Scientific Paper

Degradation and Preservation of Organic Matter in Marine Macroaggregates

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Abstract

Solid-state ^{13}C NMR and FTIR spectroscopy were applied to establish the chemical features of bulk mucous macroaggregates of phytoplanktonic origin at two different depths, surface and bottom, in the Gulf of Trieste (northern Adriatic Sea) in June 2000. The bottom sample was poor in organic matter (5% C_{org}, 0.5% N_{tot}) compared to the surface sample (17.2% C_{org}, 1.2% N_{tot}) and contained mostly senescent and degraded cells. An increase in mineral particles (quartz and calcite) was also evident. This was due to the degradation of the organic fraction and the contribution of bottom sediment resuspension. The ^{13}C-NMR–based estimate showed the approximate composition of sampled macroaggregates: 26% aliphatic C, 14% O/N alkyl structures, 39% carbohydrates, 15% aromatic and olefinic C and 6% ester and/or amide C. The solid-state ^{13}C NMR spectrum of the sedimented macroaggregate revealed the preservation of aliphatic (lipidic) material and a portion of the labile nitrogen-containing compounds.

Key words: macroaggregates, FTIR, solid-state ^{13}C NMR, northern Adriatic

Introduction

Periodically observed macroaggregates in the northern Adriatic sea are primarily the product of the agglomeration of macromolecules originating from phytoplankton (mostly diatom) exudates into macrogels.[1,2] This process is important in understanding the cycling of organic matter in the sea (an important natural reservoir of organic carbon on the Earth)[3] as well in other natural waters. The macroaggregates in the northern Adriatic offer a rare opportunity to study the agglomeration of marine macromolecular dissolved organic matter into macrogels and particulate organic matter. The mucous macroaggregates accumulate at boundaries, such as the sediment-water, air-sea interfaces and the pycnocline, due to the tendency of dissolved organic matter to concentrate in these layers.[4]

Different spectroscopic techniques were used to study the composition of dissolved or particulate organic matter. Among them, NMR and FTIR spectroscopy emerged as the most useful techniques.[5-10] In many cases only the combination of different techniques enables adequate composition determination, especially in the cases of complex structures and/or low solubility.

Previous chemical analyses of mucous macroaggregates revealed a very complex chemical composition. The aggregates are composed of four major classes of structural elements: heteropolysaccharides, ester and amide functional groups, aliphatic and organosilicon components.[2,11,12] The macroaggregates are predominately composed of a saccharidic matrix with accumulated lipidic refractory substances.[13,14] This composition is supported by a higher C/N ratio which is due to a lower protein content,[15,16] mostly from plankton cells.[17] The macroaggregate gel is stabilized by organo-mineral interactions with calcite, quartz and clay minerals.[2,12] The study of temporal changes in macroaggregate composition revealed a relative increase of organosilicon and aliphatic components bonded to carbohydrates through the ester and amide groups, and a decrease in the carbohydrate component.[2] The temporal decrease in carbohydrate content is due to microbial and photochemical degradation, which cleaves the glycoside bonds.[11]

In the present study, FTIR and the solid-state ^{13}C NMR spectroscopy were applied to establish the chemical features of two different samples of mucous macroaggregates from the Gulf of Trieste, one collected at the sea surface (surface sample) and the other at the sea bottom (bottom sample).

Experimental

Sampling

Mucous macroaggregates were collected during the mucilage event in June 2000 in the southeastern part of the Gulf of Trieste (northern Adriatic Sea, Slovenia). The first sample was collected by hand on June 13 at the sea surface. SCUBA divers collected the second sample at the sea bottom on June 26. Surface aggregates formed huge white- yellowish gelatinous surface layers of spongy consistency while the bottom macroaggregate was in the form of a cloud of grey/brown coloured non sticky material. Samples were freeze-dried and subsequently washed several times with a small volume of Milli-Q water to remove salt. Dried samples were used for C and N elemental, FTIR and solid-state ^{13}C NMR analyses. For biological analyses, formalin-fixed samples of gelatinous material were used (volume approx. 100 ml, 2% final concentration).

Analyses

The microscopic composition of the mucous was determined by using transmittal and epifluorescent microscopy to check for live autotrophic organisms. A small piece of gel was pinched off the spongy material and placed on a microscope slide. Microscopic observations of three replicates of each sample were made at 200x and 400x magnification. The nature of the examined material, i.e. its stickiness and heterogeneity, allowed us to make only a rough estimation of the abundance of organisms and particles found.

The organic carbon (OC), total nitrogen (N) and total hydrogen (H) contents of the freeze-dried and acid-washed (1M HCl) samples were determined with a Carlo Erba model 1108 elemental analyzer.[18]

FTIR spectra were obtained on a Perkin-Elmer System 2000 using KBr pellets. Solid-state ^{13}C NMR spectra were acquired using a Varian Unity plus 300 MHz spectrometer. The rotor was spun at the magic angle (54.7°). The experimental conditions were: spectrometer frequency 76.19 MHz, number of scans 22884 and 32576, pulse width 9 μs, spectral width 20 kHz and pulse delay 2 s.

Results

Microscopic composition of mucous

Although sampled at different times and depths (surface *vs.* bottom samples), the two types of macroaggregates showed similarities, which revealed the heterogeneous nature of the samples with regard to organisms, particles and unidentified structures, and in phytoplankton composition.

The material constituting the surface macroaggregates was very dense and gelatinous, white-yellow to brown with many gas bubbles (Figure 1), while that of the bottom aggregates was more compact/firm and grey/brown probably due to many sediment particles embedded within. In both samples the predominant phytoplankton group was that of diatoms and among them *Cylindrotheca closterium* was by far the predominant species.

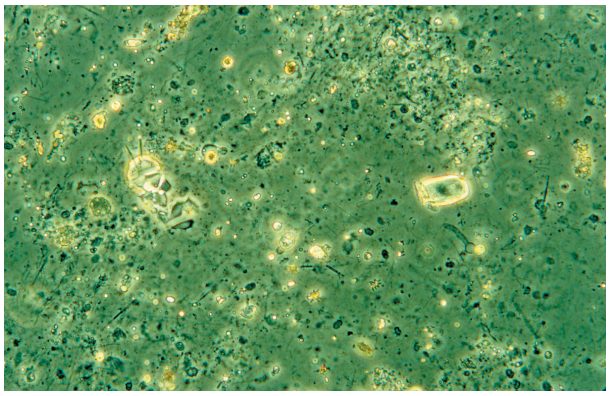

Figure 1. Light microscopy (200x magnification) of the dense and gelatinous material of surface macroaggregate.

In addition to *C. closterium*, pelagic diatoms like *Cyclotella* sp. and *Pseudo-nitzschia pseudodelicatissima* were also abundant in the surface mucous sample, the latter being mostly senescent. Other diatoms, e.g. genus *Rhizosolenia*, were present mainly as empty frustules. A high species diversity of dinoflagellates was observed in the same sample, especially of the genus *Prorocentrum*; however, empty thecae prevailed over live cells. Live specimens were found associated with the species *P. triestinum, P. minimum, P. micans, P. gracile, Heterocapsa* sp., and a naked *Gymnodinium*-like dinoflagellate. Some dinoflagellates went through encystment. In addition to diatoms, small (~10 μm) autotrophic unidentified flagellates were also very abundant and alive. Members of a class of pelagic unicellular phytoplankters with a calcite skeleton, i.e. coccolithophorids, were mainly dead and broken, so quantities of their skeletal elements, coccoliths, were dispersed in the gelatinous organic material. A variety of other organisms and/or parts of organisms (bacteria, zooplankton and related remains such as crustacean cuticles and antennae, faecal pellets), detritus and mineral particles were also found enclosed in the matrix, indicating intense scavenging processes.

As already mentioned, a "community" of organisms and particles and the same predominant live species – *C. closterium,* quite similar to the surface sample, were observed in the bottom macroaggregate, sampled two weeks later. The most evident difference was the presence of many senescent and degraded cells, as well as minerals. Although diatoms were the prevailing

group, besides *C. closterium,* only benthic live species colonized the mucous (genera *Pleurosigma, Gyrosigma, Nitzschia, Navicula, Amphora* etc.) in contrast to pelagic species in the surface sample. Pelagic diatoms were found in the bottom sample only as broken frustules. The composition of dinoflagellates was similar to that of the surface macroaggregates and, again, dead organisms and empty thecae (*P. aporum, P. gracile, Ceratium* spp.) prevailed over live forms (*P. gracile* and *Dinophysis sacculus*). Small, naked phytoflagellates were observed in high quantities as well, whereas neither coccolithophorides nor their skeletal elements were present in the bottom macroaggregate.

Elemental Analyses

Elemental analyses of both samples showed different contents of organic carbon and total nitrogen, 17.2% C_{org} and 1.2% N_{tot} for the surface sample and 5% C_{org} and 0.5% N_{tot} for the bottom sample. During the acid treatment of samples some hydrolysis could proceed. The maximal loss of acid-soluble components up to 17 wt.% of suspended particulate matter was previously estimated.[18]

FTIR

The FTIR spectra of both samples (Figs. 2a and 2b) showed similar bands originating from vibrations of organic (proteins, polysaccharides) and inorganic (carbonates and silicates) components, although differences were evident in their relative intensities.

The broad band between 3700 and 3000 cm^{-1} indicates a wide range of hydrogen bond lengths and orientations[19] mostly corresponding to the OH and NH groups. The presence of CH_2 and CH_3 alkyl groups is indicated from a sharp stretching absorption around 2922 cm^{-1} and a weaker one around 2852 cm^{-1}. Aliphatic C-H deformation vibrations of the methyl and methylene groups could contribute to the bands around 1430 cm^{-1}.[20] The 1636 cm^{-1} absorption was more pronounced in the sample of surface macroaggregates. It can be assigned to OH bending of water, overlapping with the Amide I (predominantly β-sheet structure) primarily consisting of the carbonyl stretching vibration of the peptidic bond. The Amide I band lies close to the H_2O band (OH bending) and is the most characteristic band for proteins in water solutions.[21,22] However, other groups such as COO^-, C=C bands of aromatic ring and/or olefins C=C could contribute to this band as well.[23,24]

The Amide II vibration can be found around 1544 cm^{-1} consisting of a C-N stretching vibration coupled with a C-N-H bending vibration. In the spectrum of the bottom sample, the Amide II peak is probably masked by the strong band at 1430 cm^{-1}. This band could be attributed to the carbonates[25] together with the band at 876 cm^{-1} and low-intensity bands at 1796 and 712 cm^{-1}. Furthermore, the peak at 2524 cm^{-1} (combination band $\nu_s(CO_3^{2-}) + \nu_{as}(CO_3^{2-})$), present in the spectrum of the bottom macroaggregate (Figure 2b), demonstrates the higher carbonate content in this sample.[26]

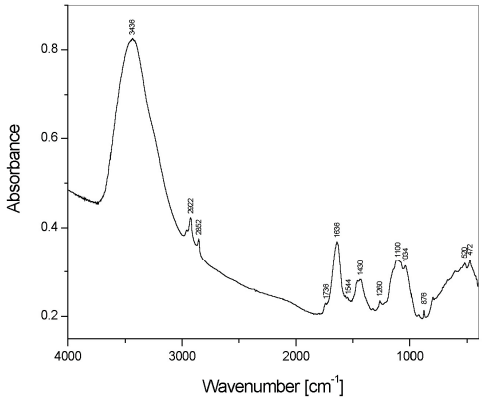

Figure 2a. FT-IR spectrum of macroaggregate collected on June 13, 2000 at the sea surface.

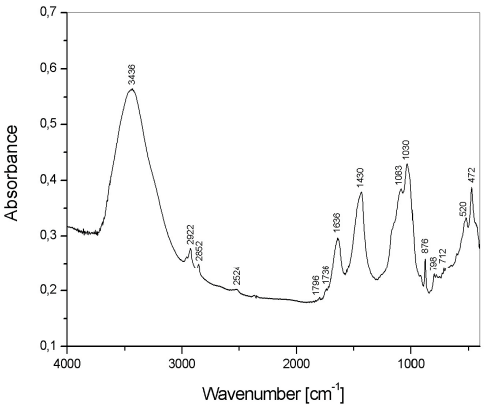

Figure 2b. FT-IR spectrum of macroaggregate collected on June 26, 2000 at the sea bottom.

In addition to carbonates, we also observed the existence of silicates[27,28] with the absorption bands at 1083, 1030, ~800 and 472 cm^{-1}. Normalization to the silicate band at 1030 cm^{-1} clearly showed that modes other than silicates are present in the band at 1083 cm^{-1} (Figure 3). This band can be ascribed to polysaccharides with characteristic bands at 1100 and 1083 cm^{-1}. It is more intense in the spectrum of the surface sample thus confirming its higher content of organic matter. Normalization also confirmed that, with regard to silicates, more carbonates are present in the bottom sample. The band around 920 cm^{-1} is probably due to Si-OH stretching (silanes/silanols),[6] and was more pronounced in the spectrum of the surface sample. The most characteristic bands of silicates[29] and organosilicon compounds[28,30,31] appear in the spectral range 900–1200 cm^{-1} coinciding with the most characteristic absorption bands of polysaccharides (900–1200 cm^{-1}) and other C-O

stretching vibrations. Another weak band was identified in the FTIR spectrum of the surface sample, i.e. at 1260 cm^{-1}, which is probably due to C-O stretching of ethers[32] and/or OH in-plane bending. Weak signals between 1720-1740 cm^{-1} indicate the presence of C=O carboxylic and/or carbonylic groups.

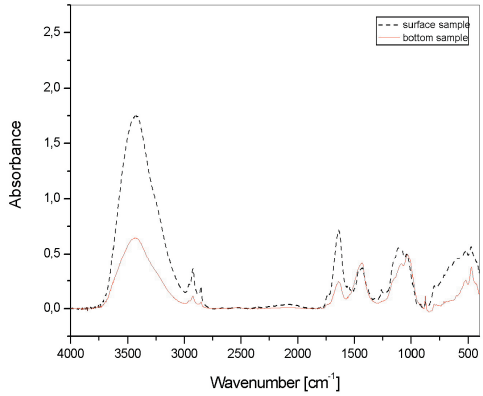

Figure 3. Normalization to the silicate band at 1030 cm^{-1} showed that modes other than silicates are present in the band at 1083 cm^{-1}. This band can be ascribed to polysaccharides with characteristic bands around 1100 and 1084 cm^{-1}.

NMR

^{13}C NMR spectra of analyzed macroaggregates (Figs. 4a and 4b) showed major spectral bands including alkyl C (δ = 0-45 ppm), O/N-alkyl C (δ = 45-110 ppm), olefinic/aromatic C (δ = 110-160 ppm) and carboxyl/carbonyl/amide C (δ = 160-220 ppm) resonances.[7,33] The broad signal between δ = 15-50 ppm indicates the heterogeneity of alkyl carbon.[23] The peak at δ = 30 ppm corresponds to $(CH_2)n$ chains and the signal at δ = 22-23 ppm is due to tertiary or quaternary carbons while the peaks around δ = 15 ppm indicate the contribution of CH_3 groups.[20] The other main peaks were assigned to carbons α to C-O or C-N functions (δ = 57 ppm), while the signals around δ = 72 ppm and δ = 103-105 ppm (glycosidic C-O) represent mostly polysaccharides. The olefinic and/or aromatic C (δ = 120-130 ppm), and ester and/or amide C (δ = 173 ppm) signals are also present.

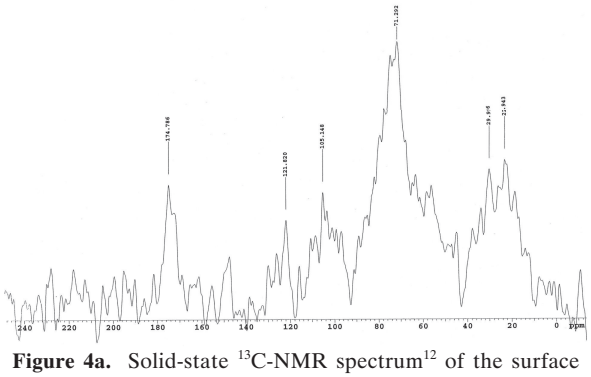

Figure 4a. Solid-state ^{13}C-NMR spectrum[12] of the surface macroaggregate sample collected in the Gulf of Trieste on June 13, 2000.

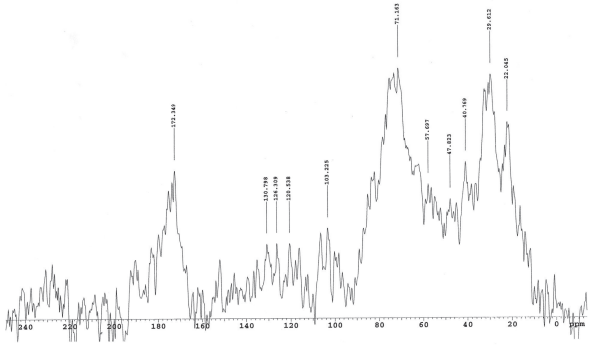

Figure 4b. Solid-state ^{13}C-NMR spectrum of the sedimented macroaggregate sample collected in the Gulf of Trieste on June 26, 2000.

Discussion

FTIR and ^{13}C NMR spectroscopic analyses supported the general composition of the organic matrix of mucous macroaggregates consisting of four major structural elements: polysaccharides, aliphatic component, functional groups such as the ester and amide groups, and organosilicon compounds, as has been previously established.[2,12] Accordingly to our previous results,[2] the FTIR spectra showed the presence of an inorganic component. However, the spectra of both samples revealed some differences in the vibrational modes of organic components indicating ongoing transformation processes within the macroaggregates.

Both FTIR spectra showed the same general pattern and the main absorptions, but the relative intensities of bands characteristic for minerals such as quartz and calcite were higher in the bottom sample spectrum. This higher relative abundance of a mineral component in the sedimented macroaggregates is due to degradation processes and the contribution of sediment resuspension. Compared to the surface sample, the bottom macroaggregates were poor in organic material. The elemental analyses of surface macroaggregates showed a higher content of organic matter with a relatively high C_{org}/N atomic ratio of 16.7 indicating fresher and less degraded organic material. The same was observed from the microscopic composition indicating that the surface sample consisted mostly of live phytoplankton cells. The presence of very abundant and live diatoms (fresh) was also indicated by the FT-IR spectrum of the surface sample including a more pronounced band due to Si-OH stretching (silanes/silanols). This is in accordance with the statement that fresh diatoms have relatively high amounts of Si-OH groups.[34,35] In contrast, the bottom sample contained a much greater quantity of organisms and particles, including sediment grains, embedded in the compact bottom-mucous sample. Many of zooplankton remains

(mainly crustacean), pollen grains, dinoflagellate cysts and unidentified, highly decomposing particles were also found.

Using the relative intensities of the main ^{13}C-NMR regions[36,37] in the surface sample, aliphatic C comprises approximately 26%, O/N alkyl structures 14%, carbohydrates 39%, aromatic and olefinic C 15% and ester and/or amide C 6%. Despite the direct comparison of these data with "classic" chemical analyses is not possible (heterogenous samples, different methods, standards and specific compunds) our previous results on macroaggregate composition[17] using colorimetric method (phenol-sulphuric acid method) showed similar total carbohydrate content. Some differences in the relative intensities in the spectrum of the bottom macroaggregate sample were observed. A decrease of peak intensities in the glycosidic C region indicates the high degradation of polysaccharides[2,12] in the bottom sample. A lower content of carbohydrates was also evident from the FT-IR spectrum of the bottom sample (Figure 2b). The most characteristic absorption of polysaccharides at 1110 cm^{-1} was more evident in the FT-IR spectrum of the surface sample (Figure 2a). The ^{13}C NMR spectrum of the bottom sample of macroaggregates also revealed an increase of signals in the region from 45 to 60 ppm, which could be assigned to alkyl C atoms bound to different heteroatoms. These signals could be attributed to different branched alkyl C atoms (secondary, tertiary C atoms). Taking into account the lower C/N ratio of the bottom sample, the contribution of N-alkyl C atoms seems to be more relevant. A marked increase in C/N ratio is usually consistent with the hydrolysis of amide bonds.[24] The observed increase of signals in the O/N-substituted alkyl-C region indicates the preservation of a portion of the labile nitrogen-containing materials during the mucilage event. Additionally, a more pronounced resonance around 173 ppm (about 13%) suggests a higher degree of oxidative degradation or/and a greater contribution of amide-C.

These features might result from the degradation of proteinaceous matter and the subsequent reaction of bioorganic residues to complex and extensive crosslinked matured structures. The macroaggregate biopolymers are subjected to various chemical transformations including degradation-recondensation and condensation-polymerization with other low molecular weight compounds, as well as photochemical transformations.[11] During degradation, proteins and polypeptides may undergo chemical transformations, including Shiffs-base condensation with sugars, to become insoluble and resistant to enzymatic attack.[38] It was also suggested that proteinaceous material could be stabilized and preserved through encapsulation inside the macromolecular matrix.[39-41] On the other hand, minerals can play an important role in organic matter preservation through sorptive protection on minerals[42-44] and they may also promote condensation reactions.[45] The preservation of organic matter has been also found in sinking marine particles where minimal changes occurred in the bulk organic composition, despite extensive degradation, because the organic matter was protected from degradation by inorganic components.[5] In this context, the silica matrix was suggested to be important for the preservation of amino acids through a refractory protein-silica complex of diatom cells.[46]

In the diatom cell wall, silica is surrounded by an organic layer (silicalemma), which plays a protective role in preventing dissolution of silica into the aqueous environment.[47] Moreover, it resists dissolution even under treatments that completely dissolve the silica. Insight into the nature of this organic matrix has been recently gained through the work of Kröger et al.[48-50] and Poulsen et al.[51] identifying silaffins (biosilica-associated peptides) and long-chain polyamines, both of which accelerate silica formation from a silicic acid solution *in vitro*, as constituents of biosilica. The silicalemma proteins are most probably highly cross-linked and unisolatable as individual entities.[52] According to the importance of diatoms in mucilage events, the contribution of the previously mentioned proteins (through the maturation processes) to preserved N-organic component of macroaggregates could be proposed. In addition, the cell walls of other marine phytoplankton (also present in macroaggregates samples such as dinoflagellate, cyanobacterium…)[53] and bacteria could also be the source of resistant (refractory) proteinaceous or/and lipidic material.

Previous study of long-term (3 months) transformation of organic components in mucous macroaggregates showed that "maturation/ageing" processes proceeded through a relative increase of aliphatic structures - i.e., lipids, and a decrease in carbohydrates,[2] which was probably due to the microbial and photochemical degradation[2,11] of algal reserve polysaccharides. The study of the chemical composition, presented in this work, showed similar transformations of the bottom sample, i.e., an increase of aliphatic structures and the degradation of glycoside linkages. The increased hydrophobic character of organic material during diagenesis progression has already been suggested (indicated) for detritus and kerogen.[39]

Conclusions

Bulk macrooaggregates collected in the Gulf of Trieste revealed that the bottom sample was poor in organic matter, i.e. organic carbon and nitrogen, compared to the surface sample, due to degradation processes and sedimentation. Microscopic analyses

of surface samples showed a predominance of live phytoplankton cells in contrast to the bottom sample which contained mostly senescent and degraded cells and mineral particles. The higher relative abundance of the mineral component of quartz and calcite in the bottom macroaggregates, decoded by relative intensities in FTIR spectra, was due to degradation of the organic fraction and the contribution of bottom sediment resuspension. The relative increase of aliphatic structures in the bottom macroaggregates, decoded by ^{13}C NMR, is most probably due to the microbial and photochemical transformation of olefins. FTIR and solid-state ^{13}C NMR spectra of bottom macroaggreagtes revealed that a portion of the labile nitrogen-containing compounds in macroaggregates is preserved during macroaggregate degradation and sedimentation. Our results confirm that FTIR and solid-state ^{13}C NMR are powerful and complementary methods for chemical composition studies of complex organic matter in natural waters. Undoubtedly, the study of the origin and preservation of organic matter in the marine environment is a very complex problem. However, this work contributes an insight into the cycling of organic matter in the sea.

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Povzetek

Kemijske lastnosti sluzastih makroagregatov fitoplanktonskega izvora, vzorčenih v juniju 2000 na površini in pri morskem dnu v Tržaškem zalivu (severni Jadran), smo določali s pomočjo ^{13}C NMR trdnih vzorcev in FTIR spektroskopije. Glede na površinski vzorec je pridneni vzorec vseboval manj organske snovi, več pa odmrlih celic ter celic v fazi razgradnje. V pridnenem vzorcu smo zasledili tudi večjo vsebnost mineralnih delcev (kremen in kalcit), kar je predvsem posledica razgradnje organske frakcije in prispevka resuspenzije sedimenta. ^{13}C NMR spekter trdnega sedimentiranega pridnenega vzorca kaže tudi na ohranjanje alifatske komponente (lipidi) in dela labilne, dušik vsebujoče snovi.