de la composition spécifique de la communauté bactérienne en réponse à des substrats différents (ici des sédiments ayant une biodégradabilité et une qualité différentes).

En se basant sur les résultats du chapitre 2, l'étude décrite dans le chapitre 3 a eu pour but de déterminer dans quelle mesure la différence de biodégradabilité entre deux sédiments avait un impact sur le fonctionnement des écosystèmes à plus grande échelle. Dans cette expérience conduite dans des mésocosmes plongés dans le lac de Créteil, deux sédiments de nature très différente ont été placés au fond des mésocosmes. Durant environ cinq mois, la biomasse et la composition élémentaire des compartiments pélagiques ainsi que les taux de sédimentation et la composition élémentaire du sédiment récent ont été régulièrement déterminés. De plus, la composition lipidique et les teneurs en sucres et protéines du sédiment récent ainsi que la composition lipidique des compartiments pélagiques ont été déterminées pour une date de prélèvement.

L'un des sédiments ($S_1$) est ancien et provient directement du lac de Créteil, le second ($S_2$) beaucoup plus récent provient d'anciennes enceintes expérimentales. La différence de biodégradabilité potentielle de ces deux sédiments (biodégradabilité $S_2$ > biodégradabilité $S_1$) est clairement révélée par leur analyse lipidique et leurs teneurs en protéines et en sucres.

Ces deux traitements ont eu des effets contrastés sur la biomasse des compartiments pélagiques. Comparé au contrôle (mésocosmes sans sédiment, $S_0$), le traitement $S_1$ n'a pas eu d'effet sur les biomasses du seston (particules de taille comprise entre 0,7 et 50 µm) et du zooplancton ni sur la composition spécifique de la communauté zooplanctonique. Cette absence d'effet ascendant sur les chaînes alimentaires est probablement due à la faible biodégradabilité de $S_1$ ainsi qu'à ses faibles teneurs en carbone organique et en azote. En revanche, les biomasses de seston et de zooplancton, supérieures dans les enceintes soumises au traitement $S_2$ que dans celles soumises aux traitements $S_1$ et $S_0$, indiquent un effet positif de la biodégradabilité potentielle plus élevée de $S_2$. Cet effet s'est aussi traduit par une augmentation significative de l'abondance des Chydoridae (Cladocères benthiques) dans les enceintes expérimentales. Les variations saisonnières de ces effets semblent indiquer que l'effet ascendant (ou effet « bottom-up ») de $S_2$ s'est dans un premier temps transmis au seston puis dans un second temps au zooplancton, probablement par le broutage du phytoplancton

par les herbivores. Toutefois, on observe que les biomasses de seston et de zooplancton du traitement $S_2$ ont, en fin d'expérimentation, des valeurs similaires à celles des traitements $S_0$ et $S_1$. Ceci pourrait signifier que l'effet positif exercé par $S_2$ sur la biomasse de seston et transmis au zooplancton, n'est pas suffisamment intense pour se maintenir dans le temps et que le zooplancton se retrouve finalement limité par la quantité de phytoplancton disponible malgré la richesse potentielle élevée en nutriments du sédiment ajouté, ce qui a été confirmé par les teneurs en phosphates plus grande dans l'eau des enceintes $S_2$ que dans les enceintes $S_0$ et $S_1$. Ce résultat suggère que le contrôle « bottom-up », dû notamment au relargage de nutriments (Søndergaard et al., 2003) exercé par le sédiment $S_2$ sur les biomasses des organismes pélagiques, peut être masqué par le contrôle descendant (ou effet « top-down ») exercé par la prédation des herbivores sur le phytoplancton.

L'effet ascendant induit par $S_2$ sur la biomasse du seston a également été observé sur sa composition élémentaire et suggère que le seston de ce traitement a une qualité nutritive supérieure (notamment une teneur en azote supérieure et un rapport C/N inférieur) à celle du seston des traitements $S_1$ et $S_0$. Par contre, malgré les différences de composition élémentaire du seston observées, la composition élémentaire du zooplancton n'est pas influencée par les traitements sédiments. Ce résultat confirme que le zooplancton est capable de réguler sa stœchiométrie indépendamment de celle de sa ressource selon le principe d'homéostasie (Hessen, 1990). De plus, ceci suggère que les changements de composition élémentaire des organismes à la base des réseaux trophiques aquatiques ne sont pas nécessairement transmis aux organismes d'un niveau trophique supérieur, restreignant ainsi les effets du recyclage des nutriments des sédiments aux organismes basaux en termes de composition élémentaire.

L'analyse des lipides des compartiments pélagiques a mis en évidence le fait que l'effet « bottom-up » de $S_2$, qui se traduit sur les biomasses de seston et de zooplancton et sur la composition élémentaire du seston, n'induit pas de différences notables sur la distribution des lipides de ces deux compartiments.

Les taux de sédimentation ne sont influencés par aucun des différents traitements sédiments. Ce résultat est inattendu puisque les biomasses de seston et de zooplancton, qui contribuent largement à la sédimentation, sont plus grandes dans les mésocosmes soumis au traitement $S_2$. Cette contradiction soulève le problème du manque de précision des mesures de sédimentation dans des systèmes expérimentaux peu profonds et peu productifs, pour lesquels les taux de sédimentation sont relativement faibles comparés, par exemple, à des systèmes eutrophes (Bloesch, 2004).

La composition des lipides des sédiments récemment déposés indique que le phytoplancton et le zooplancton contribuent tous les deux à la sédimentation sans qu'il soit possible de se prononcer quant à une contribution majoritaire du phytoplancton ou du zooplancton. L'absence d'effet « bottom-up » sur la sédimentation à court terme est confirmée par différents biomarqueurs de biodégradabilité de la matière organique tels que les acides gras insaturés, les protéines, les sucres, et les acides bactériens.

Cette étude suggère donc que les effets du contrôle ascendant induits par la biodégradabilité potentielle de la matière organique des sédiments lacustres sur les compartiments pélagiques restent limités. Les effets ne sont visibles que pour $S_2$, sédiment constitué de matière organique hautement biodégradable et donc non vraiment représentative de la matière organique des sédiments lacustres naturels. Les résultats confirment que dans des systèmes aquatiques à faibles charges en poissons planctonophages ou omnivores (ou de manière plus caricaturale en absence de poissons comme c'était le cas dans cette expérience), le relargage de nutriments par le sédiment peut être ralenti, la faible bioturbation du sédiment jouant probablement un rôle majeur dans ce ralentissement (Søndergaard et al., 1992). Ceci suggère que les biomanipulations, utilisées pour la remédiation des écosystèmes eutrophes et consistant à diminuer la charge en poissons planctonophages ou en augmentant la charge en poissons carnivores (Jeppesen et al., 1990), pourraient favoriser un retour à des eaux claires, non seulement à travers l'accentuation du contrôle du phytoplancton par le zooplancton herbivore (contrôle « top-down »), mais aussi en limitant le recyclage interne des nutriments (faible taux de sédimentation, biodégradabilité réduite de la matière organique nouvellement formée, et faible relargage de nutriments du fait d'une bioturbation limitée des sédiments, contrôle « bottom-up). Il convient bien-sûr de rester prudent, car nos systèmes expérimentaux n'étaient pas soumis à des apports en nutriments extérieurs et la durée de l'expérience était limitée à 5 mois. Dans des écosystèmes soumis à d'importants apports extérieurs de nutriments, l'efficacité des biomanipulations semble être limitée à quelques années si les apports externes de nutriments sont arrêtés (Jeppesen et al., 2007 ; Søndergaard et al., 2007). Cependant, l'ensemble des résultats obtenus dans les chapitres 2 et 3 suggère que les biomanipulations pourraient avoir un effet positif sur la qualité de l'eau plus accentué que ce qui est attendu avec la seule théorie des cascades trophiques.

Dans le chapitre 4 nous nous sommes intéressés à la biodégradation de la matière organique des sols lorsqu'elle est transportée du milieu terrestre au milieu aquatique. Pour ce

faire, différents sols (sols de prairie, de forêt, de jachère et agricole) ont été incubés en présence d'une communauté bactérienne de lac en milieu aqueux minéral simulant deux écosystèmes, l'un méso-oligotrophe (faible concentration en nutriments) et le second eutrophe (forte concentration en nutriments). La cinétique de la minéralisation de la matière organique de ces sols en milieu aquatique a été suivie pendant 45 jours. Les cinétiques de minéralisation en milieu aquatique ont été comparées à celles obtenues en environnement terrestre. Nous avons également étudié l'impact d'un ajout de matière organique labile, simulant les exsudats phytoplanctoniques en milieu aquatique, sur la minéralisation. Pour cette étude, du glucose marqué uniformément au carbone 13 a été ajouté aux microcosmes pour permettre la distinction entre la minéralisation de la matière organique des sols et celle du glucose.

Comparée aux incubations reproduisant un système terrestre, la minéralisation de la matière organique des sols augmente en moyenne de 63 % dans des conditions aquatiques. Cette surminéralisation en milieu aquatique ne dépend pas des conditions trophiques d'incubation (faible ou forte concentration en N et P) et est plus importante pour les sols de forêt et de prairie que pour le sol agricole et le sol de jachère. Ces résultats sont interprétés par une différence dans la cinétique de désagrégation des sols en milieu aquatique et donc par une différence d'accessibilité des micro-organismes à la matière organique. En effet, le sol de jachère et le sol agricole ont été, depuis très longtemps, labourés tous les ans et contiennent vraisemblablement des agrégats moins stables que ceux présents dans les sols de forêt et de prairie, non impactés par des actions anthropiques (Balabane et Plante, 2004).

Cette expérience en laboratoire suggère que certains mécanismes responsables de la préservation de la matière organique dans les sols sont atténués en conditions aquatiques. Ces mécanismes concernent non seulement la stabilité physique des sols qui limite l'accessibilité des micro-organismes à la matière organique, mais également la stabilité chimique de cette matière organique (von Lützow et al., 2006). Cependant, les compositions élémentaires et biochimiques de la matière organique des différents sols utilisés ne semblent pas être des facteurs primordiaux pour expliquer l'intensité et la cinétique du processus de minéralisation des sols en contexte aquatique. De plus, la surminéralisation en milieu aquatique n'apparaît pas être dépendante des conditions trophiques. Il semblerait donc que dans ces conditions, les micro-organismes décomposeurs de la matière organique ne soient pas limités par les nutriments mais plutôt par la quantité de carbone organique disponible.

Cette hypothèse a été validée par la mise en évidence d'une surminéralisation de la matière organique allochtone en milieu aquatique en présence d'une source de matière

organique labile (« priming effect », Kuzyakov et al., 2000). En effet, l'ajout de glucose en tant que matière organique labile augmente de 12 % (en conditions oligo-mésotrophes) et de 22% (en conditions eutrophes) la minéralisation de la matière organique des sols en milieu aquatique. Le « priming effect » cumulé (c.a.d. la différence entre la minéralisation avec et sans glucose) est très différent selon le sol considéré. On observe en effet un « priming effect » cumulé positif pour le sol agricole et le sol de prairie. Le sol de jachère présente quant à lui un comportement particulier. En effet après un « priming effect » cumulé négatif durant les premiers jours de l'incubation, un « priming effect » cumulé positif est observé durant le reste de l'expérience. Ces différents comportements sont interprétés en fonction de la récalcitrance et de la qualité (dont les indicateurs sont ici la composition élémentaire, la composition lipidique et la teneur en protéines et en sucres des sols). Ainsi la matière organique du sol de jachère est considérée comme un modèle de matière organique stable et hautement récalcitrante, et la communauté bactérienne a besoin de plus d'énergie pour la minéraliser. Cette communauté bactérienne aura donc tendance à utiliser prioritairement le glucose comme source d'énergie. Un « priming effect » cumulé négatif est observé pour le sol de forêt durant la majeure partie de l'expérience, une surminéralisation de la matière organique ne survenant qu'en fin d'expérience et seulement pour la faible charge en nutriments. Ce « priming effect » cumulé négatif ne peut pas être expliqué uniquement par une trop grande récalcitrance de la matière organique. En effet, les compositions élémentaires, lipidiques et les teneurs en protéines et en sucres du sol de forêt montrent que la matière organique de ce sol est très certainement moins récalcitrante que celle issue du sol de jachère. Des paramètres tels que le rapport C/N élevé et la forte concentration en tannins, composés inhibiteurs d'exoenzymes (Kraus et al., 2003), des sols de forêt ont été avancés pour expliquer le « priming effect » cumulé négatif observé pour ce sol.

Généralisés à l'échelle de l'écosystème aquatique, dans lequel les apports de matière organique labile seraient assurés par les exsudats phytoplanctoniques (Myklestad, 1995) et les apports de matière allochtone par l'érosion des bassins versants, nos résultats renforcent les précédentes observations sur la surminéralisation de la matière organique en milieu aquatique et ses conséquences potentielles à l'échelle de l'écosystème. L'une des principales conséquences, qui semble désormais acquise au vu des résultats de nombreux travaux effectués durant ces deux dernières décennies à l'échelle de l'écosystème, est que les lacs se comportent comme une source de $CO_2$ pour l'atmosphère plutôt que comme un puits de carbone (del Giorgio et al., 1997, 1999 ; Duarte et Prairie, 2005).

C'est dans ce contexte que nous avons mis en place l'étude présentée dans le chapitre 5. Dans un premier temps, ce travail a eu pour but d'étudier, l'influence d'apports réguliers de matière organique allochtone sur les écosystèmes lacustres. Par la suite, l'ajout de poissons zooplanctivores dans la moitié des systèmes expérimentaux nous a permis d'étudier l'influence de la structure du réseau trophique et de ses interactions avec les ajouts de matière organique allochtone sur les compartiments pélagiques.

La composition lipidique du sol utilisé pour simuler les apports allochtones est largement dominée par des biomarqueurs généralement attribués à la présence de plantes supérieures.-Sur toute la durée de l'expérience (1 an ½), les ajouts de terre n'ont affecté ni les biomasses du seston et du zooplancton ni leur composition élémentaire. L'absence de différences entre les concentrations en chlorophylle-*a* des mésocosmes soumis aux deux traitements (avec [S+] et sans [S-] ajout de terre) suggère que les apports de terre n'ont pas influencé la biomasse de phytoplancton. De même, le traitement terre n'a eu aucune influence sur la composition lipidique du seston et a très peu modifié celle du zooplancton. Les faibles différences observées entre les compositions lipidiques du seston et du zooplancton issus des deux traitements ainsi que la faible abondance des biomarqueurs allochtones dans le seston et le zooplancton des mésocosmes S+ suggèrent que les apports de matières allochtones ont eu peu d'effets sur la composition lipidique de ces compartiments à l'échelle de la communauté. Toutefois, l'analyse de la composition lipidique du zooplancton à des échelles plus fines (groupe fonctionnel, ordre, famille…) pourrait révéler des effets significatifs sur la contribution de la matière organique allochtone au régime alimentaire du zooplancton puisque la concentration de certains groupes (daphniidae et calanoïdes) a été augmentée par les apports de terre.

Si l'ajout de terre n'a eu que très peu d'effet sur le seston et le zooplancton, la croissance des poissons des mésocosmes S+ a été plus importante que celle des poissons des mésocosmes S-. Ce résultat suggère que les apports de matière allochtone ont eu un effet positif indirect sur les prédateurs en sommet de chaîne trophique, probablement du fait d'une stimulation des chaînes benthiques, qui pourraient avoir constitué des voies trophiques majeures pour les poissons introduits dans les mésocosmes. Cette hypothèse est corroborée par le fait que, en absence de poisson, les apports de terre n'ont pas eu d'effet positif sur la biomasse du zooplancton, qui était le compartiment en sommet du réseau pélagique, alors que

l'abondance et la croissance d'organismes benthiques comme les gastropodes ont été stimulées.

Les apports de terre n'ont pas eu d'effet sur les taux de sédimentation mais ont entraîné des modifications de la composition élémentaire des sédiments récemment déposés, puisque les sédiments des mésocosmes soumis aux apports de terre avaient des teneurs en carbone total, carbone organique, et azote plus faibles que ceux des mésocosmes témoins. En plus de cette absence d'effet terre sur le taux de sédimentation, la faible valeur du rapport CO/N et la faible contribution des biomarqueurs allochtones à la composition lipidique des sédiments, qu'ils soient issus des mésocosmes S- ou S+, suggèrent que les sédiments récemment déposés ont une origine majoritairement autochtone.

Aucune influence de l'ajout de terre n'a été observée sur les teneurs en protéines, sucres et en biomarqueurs bactériens des sédiments récemment déposés. Ce résultat suggère que les apports de matière allochtone n'ont pas d'effet sur la qualité des sédiments récemment déposés et sur l'état de dégradation de la matière organique composant ces sédiments.

Comparé aux apports de terre, l'ajout des poissons zooplanctivores a eu des effets marqués sur les compartiments pélagiques. La cascade trophique induite par la prédation du zooplancton par les poissons a eu un effet positif sur la biomasse du seston et sur la concentration en chlorophylle-*a* des mésocosmes, ce qui suggère une augmentation de la biomasse du phytoplancton (Carpenter, 1993 ; Danger et al., 2012). Les teneurs en carbone et en azote du seston se sont avérées plus grandes dans les mésocosmes avec poissons que dans les mésocosmes sans poisson. Ce résultat pourrait être expliqué par une resuspension de particules contenant peu de carbone et d'azote par les fouilles benthiques des poissons, phénomène d'autant plus important que les systèmes expérimentaux sont relativement peu profonds (Bloesch, 2004).

Au contraire, la présence des poissons n'a pas d'influence sur la biomasse du zooplancton. Ceci pourrait être dû aux changements des communautés zooplanctoniques en réponse à la prédation, phénomène n'entrainant pas nécessairement un changement de biomasse (Bertolo et al., 1999 ; Danger et al., 2012). L'absence d'influence de la présence de poissons est également observée sur la composition élémentaire du zooplancton. Ceci pourrait être dû soit à un changement de la composition de la communauté du zooplancton soit à une prédation sélective du zooplancton sur certaines algues ayant des compositions élémentaires particulières.

Les taux de sédimentation sont positivement impactés par la présence de poisson en accord avec de précédentes études (Vanni et al., 1997 ; Sarnelle, 1999 ; Danger et al., 2012). De plus, les variations saisonnières similaires des biomasses de seston, de zooplancton et des taux de sédimentation suggèrent que, dans nos systèmes expérimentaux, le processus de sédimentation est principalement contrôlé par le seston et le zooplancton. Les similarités entre les compositions élémentaires, principalement la teneur en azote, de ces trois compartiments corroborent cette hypothèse.

Comme suggéré par l'impact positif indirect des poissons sur la biomasse du phytoplancton, la différence de contribution relative du phytoplancton et du zooplancton à la sédimentation induite par le contrôle « top-down » des poissons a été confirmée par certains biomarqueurs lipidiques (proportions relatives de phytostérols, de cholestérol et de diols à longue chaine par exemple). Toutefois, la contribution relative du phytoplancton et du zooplancton à la sédimentation reste difficile à estimer de façon précise sur la seule base des biomarqueurs lipidiques.

Les abondances relatives des acides carboxyliques mono- et polyinsaturés et des biomarqueurs bactériens suggèrent que la présence de poissons n'induit pas de changement de biodégradabilité des sédiments récemment déposés. Les pertes de sédiment à long-terme, identiques en pourcentages dans les enceintes avec et sans poissons, confirment que les poissons n'ont pas modifié la biodégradabilité de la matière organique sédimentée en provenance du domaine pélagique.

Le peu d'effets induits par les apports de sol comparés à ceux entrainés par l'ajout de poisson ainsi que l'absence d'interaction entre ces deux traitements suggèrent que le contrôle « bottom-up » exercé par les apports de terre n'a eu qu'un impact mineur sur les écosystèmes aquatiques comparé au contrôle « top-down » exercé par les prédateurs en sommet de chaîne trophique. L'absence de différences entre les compositions lipidiques du seston, du zooplancton et des sédiments récemment déposés des mésocosmes soumis ou non aux apports de terre suggère que l'analyse des biomarqueurs lipidiques doit être conduite à une échelle plus fine (groupe fonctionnel, famille, genre…) et non des compartiments si l'on veut mettre en évidence le rôle des apports de matières allochtones dans les transferts d'énergie et de nutriments au sein des réseaux trophiques aquatiques (Perga et al., 2006, 2009).

Notons que l'étude réalisée n'a pas porté sur le devenir de la matière organique totale (autochtone plus allochtone) dans les systèmes expérimentaux, mais uniquement sur le devenir de la matière organique sédimentée en provenance des communautés pélagiques. Des

pots à ouverture large (« pommadiers ») ont été placés en début d'expérience au fond des bassins pour mieux comprendre le devenir de la totalité de la matière sédimentée. Ces récipients à large ouverture ont été choisis pour permettre un accès à la faune (poissons et invertébrés) et donc permettre une mesure de perte réelle et non une mesure de dégradabilité potentielle. Ces pots ont reçu non seulement les apports mensuels de sol (apports quantifiés à l'échelle des bassins expérimentaux et donc calculables à l'échelle des récipients), mais aussi les apports de matière organique en provenance des communautés de pleine eau (apports estimés dans chaque bassin grâce à l'utilisation des tubes à sédimentation). Le taux de dégradabilité potentiel de cette matière organique originaire des communautés pélagiques a été estimé à 90,5 % sur la période, indépendamment du traitement expérimental. Connaissant la quantité finale de matière dans les pots, il sera possible en théorie d'estimer grossièrement quel a été le taux de perte de la matière allochtone sur la durée de l'expérience. En particulier, nous espérons vérifier si la présence d'une plus grande quantité de producteurs primaires dans les bassins avec poissons a stimulé la dégradation des molécules organiques allochtones « récalcitrantes » initialement présentes dans les sols. Une telle analyse permettrait de tester en conditions proches de conditions naturelles l'hypothèse de Guenet et al. (2010) et les résultats obtenus en laboratoire (chapitre 4) sur le rôle potentiel du « priming effect » dans la dégradation de la matière organique allochtone en milieux aquatiques. Les échantillons, récoltés et stockés, seront analysés au cours des prochains mois.

En couplant des expériences en microcosmes et en mésocosmes menées à différentes échelles temporelles et des approches d'écologie aquatique et de biogéochimie, ces travaux de thèses ont permis de mettre en évidence les points suivants :

- En modifiant la biomasse de phytoplancton qui sédimente et donc la composition biochimique des sédiments, la structure des réseaux trophiques aquatiques induit des changements de biodégradabilité de ces sédiments.

- La biodégradabilité et donc la qualité des sédiments sont des paramètres qui peuvent modifier le recyclage interne des nutriments et les biomasses des compartiments pélagiques par un contrôle « bottom-up ».

- La minéralisation de la matière organique des sols dans les lacs dépend des conditions trophiques des écosystèmes étudiés.

- Le transport des sols dans les écosystèmes aquatiques favorise le recyclage de la matière organique et peut aussi avoir un effet « bottom-up » positif sur les organismes en sommet de chaîne trophique ou situés à des niveaux intermédiaires.

- Le contrôle « top-down » des prédateurs a un effet marqué qui peut masquer l'impact du contrôle « bottom-up » des sédiments ou des apports allochtones sur le fonctionnement des écosystèmes lacustres.

- Les interactions entre contrôles « bottom-up » de la matière organique et « top-down » des prédateurs sont faibles.

- La stoechiométrie écologique et les biomarqueurs lipidiques sont des outils complémentaires dans l'étude du fonctionnement des écosystèmes aquatiques qui peuvent cependant présenter certaines limites lorsque les processus étudiés sont peu intenses.

En utilisant les mêmes outils à l'échelle du groupe ou de l'ordre au lieu du compartiment, l'impact des processus étudiés ici sur le fonctionnement des écosystèmes lacustres pourrait être mieux compris. Par exemple, rotifères, copépodes et cladocères, principaux groupes constituant le zooplancton des eaux douces (Gliwicz, 2004), ont des comportements alimentaires et des traits de vie différents qui pourraient conduire à des différences de composition lipidique non nécessairement visibles lorsque que l'on travaille à l'échelle du compartiment zooplanctonique (von Elert, 2004).

Le processus de biodégradation de la matière organique étant principalement contrôlé par les micro-organismes, l'étude de l'influence de la structure des réseaux trophiques et de la composition de la matière organique sur la biodégradabilité des sédiments devrait également intégrer différentes techniques de biologie moléculaire pour mieux comprendre l'utilité des communautés de micro-organismes sur ces processus (del Giorgio et al., 1999). Par exemple, il serait intéressant d'étudier les réponses fonctionnelles (croissance, respiration, composition spécifique…) des communautés bactériennes à des sédiments présentant des biodégradabilités et des qualités différentes. Ce type d'expérience se ferait par des incubations de sédiments, soumis par exemple à des réseaux trophiques contrastés, durant lesquelles la composition biochimique de la matière organique, la croissance, la respiration et la composition spécifique de la communauté bactérienne seraient suivies tout au long de l'incubation.

En complément de l'utilisation des biomarqueurs lipidiques et des techniques de biologie moléculaire, l'analyse des pigments du seston, du zooplancton et des sédiments apporterait des informations supplémentaires sur la composition de la communauté phytoplanctonique (Waters et al., 2005), sur l'origine des sédiments (phytoplanctonique *vs* zooplanctonique), et sur l'état de dégradation (pigments bactériens) puisque certains pigments sont hautement spécifiques (Castaneda et Schouten, 2011).

L'analyse des isotopes stables (principalement du carbone, $\delta^{13}C$, et de l'azote, $\delta^{15}N$) des différents compartiments des écosystèmes aquatiques a démontré son utilité, aussi bien dans l'étude des transferts d'énergie et des interactions entre les communautés des réseaux trophiques aquatiques (signature isotopique naturelle, Peterson et Fry, 1987 ; Post, 2002 ; Ventura et Catalan, 2008 ; Seifert et Scheu, 2012) que dans celle des contributions relatives des matières organiques autochtone et allochtone comme ressources pour les réseaux trophiques (signature isotopique naturelle ou enrichissement du phytoplancton en $\delta^{13}C$, Canuel et al., 1997 ; Pace et al., 2004 ; Perga et al., 2006 ; Weidel et al., 2008). Par exemple, l'utilisation de cet outil dans une étude telle que celle présentée dans le chapitre 5 pourrait permettre d'étudier : i) la contribution relative des apports de terre comme ressource pour le zooplancton et les poissons, ii) les changements de la communauté zooplanctonique et de la position trophique des différentes espèces (en complément de comptages taxonomiques) en fonction des différents traitements étudiés et iii) la contribution relative du phytoplancton et du zooplancton à la sédimentation.

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