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Intense photooxidative degradation of planktonic and bacterial lipids in sinking particles collected with sediment traps across the Canadian Beaufort Shelf (Arctic Ocean)

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Abstract. The lipid content of seven samples of sinking particles collected with sediment traps moored at ∼ 100 m depth in summer and fall across the Canadian Beaufort Shelf (Arctic Ocean) was investigated. Our main goal was to quantify and characterize the biotic and abiotic degradation processes that acted on sinking material during these periods. Diatoms, which dominated the phytoplanktonic assemblage in every trap sample, appeared to be remarkably sensitive to Type II (i.e. involving singlet oxygen) photodegradation processes in summer, but seemed to be relatively unaffected by biotic degradation at the same time. Hence, the relative recalcitrance of phytodetritus towards biodegradation processes during the Arctic midnight sun period was attributed to the strong photodegradation state of heterotrophic bacteria, which likely resulted from the efficient transfer of singlet oxygen from photodegraded phytoplanktonic cells to attached bacteria. In addition, the detection in trap samples of photoproducts specific to wax ester components found in herbivorous copepods demonstrated that zooplanktonic faecal material exported out of the euphotic zone in summer were affected by Type II photodegradation processes as well. By contrast, sinking particles collected during the autumn were not influenced by any light-driven stress. Further chemical analyses showed that photodegraded sinking particles contained an important amount of intact hydroperoxides, which could then induce a strong oxidative stress in underlying sediments.

1 Introduction

Continental shelves of the Arctic Ocean receive a considerable amount of terrestrial matter from river runoff, mixed with important autochthonous production from microalgal photosynthesis during spring and summer (Rachold et al., 2004; Wassmann et al., 2004). The ongoing trend of declining sea ice extent and thickness in the Arctic Ocean appears to induce a steady increase in pelagic primary production (Arrigo et al., 2008), whereas permafrost thawing combined with enhanced river discharge are currently increasing the seaward flux of terrigenous material (Frey and McClelland, 2009). In turn, the annual lengthening of the ice-free period and the rise in river run-off could lead to an increase in particulate matter export that could modify the biogeochemistry and trophic balance of Arctic ecosystems through the coastal-marine realm (Vallières et al., 2008; Wassmann and Reigstad, 2011). Therefore, it is essential to understand how abiotic (autoxidation and photooxidation) and biotic (bacterial degradation) processes affect the dynamic of sinking fluxes of particulate organic matter in such environments.

Particles in the water column exist in a continuum of sizes (McCave, 1984), with two classes usually operationally recognized (Bacon et al., 1985; Wakeham and Lee, 1989): (i) suspended particles ($\leq 10^2$ µm diameter) sinking very slowly through the water column and constituting most of the standing stock of particulate matter in the ocean and (ii) sinking

particles ($\geq 10^2$ µm diameter) (including zooplankton fecal pellets and marine snow aggregates) numerically less abundant but responsible for most of the downward flux of material from the upper ocean to the sea floor. Suspended particles are typically collected by filtration, whereas sinking material is commonly collected using sediment traps. It may be noted that a continual exchange exists between these two particle classes owed to the complex suite of aggregation and disaggregation processes that occur in the water column (Wakeham and Lee, 1989; Hill, 1998). The sum of these processes affects particle settling velocity, residence time, and thus the efficiency of organic matter remineralization.

In a companion paper (Rontani et al., 2012b), we examined the lipid content of suspended particulate matter (SPM) samples collected in August 2009 in the Mackenzie River and in surface waters of the adjacent Beaufort Sea. Lipid biomarkers, although representing a very minor fraction of the total organic matter (OM), convey important information on the source (terrigenous, marine or bacterial) and degradation state of OM, which is commonly more diagnostic than that provided by bulk parameters (Saliot et al., 2002). Using specific lipid degradation products that have been proposed for distinguishing biotic from abiotic processes (Rontani et al., 2011; Christodoulou et al., 2009), we showed that marine particulate organic matter (POM) was weakly degraded across the study area, while biodegradation and autoxidation processes acted intensely on terrigenous POM present in seawater (Rontani et al., 2012b). This result was unexpected as POM originating from land is generally considered to be well preserved due to its previous degradation during transit to the sea. In order to explain the specific induction of autoxidative processes on vascular plant-derived material, a mechanism involving homolytic cleavage of photochemically produced hydroperoxides resulting from the senescence of higher plants on land was proposed (Rontani et al., 2012b). This cleavage could be catalyzed by some redox active metal ions released from SPM in the mixing zone of riverine and marine waters. In contrast, the intense biodegradation of terrestrial POM observed was attributed to the well known (Bianchi, 2011) high "priming effect potential" of deltaic regions.

It was previously observed in the Mediterranean Sea (Rontani et al., 2009; Christodoulou et al., 2009) and the equatorial Pacific Ocean (Rontani et al., 2011) that the mechanisms of POM degradation vary according to particle size. In the present work, we present biogeochemical data based on specific lipid biomarkers studies for samples collected by sediment traps deployed at 100 m depth over the shelf of the Canadian Beaufort Sea and Amundsen Gulf during the period of August 2009 and October 2003.

2 Material and methods

2.1 Study area

The Canadian Beaufort Shelf (Fig. 1) represents around 2 % (i.e. 64 000 km^2) of the Arctic Ocean. The shelf is delimited on the west by the Mackenzie Canyon and on the east by Amundsen Gulf. The Mackenzie River is the largest river draining into the Arctic in terms of sediment and particulate organic carbon supply (127×10^{12} g y^{-1} of sediment and 2.1×10^{12} g y^{-1} of particulate organic carbon respectively; Macdonald et al., 1998) and the fourth largest in terms of freshwater discharge (3.3×10^{11} m^3 y^{-1}; Milliman and Meade, 1983; Brunskill, 1986; Macdonald et al., 1998). The Mackenzie River supplies about 95–99 % of the sediment to the Beaufort Shelf, with coastal erosion and other rivers (Hill et al., 1991; Rachold et al., 2004). The main river load occurs between end of May and the end of August with considerable interannual variance (O'Brien et al., 2006). Primary productivity over the Mackenzie Delta/Beaufort Shelf (3.3×10^{12} g y^{-1} of particulate organic carbon) is mainly due to phytoplanktonic blooms during late spring and summer (Macdonald et al., 1998). Production by ice algae accounts for less than 10 % of the marine production in this area (Horner and Schrader, 1982).

2.2 Sample collection

Time series sediment traps (Technicap PPS 4/3; 24 cups; cylindrical-conical shape; collecting area: 0.125 m^2) were deployed on 4 mooring lines located in the Amundsen Gulf (CA16, CA05) and on the Mackenzie Shelf (CA10, G09) in the Beaufort Sea (Fig. 1; Table 1). Baffled lids covered the opening of the sediment traps to reduce internal turbulence. Before deployment, sediment traps were thoroughly rinsed with freshwater and seawater following the JGOFS protocol (Knap et al., 1996). Sample cups were filled with filtered seawater (GFF 0.7 µm) adjusted to 35 PSU with NaCl. Formalin was added to preserve the material collected (5 % v/v, sodium borate buffered).

2.3 Sample treatment

After retrieval, sample cups were checked for salinity and put aside 24 h to allow particles to settle down. Swimmers were removed from the samples then quantitative splitting into several fractions was completed using a McLane Wet Samples Divider or peristaltic pump. Subsamples for the determination of particulate organic carbon (POC) and lipids and their degradation products were filtered in triplicates through preweighted Whatman glass fiber filters (GFF 0.7 µm, 25 mm, combusted 4 h at 450 °C). For POC analysis, filters were dried for 12 h at 60 °C and weighed again for dry weight. After exposure for 12 h to concentrated HCl fumes to remove inorganic carbon fraction, the samples were analyzed with a Perkin Elmer CHNS 2600 Series II. Total and

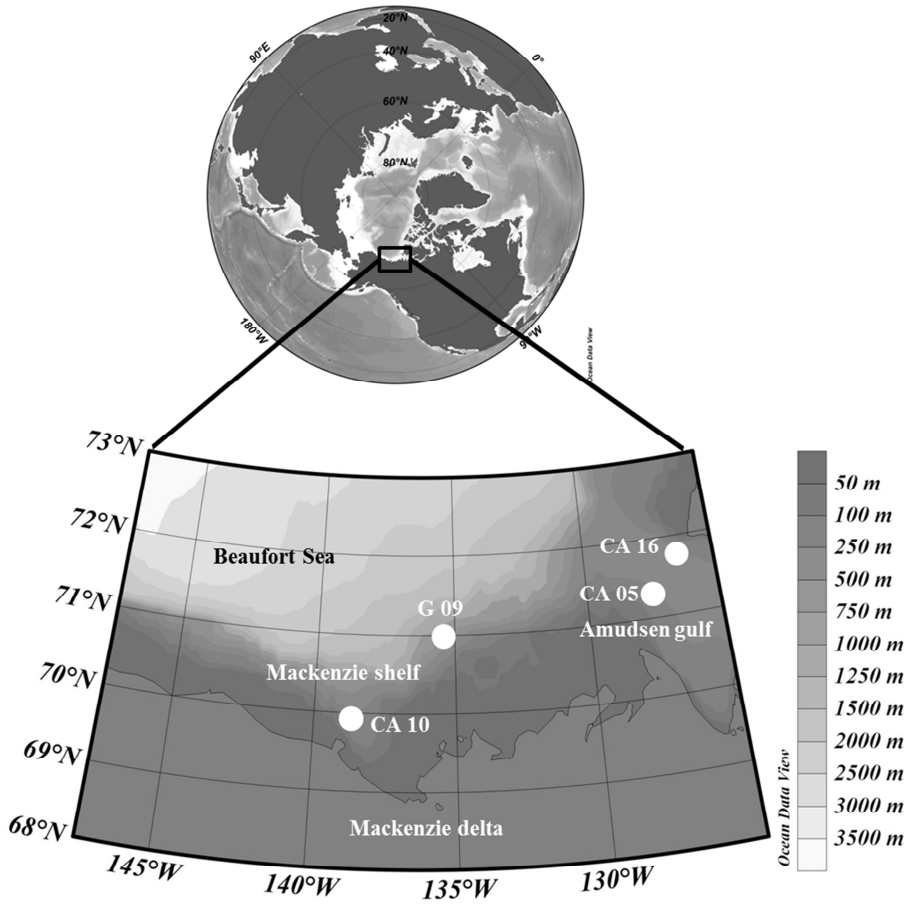


Fig. 1. Map of the studied area with locations of the different stations investigated.

Table 1. Mooring location and deployment information.

Mooring	Location	Latitude	Longitude	Deployment period	Water depth (m)	Trap depth (m)
CA05 A22	Amundsen Gulf	71.31245	127.58237	2 August 2009–7 August 2009	204	97.3
CA05 A23	Amundsen Gulf	71.31245	127.58237	8 August 2009–15 August 2009	204	97.3
CA05 A24	Amundsen Gulf	71.31245	127.58237	16 August 2009–31 August 2009	204	97.3
CA16 A23	Amundsen Gulf	71.78677	126.49695	8 August 2009–15 August 2009	314	110.2
G09 A2	Mackenzie Shelf	71.00254	135.47930	31 July 2009–14 August 2009	702	100.5
G09 A3	Mackenzie Shelf	71.00254	135.47930	30 August 2009–30 August 2009	702	100.5
CA10 A1	Mackenzie Shelf	69.95512	138.67373	7 October 2003–31 October 2003	250	105

POC fluxes were expressed as daily fluxes (mg C m^{-2} d^{-1}) (Heussner et al., 1990; Lalande et al., 2009). The collected samples were processed in the laboratory according to the method described by Heussner et al. (1990). The total sample was divided into several aliquots to obtain different subsamples for analyzing total mass flux, TOC, lipids and their degradation products. Subsamples were filtered through a precombusted quartz fiber filter (Whatman GF/F, 0.7 µm) under low vacuum.

2.3.1 Lipid extraction

All solvents employed in this study were glass distilled analytical grade. Each filter was extracted four times with $CHCl_3$-MeOH-H_2O (1 : 2 : 0.8, $v/v/v$) using ultrasonication (separation of particles and solvents by centrifugation at 3500 G for 9 min). To initiate phase separation after ultrasonication, $CHCl_3$ and purified H_2O were added to the combined extracts to give a final volume ratio of 1 : 1 : 0.9 ($v/v/v$). The upper aqueous phase was extracted twice with $CHCl_3$ and the combined $CHCl_3$ extracts were dried over anhydrous

Na_2SO_4, filtered and the solvent removed via rotary evaporation.

2.3.2 Hydroperoxide-reduction

$NaBH_4$-reduction of the lipid extracts was carried out to reduce labile hydroperoxides resulting from photooxidation and autoxidation to alcohols that are amenable to gas chromatography-electron impact mass spectrometry (GC-EIMS). The filters were put in methanol (15 ml) and hydroperoxides were reduced to the corresponding alcohols by excess $NaBH_4$ (70 mg) (30 min at room temperature). During this treatment, ketones are also reduced and the possibility of some ester cleavage cannot be excluded.

2.3.3 Alkaline hydrolysis

Metal ions can promote autoxidation during hot saponification procedures, so the prior reduction of hydroperoxides with $NaBH_4$ allowed us to avoid such autoxidative artifacts during the alkaline hydrolysis. After $NaBH_4$ reduction, 15 ml of water and 1.7 g of potassium hydroxide were added and the mixture was directly saponified by refluxing for 2 h. After cooling, the content of the flask was acidified with HCl (pH 1) and subsequently extracted three times with dichloromethane. The combined dichloromethane extracts were dried over anhydrous Na_2SO_4, filtered and concentrated to give the total lipid fraction.

2.3.4 Derivatization

After solvent evaporation, residues were taken up in 300 µl of a mixture of pyridine and N,O-bis(trimethysilyl)trifluoroacetamide (BSTFA; Supelco) (2 : 1, v/v) and silylated for 1 h at 50 °C to convert OH-containing compounds to their TMSi-ether derivatives. After evaporation to dryness under a stream of N_2, the derivatized residues were taken up in a mixture of ethyl acetate and BSTFA (to avoid desilylation of fatty acids) for analysis using GC-EIMS. It should be noted that under these conditions steran-3β, 5α, 6β-triols were only silylated at the 3 and 6 positions and thus need to be analyzed with great care (Rontani et al., 2012b).

2.3.5 Osmium tetroxide oxidation

Double bond positions of monounsaturated fatty acids were determined unambiguously after OsO_4 treatment. A fraction of total lipid extracts and OsO_4 (1 : 2, w/w) were added to a pyridine-dioxane mixture (1 : 8, v/v, 5 ml) and incubated for 1 h at room temperature. Then, 6 ml of Na_2SO_3 suspension (16 % Na_2SO_3 in water-methanol, 8.5 : 2.5, v/v) was added and the mixture was again incubated for 1.5 h. The resulting mixture was acidified (pH 3) with HCl and extracted three times with DCM (5 ml). The DCM extracts were combined and subsequently dried over anhydrous Na_2SO_4, filtered and concentrated.

2.4 Gas chromatography-electron impact mass spectrometry (GC-EIMS)

Compounds were identified by comparison of retention times and mass spectra with those of standards and quantified (calibration with external standards) by GC-EIMS. For low concentrations, or in the case of co-elutions, quantification was achieved using selected ion monitoring (SIM). GC-EIMS analyses were carried out with an Agilent 6890 gas chromatograph connected to an Agilent 5973 Inert mass spectrometer. The following conditions were employed: 30 m × 0.25 mm (i.d.) fused silica column coated with HP-1-MS (Agilent; 0.25 µm film thickness); oven temperature programmed in three sequential steps: (i) 70 °C to 130 °C at 20 °C min^{-1}; (ii) 130 °C to 250 °C at 5 °C min^{-1}; and (iii) 250 °C to 300 °C at 3 °C min^{-1}; carrier gas (He) maintained at 0.69 bar until the end of the temperature program and then programmed from 0.69 bar to 1.49 bar at 0.04 bar min^{-1}; injector (on column with retention gap) temperature 50 °C; electron energy 70 eV; source temperature 190 °C; cycle time 1.99 and 8.3 cycles s^{-1} in SCAN and SIM modes, respectively.

2.5 Lipid degradation products employed for photooxidation, autoxidation and biodegradation estimation

5α (H)-stan-3β-ols, Δ^4-stera-3β, 6α/β-diols and 3β, 5α, 6β-steratriols (deriving from cholest-5-en-3β-ol (cholesterol), 24-ethylcholest-5-en-3β-ol (sitosterol), 24-methylcholesta-5,22E-dien-3β-ol (brassicasterol) and 24-methylcholesta-5,24(28)-dien-3β-ol (24-methylenecholesterol)) were used to estimate biodegradation, photooxidation and autoxidation state of the different components of the samples, respectively (Fig. 2) (Rontani et al., 2009, 2011; Christodoulou et al., 2009). Abiotic oxidation of the non-specific Δ^9 monounsaturated fatty acids (oleic and palmitoleic acids) affords 8-E, 8-Z, 9-E, 10-E, 11-E and 11-Z hydroxyacids (Frankel, 1998), which were employed to estimate the importance of autoxidation and photooxidation of bulk organic matter (Fig. 2) (Marchand and Rontani, 2001; Rontani et al., 2011). In contrast, abiotic oxidation of *cis*-vaccenic acid (a typical biomarker for Gram-negative bacteria, Sicre et al., 1988; Keweloh and Heipieper, 1996) produces 10-E, 10-Z, 11-E, 12-E, 13-E and 13-Z hydroxyacids, which were useful to estimate autoxidation and photooxidation state of bacteria (Fig. 2; Rontani et al., 2003; Christodoulou et al., 2010).

2.6 Quantification of hydroperoxides and their ketonic and alcoholic degradation products

A different treatment was employed to quantify hydroperoxides and their ketonic and alcoholic degradation products.

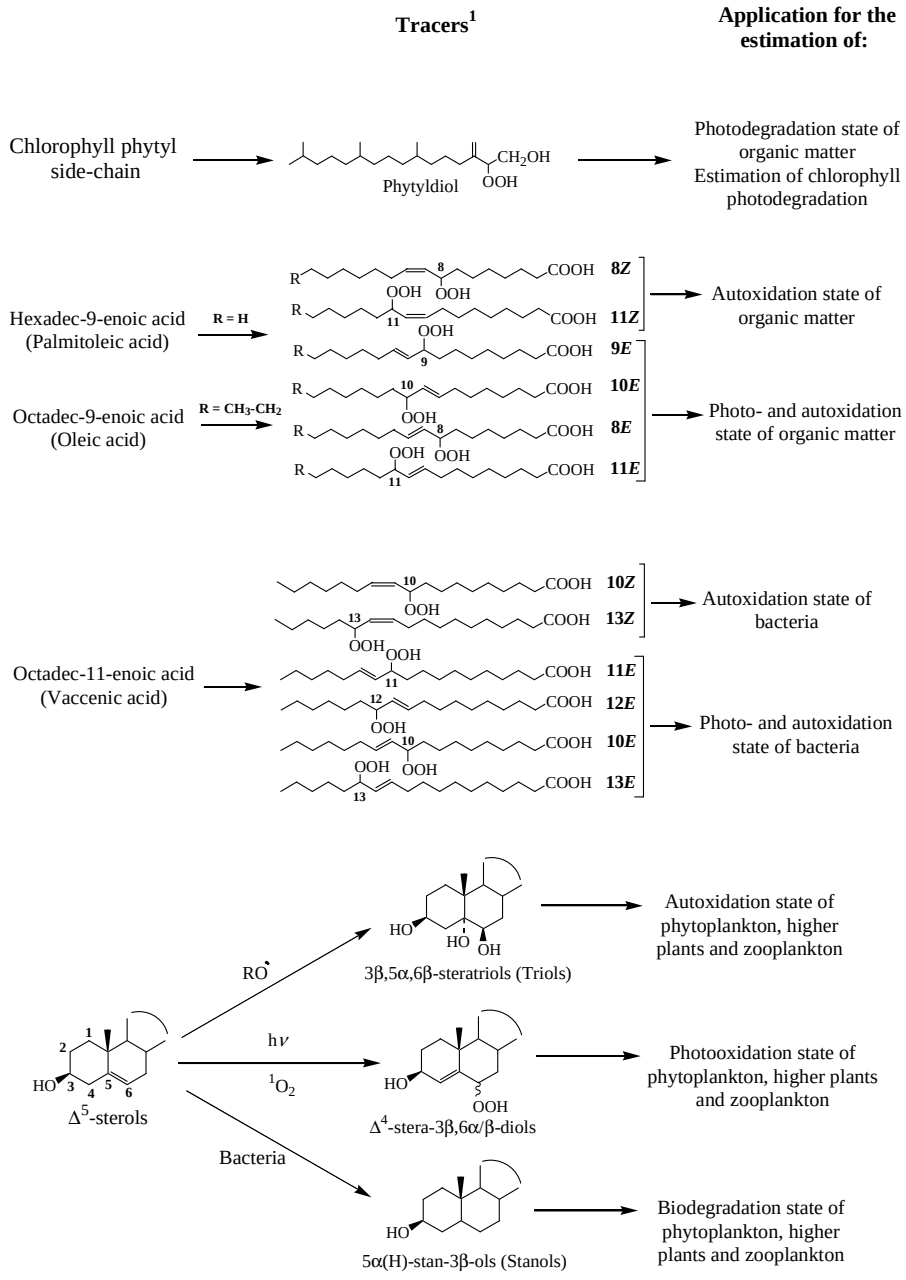


Fig. 2. Formulae, vernacular names and potential applications of the main (non-exhaustive list) lipid tracers of degradation processes employed in the present work. [1]Quantified after $NaBH_4$-reduction of hydroperoxides to the corresponding alcohols and subsequent silylation.

The residue obtained after extraction was dissolved in 4 ml of dichloromethane and separated in two equal subsamples. After evaporation of the solvent, degradation products were obtained for the first subsample after acetylation (inducing complete conversion of hydroperoxides to the corresponding ketones, Mihara and Tateba, 1986) and saponification and for the second after reduction with $NaBD_4$ and saponification. Comparison of the amounts of alcohols present after acetylation and after $NaBD_4$ reduction made it possible to estimate the proportion of hydroperoxides and alcohols present in the samples, while after $NaBD_4$-reduction deuterium labelling allowed to estimate the proportion of ketones really present in the samples (Marchand and Rontani, 2003).

Acetylation was carried out in 300 µl of a mixture of pyridine and acetic anhydride (2 : 1, v/v), allowed to react at 50 °C overnight and then evaporated to dryness under nitrogen.

Table 2. Relative percentage of sterols in the different samples.

Sterols	CA05-A22	CA05-A23	CA05-A24	CA16-A23	CA01-A1	G09-A2	G09-A3
24-Nor-cholesta-5,22*E*-dien-3β-ol	6.9	6.8	6.8	7.0	9.6	7.8	7.1
27-Nor-24-methylcholesta-5,22*E*-dien-3β-ol	2.9	2.5	3.4	2.8	2.1	3.2	3.7
Cholesta-5,22*E*-dien-3β-ol	3.2	3.7	3.1	3.2	4.0	5.0	5.9
Cholesterol	9.6	21.0	30.7	17.9	18.6	18.8	29.1
Brassicasterol	5.6	5.9	5.0	6.3	3.9	8.3	5.8
24-Methylenecholesterol	10.1	12.4	9.0	9.1	6.5	11.0	15.2
Campesterol	2.8	2.4	2.0	1.8	1.8	2.2	2.7
Stigmasterol	5.9	5.1	4.3	5.9	5.4	5.6	3.8
Sitosterol	45.0	33.5	28.3	39.2	38.8	31.5	22.5
Fucosterol	8.1	6.7	7.4	6.8	9.3	6.6	4.2

Table 3. Chlorophyll phytyl side-chain degradation products detected in the different samples and CPPI-based estimates of chlorophyll photodegradation.

Mooring	4,8,12-TMTD acid (%)*	Pristanic acid (%)*	Phytanic acid (%)*	Dihydrophytol (%)*	Pristane (%)*	CPPI	Chlorophyll photodegradation %
CA05-A22	18.8	7.9	69.0	8.1	0.4	40.0 ± 2.5	99.8 ± 0.1
CA05-A23	41.6	19.4	108.9	5.8	1.9	53.3 ± 0.4	100
CA05-A24	66.1	39.2	72.7	11.5	3.1	35.6 ± 3.7	99.6 ± 0.2
CA16-A23	55.0	27.4	87.3	15.9	2.4	104.1 ± 0.1	100
G09-A2	37.2	27.9	218.9	5.4	–	120.9 ± 41.7	100
G09-A3	37.6	10.1	110.5	6.7	14.2	36.7 ± 4.9	99.6 ± 0.2
CA10-A1	–	–	120.0	–	–	22.7 ± 9.9	94.3 ± 5.1

* Relative to phytol.

3 Results and discussion

3.1 Classical lipid biomarker analyses

3.1.1 Sterols

In the different samples investigated the major sterols were cholesterol (10–31 %) and sitosterol (28–45 %) (Table 2). Although a substantial amount of cholesterol may be derived from diatoms or Prymnesiophycean algae (Volkman, 1986), its dominance suggests an important contribution of zooplanktonic faecal material to these samples. Indeed, it is well known that zooplankton convert much of the sterols produced by algae into cholesterol (Volkman et al., 1980; Prahl et al., 1984). Sitosterol is commonly associated with terrestrial higher plants inputs (Lütjohann, 2004), but some microalgae (and notably diatoms) are now known to produce this sterol (Volkman, 1986, 2003). The other sterols, found in lower ranges in this study, include 24-nor-cholesta-5,22*E*-dien-3β-ol, 27-nor-24-methylcholesta-5,22*E*-dien-3β-ol, cholesta-5,22*E*-dien-3β-ol, brassicasterol, 24-methylenecholesterol, 24-methylcholest-5-en-3β-ol (campesterol), 24-ethylcholesta-5,22*E*-dien-3β-ol (stigmasterol) and 24-ethylcholesta-5,24(28)*E*-dien-3β-ol (fucosterol) (Table 2). 24-nor-cholesta-5,22-dien-3β-ol, has been previously identified in a phytoplankton sample composed principally of diatoms (Boutry et al., 1971). The important contribution of diatoms to these samples is also well supported by the presence of brassicasterol and 24-methylenecholesterol, which are major constituents of several diatom species (Lee et al., 1980). However, it may be noted that brassicasterol is also present in some dinoflagellates and in many haptophytes (Volkman, 1986, 2003). If the lack of dinosterol, which is present in some dinoflagellates (Mansour et al., 1999), does not support the presence of such organisms, a significant contribution of dinoflagellates to the samples cannot be totally excluded since they do not systematically produce dinosterol (Leblond and Chapman, 2002). In contrast, a contribution of haptophytes to the samples is very likely. Indeed, it was previously observed that larger haptophytes and diatoms co-dominated in near-surface assemblages of the Beaufort Sea in summer (Hill et al., 2005).

3.1.2 Isoprenoids

Dihydrophytol, pristane, 3,7,11,15-tetramethylhexadecanoic (phytanic), 2,6,10,14-tetramethylpentadecanoic (pristanic) and 4,8,12-trimethyltridecanoic (4,8,12-TMTD) acids could be detected in most of the total lipid extracts analysed (Table 3). The presence of relatively high proportions of these degradation products of the chlorophyll phytyl side-chain well supports the contribution of zooplanktonic faecal pellets

Table 4. Flux ($\mu g\, m^{-2}\, d^{-1}$) of fatty acids and *n*-alkan-1-ols.

Compounds	CA05-A22	CA05-A23	CA05-A24	CA16-A23	CA10-A1	G09-A2	G09-A3
Fatty acids							
$C_{14:0}$	227.2	802.0	317.9	523.6	16.5	275.3	404.2
$C_{15:0}$	35.4	99.2	86.3	160.3	19.1	32.8	85.3
$C_{16:1\Delta9}$ (Palmitoleic)	465.3	1066.5	306.8	570.9	81.8	457.2	507.7
$C_{16:0}$	971.0	2907.3	1024.7	4572.9	506.6	1581.8	1443.4
$C_{17:1}$	–	21.8	38.5	–	11.4	–	–
$C_{17:0}$	14.1	39.5	36.3	95.3	15.0	23.2	–
$C_{18:1\Delta9}$ (Oleic)	170.4	438.2	248.3	442.8	183.1	181.6	353.1
$C_{18:1\Delta11}$ (Vaccenic)	73.4	310.5	114.3	183.8	55.1	82.2	167.8
$C_{18:1\Delta13}$	12.0	88.1	34.7	62.0	15.6	18.2	41.7
$C_{18:0}$	368.6	992.1	172.5	1999.0	131.0	451.1	260.6
$C_{20:1\Delta11}$	34.0	123.3	79.8	217.5	68.9	–	–
$C_{20:0}$	6.0	17.4	10.5	49.8	6.7	12.0	9.2
$C_{22:1\Delta11}$	5.7	23.7	16.1	28.6	3.8	5.6	21.7
$C_{22:0}$	4.7	12.4	4.2	31.4	3.2	6.9	6.6
$C_{24:1\Delta11}$	3.3	37.7	18.3	14.3	2.0	5.7	26.3
$C_{24:0}$	2.7	16.4	5.8	41.3	4.9	7.2	5.7
n-Alkan-1-ols							
$C_{14:0}$	5.3	105.2	73.9	94.3	15.9	24.6	236.2
$C_{16:1}$	7.8	81.3	46.1	61.5	5.2	29.1	109.8
$C_{16:0}$	58.9	357.1	273.8	408.1	32.1	122.6	471.0
$C_{18:0}$	25.1	117.4	46.0	257.3	23.1	62.0	81.7
$C_{20:1\Delta11}$	122.0	204.6	186.2	111.6	66.0	20.4	130.7
$C_{22:1\Delta11}$	605.9	500.4	217.5	120.9	43.8	20.7	213.7

to the sampling material. Indeed, pelagic crustaceans decrease the abundance of the chlorophyll phytyl side-chain when feeding herbivorously (Prahl et al., 1984; Harvey et al., 1987; Bradshaw et al., 1990). Any phytol remaining in the faeces of pelagic zooplankton after herbivorous feeding will be quickly removed on subsequent reprocessing of the faecal material (Bradshaw and Eglinton, 1993). Several phytol degradation products have been thus identified in zooplanktonic faecal pellets during feeding experiments, including pristane, isomeric pristenes, isomeric phytadienes, dihydrophytol and phytanic, pristanic, 4,8,12-TMTD and isomeric phytenic acids (for a review see Rontani and Volkman, 2003).

3.1.3 Fatty acids and *n*-alkan-1-ols

Total lipid extracts of the different samples exhibited a distribution of even-carbon number dominated fatty acids ranging from C_{14} to C_{24} (Table 4), suggesting the presence of a material dominated by marine organisms (plankton and bacteria). Long-chain ($> C_{24}$) saturated fatty acids, which are characteristic of epicuticular waxes of terrestrial higher plants (Kolattukudy, 1977; Gagosian et al., 1987), could not be detected. The three dominant monounsaturated fatty acids appeared to be hexadec-9*cis*-enoic (palmitoleic), octadec-9*cis*-enoic (oleic) and octadec-11*cis*-enoic (vaccenic) acids (Table 3). Palmitoleic and oleic acids have numerous possible biological origins (plants, fungi, yeasts, bacteria, animals or algae) (Harwood and Russell, 1984), while vaccenic acid is a typical biomarker for Gram-negative bacteria (Sicre et al., 1988; Keweloh and Heipieper, 1996). Small amounts of the very unusual octadec-13-enoic acid could be also detected (Table 4). The production of this compound was previously observed during linolenic acid biohydrogenation by rumen microorganisms (Ward et al., 1964). In these samples it could thus result from biohydrogenation of phytoplanktonic linolenic acid in the gut of large calanoid copepods that feed herbivorously and dominate the zooplankton assemblage in the area (Forest et al., 2012a). Despite the apparent strong contribution of diatom and zooplankton material to the samples (see previous sections), polyunsaturated fatty acids (PUFA) were not detected. The lack of these compounds could be attributed to their well known, very high reactivity towards photooxidation (Kawamura and Gagosian, 1987) and autoxidation (Frankel, 1998) processes and to the intense abiotic degradation state of the samples investigated (see Sect. 3.2).

Interestingly, although sinking particles are generally considered as the main contributors to the sedimentary record (Wakeham and Lee, 1989), after OsO_4 treatment of the different trap samples investigated, we failed to detect significant amounts of monounsaturated fatty acids with a *trans* double bond, which were previously observed in surface

sediments of this zone in very high proportions (Rontani et al., 2012a). The isomerization process responsible for the formation of *trans* monounsaturated fatty acids seems thus to act in sediments and not in sinking particles.

Four principal types of storage lipids have been found in marine zooplankton: triacylglycerols, wax esters, phospholipids and diacylglycerol ethers (Lee et al., 2006). Wax esters are generally the major storage lipids in high latitude species (Lee et al., 2006). The most common alkan-1-ols of the wax esters found in herbivorous zooplankton are $C_{20:1\Delta11}$ and $C_{22:1\Delta11}$, while omnivorous or carnivorous zooplankton have a predominance of $C_{14:0}$ and $C_{16:0}$ alkan-1-ols (Lee and Nevenzel, 1979; Albers et al., 1996). $C_{20:1\Delta11}$ and $C_{22:1\Delta11}$ alcohols are only known to occur in copepods that undergo diapause (Graeve et al., 1994), which are largely distributed in the Arctic. The detection of high proportions of these two specific compounds in most of the total lipid extracts (Table 4) confirmed the presence of high amounts of herbivorous zooplanktonic material in the different samples. The source of this material is probably lipid droplets remaining "trapped" in faecal pellets (Najdek et al., 1994) produced by the large herbivorous copepods *Calanus hyperboreus* and *C. glacialis* that undergo diapause.

3.2 Lipid degradation product analyses

3.2.1 Chlorophyll

Although the visible light-dependent degradation rate of the chlorophyll tetrapyrrole ring is three to four times higher than for its phytyl side-chain (Cuny et al., 1999), no specific and stable tetrapyrrole photodegradation products could be identified in the literature. Type II photosensitized oxidation (i.e., involving $^1O_2$) of the phytyl side-chain, however, leads notably to the production of 3-methylidene-7,11,15-trimethylhexadecan-1,2-diol (phytyldiol) (Rontani et al., 1994). Phytyldiol is ubiquitous in the marine environment and constitutes a stable and specific tracer for photodegradation of chlorophyll phytyl side-chain (Rontani et al., 1996; Cuny and Rontani, 1999). Further, the molar ratio phytyldiol : phytol (Chlorophyll Phytyl side-chain Photodegradation Index, CPPI) was proposed to estimate the extent of chlorophyll photodegraded in natural marine samples (Cuny et al., 2002).

CPPI ranges from 36 to 121 in the case of the samples collected in summer (Table 3). These values are particularly high when compared with CPPI previously measured in particulate matter collected in summer in the Equatorial Pacific (Rontani et al., 2011) and in the northwestern Mediterranean Sea (Cuny et al., 2002) (ranging from 1 to 8 and from 1 to 24, respectively). This attests to the exceptional efficiency of photooxidation processes in the Arctic Ocean region in summer, most probably because of the midnight sun that persists for 3 months (May–July) at 70° N. On the basis of these very high CPPI values, it could be estimated that during this period chlorophyll was practically entirely photodegraded in sinking particles (Table 3). In the sample CA10 A1 collected in October, a strong photodegradation state of chlorophyll (> 94 %) was also observed (Table 3).

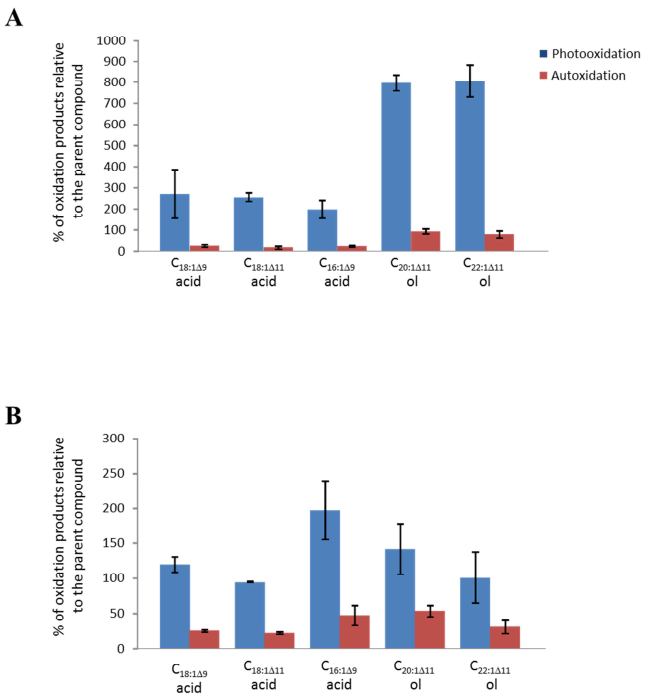


Fig. 3. Percentages of photooxidation and autoxidation products (relative to the residual parent compound) of monounsaturated fatty acids and alkan-1-ols observed in G09-A2 **(A)** and G09-A3 **(B)** samples.

3.2.2 Monounsaturated fatty acids and *n*-alkan-1-ols

Due to the lack of specificity of palmitoleic and oleic acids, their oxidation products have been used to assess abiotic degradation of bulk OM. The results obtained are summarized in Figs. 2–4. Photooxidation percentages of these two acids appeared to be very high (values ranging from 45 to 270 % relative to the residual parent compound) in summer, but not in fall (values < 20 %). These results, which are in good agreement with the total photodegradation of chlorophyll observed in summer (Table 3), confirm that during this period, photooxidation processes act very intensely on sinking particles of the Beaufort Sea. Autoxidation (free radical oxidation) processes also contributed to the degradation of these two fatty acids (10–30 %), but to a lesser extent than light-driven degradation (Figs. 3–5). The strong spatial variability in the photooxidation stress (Figs. 3–5) could likely be attributed to differences in water clarity at the different sampling stations that typically increases from a shelf-edge location (CA05), to a mid-slope area (CA16), up to a basin-close environment (G09) (Table 1). Alternatively, visual inspection of sediment trap samples revealed that particles collected at

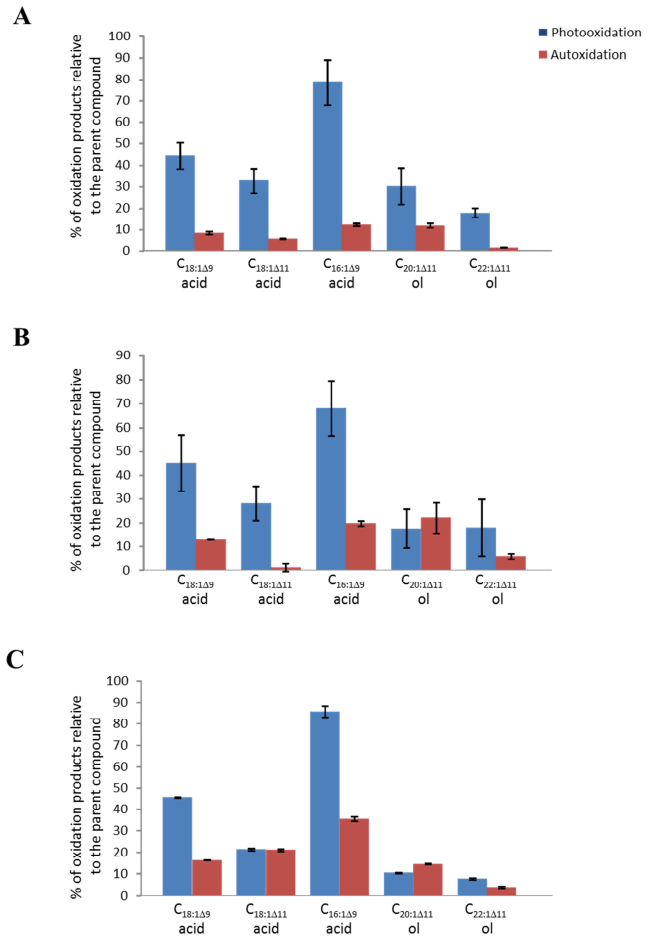


Fig. 4. Percentages of photooxidation and autoxidation products (relative to the residual parent compound) of monounsaturated fatty acids and alkan-1-ols observed in CA05-A22 **(A)**, CA05-A23 **(B)** and CA05-A24 **(C)** samples.

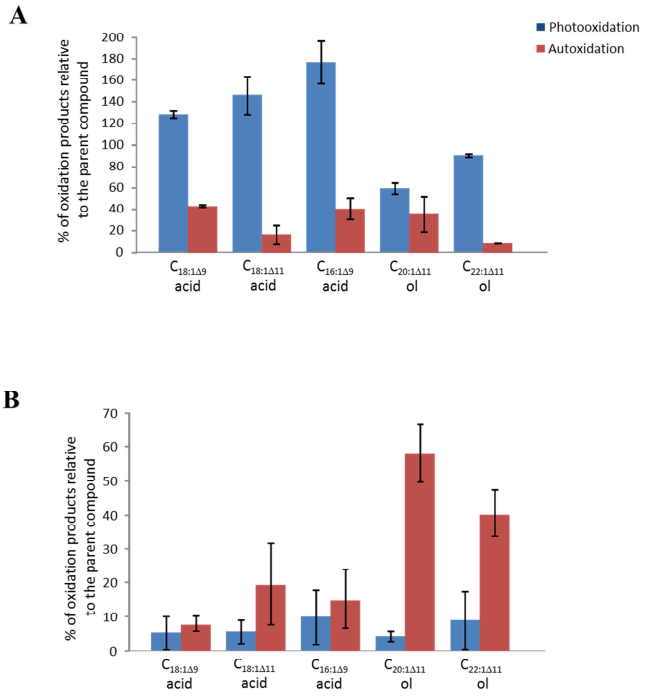


Fig. 5. Percentages of photooxidation and autoxidation products (relative to the residual parent compound) of monounsaturated fatty acids and alkan-1-ols observed in CA16-A23 **(A)** and CA10-A1 **(B)** samples.

G09 were generally finer and less aggregated than at CA16 and CA05, with the latter being obviously affected by the sinking of large diatom colonies (A. Forest, personal observation, 2009). Organic matter contained in large aggregates could then be relatively more protected against photooxidation than in fine particles that might offer a high surface-to-volume ratio.

Oxidation products of vaccenic acid allowed us to estimate photo- and autoxidation state of heterotrophic bacteria associated to sinking particles. These bacteria were also strongly photodegraded in summer (photodegradation percentage ranging from 45 to 260 %) (Figs. 3–5) and weakly in fall (photodegradation percentage < 10 %). During the summer period, transfer of singlet oxygen from senescent phytoplanktonic cells to bacteria (Rontani et al., 2003; Christodoulou et al., 2010) seems thus to have been especially efficient. Vaccenic acid also appeared to be affected by autoxidation but less intensively (Figs. 3–5). Indeed, reaction of singlet oxygen with unsaturated components of the outer lipopolysaccharide membrane of Gram negative bacteria (the dominant bacteria in the ocean) leads to the formation of reactive secondary products, such as peroxyl radicals, which may in turn accentuate cell death (Dahl et al., 1989). The intense oxidative stress resulting from singlet oxygen damages in bacteria should limit their growth (and thus biodegradation processes) during the settling of sinking particles.

Important amounts of oxidation products of $C_{20:1\Delta11}$ and $C_{22:1\Delta11}$ alkan-1-ols (values ranging from 10 to 800 % of the residual parent compound), which are specific components of zooplankton wax esters (Lee and Nevenzel, 1979; Albers et al., 1996), could be also detected in the different samples (Figs. 3–5). The major part of these compounds results from the involvement of Type II (i.e. involving singlet oxygen) photoprocesses (Fig. 6). It is important to note that these oxidation products disappeared when the alkaline hydrolysis step was avoided during the treatment. These results clearly showed that photooxidation processes acted directly on wax esters and not on the corresponding *n*-alkan-1-ol after enzymatic hydrolysis. The high efficiency of Type II photooxidation processes in such micro-environments may be attributed to: (i) the high concentration of wax esters in the droplets trapped in faecal pellets (as discussed above) favoring the likelihood of interaction between singlet oxygen (produced from chlorophyll and phaeopigments contained in the pellets) and their double bonds and (ii) the apolar character of

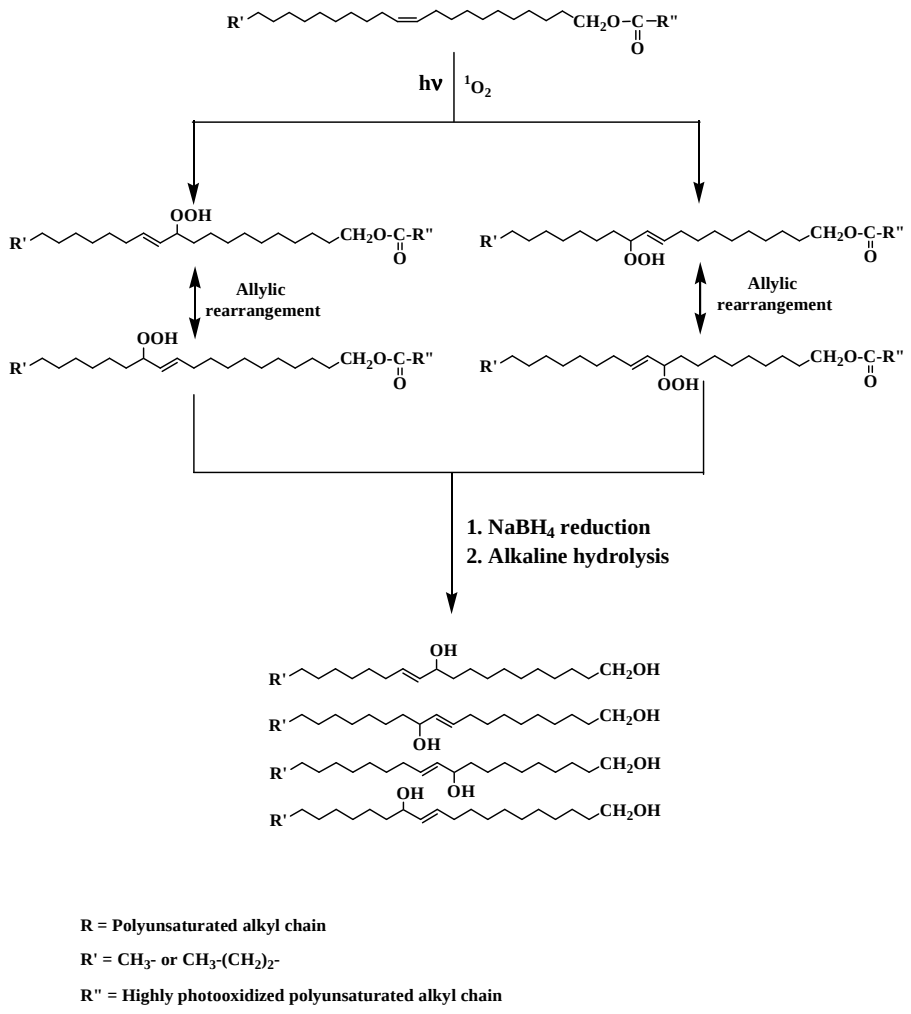


Fig. 6. Type II (i.e. involving singlet oxygen) photooxidation of $C_{20:1\Delta11}$ and $C_{22:1\Delta11}$ alkan-1-ols.

these droplets. Indeed, the lifetime of singlet oxygen in apolar environments is longer, and its potential diffusion distance greater, than under polar conditions (Suwa et al., 1977). To our knowledge, this is the first in situ demonstration of photodegradation of zooplanktonic faecal material.

Allylic hydroperoxides resulting from photo- and autoxidation of monounsaturated fatty acids may undergo: (i) heterolytic cleavage catalyzed by protons (Frimer, 1979) leading to the formation of ω-oxocarboxylic acids and other volatile products, and (ii) homolytic cleavage induced by transition metal ions (Pokorny, 1987; Schaich, 2005) or UVR (since hydroperoxides absorb in the UVR range; Horspool and Armesto, 1992). Homolytic cleavage of hydroperoxyacids would lead to the formation of alkoxyl radicals, which can then: (i) abstract a hydrogen atom from another molecule to give hydroxyacids, (ii) lose a hydrogen atom to yield ketoacids, or (iii) undergo β-cleavage reaction affording volatile products. It may be noted that hydroxyacids and ketoacids may also result from disproportionation of two alkoxyl radicals. During $NaBH_4$-reduction (carried out in order to avoid thermal breakdown of hydroperoxides during the treatment), hydroperoxides and ketones were reduced to the corresponding alcohols. The sum of hydroperoxy acids, ketoacids and hydroxy acids was thus quantified in the form of hydroxyacids. A different treatment was employed (see Sect. 2.6.) in order to specifically quantify hydroperoxyacids and their main degradation products: hydroxyacids and ketoacids. The results obtained in the case of the sample G09-A2 are summarized in Fig. 7a. It appears that in sinking particles, a significant proportion (ranging from 12 to 22 % of the sum of hydroperoxides, ketones and alcohols) of oxidation products of monounsaturated fatty acids are still under the form of hydroperoxides. An important flux of these compounds should thus reach the seafloor, inducing a strong oxidative stress in surface sediments. These results support the mechanisms proposed in our companion paper to explain the presence of unusual very high proportions of epoxyacids and monounsaturated fatty acids with a *trans* double bond in

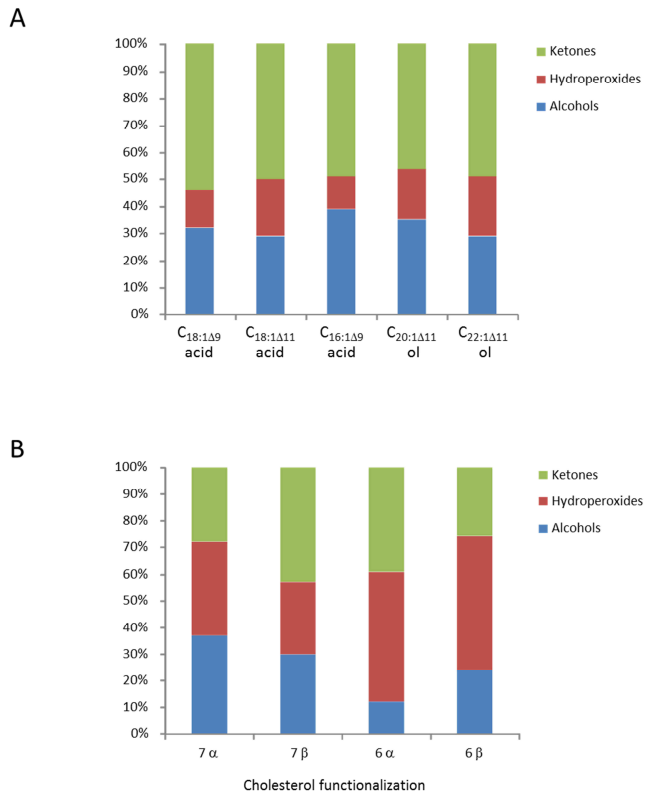


Fig. 7. Relative percentages of intact hydroperoxides and their ketonic and alcoholic degradation products measured in the case of monounsaturated fatty acids and alkan-1-ols **(A)** and cholesterol **(B)** oxidation products.

sediments of this zone (Rontani et al., 2012a). Indeed, the formation of the formers was attributed to the involvement of enzymes catalyzing epoxidation of unsaturated fatty acids in the presence of alkylhydroperoxides as co-substrates, and this of the latters to *cis/trans* isomerization reactions induced by thiyl radicals resulting from the reaction of thiols with hydroperoxides.

3.2.3 Sterols

Degradation products of four model Δ^5−sterols (cholesterol, 24-methylenecholesterol, brassicasterol and sitosterol) were quantified. The results obtained are summarized in Fig. 8. Photooxidation of Δ^5−sterols appears less important than that of chlorophyll phytyl side-chain or monounsaturated fatty acids (see Sects. 3.2.1 and 3.2.2). Indeed, degradation rate constants of $^1O_2$-mediated photooxidation (type II photoreactions) are generally lower for Δ^5−sterols than for chlorophyll phytyl side-chain and monounsaturated fatty acids (Rontani et al., 1998), possibly due to steric hindrance during the attack of the sterol Δ^5 double bond by $^1O_2$ (Beutner et al., 2000). Photodegradation processes acted more intensively on 24-methylenecholesterol (mainly arising from diatoms) (photodegradation percentage ranging from 40 to 81 % relative to the parent sterol) than on brassicasterol (arising from diatoms and/or Prymnesiophytes) (values ranging from 18 to 33 %) (Fig. 8). These differences suggest a higher efficiency of photodegradation processes in diatoms than in Prymnesiophytes. The similarity observed between the overall behaviors for brassicasterol and sitosterol (Fig. 8) with respect to degradation well supports a major contribution of Prymnesiophytes to sitosterol. Interestingly, the sitosterol and campesterol contained in suspended particles collected in this zone (mainly arising from terrestrial higher plants) were strongly autoxidized (Rontani et al., 2012b). The lack of sitosterol autoxidation products in all the total lipid extracts obtained from sediment trap samples thus confirms that terrestrial higher plant material does not contribute significantly to this sterol in sinking particles. A release of sub-Arctic terrestrial POM in two different pools was recently proposed (Vonk et al., 2010a, b). A pool composed of mineral-bound POC derived from erosion, which has short initial residence times in the surface water and quickly settles to the sea floor, and another pool composed of higher plants debris mainly contributing to suspended particulate matter. These two pools probably settle too quickly or too slowly, respectively, to contribute significantly to the material collected by the different traps deployed.

Low proportions of 5α-stanols corresponding to 24-methylenecholesterol and brassicasterol could be observed in the different samples (values ranging from 3 to 15 % of the corresponding sterol) (Fig. 8). These values, which are very close to those generally considered as typical of healthy phytoplanktonic cells (5–10 %, Wakeham et al., 1997), suggest that biodegradation processes acted only very weakly on phytoplanktonic material. The lack of the corresponding ster-4-en-3-ones, which are classical bacterial metabolites of Δ^5-sterols (de Leeuw and Baas, 1986; Wakeham, 1989) often detected in sinking particles (Bayona et al., 1989; Christodoulou et al., 2009), well supports this assumption. This apparently good resistance of phytodetritus against bacterial degradation might result from the inhibition of bacterial growth when $^1O_2$ generated by the photolysis of senescent phytoplanktonic cells in the euphotic zone is efficiently transferred to attached bacteria, as it was observed in the previous section.

As in the case of monounsaturated fatty acids, the specific proportion of hydroperoxysterols and their alcoholic and ketonic degradation products have been also determined. The results obtained are summarized in Fig. 7b. Hydroperoxysterols appeared to be more stable than hydroperoxyacids in sinking particles (Fig. 7a); significant amount of these compounds should thus reach the sediments. This observation is in good agreement with the previous detection of intact hydroperoxysterols in recent surficial sediments (Rontani and Marchand, 2000). While ratio Δ^4-6α/6β-hydroperoxides/ Δ^5-7α/7β-hydroperoxysterols produced during irradiation of senescent phytoplanktonic cells ranged from 0.30 to 0.35 (Rontani et al., 1997), very high

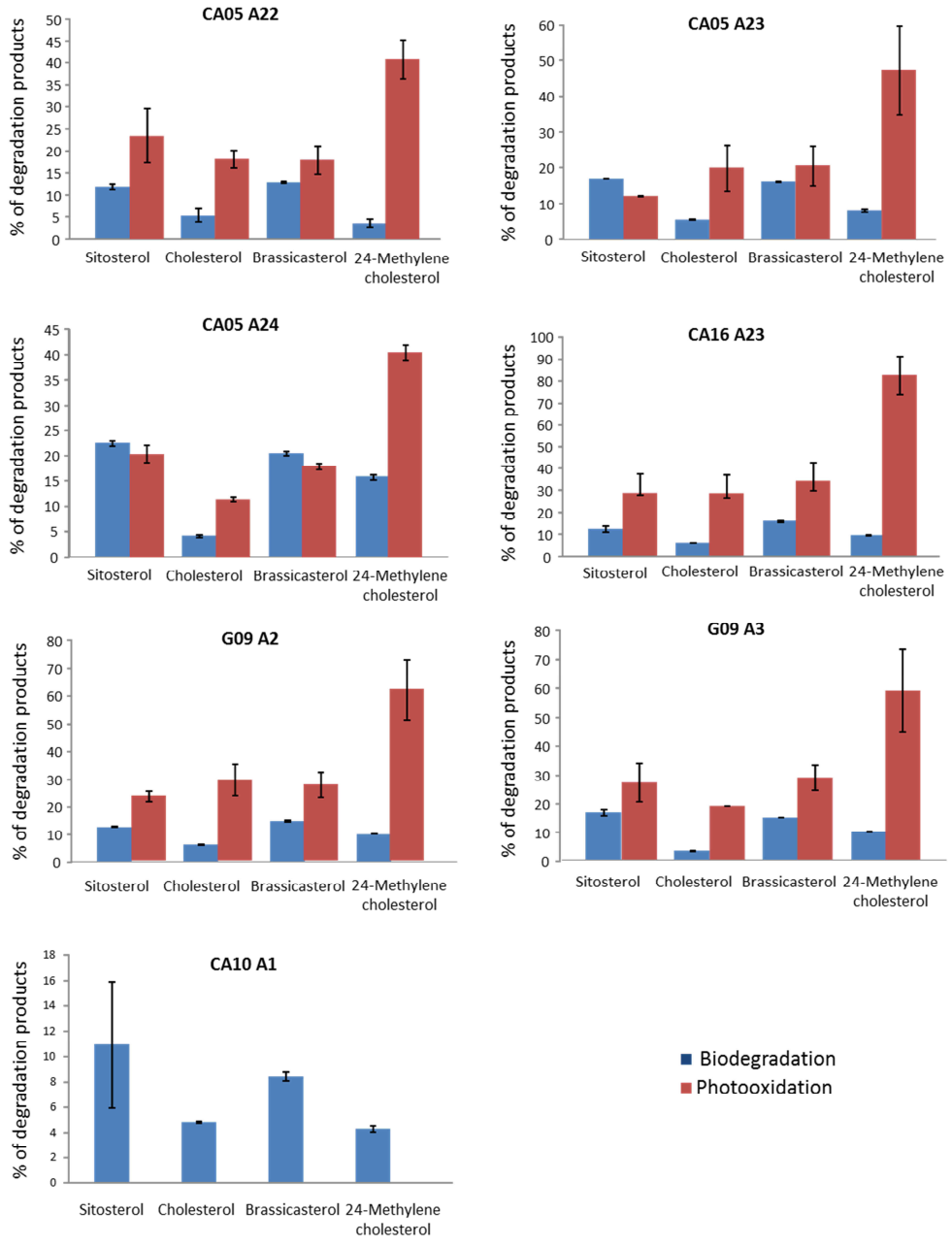


Fig. 8. Percentages of photooxidation and autoxidation products (relative to the residual parent compound) of sitosterol, cholesterol, brassicasterol and 24-methylenecholesterol in the different samples investigated.

values (ranging from 0.4 to 2.55) of the ratio cholest-4-en-3β,6α/6β-diols/cholest-5-en-3β, 7α/7β-diols were previously measured (after $NaBH_4$-reduction) in sediment trap samples collected in Mediterranean Sea (Christodoulou et al., 2009). These high values were attributed to a faster degradation of Δ^5-7-hydroperoxysterols than Δ^4-6-hydroperoxysterols during settling through the water column (Christodoulou et al., 2009). According to the theoretical stability of the alkyl radicals formed during β-scission of the corresponding alkoxyl radicals, the following order of stability was tentatively proposed by Christodoulou et al. (2009): Δ^4-6-hydroperoxysterols > Δ^5-7-hydroperoxysterols > Δ^6-5-hydroperoxysterols. The results obtained in the present study (Fig. 7b) well support this assumption.

4 Conclusions

Lipids and their degradation products were quantified in seven samples of sinking particles collected with sediment traps in summer and fall across the Canadian Beaufort Shelf. These samples were dominated by diatoms and zooplanktonic faecal pellets. Terrestrial higher plants resulting from Mackenzie River discharge did not contribute significantly to the sinking material. During the summer period, Type II (i.e. involving singlet oxygen) photooxidation processes acted strongly on senescent phytoplanktonic cells, heterotrophic bacteria and zooplanktonic faecal material. Diatoms, which dominated the phytoplanktonic assemblage, appeared to be remarkably sensitive to photodegradation. Singlet oxygen transfer from phytodetritus to attached bacteria was particularly efficient inducing strong oxidative damages in these heterotrophic organisms. The presence of high amounts of photoproducts of $C_{20:1\Delta11}$ and $C_{22:1\Delta11}$ alcohols, which are specific components of wax esters found in herbivorous copepods (Lee and Nevenzel, 1979; Albers et al., 1996), allowed us to demonstrate for the first time the high efficiency of Type II photodegradation processes in zooplanktonic faecal material.

In contrast, phytoplanktonic cells seemed to be relatively preserved towards biodegradation processes in sinking POM. As proposed by Rontani et al. (2011), there is a synergy between senescing phytoplanktonic cells and attached bacteria and between photooxidation and biodegradation. Photolysis of chlorophyll in senescing algal cells produces singlet oxygen, which if transferred from algal cells to attached bacteria may inhibit bacterial growth and reduce the extent of heterotrophic degradation. Therefore, it seems that there is a direct link between the photooxidation state of lipids of senescent phytoplanktonic cells in particles and their resistance towards biotic degradation. However, this does not exclude that the flux of labile dissolved organic matter produced through the photo-cleavage of phytodetritus might sustain an active community of free-living bacteria around sinking particles (as proposed by Forest et al., 2012b).

In addition, we demonstrated that strongly photodegraded sinking particles contained an important amount of intact hydroperoxides. After sedimentation, these compounds should induce a strong oxidative stress in surface sediments, which could be at the origin of the formation of epoxyacids and monounsaturated fatty acids with a *trans* double bonds previously detected in unusual high proportion in this zone (Rontani et al., 2012a).

In order to put the current global warming trend into the context of natural climate variability, it is essential to reconstruct sedimentary palaeoenvironments. Lipid biomarkers preserved in bottom sediments are particularly useful for this purpose, since they represent the ultimate signature of sympagic and pelagic productivity (e.g. Volkman et al., 1998; Wakeham et al., 1997; Rontani and Volkman, 2005; Bianchi and Canuel, 2011). However, reconstructions based on sediment biomarkers are incomplete without a careful consideration of particle alteration and/or preservation during their transport from the euphotic zone to the benthic boundary layer. It is thus critical to understand how biotic and abiotic processes may alter the environmental signal encoded by the biomarker proxy. This is particularly important for Arctic regions, which indeed provide the earliest and most dramatic manifestations of global change (Hansen et al., 2012). Here, we have observed an extraordinary efficiency of photooxidation processes acting on sinking particles collected during summer in the Beaufort Sea. These processes, which should gradually increase as ice-free waters increase in extent and duration (NSIDC, 2012), appear to destroy most of the unsaturated components of organisms initially present in the settling material – thus strongly altering their lipid signature. Although it is generally considered that sinking particles are the main contributors to the sedimentary record (Wakeham and Lee, 1989), it may be noted that zooplanktonic monounsaturated *n*-alcohols and their photooxidation products (present in very high proportion in these particles) were totally absent in the underlying surface sediments (Rontani et al., 2012a). The disappearance of those products as they transit through the aphotic layer of the water column might result from the involvement of free radical oxidation processes (induced by the cleavage of photochemically produced hydroperoxides), rather than from biodegradation processes limited by the photochemical alteration of attached bacteria. In the future, it will thus be essential to take into account the effects of abiotic degradation processes (relatively ignored until now in the literature) within sedimentary palaeoenvironmental reconstructions.

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