# 7.5 Carbon isotope composition of phytoplankton in the Yenisei riverestuary-open sea system and the application of isotopic approach for evaluation of phytoplankton contribution to the Yenisei POC load

## L.A. Kodina

V.I.Vernasky Institute of Geochemistry and analytical Chemistry RAS. Moscow <u>kodina@geokhi.ru</u>

### Abstract

Measurement of the phytoplankton carbon isotope composition along the extended meridional section Yenisei-Kara Sea was carried out to identify the "marine" (planktonderived) and terrestrial endmembers both types of organic matter contributions to the POC load in the framework of a two- compound mixing model. The phytoplankton samples were previously cleaned from detritus through a multiple decantation procedure. A high variability of the stable carbon isotope ratio caused by river run-off was revealed: plankton in the open sea differed from the freshwater plankton by about 12%. A correlation was made between the plankton and particulate organic carbon isotope ratio distributions along the meridional section and the salinity. Both isotopic curves run in parallel each other, but in the frontal zone they intersect. The intersection point of the curves corresponds to the averaged  $\delta^{13}$ C-value of -27,5%. This value is common to the plankton carbon, POC and hence to the second POC compound, namely to the terrigenous organic carbon. The value was used as the terrigenous endmember for calculation the both OM type contribution by the isotope-mass balance equation. The second endmember was represented by the  $\delta^{13}$ C-value of the clean phytoplankton sample for each station of the section. In the fresh water part, the contribution of plankton-derived carbon is 36-40%, in the open sea from 60 to 71%, with a very low particulate organic carbon concentration.

#### Introduction

Stable carbon isotope analysis is commonly used for tracing sources of sedimentary organic matter (OM) in marine systems. The present work aimes to continue our study of phytoplankton isotope composition of the both great Siberian rivers and adjacent Kara Sea area to get further proofs for the influence of the river run-off on the biogeochemical carbon cycle in the Kara Sea (Kodina 2001). Up to now, only few data on the carbon isotopic composition of Arctic phytoplankton exist. More typically, particulate organic carbon (POC) collected on a filter is measured. POC is representative of phytoplankton carbon in that it is largely derived from phytoplankton. However, two additional circumstances should be taken into account when studying the Arctic shelf seas. The first is that the POC load of the great Siberian rivers involves a substantial proportion of terrestrial material. Second, the dissolved inorganic carbon available for growth of phytoplankton algae might be depleted in the <sup>13</sup>C-isotope due to input of dissolved inorganic carbon transported with river water from the land (Erlenkeuser et al. 1999; Kodina 2001).

The objective of the present work involved preparation of clean algae samples and to identify the "marine" (plankton-derived) and terrigenous endmembers for assessment of the both typeorganic matter contribution to POC load of the Yenisei.

### Material and methods

The work was carried out in the 35 cruise of R/V"Akademik Boris Petrov" (2000) along the meridional section river Yenisei-estuary-open sea, between 70 and 77°N, in the period of 7-19 September 2000. 14 ptytoplankton sampling stations covered three basic part of the transect (Fig.7.7). Stations 17 and 19 were situated in the river part (fresh water from surface to bottom); estuary (surface water salinity is of 2,3-6,7 psu) included st. 16, 15 and 22; stations 23, 24, 8, 9, 28, 30, 35, 36 were taken in the open Kara Sea area. Most stations of the open sea situated close to drifting ice fields and were influenced by the ice thawing. The temperature of the thin uppermost water layer sank below 0°C, and the salinity sharply decreased. The stations 13-19 were taken 9-12 September, during the direct vessel trip southwards, stations 22-36 - on the vessel return trip in the period of 13-19 September. It is reasonably to consider separately the two parts of the cumulative section (direct and return vessel trips). Figure 7.8 shows the stations on the direct trip (upper part) and on the return trip (lower part of the Fig 7.8).

# Geochemistry

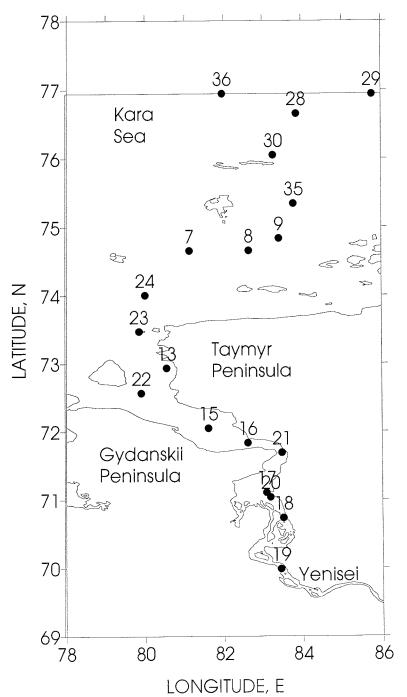


Figure 7.7. Map of phytoplankton sampling stations. 35 Cruise of R/V "Akademik Boris Petrov", September 2000.

#### **Results and discussion**

#### Plankton sample preparation

The starting material was sampled from subsurface water by traditional net technique. A hand net with pore size of 90  $\mu$ m was used. Sometimes, a ship pump and a bucket were used for water sampling. The raw samples were poisoned with saturated HgCl<sub>2</sub> solution and left in a cold room until all particles settle down. The bulk of transparent water was removed, and the concentrated suspension was further separated into phytoplankton and detritus by a repeated careful decantation. The decantation procedure was repeated with the detritus samples as well to remove as much algae cells as possible. The cleaning of the algae samples was assessed by use of light microscopy. Within the species present in the raw material (natural population), usually only a few make up the bulk of biomass. Phytoplankton samples cleaned by this way, contained less than 5% detritus in most cases. The initial ratio of the dominating algae in the natural population was preserved with the following exception:

The samples from St. 15 and 16 (and to some extent St. 22) comprise mixture of separate freshwater algae cells and the bulk of brown colloidal aggregates and unidentified particles.

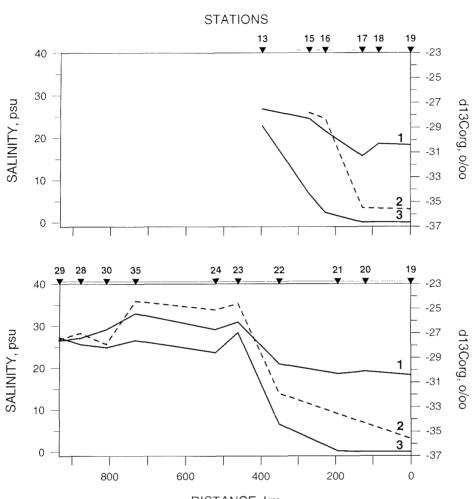
#### Phytoplankton isotope composition

Data on the organic carbon isotope composition of the clean phytoplankton samples together with a short description of the dominating species (Dr. V. Larionov, Tab. 7.5). At St. 19-22, the algae population was represented almost exclusively by freshwater species. The main contribution to the total biomass was due to diatoms *Melosira granulata, Asterionella formosa, Fragillaria crotonensis.* At St. 17, 19 green algae (*Rhizolclonium*) and blue-green *Aphanizomenon flos-aquae* accounted for a great percentage of the total biomass. A typical marine population is present at St. 23, with rare freshwater algae cells being observed. St. 24 shows an exclusively marine species assemblage. Diatoms of *Chaetoceros* species and some *Dinophyceae* were predominant (Larionov & Makarevich 2001).

One can see a wide range of  $\delta^{13}$ C variations along the coupled Yenisei-Kara Sea transect : from - 36,2‰ and -35,6‰ in the Yenisey fresh water to -24,4‰ in the open sea, northwards of the estuary (Tab. 7.5). POC isotope composition along the transect ranged from -30,4 ‰ to -25,2‰ (Bogacheva et al. 2001). POC isotope composition in the Yenisei estuary has been found to fit well with the dissolved inorganic carbon isotope composition and water salinity (Kodina et al. 1999). The same regularity was valid as a whole for the Ob phytoplankton (Kodina 2001), as well as for the phytoplankton in this study. Curve 2 (Fig. 7.8) demonstrates the distribution of the phytoplankton isotope composition along the section, as compared with the POC isotope data (curve 1) and water salinity (curve 3). However, in the northerneastern part of the section the presence of the thawing ice and the stormy weather disturbed the regularity to some extent (e. g. St. 30 and 36 show anomalous depleted  $\delta^{13}$ C- values (-27,9‰ and -28,1‰).

Detritus and plankton differ in the carbon isotope composition (Tab. 7.5). The freshwater algae were noticeably depleted relative to reciprocal detritus. Conversely, in the marine part of the section (St. 23, 24, 28) the detritus is more depleted than the plankton.





DISTANCE, km

Figure 7.8. Distributions of  $\delta^{13}$ C- values (% PDB) for particulate organic carbon (curve 1), phytoplankton (curve 2) and subsurface water salinity (psu) along section Yenisey-Kara Sea in the periods of 9-12 September (upper part) and 12-19 September (lower part). Locations of the stations are shown in Figure 7.7.

# Phytoplankton as a marker of the frontal zone.

Distribution pattern of the plankton carbon isotope composition along the section together with isotopic data for POC samples are given in Figure 7.8. One can see that a rather good agreement exists between the curves of water salinity,  $\delta^{13}C_{\text{plankton}}$  and  $\delta^{13}C_{\text{POM.}}$ . It is particularly remarcable that the phytoplankton  $\delta^{13}C$  and salinity curves run almost parallel.

A sharp change of the phytoplankton isotopic signals in both parts of the cumulative transect are seen in Figure 7.8 (curve 2). The first is of 7,9% in magnitude and located between st. 17-16. The second - of 7,3% coincides with the frontal zone pronounced through salinity – temperature gradients between st. 22-23 (Stephantsev & Shmel'kov

2001). We suppose, that during the st. 13 and 14 (9 September, direct ship trip) due to the stormy weather, the hydrological front had been driven with a strong north-eastern wind at the distance of 224 km upstream. The frontal zone has been detected between the st. 16-17 through the sharp isotopic signal of the phytoplankton (Fig.7.8, upper part, curve 2). In the lower part of the Figure 7.8 we could observe that 53 hours later (return ship trip) the hydrological front came back to its initial position. Almost the same change of the phytoplankton isotopic signal of 7,3% was identified between st. 22 (salinity 6,6 psu) and st. 23 (salinity 28,4 psu).

The run of the POC curve is much more gentle than that of the plankton, in the frontal zone: 3,2% for POC against 7,3% for the clean plankton samples.

In the frontal zone POM sedimentation was shown to occur. The bulk of the river runoff POC was precipitated when water salinity changes from 6,6 psu to 28,4 psu (Bogacheva et al. 2001). The narrow interval (about 100 km) between st.22 and 23 corresponds to a depocenter of the marginal filter. It is known that about 90% of the sedimentary material carried with river water from the land, including freshwater plankton is precipitated in the marginal filter area (Lisitzin 1994). The freshwater plankton sedimentation is represented by the steep change of the carbon isotope composition from -31,9% (st. 22) to -24,6% (st. 23). An equal steep change of the species composition of algae population was observed in the marginal filter depocenter (Tab. 7.5).

It is significant that the  $\delta^{13}C_{plankton}$  and  $\delta^{13}C_{POM}$  curves cross at the point corresponding to the frontal zone. The intersection point corresponds to a  $\delta^{13}C$  value of -27,5% . At this point, the phytoplankton, POC and hence the second averaged POC compound are of similar carbon isotopic composition.

#### Endmembers for the two-compound mixing model

The model of simple mixing of two endmembers – terrigenous and marine algaederived organic material is widely accepted to explain variations of  $\delta^{13}C$  –values of marine particulate material and to determine the ratio between autochthonous material and terrigenous supply in organic carbon pools of sediment and water masses (Tan et al. 1991; Rachold & Hubberten 1999).

The central problem for a reliable application of the model consists in the selection of the both endmembers. A problem consists in, that for the system river-estuary-open sea it is not enough to get only the average value for primary bioproduction. The present paper demonstrates the wide variability of phytoplankton isotope composition (about 12%c) caused by the inorganic carbon variability and organic load transformation in the shallow shelf sea influenced by the great river run-off.

The study of isotope composition of phytoplankton in parallel with water particulates enables us to determine the representative  $\delta^{13}C$  –values for both endmembers.

We assume that the experimental  $\delta^{13}$ C- value for the bulk organic material precipitated in the depocenter of the marginal filter is representative of the average organic terrigenous load of the river water. We found it is equal to -27,5%c. The value seems to be rather reliable and fits well literature data on the tundra and taiga vegetation, soil and peat organic matter (Schell & Ziemann 1989; Balesdent et al.1993; Fogel & Cifuentes 1993; Huang et al. 1999), as well as an average of Kara Sea samples terrigenous UDOM  $\delta^{13}$ C- value of -27,3% (Opsahl et al. 1999).

Many factors, involving temperature, DIC isotope composition, nutrient supply,  $CO_2$  availability, growth rate, as well as variations in both carbon source and carbon metabolism have been proposed to influence  $\delta^{13}C$  composition of marine phytoplankton. Species composition may be an additional controlling factor, as specific groups of marine phytoplankton may show significant difference in their carbon isotope ratio. Consequently, the calculation of the isotope ratios based on some of the available parameters seems to be problematic at the present time (Thompson & Calvert 1994; Fogel & Cifuentes 1993; Lajtha & Michener 1994).

We intend to get reliable data on the phytoplankton precisely and to use them as "marine"endmembers for three different parts of the extended meridional section "riversea". The experimental data displayed in Table 7.5 were used as "marine" endmembers, different for each station to calculate the contribution of allochthonous supply and aquatic bioproductivity along the cumulative transect, except when a hydrological situation was unstable (examplified by mixing zone or ice field vicinity). The standard equation of the isotope- mass balance for the two-member mixing model was applied. The experimentally determined average value of -27,5% was used in each case as the terrigenous endmember.

In the freshwater part of the transect, the contribution of plankton-derived carbon in the POC pool is 36 - 40%; in the Yenisei Estuary, it is 45 - 50%. Selective sedimenation of the bulk freshwater plankton and flocculated terrestrial OM resulted in a drastic decline of the total POC concentration in the marine part of the transect, with the autochthonous bioproduction dominating (60-71%) in the open sea.

### Acknowledgement

I am grateful to Dr. S. Meschanov for his help in preparation of the hydrological material for this paper and discussion. The paper was prepared under support of the Russian Foundation of Basic Research, Grant N 00-05-64575

	toplankton (70-77° N)		ected along the meridional transect Yeni	se1-Kara
Station number	Water salinity, psu	De trit us content, % $\delta^{13}C$ , %o	Phytoplankton sample description (By Larionov V.V.) (Predominant species, rel.%)	δ <sup>13</sup> C, %c PDB
19	0,0	< 5% -30,6	Melosira granulata (73), Asterionella formosa (13), Chlorophyceae(12), Cyanophyceae(2)	-35,6
17	0,0	<5%	Asterionella formosa (50), Melosira sp.(30),Chlorophyceae (20)	-36,2
16	2,3	<50% -28,3	M. granulata (70), A. formosa (10), Synedra sp. (5) Chlorophyceae (15)	-28,3
15	6,7	~50%	M. granulata (50), Pennatophyceae(23), A. formosa (10), Synedra (10), Cyanophyceae(5), Chlorophyceae	-27,8
22	6,6	<50%	Melosira sp. (80), Thalassiosira nordenskioeldii (5), Nitzschia grunowii, Synedra, A.formosa, Chlorophyceae	-31,9
23	28,5	<5% -25,4	Chaetoceros socialis(55), Nitzschia grunowii(20), Thalassiosira sp.(15), Melosira sp.(5) Dinophyceae	-24,6
24	23,7	5% -26,3	Ch. socialis (50),Ch.sp.(25), Th.nordenskioeldii.(15), Dinophyceae(5), Nitzschia grunowii A.formosa	-25,1
8	21,1	10%	Nitzchia grunowii(60), Th.nordenskjoldii.(30), Ch.sp.(10),	-25,9
9	23,8	10%	Nitzchia grunowii(75), Th.nordenskioeldii (15),) Chaetoceros sp.( 5), Dinophyceae	-25,9
26	19,2	<5%	Ch. decipiens(35), Ch.sp.(50), Th.nordenskioeldii. (15), Ceratium arcticum	-27,5
28	25,6	~10% -27,1	Ch. sp.(95), Th.nordenskioeldii, Nitzschia grunowii, Ceratium arcticum	-27,0
30	24,9	<5% -27,6	Ch.sp (85), Dinophyceae (10), Nitzschia grunowii	-27,9
35	26,6	<5%	Ch. socialis (90,) Th.nordenskioeldii(5); Nitzschia grunowii, Dinophyceae, Anabaena	-24,4
36	27,2	<5%	Ch. decipiens (>90),Thalassionema sp., Ceratium arcticum	-28,1

Table 7.5: Organic carbon isotope composition and description of the subsurface phytoplankton samples collected along the meridional transect Yenisei-Kara Sea (70-77° N)

150