

**Degradation state of
organic matter in
surface sediments**

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Degradation state of organic matter in surface sediments from the Beaufort Shelf: a lipid approach

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Abstract

The lipid content of surface sediments collected on the Beaufort Shelf was examined. Particular attention was given to biotic and abiotic degradation products of sterols and monounsaturated fatty acids. By using sitosterol and campesterol degradation products as tracers of the degradation of terrestrial higher plant inputs and brassicasterol degradation products as tracers of degradation of phytoplanktonic organisms, it could be observed that autoxidation, photooxidation and biodegradation processes act much more intensively on higher plant debris than on phytoplanktonic organisms. Examination of oxidation products of monounsaturated fatty acids showed that photo- and autoxidation processes act more intensively on bacteria than on phytodetritus. Enhanced damages induced by singlet oxygen (transferred from senescent phytoplanktonic cells) in bacteria were attributed to the lack of an adapted antioxidant system in these microorganisms. The strong oxidative stress observed in the sampled sediments resulted in the production of significant amounts of epoxyacids and unusually very high proportions of monounsaturated fatty acids with a *trans* double bond. The formation of epoxyacids was attributed to peroxygenases (enzymes playing a protective role against the deleterious effects of fatty acid hydroperoxides *in vivo*), while *cis/trans* isomerization was probably induced by thiyl radicals produced during the reaction of thiols with hydroperoxides. Our results confirm the important role played by abiotic oxidative processes in the degradation of marine bacteria and do not support the generally expected refractory character of terrigenous material deposited in deltaic systems.

1 Introduction

River-dominated shelves are some of the most important sites of organic carbon (OC) burial in the marine environment (Berner, 1982; Hedges and Keil, 1995). The flux of OC to the sediments of these zones includes autochthonous contributions from primary

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production in overlying waters as well as allochthonous inputs from terrigenous sources such as vascular plants, soils and anthropogenic contaminants (Hedges et al., 1997).

The large amounts of terrigenous compounds deposited in deltaic systems are generally considered as being refractory to decomposition due to the presence of protective lignin structures (de Leeuw and Largeau, 1993; Wakeham and Canuel, 2006). However, recent findings have questioned this paradigm (Bianchi, 2011). Indeed, several studies demonstrated that terrestrial organic matter (OM) was more degraded in coastal sediments than in river suspended particulate matter (Ingalls et al., 2003; Unger et al., 2005a,b). Moreover, relatively depleted $\delta^{13}\text{C}$ signatures of bacteria-specific fatty acids were measured in Rhône Prodelta indicating a preferential utilization of terrestrial OM by bacteria (Bourgeois et al., 2011). Recently, we studied the degradation of suspended particulate organic matter (POM) from the Mackenzie River to the Beaufort Sea by using specific lipid degradation tracers (Rontani et al., 2012). The results obtained allowed to demonstrate that biodegradation and especially autoxidation processes strongly affect vascular plant POM delivered by the Mackenzie River to the Beaufort Shelf.

To further investigate and confirm these previous results, we examined the lipid content of surface sediments from the Beaufort Shelf. Using specific lipid degradation products from Δ^5 -sterols and monounsaturated fatty acids that have been proposed for distinguishing biotic from abiotic processes, and photooxidation from autoxidation (Christodoulou et al., 2009; Rontani et al., 2009, 2011), we evaluated the roles played by heterotrophic, photodegradative, and autoxidative processes in the degradation of the main components of OM (higher plants, micro-algae and bacteria).

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2 Material and methods

2.1 Study area

The major input of sediment and particulate organic carbon to Beaufort Sea comes from the Mackenzie River. The Mackenzie is the largest river draining into the Arctic in sediment and particulate organic carbon supply ($127 \times 10^6 \text{ tyr}^{-1}$ of sediment and $2.1 \times 10^6 \text{ tyr}^{-1}$ of particulate organic carbon, respectively, Macdonald et al., 1998) and the fourth largest in terms of freshwater discharge ($3.3 \times 10^{11} \text{ m}^3 \text{ yr}^{-1}$, Milliman and Meade, 1983; Brunskill, 1986; Macdonald et al., 1998). It 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). Primary productivity over the Mackenzie Delta/Beaufort Shelf ($3.3 \times 10^6 \text{ tyr}^{-1}$ 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).

Sediments of the Beaufort shelf are characterized by high silt and clay content and very low sand content (Hill et al., 1991; Conlan et al. 2008). It is generally considered that the particulate organic carbon derived from primary production is rapidly recycled in the water column and/or at the sediment interface (Magen et al., 2010), while a large fraction of land-derived particulate organic carbon (50–60 %) accumulated in shelf and slope sediments (Macdonald et al., 1998). The sedimentation rates varied from 0.040 to 0.12 cm yr^{-1} in the Mackenzie Canyon axis (Richerol et al., 2008) and were around 0.13 cm yr^{-1} in stations located in the deepest area of the Mackenzie Shelf (isobaths 200 m depth; Scott et al., 2009; Bringué and Rochon, 2012). In shallow sediments of the shelf, seasonal landfast ices can scour the sediment to water depths of 15 to ~ 50 m (Blasco et al., 1994). This frequently resuspends and exports material to the slope and deep Arctic basins.

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2.2 Sediment sampling

Samples were collected at eight sites ranging in water depth from 45 m to 580 m in August 2009 onboard the icebreaker CCGS Amundsen (Fig. 1). At each sampling station, an USNEL box corer was deployed for collecting seafloor sediments. Water overlying the box core sediments was drained with a silicone tube. From each box core, one sample of ca. 50 cm² was collected from intact sediment surface (0 to 1 cm) (integrating 7 to 25 years of sedimentation) and frozen immediately at -80 °C for later analysis.

2.3 Treatment of the samples

Each frozen sediment sample was extracted four times with CHCl₃-MeOH-H₂O (1:2:0.8, v/v/v) using ultrasonication (separation of sediment and solvents by centrifugation at 4000 G for 10 min). To initiate phase separation after ultrasonication, CHCl₃ and purified H₂O 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 CHCl₃ and the combined CHCl₃ extracts were dried over anhydrous Na₂SO₄, filtered and the solvent removed via rotary evaporation.

The residues thus obtained were then reduced with excess NaBH₄ (70 mg) at room temperature in MeOH (25 ml; 30 min). This was carried out to reduce labile hydroperoxides (resulting from photo- and autoxidation) to alcohols which were more amenable to analysis using Gas Chromatography/Electron impact Mass spectrometry (GC-EIMS). During this treatment, ketones are also reduced and the possibility of some ester cleavage cannot be excluded. After NaBH₄ reduction, water (25 ml) and KOH (2.8 g) were added and the resulting mixtures saponified by refluxing (2 h). After cooling, the contents were acidified (dilute HCl, 2 N) to pH 1 and extracted with dichloromethane (DCM, 3 × 10 ml). The combined DCM extracts were dried over anhydrous Na₂SO₄, filtered and concentrated by way of rotary evaporation at 40 °C to give the total lipid extract (TLE).

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2.4 Osmium tetroxide oxidation

A fraction of TLE and OsO₄ (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 Na₂SO₃ suspension (16 % Na₂SO₃ 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 gently acidified (pH 3) with HCl and extracted three times with DCM (5 ml). The combined DCM extracts were subsequently dried over anhydrous Na₂SO₄, filtered and concentrated.

2.5 Silylation

After evaporation of solvent, residues were taken up in 300 µl of a 2 : 1 (v/v) mixture of pyridine and pure bis(trimethylsilyl)trifluoroacetamide (BSTFA; Supelco) and silylated at 50 °C for 1 h. The solution was re-evaporated to dryness under a stream of N₂ and the derivatized residue was taken up in a mixture of EtOAc and BSTFA (to avoid desilylation of the more easily silylated compounds) for GC-EIMS analysis. It may be noted that derivatization of stera-3β,5α,6β-triols with pyridine/BSTFA results in the silylation of only the positions 3 and 6. The use of more powerful silylating reagents such as trimethylsilylimidazole/N,O-bis(trimethylsilyl)acetamide/trimethylchlorosilane (Bortolomeazzi et al., 1999) or BSTFA/dimethylsulfoxide (Aubert, unpublished data, 2012) yields complete silylation of 3β,5α-dihydroxysterols. Unfortunately, the presence of an additional (easily silylated) 6β-hydroxyl group in steran-3β,5α,6β-triol molecules induces a supplementary steric hindering, which precludes silylation at the 5 position.

2.6 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). The main characteristic mass fragment ions used to

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quantify degradation products of sterols and monounsaturated fatty acids were previously described (Marchand and Rontani, 2001; Christodoulou et al., 2009; Rontani et al., 2009). Standard oxidation products of palmitoleic, oleic and vaccenic acids and sterols were obtained according to previously described procedures (Rontani and Marchand 2000; Marchand and Rontani, 2001).

Due to their only partial silylation, steran-3 β ,5 α ,6 β -triols need to be analyzed with great care. The use of hot splitless injectors (which can discriminate against high-boiling compounds and induce thermal degradation) should be avoided. The best results were obtained with an on-column injector coupled to a deactivated retention gap.

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 \times 0.25 mm (i.d.) fused silica column coated with HP-1-MS (Agilent; 0.25 μ m film thickness); oven temperature programmed in three sequential steps: (i) 70 $^{\circ}$ C to 130 $^{\circ}$ C at 20 $^{\circ}$ C min $^{-1}$; (ii) 130 $^{\circ}$ C to 250 $^{\circ}$ C at 5 $^{\circ}$ C min $^{-1}$; and (iii) 250 $^{\circ}$ C to 300 $^{\circ}$ C at 3 $^{\circ}$ 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 $^{\circ}$ C; electron energy 70 eV; source temperature 190 $^{\circ}$ C; cycle time 1.99 and 8.3 cycles s $^{-1}$ in SCAN and SIM modes, respectively.

2.7 Choice of Δ^5 -sterol degradation tracers and estimation of photooxidation, autoxidation and biodegradation

The relative importance of biodegradation, photooxidation, and autoxidation for different components of sediments was estimated by quantifying specific degradation products of three "model" Δ^5 -sterols: 24-methylcholest-5,22 E -dien-3 β -ol (brassicasterol) (indicative of phytoplanktonic sources, Volkman, 1986; 2003), 24-methylcholest-5-en-3 β -ol (campesterol), and 24-ethylcholest-5-en-3 β -ol (sitosterol) (both indicative of terrestrial higher plant source in the zone considered, Goñi et al., 2000). Stera-3 β ,5 α ,6 β -triols, Δ^4 -stera-3 β ,6 α / β -diols and 5 α (H)-stan-3 β -ols were selected as specific tracers

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of autoxidative, photooxidative and biological degradation processes, respectively (Rontani et al., 2009; Christodoulou et al., 2009; Fig. 2).

Autoxidation of Δ^5 -sterols mainly affords non-specific and unstable Δ^5 -7 α /7 β -hydroperoxides and to a lesser extent 5,6-epoxysterols and stera-3 β ,5 α ,6 β -triols, the epoxides being converted to the corresponding triol during the treatment (Christodoulou et al., 2009). On the basis of their high specificity and stability, stera-3 β ,5 α ,6 β -triols were selected as tracers of autoxidative processes (Fig. 2) and autoxidation percentage was estimated with the following equation: autoxidation % = (stera-3 β ,5 α ,6 β -triol % \times 2.4) on the basis of the results of different incubation experiments (Rontani et al., 2012) and autoxidation rate constants previously calculated by Morrissey and Kiely (2006).

Type II (i.e. singlet oxygen mediated) photooxidation of Δ^5 -sterols produces mainly unstable Δ^6 -5 α -hydroperoxides with low amounts of Δ^4 -6 α /6 β -hydroperoxides (Smith, 1981). Δ^4 -6 α /6 β -hydroperoxides were selected as tracers of photooxidation of Δ^5 -sterols (Fig. 2) due to their high specificity and relative stability (Rontani et al., 2009; Christodoulou et al., 2009). These compounds were quantified after NaBH₄ reduction to the corresponding diols and photooxidation percentage was obtained from the equation: photooxidation % = (Δ^4 -stera-3 β ,6 α / β -diols % \times (1 + 0.3)/0.3) (Christodoulou et al., 2009) based on the ratio Δ^4 -6 α /6 β -hydroperoxides/ Δ^6 -5 α -hydroperoxides measured in biological membranes (0.30) (Korytowski et al., 1992).

Although complete mineralization of Δ^5 -sterols may be achieved in the marine environment by bacteria belonging to several genera, these compounds can also undergo aerobic bacterial hydrogenation leading mainly to ster-4-en-3-ones, 5 α (H)-stanones and 5 α (H)-stanols (de Leeuw and Baas, 1986; Wakeham, 1989). 5 α (H)-stanols, which are also produced by NaBH₄-reduction of the corresponding stanone during the treatment, were selected as specific tracers of Δ^5 -sterol biodegradation (Fig. 2).

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2.8 Choice of fatty acid degradation tracers and estimation of photooxidation and autoxidation

The reactivity of unsaturated fatty acids relative to auto- and photooxidative processes logically increases with the number of double bonds (Frankel, 1998; Rontani et al., 1998). Oxidation products of polyunsaturated fatty acids (PUFA) are thus considered as very sensitive tracers of these processes. Unfortunately, they are too labile to be used for this purpose. In contrast, autoxidation and photooxidation products of monounsaturated fatty acids, although produced much more slowly, are stable enough in the environment to act as markers of these processes (Marchand and Rontani, 2001, 2003; Marchand et al., 2005; Rontani et al., 2011).

Singlet oxygen ($^1\text{O}_2$)-mediated photooxidation of monounsaturated fatty acids involves a direct reaction of $^1\text{O}_2$ with the carbon-carbon double bond by a concerted 'ene' addition (Frimer, 1979) and leads to formation of hydroperoxides at each carbon of the original double bond with an allylic *trans*-double bond, which can subsequently undergo highly stereoselective radical allylic rearrangement (Porter et al., 1995; Fig. 2). In contrast, free radical oxidation of monounsaturated fatty acids produces six isomeric hydroperoxyacids (Frankel, 1998; Fig. 2). Autoxidative processes can be easily characterised based on the presence of *cis* allylic hydroperoxyacids, which are specific products of these degradation processes (Porter et al., 1995; Frankel, 1998). In order to evaluate autoxidation, we needed to calculate (after NaBH_4 -reduction of hydroperoxides to the corresponding alcohols) the amounts of the four *trans*-hydroxyacids arising from autoxidation according to the proportions of the two *cis*-hydroxyacids observed (Frankel, 1998; Marchand and Rontani, 2001; Fig. 2) and the ambient seawater temperature (-1°C). The temperature of oxidation has a significant effect on the *cis* and *trans* configuration of the initial hydroperoxides formed (Frankel, 1998). For this purpose, we employed different equations previously proposed by Marchand and Rontani (2001). Photooxidation was estimated from *trans*-hydroxyacids (after subtraction of the amounts of these compounds arising from autoxidation processes).

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We thus quantified the products of both autoxidation and photooxidation of hexadec-9(*cis*)-enoic (palmitoleic), octadec-9(*cis*)-enoic (oleic) and octadec-11(*cis*)-enoic (vaccenic) acids, which were the three dominant monounsaturated fatty acids in the different sediment samples investigated. Oleic and palmitoleic acids have diverse possible biological sources (plants, fungi, yeasts, bacteria, animals or algae) (Harwood and Russell, 1984), their oxidation products may thus only be used to assess abiotic degradation of bulk OM of sediments. In contrast, oxidation products of vaccenic acid, which is a typical biomarker for Gram-negative bacteria (Sicre et al., 1988; Keweloh and Heipieper, 1996), are very useful to estimate the extent of sedimentary bacteria degradation.

3 Results and discussion

3.1 Biotic and abiotic alteration of Δ^5 -sterol

Sterol composition of the different sediments sampled appeared to be dominated by cholesterol and sitosterol. Lesser amounts of campesterol, brassicasterol, 24-methylcholest-5,24(28)-dien-3 β -ol (24-methylenecholesterol) and 24-ethylcholest-5,22 E -dien-3 β -ol (stigmasterol) could be also detected.

Degradation tracers of brassicasterol, sitosterol and campesterol, which could be identified in all investigated sediments (see example for sitosterol in Fig. 3), were quantified. The results obtained are summarized in Fig. 4. The three sterols exhibited well distinct degradation states, with the following order of reactivity: sitosterol > campesterol \gg brassicasterol. Brassicasterol (mainly arising from phytoplankton) appeared to be very weakly affected by biotic and abiotic degradation processes in Beaufort Shelf sediments (Fig. 4). In contrast, autoxidation, photooxidation and biodegradation processes acted significantly on sitosterol and campesterol (mainly arising from terrestrial higher plants). Goñi et al. (2000) previously estimated terrigenous contribution for these two sterols in sediments of the same zone and found approximately 60 % for

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campesterol and 70 % for sitosterol. The reduced degradation observed in the case of campesterol (Fig. 4) may be thus attributed to a significant contribution of weakly altered Chlorophytes or Prasinophytes, (micro-algae containing high proportions of campesterol, Volkman, 1986) to this sterol.

It was previously observed that autoxidation processes play a key role in the degradation of terrestrial suspended POM in the Beaufort Sea (Rontani et al., 2012). Although this seems to be also the case for particles accumulating at the seafloor, the proportions of autoxidation products (ranging from 20 to 120 % of the residual parent sitosterol; Fig. 4) are practically one order of magnitude lower than those previously observed in suspended particles collected in the same zone. These differences may be attributed to the fact that suspended particles, which spend a very long time in the water column (where autoxidation strongly occurs) generally only weakly contribute (after aggregation) to the sedimentary record (Wakeham and Lee, 1989).

Relatively high proportions of Type II photooxidation products of campesterol and sitosterol (e.g. 60 % of the residual parent sitosterol at station 680, for example; Fig. 4) were detected in the different samples. These results contrast with the very weak amounts of photooxidation products of these sterols previously observed in suspended POM (for example 10 % of the residual parent sitosterol at the same station 680; Rontani et al., 2012). Due to the involvement of very intensive autoxidation processes in these suspended particles, a free radical driven breakdown of photochemically-produced hydroperoxides might likely explain their unexpected very weak content of sterol photodegradation products. These findings support the idea that suspended and sinking particles that reach the seafloor have distinct origins and then distinct degradation pathways during their transit.

3.2 Biotic and abiotic alteration of monounsaturated fatty acids

The results obtained are summarized in Figs. 5a (vaccenic acid), 6a (oleic acid) and 7a (palmitoleic acid). The three selected monounsaturated fatty acids exhibited well distinct abiotic degradation states. Photooxidation processes appeared to act more

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intensively in bacteria (Fig. 5a) than in other organisms (Figs. 6a and 7a). This observation is in good agreement with the highest photoreactivity of vaccenic acid (relative to oleic and palmitoleic acids) previously observed by Christodoulou et al. (2010) during irradiation of non-axenic cells of *Emiliana huxleyi* by solar light. It was previously shown that the photodegradation of *cis*-vaccenic acid of heterotrophic bacteria was more than two orders of magnitude faster in the presence of phytoplanktonic cells (Rontani et al., 2003). Indeed, phytodetritus constitute hydrophobic microenvironments where the lifetime and potential diffusive distance of singlet oxygen may be long enough to allow its transfer to attached heterotrophic bacteria. Damages resulting from the presence of high amounts of singlet oxygen in heterotrophic bacteria may be more important than in senescent phytoplanktonic cells due to the lack of an adapted photoprotective system in these organisms (Garcia-Pichel, 1994). Vaccenic acid also appeared to be affected by autoxidation (Fig. 5a). 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 peroxy radicals, which may in turn accentuate cell damages (Dahl et al., 1989). The predominance of autoxidation relative to photooxidation observed in the case of palmitoleic acid (Fig. 7a) was attributed to a strong contribution of benthic animals (where Type II photoprocesses do not act) to this fatty acid.

We detected significant proportions of saturated hydroxyacids, methoxyhydrins, diols and chlorohydrins resulting from the degradation of 9,10-epoxyhexadecanoic, 9,10-epoxyoctadecanoic and 11,12-epoxyoctadecanoic acids in the different samples investigated (Fig. 8). Epoxyacids are in fact strongly degraded during the treatment; in addition to a partial reduction with NaBH_4 (Marchand and Rontani, 2001), they undergo alcoholysis and hydrolysis during alkaline hydrolysis and are converted to chlorohydrins and 9,10-dihydroxyacids during acidification (Holloway and Brown Deas, 1973, Fig. 8). Epoxides may be formed by classical addition of a peroxy radical to a double bond (Berti, 1973) and subsequent fast intramolecular homolytic substitution (Fossey et al., 1995). However, this reaction becomes competitive (relative to allylic hydrogen atom

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abstraction) only in the case of conjugated, terminal, or trisubstituted double bonds (Schaich, 2005). In the case of monounsaturated fatty acids, such a formation is thus very unlikely. Epoxidation of the double bonds of fatty acids may be also induced by cytochrome P-450-dependent monooxygenases (Ruettinger and Fulco, 1981); however these enzymes also catalyze monohydroxylation at the ω -1, ω -2 and ω -3 positions and we failed to detect the thus formed hydroxyacids in lipid extracts. Finally, we attributed the formation of the epoxyacids detected to the involvement of peroxygenases (hydroperoxide-dependent oxygenases) during abiotic degradation of higher plant debris, algae or bacteria. Such enzymes catalyzed epoxidation of unsaturated fatty acids in the presence of alkylhydroperoxides as co-substrates (Fig. 9) and play a protective role against the deleterious effects of fatty acid hydroperoxides in vivo (Blée and Schuber, 1990). This hypothesis is well supported by the relative good correlation observed between the proportions of epoxyacids and these of fatty acid oxidation products (quantified after NaBH_4 -reduction of the corresponding hydroperoxides) ($r^2 = 0.825, 0.702$ and 0.631 with p -value = $0.002, 0.009$ and 0.018 for vaccenic, oleic and palmitoleic acids, respectively; Figs. 5a, 6a and 7a).

In the sediments analyzed, unusually very high proportions of monounsaturated fatty acids with a *trans* double bond could be also detected. The position of the double bond of these compounds was unambiguously determined after OsO_4 oxidation and GC-EIMS analyses of the silylated foregoing diastereoisomeric diols (Fig. 10). According to the fatty acid considered, well distinct *trans/cis* ratios could be observed (Figs. 5b, 6b and 7b). *Cis-trans* isomerization of the double bond of monounsaturated fatty acids may be attributed to: (i) photosensitized isomerization processes induced by UVR (Christodoulou et al., 2010) generally involving ketonic triplet energy sensitizers (Testa, 1964; Horspool and Armesto, 1992), (ii) *cis-trans* isomerase activity enabling Gram-negative bacteria belonging to the genera *Pseudomonas* and *Vibrio* to adapt to several forms of environmental stress (Heipieper et al., 2003), or (iii) the formation of thiyl radicals (catalyzing double bond isomerization, Ferreri et al., 2004) during

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the antioxidant reactions of biologically relevant thiols (e.g. glutathione) (Chatgijialoglu et al., 2002) or from methanethiol homolytic cleavage or thiolate oxidation.

During previous irradiation of non-axenic cells of the haptophyte *E. huxleyi* by solar light, it was observed that UVR-induced photosensitized *cis-trans* isomerization processes acted not only on monounsaturated fatty acids but also on their oxidation products (Christodoulou et al., 2010). In the studied sediments, the lack of 9-*cis* and 10-*cis* hydroxyacids (arising from oleic acid oxidation) and 11-*cis* and 12-*cis* hydroxyacids (arising from *cis*-vaccenic acid oxidation) previously proposed as potential tracers of the effects of UVR in situ (Christodoulou et al., 2010) suggests that *cis-trans* isomerization of monounsaturated fatty acids observed in sediments from the Beaufort Shelf does not result from the involvement of UVR-induced photosensitized processes in the water column.

Enzymatic *cis-trans* isomerization of unsaturated fatty acids constitutes an important adaptive reaction of *Pseudomonas* and *Vibrio* species to toxic organic compounds or other environmental stress factors (Heipieper et al., 1992, 2003, 2007). Such an adaptive mechanism appears to be an alternative way to regulate membrane fluidity when the growth is inhibited (Heipieper et al., 2003). Based on the good correlation observed between the hydrophobicity of organic compounds, growth inhibition and the *trans/cis* ratio of unsaturated fatty acids, this enzymatic isomerization process was proposed as marker for stress in contaminated environments (Guckert et al., 1986; Frostegard et al., 1993; White et al., 1996). Values of the *trans/cis* ratio higher than 0.1 in environmental samples are generally considered as indicative of environmental stress conditions at the site (Guckert et al., 1986; Navarrete et al., 2000). The very high *trans/cis* ratio observed in the sediments analyzed (values ranging from 0.03 to 0.50 for oleic acid and from 0.18 to 0.78 for vaccenic acid; Figs. 5b and 6b) could thus be attributed to an adaptive reaction of sedimentary bacteria to the presence of high amounts of photochemically and autoxidatively-produced hydroperoxides (see above). However, it was previously demonstrated that this enzymatic isomerization process has a highest specificity for C₁₆ unsaturated fatty acids as substrates (Heipieper et al., 1992) and the

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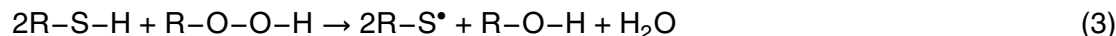
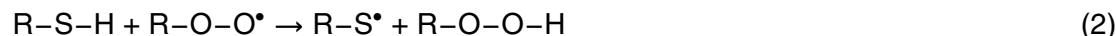
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trans/cis ratio observed in the samples for palmitoleic acid (values ranging from 0.004 to 0.1; Fig. 7b) are considerably lower than in the case of oleic and vaccenic acids (Figs. 5b and 6b). In addition, it was recently shown that the *cis-trans* isomerization is only an urgent response mechanism in these bacteria that is later substituted by other adaptive mechanisms (Fischer et al., 2010). Therefore, *trans/cis* ratio is not a good indicator of long-term oxidative stress as it is present in the investigated sediments. It seems thus very unlikely that the formation of *trans* monounsaturated fatty acids in sediments from the Beaufort Shelf results from an enzymatic *cis-trans* isomerization activity.

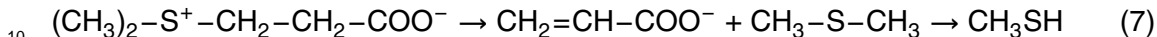
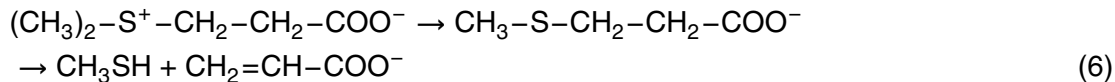
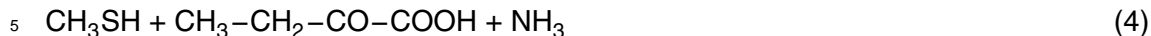
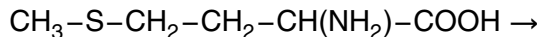
Functionalized aliphatic thiols (glutathione, methionine-containing proteins) are present in living organisms in considerable amounts (Ferreri et al., 2005). These compounds, which are very good hydrogen donors towards radicals such as alkoxy or alkylperoxy radicals, are extraordinarily efficient antioxidants protecting the cells against consequences of damage induced by free radicals (Wlodek, 2002) (Eqs. 1–3).



However, this role as repairing agents is counterbalanced by the formation of thiyl radical species, which can damage other biomolecules (Ferreri et al., 2005; Rontani et al., 2006). Indeed, thiyl radicals are efficient catalysts for *cis-trans* isomerization of lipids in biological membranes and this process cannot be ignored when considering radical damage to biological components. In sediments, the formation of thiyl radicals can also result from the homolytic cleavage of methanethiol produced by bacteria.

Several mechanisms for the bacterial production of methanethiol in the environment have been identified. It can be formed by: (i) microbial degradation of S-containing amino acids such as methionine (Eq. 4; Ferchichi et al., 1986; Kiene and Visscher, 1987), (ii) methylation of sulfide (Eq. 5; Lomans et al., 2002) and (iii) degradation of β -dimethylsulfoniopropionate (DMSP) (Eqs. 6 and 7), a tertiary sulfonium compound

produced in high concentration by certain species of algae (Keller et al., 1989; Yoch, 2002) and halophytes (Ishida, 1996) for regulation of their internal osmotic environment.



Thiyl radicals can also be produced by oxidation of thiolate ions (produced during sulfate reduction) by transition metals such as e.g., Fe^{+3} (Eq. 8; Wlodek, 2002).



15 The fact that thiyl radicals act as a catalyst for *cis-trans* isomerization is important, because even a small concentration of these radical species is able to propagate the reaction, leading to an efficient formation of *trans* isomers (Ferreri et al., 2007). Because the *trans*-configuration is energetically preferred by about $0.6\text{--}1 \text{ kcal mol}^{-1}$, a mixture dominated by *trans* olefin (about 80 %) may be theoretically obtained (Ferreri et al., 2005).
 20 Due to the strong oxidative stress observed in the sediments investigated (see above), an induction of *cis-trans* isomerization by thiyl radicals resulting from the reaction of thiols with hydroperoxides (Fig. 9) seems thus very likely. This hypothesis is well supported by the relative good correlation observed between *trans/cis* ratio and the proportions of vaccenic and oleic acid oxidation products (quantified after NaBH_4 -reduction
 25 of the corresponding hydroperoxides) ($r^2 = 0.692$ and 0.812 with p -value = 0.011 and 0.002 , respectively; Figs. 5 and 6). These processes appeared to act very intensively in bacteria and to a lesser extent in phytodetritus and higher plant debris.

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It may be noted that the *trans* configuration of double bonds is 7 to 10 times less sensitive against singlet oxygen-mediated oxidation than the classical *cis* configuration (Hurst et al., 1985). Consequently, if *cis-trans* isomerization processes took place in sinking particles, which are generally considered as the main contributors to the sedimentary record (Wakeham and Lee, 1989), selective Type II photooxidation of *cis* and *trans* monounsaturated fatty acids in euphotic layer could be an additional explanation of the unusually very high *trans/cis* ratio observed in sediments.

The spatial variability of the results obtained (Figs. 5–7) may be attributed to several factors. Sedimentation rate is lower at the deeper sites further off the Mackenzie River and in the Amundsen Gulf (stations 110, 140, 235, 345, Fig. 1) (Richerol et al., 2008). This implicates, that diagenetic reaction time in the sampled zone of sediments (0–1 cm) is longer at deeper sites which could explain the observed results of distinct degradation state of OM. Oxygenation of sediments may also strongly affect the degradation of OM. Indeed, the presence of oxygen may enhance autoxidation and aerobic degradation processes, but it can also hinder the formation of thiolates and thus limit thiy radical-induced *cis/trans* isomerization. The penetration depth of oxygen is generally limited to few millimetres below the sediment-water interface at the head of the Mackenzie Canyon (in the vicinity of our station 689) and extended between 2 and 3 cm in sediment of the shelf (Magen, 2007). Finally, well distinct phytoplanktonic communities may be also present at the different stations investigated, which will inducing the formation of different qualities of sinking material (Morata et al., 2008).

4 Conclusions

Lipids and their degradation products were quantified in eight samples of surface sediments collected in the Beaufort Sea. Brassicasterol (mainly arising from phytoplankton) appeared to be very weakly affected by biotic and abiotic degradation processes in these sediments. These results do not support the generally expected quick recycling of material derived from primary production in the water column and/or at the sediment

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interface of this zone (Magen et al., 2010). In contrast, autoxidation, photooxidation and biodegradation processes acted intensively on sitosterol and campesterol (mainly arising from terrestrial higher plants), while these compounds appeared to be only weakly affected by these degradation processes in particulate matter delivered by the Mackenzie River (Rontani, 2012). The old concept expecting that the pre-degradation of terrestrial OM on land and in the rivers should result to a good preservation of this material in the marine environment seems thus to be erroneous.

In Arctic, global warming may induce changes in vegetation from tundra toward leaf-bearing plants (Goñi et al., 2005), thus enhancing the delivery of modern vascular plant organic carbon to rivers. To estimate the consequences of climate change in this strategic zone, a good knowledge of the processes controlling degradation and burial of terrestrial OM is essential. The results obtained here confirm that vascular plant POM delivered by the Mackenzie River to the Beaufort Sea is strongly affected by biotic and abiotic degradation processes.

We used oxidation products of vaccenic acid, which is a typical biomarker for Gram-negative bacteria (Sicre et al., 1988; Keweloh and Heipieper, 1996), to estimate the extent of abiotic sedimentary bacteria degradation. In contrast, oxidation products of the non-specific oleic and palmitoleic acids could only be used to assess abiotic degradation of bulk OM of sediments. Surprisingly, photo- and autoxidation processes appeared to act more intensively in bacteria than in other organisms. We suggest that singlet oxygen is efficiently transferred from phytodetritus, where it is produced by photolytic excitation of chlorophyll, to the heterotrophic bacteria (and their lipids) that are associated with the detritus. This transfer has been observed previously in vitro (Rontani et al., 2003; Christodoulou et al., 2010). The highest efficiency of oxidative damages in bacteria should result from the lack of an adapted antioxidant system in these microorganisms (Garcia-Pichel, 1994).

In parallel to the intensive abiotic degradation of monounsaturated fatty acids observed, significant amounts of epoxyacids could be detected. The formation of these compounds was attributed to the involvement of peroxygenases

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(hydroperoxide-dependent oxygenases) during abiotic degradation of higher plant debris, algae or bacteria contained in sediments. Such enzymes play a protective role against the deleterious effects of fatty acid hydroperoxides in vivo.

Unusually very high proportions of monounsaturated fatty acids with a *trans* double bond could be also detected in these sediments. Vaccenic, oleic and palmitoleic acids exhibited well distinct *trans/cis* ratios, the highest values (ranging from 0.18 to 0.78) being observed in the case of vaccenic acid. Due to the strong oxidative stress observed in the sediments investigated, induction of *cis-trans* isomerization was attributed to the presence of thiyl radicals resulting from the reaction of thiols with hydroperoxides. These processes appeared to act very intensively in bacteria and to a lesser extent in phytodetritus and higher plant debris.

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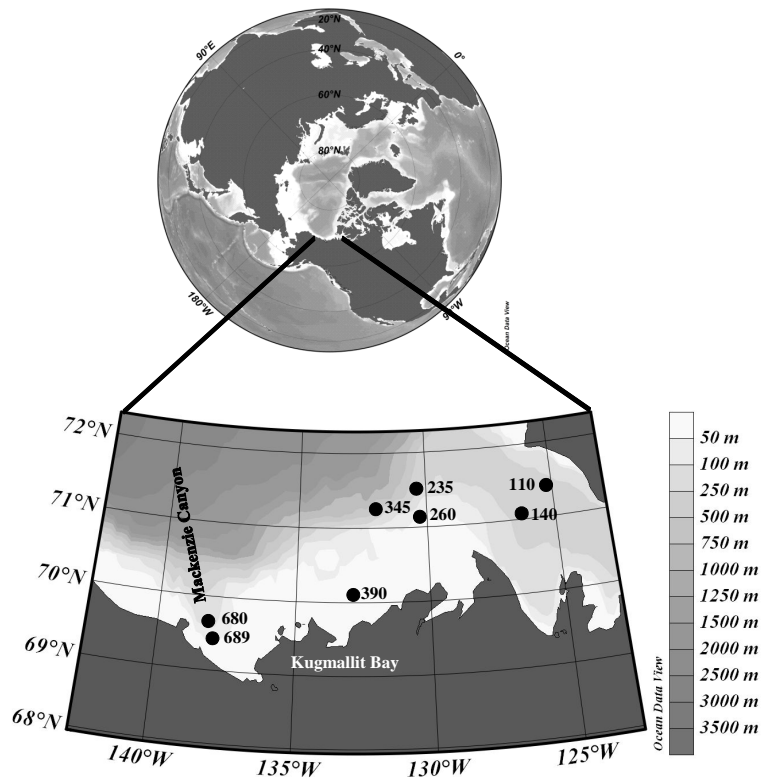


Fig. 1. Map of the studied area with locations of the different stations investigated.

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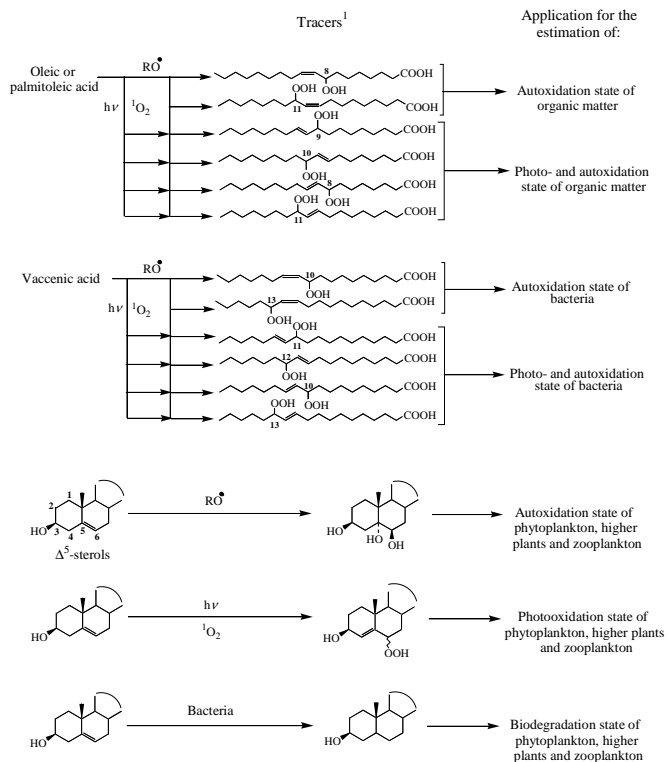


Fig. 2. Formulae and potential applications of the different lipid tracers of degradation processes employed in the present work. ¹Quantified after NaBH₄-reduction to the corresponding alcohols and subsequent silylation.

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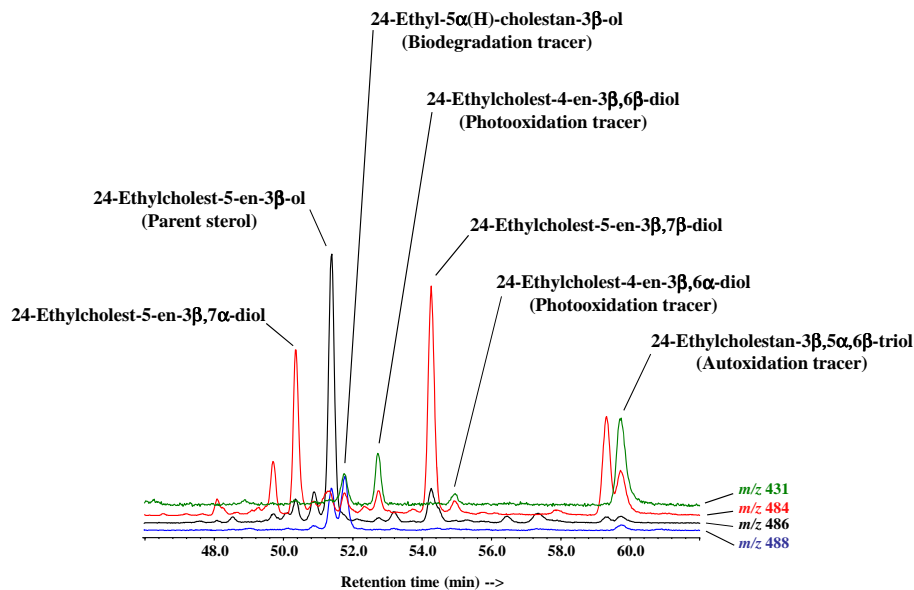


Fig. 3. Partial m/z 486, 488, 484 and 431 ion chromatograms showing presence of sitosterol degradation products in the total lipid extract of surface sediments (0–1 cm) collected at the station 680.

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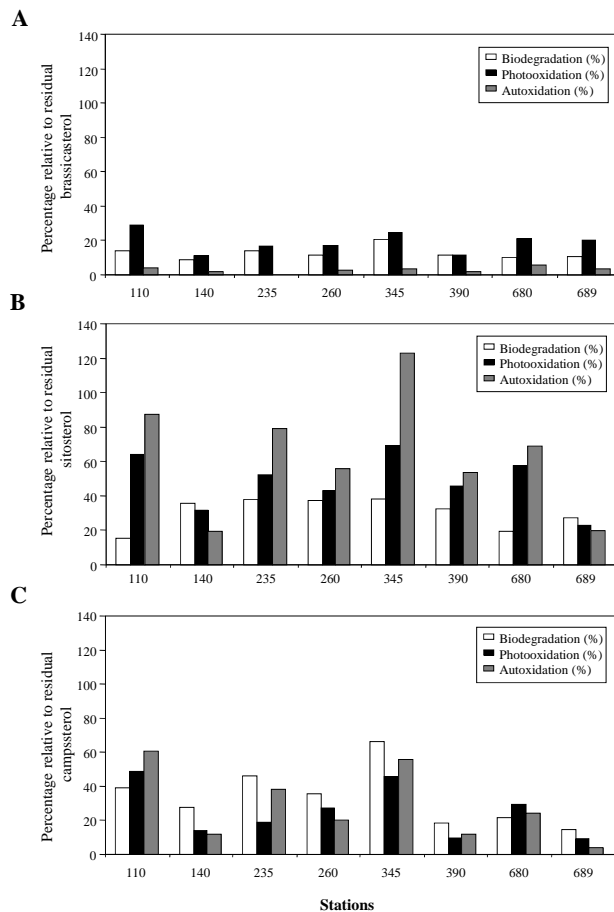


Fig. 4. Estimates of relative biodegradation, autoxidation and photooxidation (as percentages relative to the residual parent compound) of brassicasterol (**A**), sitosterol (**B**) and campesterol (**C**) for the different sediments investigated.

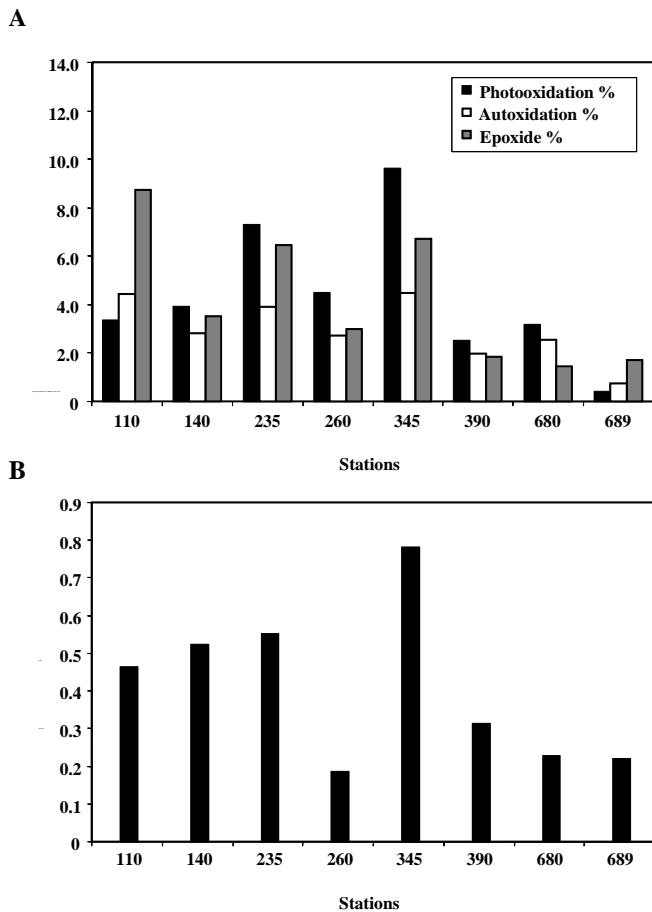


Fig. 5. Estimates of relative autooxidation, photooxidation and epoxide production (as percentages relative to the residual parent compound) **(A)** and *trans/cis* ratio measured **(B)** of vaccenic acid for the different sediments investigated.

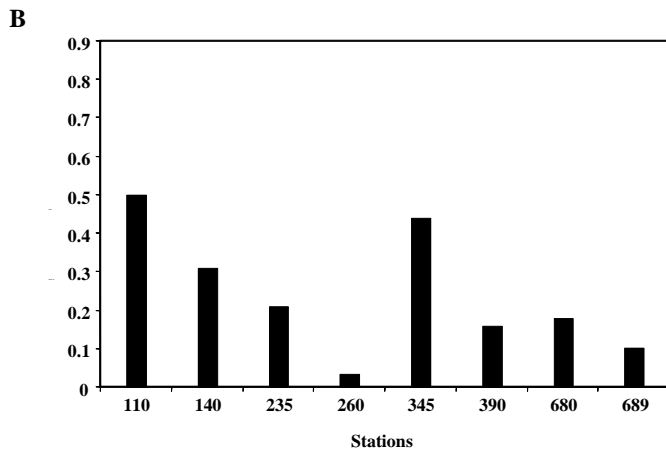
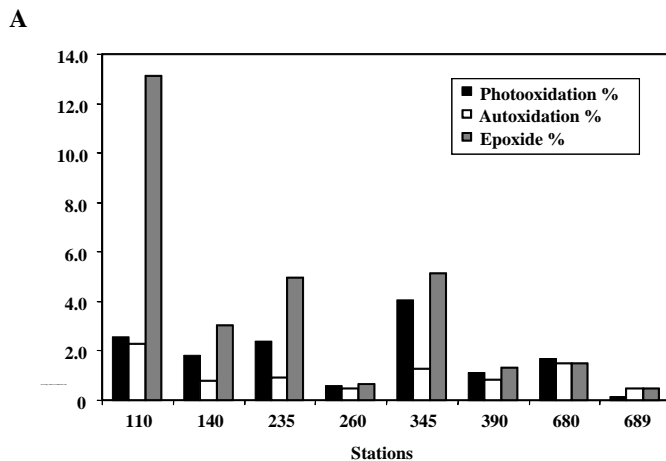


Fig. 6. Estimates of relative autooxidation, photooxidation and epoxide production (as percentages relative to the residual parent compound) **(A)** and *trans/cis* ratio measured **(B)** of oleic acid for the different sediments investigated.

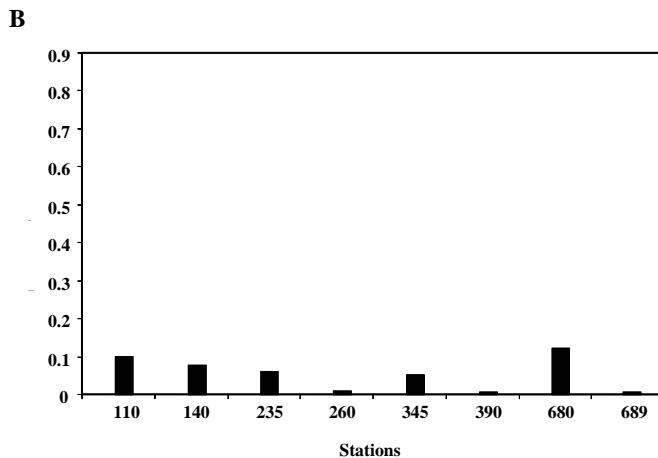
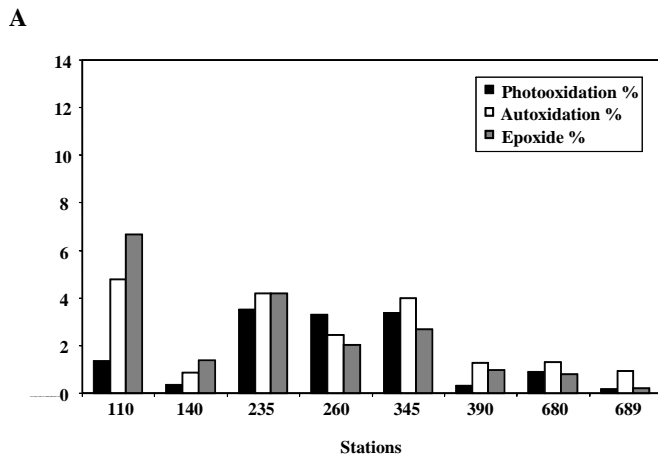


Fig. 7. Estimates of relative autooxidation, photooxidation and epoxide production (as percentages relative to the residual parent compound) **(A)** and *trans/cis* ratio measured **(B)** of palm-toleic acid for the different sediments investigated.

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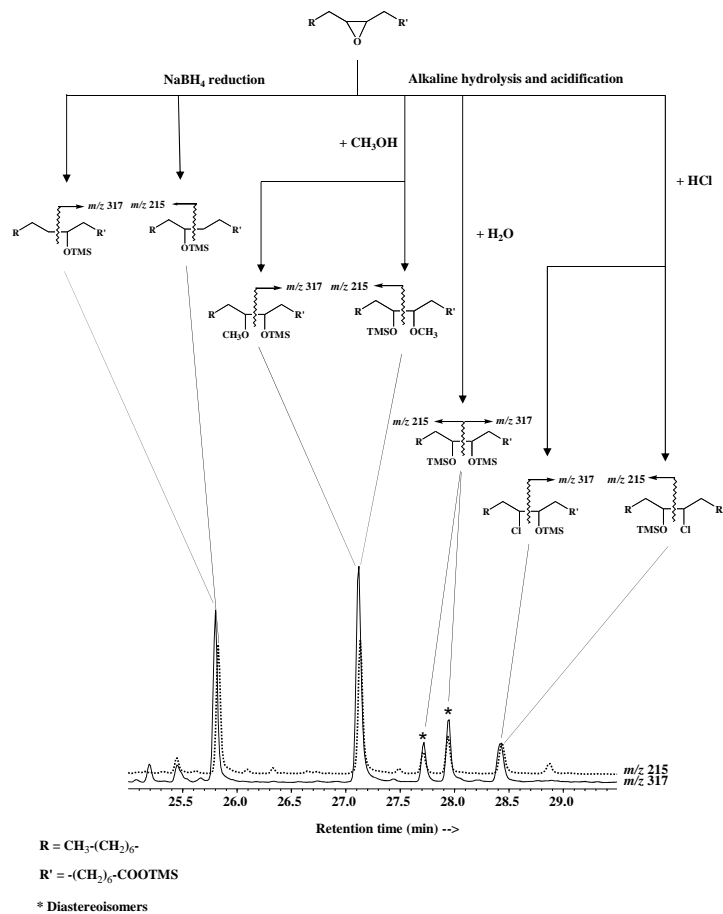


Fig. 8. Partial m/z 215 and 317 ion chromatograms showing the presence of compounds resulting from the degradation of 9,10-epoxyoctadecanoic acid during the treatment.

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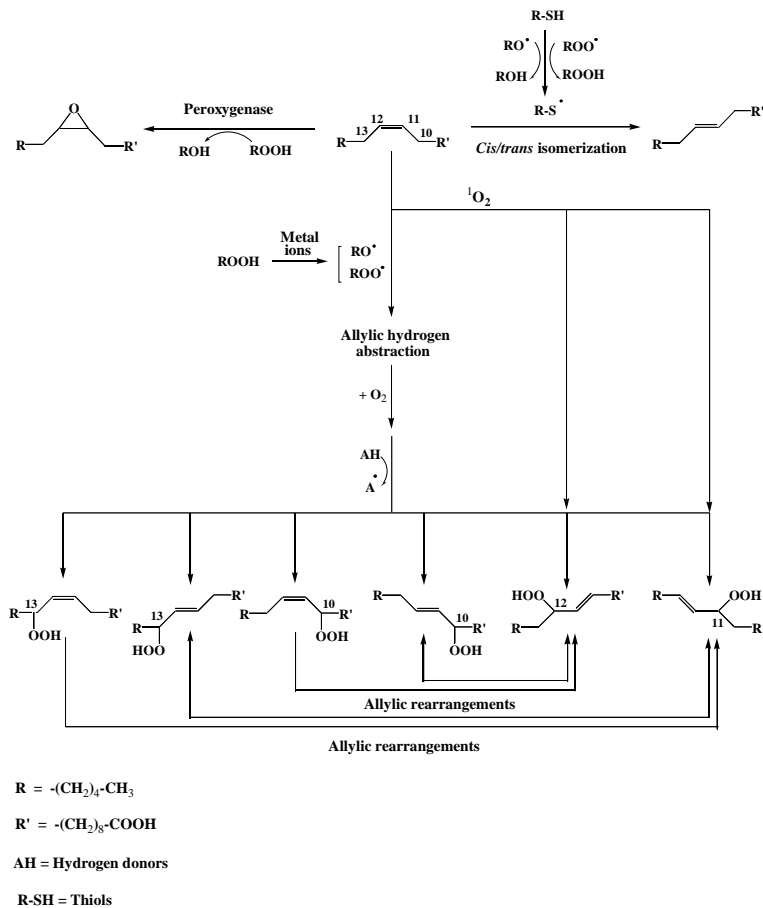


Fig. 9. Proposed mechanisms for biotic and abiotic degradation of vaccenic acid in the Beaufort Shelf.

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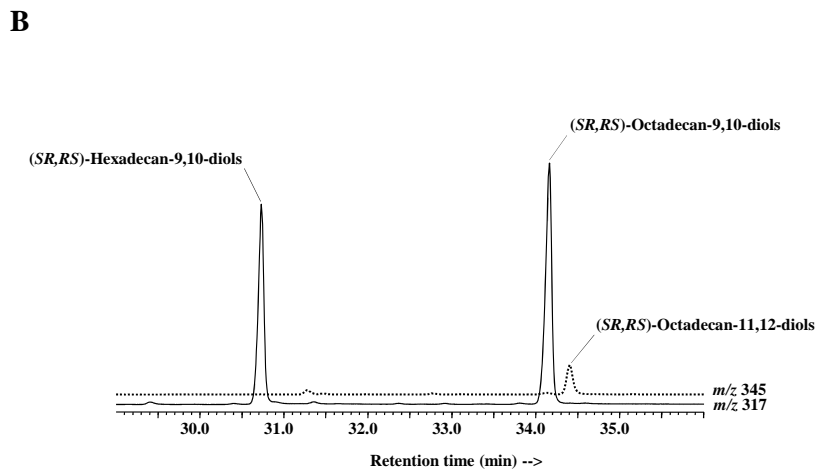
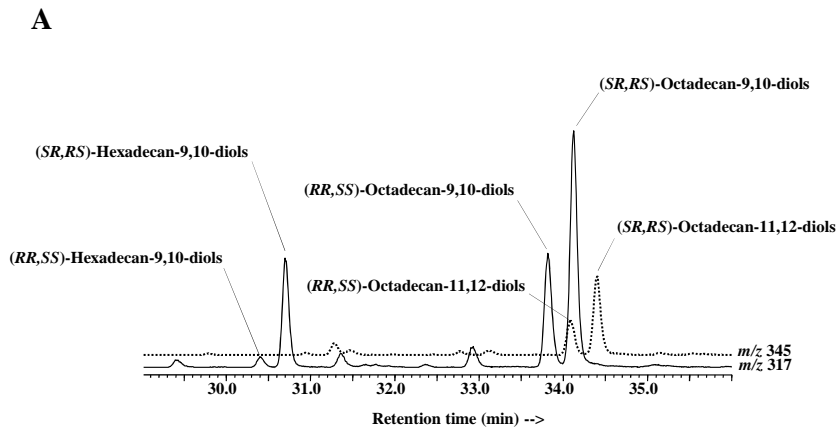


Fig. 10. Partial *m/z* 317 and 345 ion chromatograms showing the distribution of silylated OsO_4 derivatives of *cis* and *trans* monounsaturated fatty acids in surface sediments (0–1 cm) collected at the stations 110 (**A**) and 260 (**B**).