7.4 Stable carbon isotope ($\delta^{13}C_{org}$) ratio and lignin-derived phenol distribution in surface sediments of the inner Kara Sea

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Abstract

The sources of organic carbon were studied in the inner part of the Kara Sea by a combined isotopic ($\delta^{13}C_{org}$) and molecular (n-alkanes, lignin) approach. A wide range of $\delta^{13}C_{org}$-values from –22,4‰ to –27,6‰ was determined over the study area. The organic carbon isotope composition allows to distinguish two groups of sediments: Station group I sediments are dominated by organic carbon of a planktonic origin enriched in ^{13}C ($\delta^{13}C_{org}$: –22,4 to - 23,9‰, $\varnothing$ –23,0‰). Sediments f this type are clustered in the western part of the Kara Sea area, which is influenced by the Barents Sea water.

Station group II comprises sediments are characterized by ^{13}C depleted organic carbon (from –24,3‰ to –27,6‰, $\varnothing$ –26‰). These sediments are located in the eastern part of the study area, including the Ob and Yenisei estuaries. Enhanced lignin-derived phenol concentrations are typical for these sediments. A special sub-group of station group II sediments was further distinguished in the area under indirect river influence, situated northwards of the estuaries. Isotopically depleted organic matter and the predominance of short chain n-alkanes in these sediments is typical for plankton-derived organic matter (OM). Rock-Eval pyrolysis data (HI>300mgHC/gTOC) as well as the distribution pattern of lignin phenols further supports the planktonic origin of the OM in sediments f this group. Organic carbon isotope depletion results from the great Siberian rivers run-off, meaning that marine phytoplankton assimilates the isotopically depleted inorganic carbon driven with the river water. The subdivision of sediments with respect to the predominating organic matter source was further supported by the distribution pattern of n-alkanes and lignin-derived phenols.

Introduction

This paper reports on the sources and distribution pattern of sedimentary organic carbon in the inner part of the Kara Sea. The area of investigation extends from the archipelago Novaya Zemlya in the west to a longitude of 80°30'E. Surface sediment samples were collected during the 22 cruise R/V "Akademik Boris Petrov" in September-October 1995. The study area was covered by a set of about 80 sedimentary stations (Galimov et al. 1996). For this work, 18 stations were selected (Fig. 7.3) and the nature of sedimentary organic matter was investigated by its isotopic ($\delta^{13}C_{org}$) and molecular (n-alkanes, lignin) composition.

Stable carbon isotope ratios of C_{org} are widely applied as indicator of the nature of sedimentary organic matter. This method is based upon the general observation that terrestrial OM is enriched in ^{12}C compared to marine OM. The difference between

these two genetic types of organic matter averages about 5-7‰. In some cases, an excellent correlation between lignin-derived phenol concentrations and light $\delta^{13}C_{org}$-values was reported for recent marine sediments (Hedges & Mann 1979).

Lignin is a major biopolymer of higher plants, and lignin phenols are highly specific of vascular plant tissues (Manskaya & Kodina 1975). Aldehydes, acids and ketones of vanillyl (V) -, syringyl (S) - and p-hydroxybenzyl (P)- types are the major nitrobenzene oxidation products of lignin (Sarkanen & Ludwig 1971; Hedges & Mann 1979). In aquatic environments, lignin phenols are unique tracers for terrestrial organic matter (Opsahl et al. 1999; Huang et al. 1999).

n-Alkane concentrations and their carbon atom number distribution are considered to be a geochemical indicator to distinguish between autochthonous, aquatic bioproduction and terrigenous OM. The predominance of long cahin ($C_{25} - C_{33}$), odd-numbered n-alkanes and high CPI values are characteristic of aliphatic hydrocarbons derived from terrestrial plants, whereas short chain alkanes (C15-C19) are indicative for enhanced bioproductivity in the Arctic basin (Schubert & Stein 1997; Fahl & Stein 1999; Fernandes & Sicre 2000).

Methods

The air-dried crushed sediment samples were oxidized with alkaline (8% NaOH) nitrobenzene at 175°C in small stainless steel autoclaves for 2.5 h, followed by centrifugation. Nitrobenzene reduction products were removed from the alkaline supernatant with dimethyl chloride. Lignin derivatives were extracted from the acidified solution with methylene chloride, silylated with trimethylsilyldiethylamine in pyridine (1:1v/v) at room temperature and analysed by high resolution gas chromatographic procedure (Peresypkin 1990). Lignin-derived phenols are quantified on a Yanako G180-T.F.R. (Japan) instrument equipped with a FID and a silicone coated quartz capillar column (OVS-1, 30 m x 0,32 mm I.D.). Chromatographic conditions for the separation of phenols was as follows: 8 min at 80 °C, heating rate 4°/min to 280°C, detector and injector temperature 300°C, He flow rate 1,5-2,0 ml/min. Data acquisition, peak detection and peak area processing was done by the integrator Chromatopak C-R3A (Shimadzu, Japan). Calibrated standard mixtures of phenols were used for lignin phenol quantification. The lowest detection limit for individual phenols is 0,01 µg, the reproducibility is within 5%.

n-Alkanes were ultrasonically extracted from air-dried samples with methylene chloride and quantified with the GC-procedure described above, using squalane as an internal standard. C_{org} concentrations in sediments were determined by dry combustion of the samples in an oxygen flow, and coulombometric CO_2 titration by the express device AN 7529 (Russia). Reproducibility of data for a C_{org} concentration range from 0,01 to 4% is within 0,005% C. Stable carbon isotope ratios were determined on a Varian Mat-230 instrument (Finnigan) relative to a working standard related with the International standard PDB. Sample preparation for isotope analysis consisted of sediment pretreatment with acid followed by combustion in the high-vacuum glas system in an oxygen flow. The resulting CO_2 was cleaned and collected on a system of cold traps. The reproducibility for $\delta^{13}C$-values is within 0,2‰ vs. PDB.

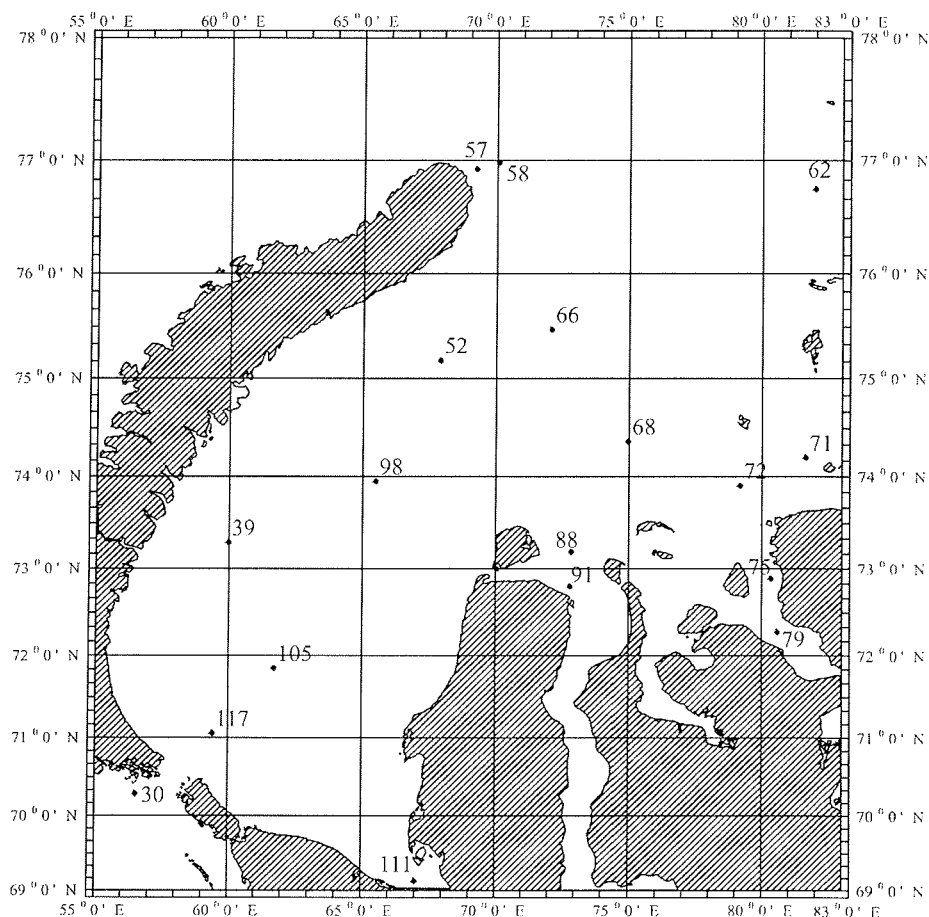Fig.7.3.Sediment sampling stations in the Kara Sea "Akademik Boris Petrov" Cruise 1995.

Results and discussion.

Stable carbon isotope ratio stands out of the other geochemical parameters as a solid indicator for bulk sedimentary organic matter. Organic carbon isotope composition forms the basis for the further classification of OM according to its genetic type. A wide range of the $\delta^{13}C_{org}$-values from -22.4 ‰ to -27.6 ‰ was determined for the sediments of the study area. The upper and lower $\delta^{13}C_{org}$-value can be considered two represent two distinct endmembers of OM:

-22.4‰ corresponds to autochthonous plankton-derived ("marine") OM, and -27.6‰ represents terrigenous land-derived OM. According to the $\delta^{13}C_{org}$-values, the stations were subdivided into two groups.

Group I ("marine") includes stations mostly enriched in ^{13}C, with the $\delta^{13}C_{org}$-values ranging from -22.4 to -23.9‰ and a mean of -23.0‰. The stations belonging to this group, and their corresponding $\delta^{13}C_{org}$-values are given below:

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St.	39	62	52	98	105	30	58	57
$\delta^{13}C_{org}$,‰	-23,9	-23,9	-23,6	-23,5	-23,4	-22,9	-22,5	-22,4

As seen in Figure 7.3, plankton-derived organic matter is most commonly encountered in the western part of the area, including clayey sediments of the Novaya Zemlya Trough and adjacent area (St. 57, 58, 52, 30). This area is influenced by the nutrient-rich Barents Sea water and ice caps of the Novaya Zemlya archipelago. Ice-edge phytoplankton blooms are considered to be the major source for the supply of ^{13}C enriched OM to the organic carbon pool in the Kara Sea.

The presence of autochthonous bioproduction over the inner Kara Sea water area (St.98, 105) may be related directly to the highly developed current system, including the circular current in the central part of the sea. In addition, the distribution pattern of sedimentary material in the Kara Sea is controlled by sea-ice transport (Kodina et al. 2000). This is in general agreement with the presence of not only isotopic but also molecular signals of algae in sediments all over the Kara Sea water area. However, from the averaged data given in Table 7.4 for n-alkane distribution clearly indicates an additional admixture of terrestrial material in sediments for some stations (e.g. St. 58, 62), where plankton-derived organic carbon dominates. Thus, some sediments of the group I, generally dominated by short chain n-alkanes, display a second maximum in the long chain n-alkane range.

Station group II is characterized by a ^{13}C depleted organic carbon isotope composition, averaging -26‰ (range from –24,3‰ to –27,6‰). Stations of group II and their sedimentary organic carbon isotope composition are given below:

St.	117	111	66	68	72	71	79	75	88	91
$\delta^{13}C_{org}$ ‰	-24,3	-24,3	-24,7	-25,3	-25,4	-26,4	-26,6	-26,8	-27,6	-27,6

The presence of terrigenous organic carbon is most prominent in the riverine-influenced area of the Yenisei and Ob estuaries (St.75, 79, 71, 72, 88, 91). The bulk of the terrestrial material driven with river water is deposited in the "marginal filter" area (Stein 2001; Bogacheva et al. 2001). This is well reflected by the n-alkane distribution pattern in the sediments of the mixing zone and adjacent area, characterized by higher CPI values (2,25 against 1,57 for group I, Tab. 7.4) and lower levels of short chain n-alkanes. Absolute maxima of n-alkane concentrations are present in the long chain carbon atom number range (C25-C31), derived from waxes of higher landplants. Nonetheless, an additional input of organic carbon derived from aquatic primary producers is indicated by enhanced C_{17} and C_{19} concentrations for some stations (St. 66, 68, 72, 117). Peaks of C_{16} and C_{23} evidence OM reworking by bacteria.
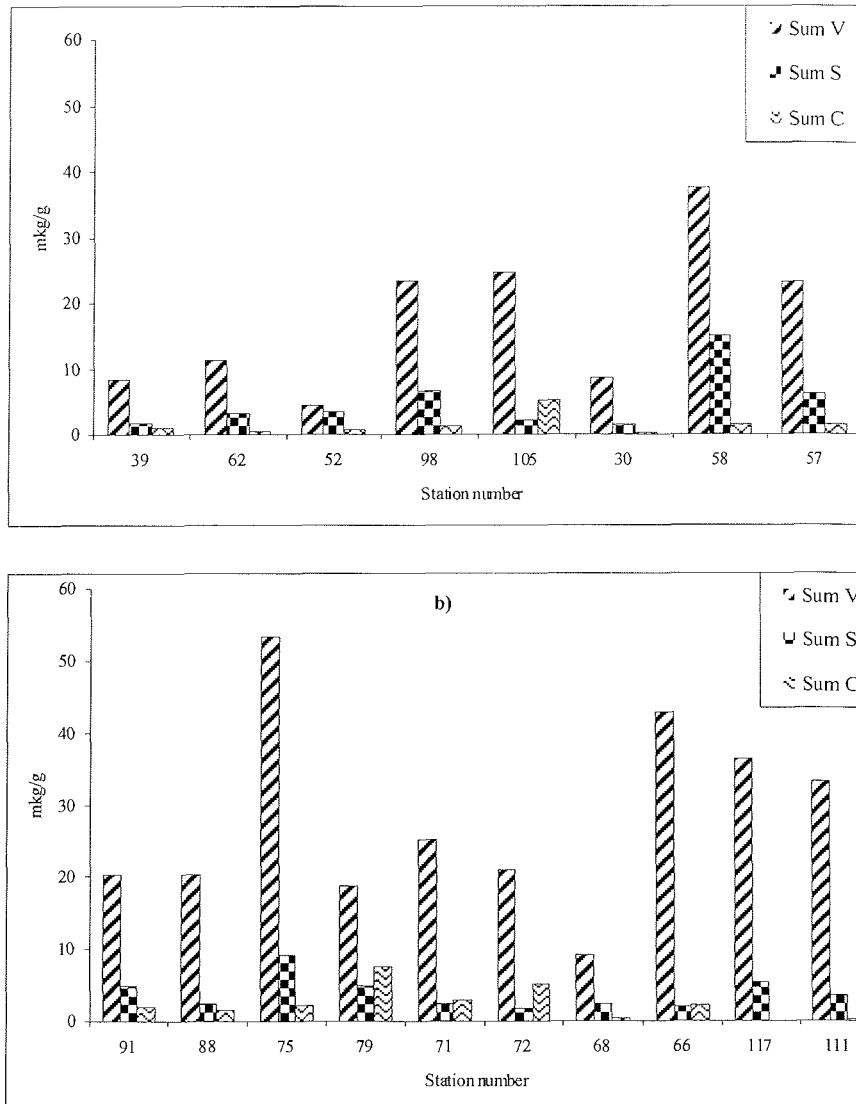
Fig. 7.4. Distribution pattern of lignin phenols in surface sediments of the groups I and II.

V- sum of vanillin, vanillic acid and acetovanillone;

S – sum of syringaldehyde, syringyl acid and acetosyringone;

C- sum of coumaric and ferulic acids.

A major part of the dissolved river discharge, namely nutrients and dissolved carbon (organic and inorganic, DOC/DIC), may pass through the marginal filter and propagate essentially northwards and northeastwards. Surface transported riverine water with dissolved compounds spreads northwards as far as 78°N. Dissolved nutrients support growth of phytoplankton and all further communities of the food

chain. DIC and DOC are included into Arctic food webs. Therefore, the terrestrial isotopic signal can travel through the marginal filter and can become incorporated into the new-formed autochthonous OM, resulting in a shift of marine $\delta^{13}C_{org}$ towards more terrestrial values.
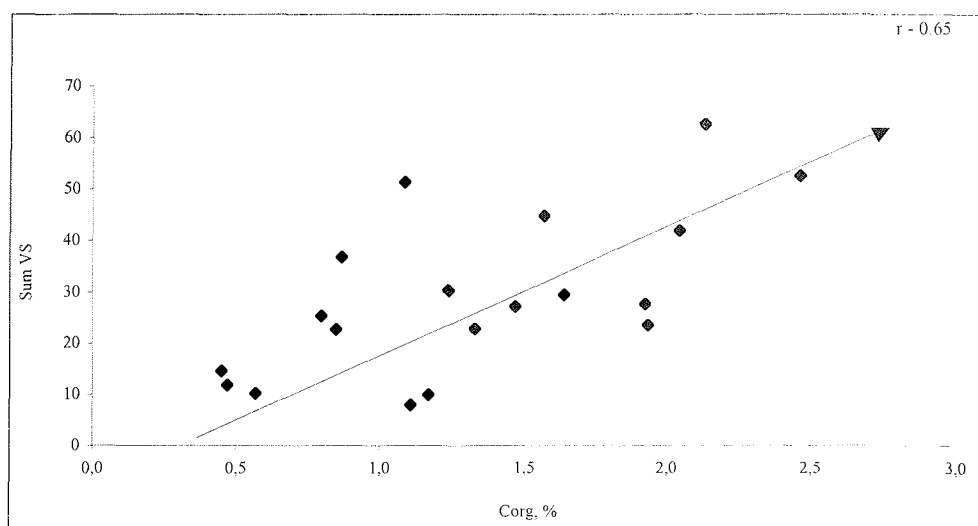

Fig.7.5. Correlation between V+S lignin structures and C_{org}.concentrations in the sediments.

The sediments recovered at stations 66 and 68 provide an example for the above mentioned influence of the Yenisei discharge and the resulting $\delta^{13}C_{org}$ shift: The stations are situated northwards of the estuaries in an area of extremely low sedimentation rate (Fig.7.3). Organic carbon isotope compositions for both stations (-24,7 and –25,3‰) correspond to the ^{13}C enriched part of the $\delta^{13}C_{org}$ range defind for terrigenous OM (group II, Table 7.4), while the n-alkane distribution is typical of plankton-derived material. The presence of specific plankton biomarkers in sedimentary OM in areas northwards of the estuaries was also noticed in a previous study (Belyaeva & Eglinton 1997). Our Rock-Eval pyrolysis data for these samples (HI>300mgHC/gTOC) further support the planktonic nature of the ^{12}C depleted sedimentary OM. We consider that the dissolved inorganic carbon of river water ($\delta^{13}C_{DIC}$= -6 ‰), assimilated in photosynthesis of phytoplankton microalgae may lead to similar isotope ratios of the planktonic and terrestrial organic matter.

Nitrobenzene oxidation of OM in the Kara Sea sediments was used to characterize the major lignin-derived phenolic compounds. According to their chemical structure, the oxidation products were summarized in the following groups:

ΣV: Vanillyl-type compounds (vanillin, vanillic acid, acetovanillone)

ΣS: Syringyl-type compounds (syringaldehyde, syringyl acid, acetosyringone)

ΣC: Coumaric and ferulic acids (cinnamyl phenols)

ΣP: p-Hydroxy-phenols

Figure 7.4 shows the concentration and distribution of lignin-derived phenols for the investigated samples. The sum of vanillyl-type compounds (ΣV, Fig. 7.4) is a distinguishing characteristic of lignin derivatives in the Kara Sea. Sediments of the

group II, directly influenced by the river discharge, in total display higher v-type phenol concentrations (max. 53,37 µg/g, Ø 28 µg/g) than sediments of group I (max. 37,48 µg/g, Ø 17,7 µg/g, Tab. 7.4, Fig. 7.4). This agrees well with the abundance of coniferous forests (taiga) in the catchment areas of Ob and Yenisei rivers.
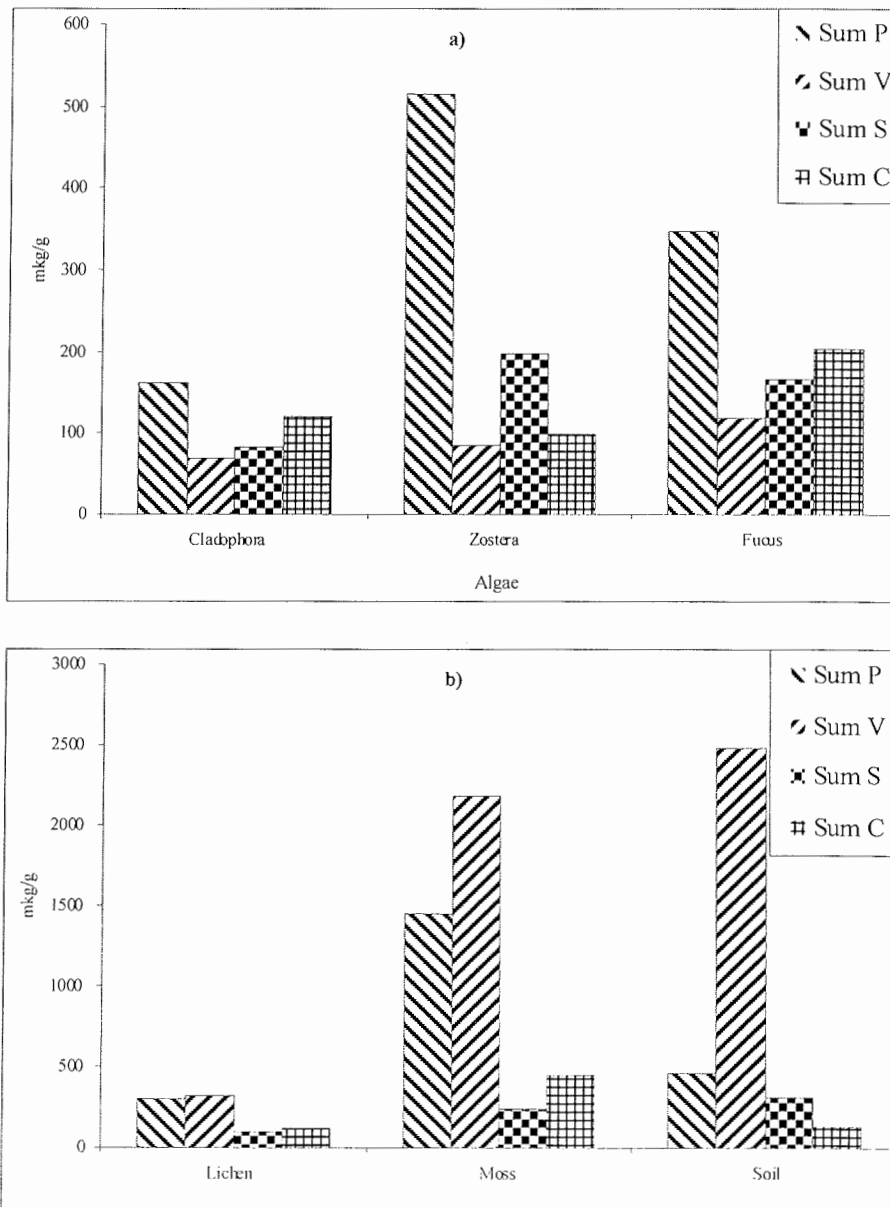

Fig.7.6. A. Lignin phenols of littoral algae (*Cladophora, Fucus*) and aquatic plant (*Zostera*), the White Sea; *B*. Lignin phenols of littoral non-vascular plants and soil, the White Sea.

Syringyl-type compounds belong to the minor compounds in the Kara Sea sediments. They are indicative for the presence fo minor inputs of dicotyledon, land grasses and pollen derived lignin to the sediments.

Vanillyl-type phenols and, even though in minor quantities, syringyl-type phenolics were detected in sediments within the whole investigation area contributing to the sedimentary organic matter. This is alos seen in the correlation of the sum of V- and S-type phenols and the sedimentary organic carbon content (ΣV+S vs. C_{org}, r=0,65, Fig. 7.5) and thus once again reflects the impact of river discharge and sea-ice transportation of terrestrial derived OM to the sediments of the Kara Sea.

Another special feature of the distribution of phenolic compounds is the prevalence of p-Hydroxy phenols, as indicated in Table 7.4 by the ratio of ΣP/ΣV for almost all investigated samples, but especially in sediments of group I (ΣP/ΣV = 0,67-7,4; Ø = 2,7). In aquatic environment, additional, non-lignin sources of p-Hydroxy phenols have been identified. They might therefore derive from the oxidation of polymeric substances common in blue-green algae, brown algae or fungi (Hedges et al. 1988). Therefore, high p-phenol yields in aquatic environments can not be unequivocally attributed to plant lignins.

The composition of aromatic phenols – products of nitrobenzene oxidation of some algae and aquatic higher plant (*Zostera*), tundra moss, lichen and soil are given in Figure 7.6. Primitive non-vascular plants, including mosses (*Sphagnum, Marchantia, Polytrichum*), lichens, higher algae (*Fucus, Laminaria*) contain lignin-like compounds with p-coumaric structures being prevalent (Manskaya & Kodina 1975). Lignin is progressively degraded in soils, to produce smaller more oxidized products, which are washed out of soil and transported to marine basins.

Spores and pollen of land vegetation might be an additional source of the P- and C-, S-, V-compounds, which were detected in sediments of the south Kara Sea area (Matthiessen and Boucsein 1999). The presence of lignin in spore and pollen grain walls was established (Manskaya & Kodina 1975). The uniform distribution pattern of the minor compounds (S,C) over the entire Kara Sea area might be considered as an evidence of spore and pollen eolian transport from the land. Non-woody plant tissues (leaves, needles, grasses) can be distinguished by their lower yields of V- and S-compounds and by production of minor C- phenols (Sarkanen & Ludwig 1971; Hedges & Mann 1979).

Acknowledgments

Table 7.3. Carbon isotope composition and some geochemical parameters of organic matter from the Kara Sea surface sediments

Parameters	St.39, 62, 52, 98, 105, 30, 58, 57 (group I) Planktonogenous OM		St. 91, 88, 75, 79, 71, 72, 68, 66, 117, 111 (group II) Terrigenous OM	
	Average	Range	Average	Range
$C_{org.}$,%	0,80	0,45 to 2,47	1,40	0,40 to 2,14
$\delta^{13}C$,‰ vs. PDB	-23,1	-22,4 to -23,9	-26,0	-24,3 to -27,6
Vanillyl phenols $(\sum V)$, µg/g	17,7	4,48 to37,48	28,0	9,24 to53,37
$\sum P/\sum V$	2,7	0,67 to 7,4	1,2	O,40 to 3,7
$\sum S/\sum V$	0,25	0,09 to 0,77	0,15	0,05 to 0,27
n-Alkane concentration, µg/g	19,93	7,08 to 74.88	10,89	4,63 to 31,87
n-Alkane C max.	C_{17}(St.105); C_{16} (St.98); C_{15}(St.52); C_{16},C_{31}(St.62); C_{15},C_{25}(St.30,); C_{17},C_{25} (St.57); C_{17},C_{31} (St.58)		C_{27}(St.88,75); C_{25}(St.111); C_{25}, C_{17} (St.117,72); C_{25},C_{27},C_{31} (St.71,79); C_{17},C_{16} (St.66,68)	
C_{10}-C_{22}/C_{23}-C_{40}	2,14	1,08 to 3,64	1,28	0,34 to 2,47
CPI	1,57	1,40 to 3,64	2,25	1,39 to 2,96

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