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

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Abstract. For the next decades significant climatic changes should occur in the Arctic zone. The expected destabilisation of permafrost and its consequences for hydrology and plant cover should increase the input of terrigenous carbon to coastal seas. Consequently, the relative importance of the fluxes of terrestrial and marine organic carbon to the seafloor will likely change, strongly impacting the preservation of organic carbon in Arctic marine sediments. Here, we investigated the lipid content of surface sediments collected on the Mackenzie basin in the Beaufort Sea. 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 epoxy acids and unusually high proportions of monounsaturated fatty acids with a *trans* double bond. The formation of epoxy acids was attributed to peroxygenases (enzymes playing a protective role against the deleterious effects of fatty acid hydroperoxides in vivo), while *cis/trans* isomerisation 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 production in overlying waters as well as allochthonous inputs from terrigenic 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 (Vonk et al., 2008; Van Dongen et al., 2008; 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) and that the reactivity of the sedimentary OM is not only influenced by its origin but also by several factors, such as water column depth, redox conditions, microbial activity, mineral composition and sediment physical characteristics (Alkathib et al., 2012; Niggemann et al., 2007; Hedges et al., 1997). Moreover, relatively depleted δ^{13}C signatures of bacteria-specific fatty acids were measured in Rhône Prodelta, indicating a preferential utilisation of terrestrial OM by bacteria (Bourgeois et al., 2011). Recently, we studied the degradation of suspended particulate matter (SPM) from the Mackenzie River to the Beaufort Sea by using specific lipid degradation tracers (Rontani et al., 2012a). Lipids of terrestrial vascular plants, which are well preserved in SPM of the Mackenzie River, appeared to be extensively degraded by bacterial and especially autoxidative degradative processes in the water column of the Beaufort Shelf, while planktonic lipids were only weakly affected. A good correlation was observed between the extent of autoxidation and salinity, suggesting that these free radical oxidation processes are enhanced by contact with seawater. In order to explain the specific induction of autoxidative processes on vascular plant-derived material, a mechanism involving metal ion-catalysed homolytic cleavage of photochemically produced hydroperoxides resulting from the senescence of higher plants on land was proposed.

Recent studies predicted that in the next decades significant changes in the Arctic zone will occur (MacGuire et al., 2009; Griffith et al., 2012). These changes should result in a river flow increase coupled with a permafrost thaw and a high coastal erosion modifying the organic and inorganic terrestrial inputs. The longer period of ice-free conditions in summer will modify light availability and thus the primary productivity and photochemical processes affecting both dissolved and particulate OM. Consequently, the relative importance of the fluxes of terrestrial and marine organic carbon to the seafloor will likely change, as will the processing and preservation of organic carbon in Arctic sediments (Katsev et al., 2006). Thus, better knowledge of the degradation processes affecting sedimentary organic matter is essential to establish a baseline to understand the impact of global change in the Arctic Ocean.

To further investigate and confirm our previous results, we examined the lipid content of surface sediments from the Beaufort Shelf. Even though this shelf accounts for only a few percent of the total Arctic Ocean surface area, it receives a large amount of freshwater from the Mackenzie River estimated at 330 km^3 yr^{-1} (Stein and Macdonald, 2004). This flux contributes vast quantities of terrigeneous organic carbon to Beaufort Sea (O'Brien et al., 2006).

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).

2 Material and methods

2.1 Study area

This study was conducted in the southeast Beaufort Sea, with an emphasis on the MacKenzie delta outflow, during summer 2009 on board the Canadian research icebreaker *CCGS Amundsen* as a part of the international Malina Program. The physical, biological and sedimentological characteristics of Malina study area are described in more details in Babin et al. (2012).

The Mackenzie Shelf is a coastal region of the Beaufort Sea located along the Arctic Ocean's Canadian coast, between Point Barrow in northern Alaska and the western part of the Canadian Arctic Archipelago. The area is dominated by a $\sim$100 km wide shelf that covers an area of 64 000 km^2 (to the isobath 200 m) which is relatively small compared to the broad Eurasian Shelf (Stein and Macdonald, 2004; O'Brien et al., 2006). The shelf is bordered on the west by the Mackenzie Trough and on the east by Amundsen Gulf. The major input of sediment and particulate organic carbon to this area comes from the Mackenzie River (O'Brien et al., 2006). The Mackenzie is the largest river draining into the Arctic Ocean in sediment and particulate organic carbon supply (127×10^6 tons yr^{-1} of sediment and 2.1×10^6 tons yr^{-1} of particulate organic carbon respectively, Macdonald et al., 1998; Holmes et al., 2002) and the fourth largest in terms of freshwater discharge (3.3×10^{11} m^3 yr^{-1}, Milliman and Meade, 1983; Brunskill, 1986; Macdonald et al., 1998). Despite the coastal erosion may be locally important, particularly in the inner shelf, the contribution of the MacKenzie River is clearly much more important (5.6×10^6 t a^{-1} vs. 64.45×10^6 t a^{-1}; Hill et al., 1991; MacDonald et al., 1998; Rachold et al., 2000) and supplies about 95–99 % of the sediment to the Beaufort Shelf (Rachold et al., 2004).

The shelf is seasonally ice covered. The sea ice usually starts to form in October and reaches its maximum 2 m-thickness in March. The landfast ice covers the inner shelf ($<$ 20 m water depth). It is bounded offshore by an hummock, or "stamucki", formed by the collision of the mobile offshore ice pack and the landfast ice edge. In winter, the stamucki retains the turbidity waters from the MacKenzie River under the landfast ice to the inner shelf. Sporadic polynya form at the edge of the landfast ice due to winter winds that push mobile ice pack away from the stamucki. Around June, the stamucki breaks and releases the Mackenzie River plume in the top 10 m of the surface layer of the MacKenzie Shelf.

This plume is pushed seaward by easterly winds (MacDonald and Yu, 2006). The sea ice break-up favors the formation of polynya and then marine organic matter production.

Primary productivity over the Mackenzie Delta/Beaufort Shelf is about 3.3×10^6 tons yr^{-1} of particulate organic carbon 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 %) accumulate in shelf and slope sediments (Macdonald et al., 1998). The sedimentation rates vary from 0.040 to 0.12 cm yr^{-1} in the Mackenzie Canyon axis (Richerol et al., 2008) and is around 0.13 cm yr^{-1} at 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 ice can scour the sediment to water depths of 15 to $\sim$ 50 m (Blasco et al., 1998). This frequently resuspends and exports material to the slope and deep Arctic basins.

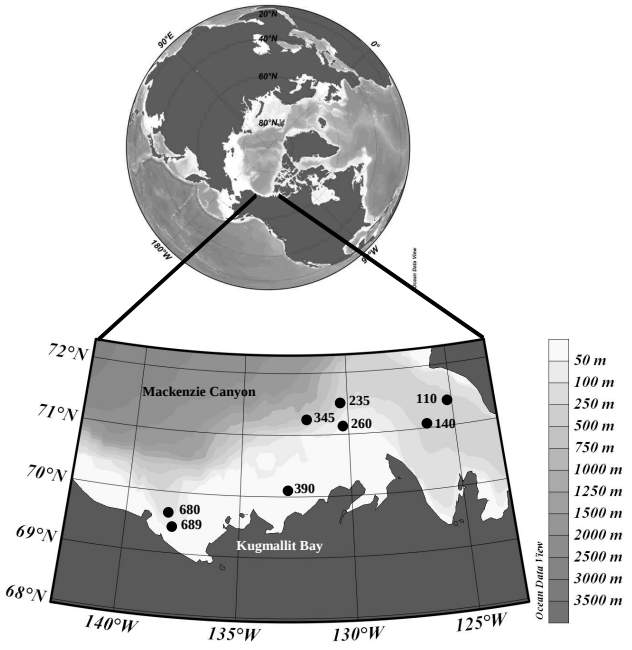

Fig. 1. Map of the studied area with locations of the different stations investigated.

2.2 Sediment sampling

Samples were collected from the MacKenzie Shelf and Slope at eight sites ranging in water depths from 45 m to 580 m in August 2009 onboard the icebreaker *CCGS Amundsen* (Fig. 1). At each sampling station, an USNEL box corer ($50 \times 50 \times 40$ cm) 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 cm^2 was collected from intact sediment surface (0 to 1 cm) (integrating 7 to 25 yr 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 $CHCl_3$-MeOH-H_2O (1 : 2 : 0.8, $v/v/v$, 3×) using ultrasonication for 15 min (separation of sediment and solvents by centrifugation at 3500 rpm 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.

The residues thus obtained were then reduced with excess $NaBH_4$ (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. It is well known that metal ions can promote autoxidation during hot saponification procedures. The prior reduction of hydroperoxides with $NaBH_4$ allowed us to avoid such autoxidative artifacts during the alkaline hydrolysis. After $NaBH_4$ 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, 2N) to pH 1 and extracted with dichloromethane (DCM, 3×10 ml). The combined DCM extracts were dried over anhydrous Na_2SO_4, filtered and concentrated by way of rotary evaporation at 40 °C to give the total lipid extract (TLE).

2.4 Osmium tetroxide oxidation

A fraction of TLE 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 gently acidified (pH 3) with HCl and extracted three times with DCM (5 ml). The combined DCM extracts were subsequently dried over anhydrous Na_2SO_4, 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 N_2 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 derivatisation 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 (C. Aubert, unpublished results), 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 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-3β,5α,6β-triols need to be analysed 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 × 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.

2.7 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-5,22E-dien-3β-ol (brassicasterol) (indicative of phytoplanktonic sources, Volkman, 1986, 2003), 24-methylcholest-5-en-3β-ol (campesterol), and 24-ethylcholest-5-en-3β-ol (sitosterol) (both indicative of terrestrial higher plant source in the zone considered, Goñi et al., 2000). Stera-3β,5α,6β-triols, Δ^4-stera-3β,6α/β-diols and 5α(H)-stan-3β-ols were selected as specific tracers 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$\alpha/7\beta$-hydroperoxides and to a lesser extent 5,6-epoxysterols and stera-3β,5α,6β-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-3β,5α,6β-triols were selected as tracers of autoxidative processes (Fig. 2) and autoxidation percentage was estimated with the following equation: autoxidation % = (stera-3β,5α,6β-triol % × 2.4) on the basis of the results of different incubation experiments (Rontani et al., 2012a) 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^6-5α-hydroperoxides with low amounts of Δ^4-6$\alpha/6\beta$-hydroperoxides (Smith, 1981). Δ^4-6$\alpha/6\beta$-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 $NaBH_4$ reduction to the corresponding diols and photooxidation percentage was obtained from the equation: photooxidation % = (Δ^4-stera-3β,6α/β-diols % × (1 + 0.3)/0.3) (Christodoulou et al., 2009) based on the ratio Δ^4-6$\alpha/6\beta$-hydroperoxides / Δ^6-5α-hydroperoxides measured in biological membranes (0.30) (Korytowski et al., 1992).

Although complete mineralisation 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, 5α(H)-stanones and 5α(H)-stanols (de Leeuw and Baas, 1986; Wakeham, 1989). 5α(H)-stanols, which are also produced by $NaBH_4$-reduction of the corresponding stanone during the treatment, were selected as specific tracers of Δ^5-sterol biodegradation (Fig. 2).

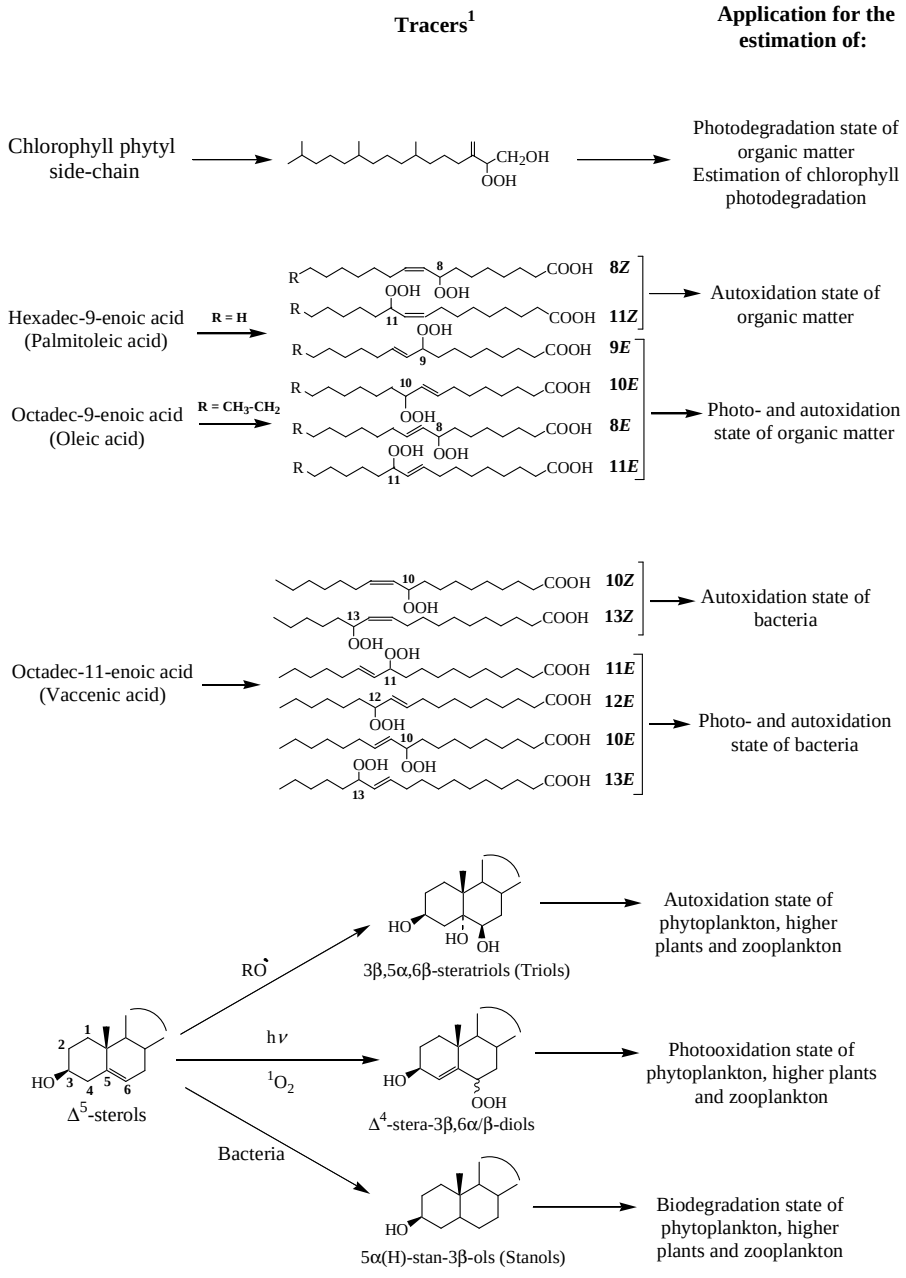

Fig. 2. Formulae and potential applications of the different lipid tracers of degradation processes employed in the present work. [1]Quantified after $NaBH_4$-reduction to the corresponding alcohols and subsequent silylation.

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 ($^1O_2$)-mediated photooxidation of monounsaturated fatty acids involves a direct reaction of $^1O_2$ 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 ($-1\,^{\circ}C$). 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).

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), thus their oxidation products may 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-sterols

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-3β-ol (24-methylenecholesterol) and 24-ethylcholest-5,22E-dien-3β-ol (stigmasterol) could be also detected (Table 1). Similar sterols were previously identified by Belicka et al. (2004) in the top layer (0–2 cm) of sediments from the Beaufort Sea. The lowest abundance of cholesterol observed by these authors in sediments collected near to the stations 235, 260 and 345 may be attributed to a progressive degradation of zooplanktonic faecal material, which contributes significantly to the sinking particles of this zone and contains a high proportion of cholesterol (Rontani et al., 2012b), deeper in the sediment in the second cm of sediments. This assumption is supported by the penetration depth of oxygen, which may reach 2–4 cm in this zone (Magen, 2007) and which may contribute to oxic degradation of the settled organic matter well deeper than the sediment-water interface.

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. It is interesting to note that Yunker et al. (2005) previously also reported a faster removal rate relative to organic carbon of campesterol and sitosterol than of brassicasterol in sediment cores from the Beaufort and Chukchi seas and Canuel and Martens (1996) observed a faster degradation rate for sitosterol than brassicasterol in nearshore sediments from North Carolina. Brassicasterol (mainly arising from marine and freshwater phytoplankton, Volkman, 1986, 2003; Fahl et al., 2003) 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 campesterol and 70 % for sitosterol. This lowest contribution of terrigenous material to campesterol was also outlined by Yunker et al. (1995, 2005). 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) and present in summer in this zone (Hill et al., 2005), 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., 2012a). 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). Lateral transport of sediments that already have known degradation and diagenetic processes could be another explanation. Indeed, in this case sediment would consist in part of particles that have settled closer to land and have thus spent less time in water column where degradation is more efficient.

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

Table 1. Sterols content (μg g^{-1}) of the sediments investigated.

Sterols	110	140	235	260	345	390	680	689
Cholesterol	9.3	3.9	1.5	31.6	1.8	2.0	1.5	4.6
Brassicasterol	3.0	2.2	0.3	17.4	0.3	1.0	0.5	1.6
24-Methylenecholesterol	1.5	0.8	0.1	8.2	0.1	0.4	0.3	0.6
Campesterol	1.1	0.6	0.1	5.8	0.1	0.5	0.4	1.1
Stigmastérol	1.3	0.3	0.1	3.3	0.1	0.3	0.2	0.4
Sitosterol	6.2	1.4	0.4	13.9	0.5	0.8	1.1	1.9

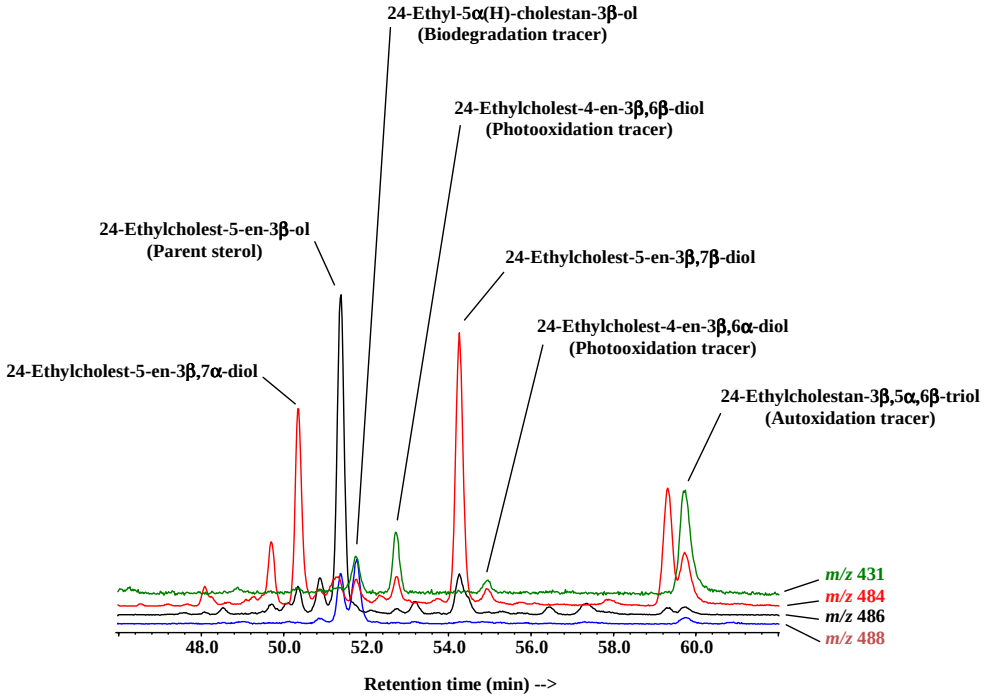

Fig. 3. Partial m/z 486, 488, 484 and 431 ion chromatograms showing presence of sitosterol degradation products in the total lipid extract of surface sediments (0–1 cm) collected at the station 680.

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., 2012a). 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

Linear fatty acids ranging from C_{14} to C_{18} have been detected in the different samples investigated (Table 2). The lack of long-chain (C_{20}-C_{28}) fatty acids, which are characteristic of epicuticular waxes of terrestrial higher plants (Kolattukudy, 1976; Gagosian et al., 1987), was attributed to bacterial degradation processes, which act intensively on terrestrial material in the mixing zone of the Mackenzie (Rontani et al., 2012). Degradation products of the main monounsaturated fatty acids present in these sediments, i.e. palmitoleic, oleic and vaccenic acids, were quantified. 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 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

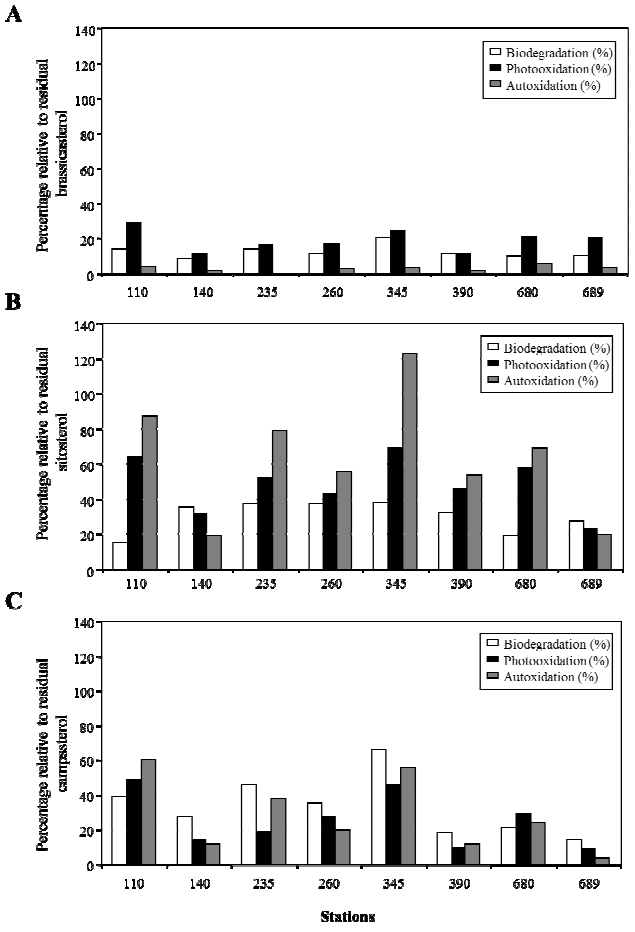

Fig. 4. Estimates of relative biodegradation, autoxidation and photooxidation (as percentages relative to the residual parent compound) of brassicasterol **(A)**, sitosterol **(B)** and campesterol **(C)** for the different sediments investigated.

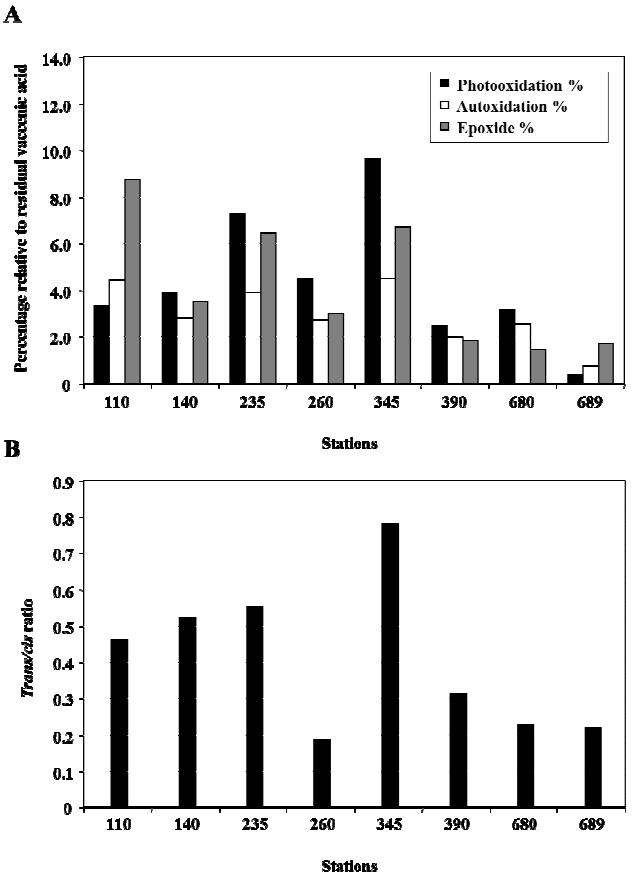

Fig. 5. Estimates of relative autoxidation, photooxidation and epoxide production (as percentages relative to the residual parent compound) **(A)** and *trans* / *cis* ratio measured **(B)** of vaccenic acid for the different sediments investigated.

cells of *Emiliania 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 thus 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 peroxyl 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). Epoxy acids 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 peroxyl 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 abstraction) only in the case of conjugated, terminal, or trisubstituted

Table 2. Fatty acid content ($\mu g\, g^{-1}$) of the sediments investigated.

Fatty acids	110	140	235	260	345	390	680	689
$C_{14:0}$ (Myristic acid)	46.4	254.3	65.9	102.0	72.3	253.9	259.2	151.9
$C_{15:0}$ (Pentadecanoic acid)	18.1	32.1	28.0	79.1	24.7	36.4	38.0	25.2
$C_{16:1\Delta9}$ (*Cis* palmitoleic acid)	30.7	2010.7	70.5	28.3	63.3	1237.3	1220.8	796.5
$C_{16:1\Delta9}$ (*Trans* palmitoleic acid)	3.0	48.3	4.2	0.2	3.2	22.3	111.1	4.8
$C_{16:0}$ (Palmitic acid)	171.7	613.0	321.4	982.8	309.3	631.9	713.7	447.5
$C_{18:1\Delta9cis}$ (Oleic acid)	45.0	230.3	135.9	338.2	153.7	208.0	157.5	133.6
$C_{18:1\Delta9trans}$ (Elaidic acid)	22.4	70.9	28.3	10.1	67.2	32.7	27.9	13.3
$C_{18:1\Delta11cis}$ (*Cis* vaccenic acid)	87.2	231.4	68.8	12.2	107.8	269.4	213.1	278.1
$C_{18:1\Delta11trans}$ (*Trans* vaccenic acid)	40.4	120.8	37.8	2.3	84.1	84.1	48.4	60.6
$C_{18:0}$ (Stearic acid)	50.1	149.7	82.7	310.4	107.4	103.0	80.6	65.7

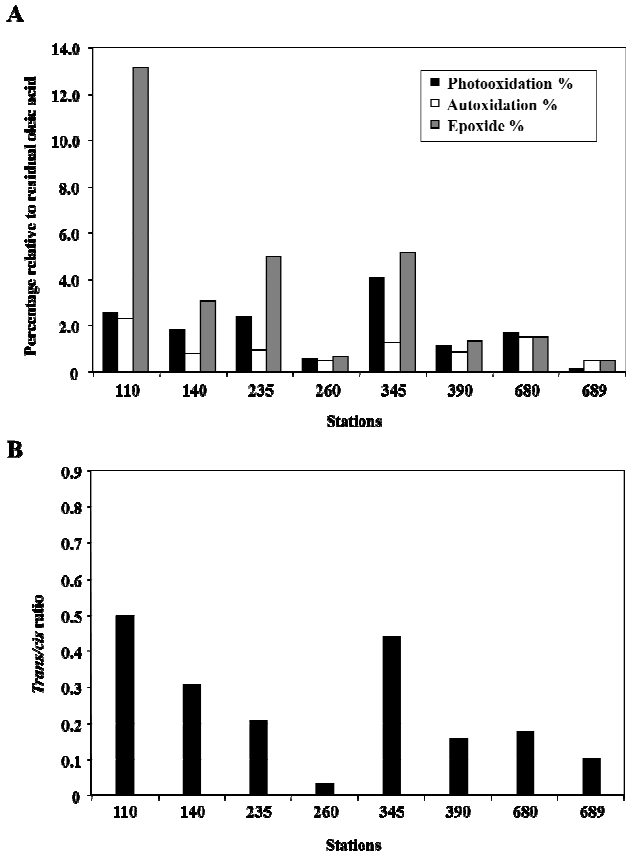

Fig. 6. Estimates of relative autoxidation, photooxidation and epoxide production (as percentages relative to the residual parent compound) **(A)** and *trans* / *cis* ratio measured **(B)** of oleic acid for the different sediments investigated.

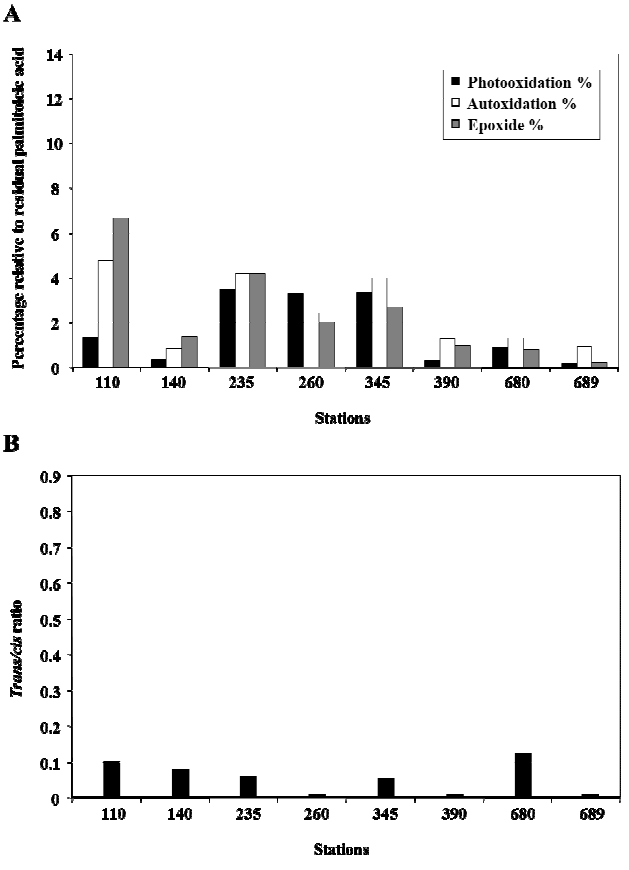

Fig. 7. Estimates of relative autoxidation, photooxidation and epoxide production (as percentages relative to the residual parent compound) **(A)** and *trans* / *cis* ratio measured **(B)** of palmitoleic acid for the different sediments investigated.

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 catalyse 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 epoxy acids detected to the involvement of peroxygenases (hydroperoxide-dependent oxygenases) during abiotic degradation of higher plant debris, algae or bacteria. Such enzymes catalysed epoxidation of unsaturated fatty acids in the

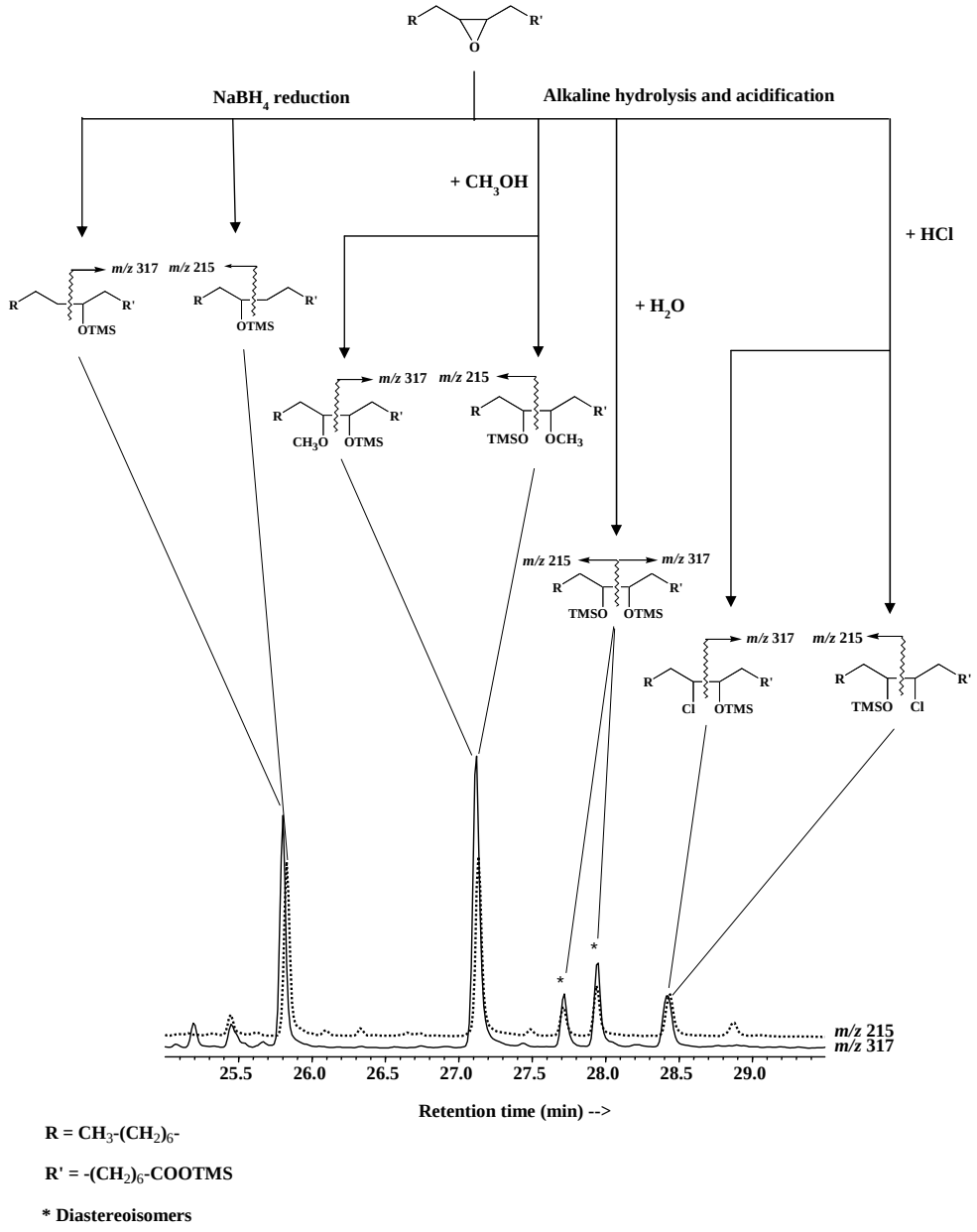

Fig. 8. Compounds resulting from the degradation of 9,10-epoxyoctadecanoic acid during the treatment.

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 epoxy acids 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).

While the *trans / cis* ratio of monounsaturated fatty acids is usually 0.05 or less in healthy non stressed bacterial populations (Navarrete et al., 2000), unusually high proportions of monounsaturated fatty acids with a *trans* double bond could be detected in the sediments analysed. 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* isomerisation 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;

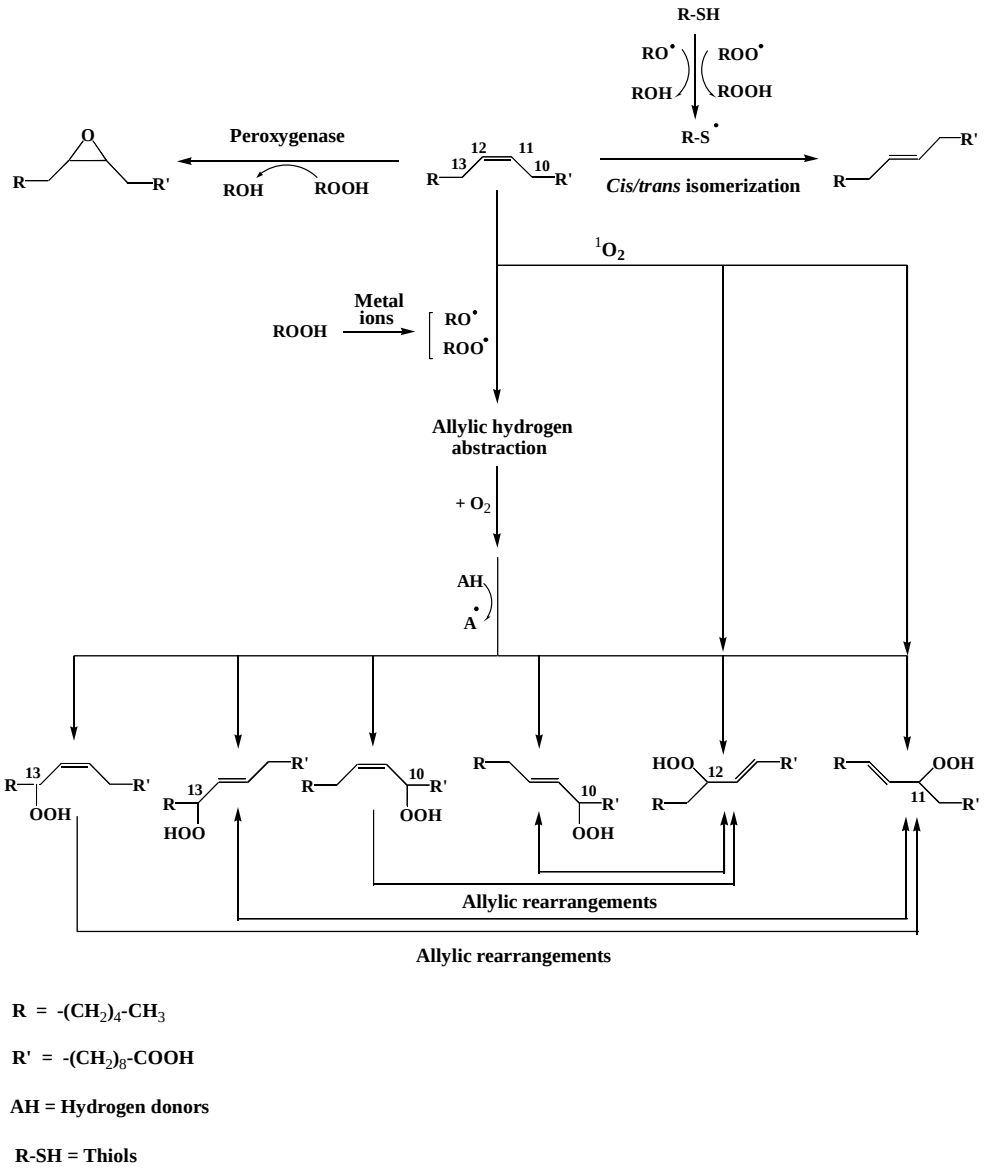

Fig. 9. Proposed mechanisms for biotic and abiotic degradation of vaccenic acid in the Beaufort Shelf.

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 isomerisation, Ferreri et al., 2004) during the antioxidant reactions of biologically relevant thiols (e.g. glutathione) (Chatgilialoglu et al., 2002) or after 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* isomerisation 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* isomerisation 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* isomerisation 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

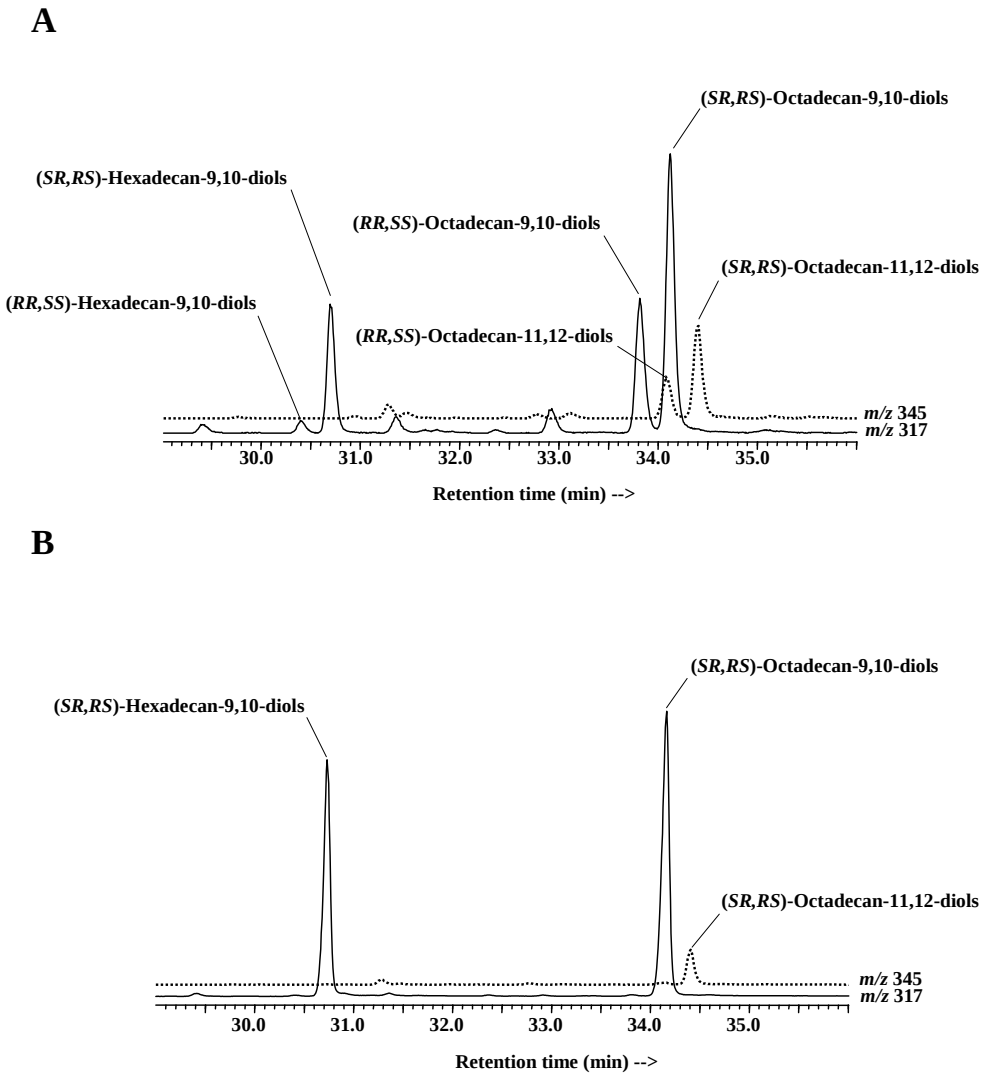

Fig. 10. Partial m/z 317 and 345 ion chromatograms showing the distribution of silylated OsO_4 derivatives of *cis* and *trans* monounsaturated fatty acids in surface sediments (0–1 cm) collected at the stations 110 **(A)** and 260 **(B)**.

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 isomerisation process was proposed as a 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 analysed (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 in sinking particles (Rontani et al., 2012b) reaching these sediments. However, it was previously demonstrated that this enzymatic isomerisation process has a highest specificity for C_{16} unsaturated fatty acids as substrates (Heipieper et al., 1992) and the *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* isomerisation is only an urgent response mechanism in these bacteria that is later substituted by other adaptive mechanisms (Fischer et al., 2010). Therefore, the *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* isomerisation activity.

Functionalised 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 alkoxyl or alkylperoxyl radicals, are extraordinarily efficient antioxidants protecting the cells against consequences of damage induced by free radicals (Wlodek, 2002) (Eqs. 1–3).

$$\text{R-S-H} + \text{R-O}^{\bullet} \rightarrow \text{R-S}^{\bullet} + \text{R-O-H} \quad (1)$$

$$\text{R-S-H} + \text{R-O-O}^{\bullet} \rightarrow \text{R-S}^{\bullet} + \text{R-O-O-H} \quad (2)$$

$$2\,\text{R-S-H} + \text{R-O-O-H} \rightarrow 2\,\text{R-S}^{\bullet} + \text{R-O-H} + \text{H}_2\text{O} \quad (3)$$

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* isomerisation 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.

$$\text{CH}_3\text{-S-CH}_2\text{-CH}_2\text{-CH(NH}_2\text{)-COOH} \rightarrow \text{CH}_3\text{SH} + \text{CH}_3\text{-CH}_2\text{-CO-COOH} + \text{NH}_3 \quad (4)$$

$$\text{(S,S)-adenosylmethionine} + \text{SH}^- \rightarrow \text{(S)-adenosylhomocysteine} + \text{CH}_3\text{SH} \quad (5)$$

$$(\text{CH}_3)_2\text{-S}^+\text{-CH}_2\text{-CH}_2\text{-COO}^- \rightarrow \text{CH}_3\text{-S-CH}_2\text{-CH}_2\text{-COO}^- \rightarrow \text{CH}_3\text{SH} + \text{CH}_2 = \text{CH-COO}^- \quad (6)$$

$$(\text{CH}_3)_2\text{-S}^+\text{-CH}_2\text{-CH}_2\text{-COO}^- \rightarrow \text{CH}_2 = \text{CH-COO}^- + \text{CH}_3\text{-S-CH}_3 \rightarrow \text{CH}_3\text{SH} \quad (7)$$

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

$$\text{HS}^- + \text{Fe}^{+3} \rightarrow \text{HS}^{\bullet} + \text{Fe}^{+2} \quad (8)$$

The fact that thiyl radicals act as a catalyst for *cis-trans* isomerisation 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 0.6–1 kcal mol^{-1}, a mixture dominated by *trans* olefin (about 80 %) may be theoretically obtained (Ferreri et al., 2005). Due to the presence of significant amounts of intact hydroperoxides in sinking particles reaching these sediments (Rontani et al., 2012b), an induction of *cis-trans* isomerisation 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 the *trans*/*cis* ratio and the proportions of vaccenic and oleic acid oxidation products (quantified after $NaBH_4$-reduction 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.

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* isomerisation 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 high *trans*/*cis* ratio observed in sediments. Recent analyses of particles collected by traps in this zone allowed us to show that the formation of *trans* monounsaturated fatty acids does not act in sinking particles (Rontani et al., 2012b) and thus to exclude such a possibility.

While algal OM appeared to be weakly degraded in all the sediments investigated (Fig. 4a), a strong spatial variability of the autoxidative degradation state of terrestrial OM was observed (Fig. 4b and c). This variability could be related to the position of the stations relative to the Mackenzie mouth. Indeed, a strong autoxidation of terrestrial OM in SPM was previously observed in the mixing zone of the Mackenzie (Rontani et al., 2012a). The extent of autoxidation appeared to be well correlated with salinity, suggesting that these free radical oxidation processes are enhanced by contact with seawater. Consequently, the stations more distant from the Mackenzie, where the residence time of terrestrial OM in seawater is expected to have been longest, should exhibit the highest autoxidation states. The results obtained well support this assumption. Indeed, the highest autoxidation states were observed at the stations 110, 235 and 345 (Fig. 4b and c), which are very distant from the Mackenzie, while the station 689 close to the mouth (Fig. 1) exhibited the weakest degradation state (Fig. 4b and c). It is interesting to note that Link et al. (2012), which used chlorophyll-a/phaeopigment ratio as a proxy of the quality or "freshness"

of the organic matter supply, also observed the highest degradation states at the stations 110, 235 and 345.

The biogeochemical fluxes measured at the same stations by Link et al. (2012) showed the highest oxygen demands for the inner shelf sediments (stations 689, 680, 390, and 260). These oxygen demands, which were associated with high production rates of metabolites (e.g. NO_2^-, PO_4^{3-}, NH_4^+), are indicative of an intense biodegradation activity in these sediments. These results are in good agreement with the weak degradation state and the *cis / trans* ratio of vaccenic acid measured at these stations (Fig. 5) attesting to the presence of non-stressed bacteria in a good healthy state and thus very active.

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 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 photodegraded in particulate matter delivered by the Mackenzie River (Rontani et al., 2012a). The old concept expecting that the pre-degradation of terrestrial OM on land and in the rivers should result in a good preservation of this material in the marine environment seems thus to be erroneous.

In the 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 epoxy acids could be detected. The formation of these compounds was attributed to the involvement of peroxygenases (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 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* isomerisation 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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