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Stable Isotopic Composition of Particulate Organic Carbon in the Caspian Sea

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Abstract—The data on the isotopic composition of particulate organic carbon ($\delta^{13}C_{POC}$) in the Caspian Sea water in summer–autumn 2008, 2010, 2012, and 2013 are discussed in the paper. These data allowed as to reveal the predominant genesis of organic carbon in suspended particulate matter of the active seawater layer (from 0 to 40 m). The $\delta^{13}C_{POC} = -27‰$ (PDB) and $\delta^{13}C_{POC} = -20.5‰$ (PDB) values were taken as the reference data for terrigenous and planktonogenic organic matter, respectively. Seasonal (early summer, late summer, and autumn) variations in the composition of suspended particulate matter in the active sea layer were revealed. A shift of $\delta^{13}C_{POC}$ towards greater values was seen in autumn (with a slight outburst in the development (bloom) of phytoplankton) in comparison with summer (with large accumulations and an extraordinary phytoplankton bloom confined to the thermocline area). The seasonal dynamics of autochthonous and allochthonous components in the suspended particulate matter of the Middle and Southern Caspian Sea was studied with the use of data on the concentration of particulate matter and chlorophyll *a*, the phytoplankton biomass and the POC content.

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INTRODUCTION

The enclosed Caspian Sea is located at the boundary between the humid climatic zone in the west and northwest and the arid climatic zone in the east. Significant successions of all components of the sea ecosystem have been seen here since about the 1930s [3, 4, 17]. They are mainly related to the change in sea level and regulation of the flows of the Volga, Ural, and other rivers of the Caspian Sea Basin. Therefore, there is a need to study the materiogenic composition of suspended particulate matter (SPM) to understand the modern sedimentation processes in the sea.

Suspended particulate matter (dispersed sedimentary matter) is formed by autochthonous phytoplaktonogenic organic matter (OM) and terrigenous material input by large and small rivers in the humid zone and by aeolian transportation in the arid zone (allochthonous OM).

These two kinds of OM differ on average by 5‰ in isotopic composition of their organic carbon (C_{org}), which makes it possible to determine the genesis of C_{org} in SPM (particulate organic carbon – POC).

The first determinations of $\delta^{13}C_{POC}$ values in the Caspian Sea (at stations of the Trans-Caspian axial transect) in May–June 2012 provided reliable data on the predominant OM genesis in the top (0–30 cm) water layer [20]. Geographical specification of the Caspian Sea into the Northern, Middle, and Southern corresponds to the C_{org} isotope analysis data in SPM of the surface water layer.

The aim of our new work was to reveal the source of C_{org} in SPM of the Caspian Sea in summer and autumn on the basis of data of isotopic markers ($\delta^{13}C_{POC}$), using a interdisciplinary approach.

MATERIALS AND METHODS

The data for the analysis were collected at 14 stations of the Trans-Caspian section during cruise 41 of the R/V *Rift* (October 5–31, 2012) and cruise 2 of the R/V *Nikifor Shurekov* (August 21–September 12, 2013) (Fig. 1, Table 1). We also used the published data on the isotopic composition of POC obtained during cruises 29, 35, and 39 of the R/V *Rift* in November 2008, June 2010, and May–June 2012, respectively [7, 10, 20].

Seawater samples for analysis of SPM were taken with Niskin bottles throughout the entire water column from the surface to the bottom (after the fluorescence intensity and oxygen distribution were determined to specify the boundary layers) using Indronaut Ocean 316 and SBE 25 plus CTD sounds. Fluffy layer was sampled with a KUM multicorer (Germany) [1, 6].

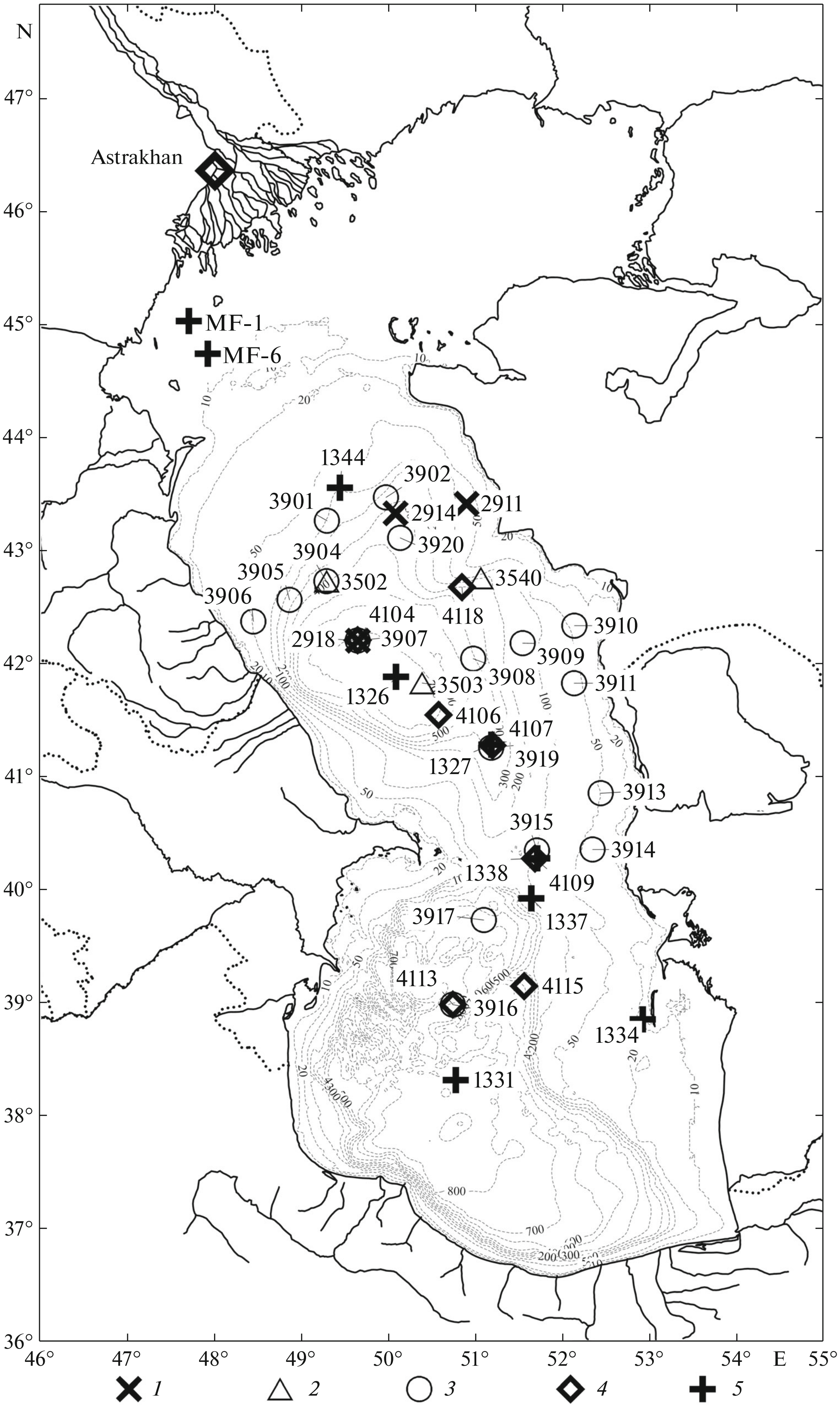


Fig. 1. Schematic maps of sampling stations for studying isotope carbon composition during cruises of research vessels of Shirshov Institute of Oceanology, Russian Academy of Sciences: (*1*) cruise 29 of R/V *Rift*, November 7–22, 2008; (*2*) cruise 35 of R/V *Rift*, June 4–19, 2010; (*3*) cruise 39 of R/V *Rift*, May 21–June 9, 2012; (*4*) cruise 41 of R/V *Rift,* October 5–31, 2012; (*5*) cruise of R/V *Nikifor Shurekov*, August 21–September 9, 2013.

Table 1. Number of samples of SPM collected in different seasons in water column of the Caspian Sea to study isotopic composition of organic carbon

Cruise, season	2008		2010		2012				2013		Total	
	cruise 29 of R/V *Rift*		cruise 35 of R/V *Rift*		cruise 39 of R/V *Rift*		cruise 41 of R/V *Rift*		cruise 2 of R/V *Nikifor Shurekov*			
	November		June		May–June		October		August–September			
region	stations	samples	stations	samples	stations	samples	stations	samples	stations	samples	stations	samples
Northern	–	–	–	–	–	–	–	–	2	2	2	2
Middle	3	17	4	20	15	38	4	16	4	24	30	115
Southern	–	–	–	–	2	8	3	14	3	14	8	36
											40	153

Prior to the determination of the POC content and its isotopic composition ($\delta^{13}C_{POC}$), water samples were filtered in a vacuum of 200 mbar through Whatman Co. fiberglass GF/F filters (Ø 47 mm, effective mesh Ø 0.7 μm).

We determined $\delta^{13}C_{POC}$ after conventional preparation of samples on a Delta Plus mass spectrometer (Germany) using the PDB standard (analyst T.S. Prusakova, Winogradsky Institute of Microbiology, Russian Academy of Sciences) with an accuracy of ±0.2‰.

The POC content was determined by the automatic coulometric method on an AN 7560 carbon analyzer (analyst L.V. Demina, Shirshov Institute of Oceanology, Russian Academy of Sciences). For a concentration of 30–100 μg C/L, the accuracy was ±15%, and the measurement range was 5–500 μg C/L.

The SPM concentration was determined by the standard filtration method in a vacuum of 0.4 atm with membrane nuclear pore filters (Ø 47 mm, mesh Ø 0.45 μm). The approaches for filtration, determination of SPM and POC concentration, and measurement of the isotopic composition of POC are given in [7, 10, 20].

The concentration of chlorophyll *a* (chl *a*) was simultaneously determined in the samples with fluorimetry (with extraction in 90% acetone) on a Trilogy 1.1 fluorimeter (Turner Designs, United States) according to the approach described in [19]. Conventional methods were used during fixation, concentration, and determination of the quantitative phytoplankton parameters [5].

Data obtained with a MODIS-Aqua satellite ocean color scanner (http://oceancolor.gsfc.nasa.gov/) were used to analyze the spatial distribution pattern of the water temperature, chlorophyll, and SPM in the surface water layer. Maps of the distribution patterns of these parameters (average of five days) were compiled, using regional algorithms developed at the Laboratory of Ocean Optics of the Shirshov Institute of Oceanology, Russian Academy of Sciences, from original field measurements made by the authors [7, 21].

RESULTS AND DISCUSSION

Hydrophysical conditions. In early summer (June 2010, May–June 2012), three layers were specified in the water column of the Middle and Southern Caspian Sea with respect to all the studied parameters: (i) the top quasihomogeneous layer (TQL) from 0 to 15 m deep with temperature range from 17 to 23°C; (ii) the thermocline (from about 20 to 60 m deep) with great changes in the parameters and a drop in temperature to 8°C; (iii) the deep-water layer with a temperature of about 6°C near the bottom. The water salinity was 11.23 PSU in TQL and rose to 11.42 PSU in the thermocline layer [1, 2, 7].

In late summer (August–September 2013), water column was also specified into three layers: the TQL, the seasonal thermocline, and the deep water layer, often including the nepheloid layer [7]. The thickness of the TQL was 15–23 m in the Middle and 25–31 m in the Southern Caspian. Its temperature varied from 22.8 to 27.3°C, and salinity was within 10.2–11.5 PSU [6]. The lower boundary of the thermocline layer was at a depth of 40–50 m, where the water temperature dropped to 7.8°C in the Middle and to 10.8°C in the Southern Caspian Sea. The deep-water layer was characterized by a gradual temperature decrease to 5.12 and 6.05°C in the Derbent and Southern Caspian Depressions, respectively.

In late autumn (October–November 2008 and 2012), the thickness of the TQL increased to 30–50 m as a result of more intensive water mixing by wind and a drop in temperature to 13.2°C in the Middle and 22.7°C in the Southern Caspian Sea [1]. Nevertheless, the water column was still specified into the same three layers, and only the positions of their boundaries differed [2].

These hydrophysical conditions in the water column were typical for autumn. Our preceding investigations have shown that the seasonal thermocline significantly determines the vertical distribution of allochthonous and autochthonous SPM in water body [7, 14].

The concentration of SPM in the surface **(**0–1 m) layer varied from 0.2 to 1.5 mg/L in August–September 2013. It was usually <0.6 mg/L in the most of the Middle and Southern Caspian Sea and exceeded 1 mg/L only in some areas: in shallow sea waters unstratified with respect to temperature and density (near Ogurchinskii Island), near the Apsheron Sill, and on the northeastern slope of the Derbent Depression.

The concentration of SPM in the 0–1 m layer of the Southern Caspian Depression was slightly higher (0.5 mg/L) than for the Derbent Depression (0.4 mg/L).

At a depth of 100 m, the concentration of SPM varied from 0.6 in the Middle to 1.0 mg/L in the Southern Caspian Sea.

Incomparably high concentrations of SPM were revealed at shallow-water stations MF-1 and MF-6 in the marginal filter zone of the Volga River in the Northern Caspian Sea (10 and 4 mg/L, respectively).

In October 2012, the concentration of SPM in the surface water of the Middle and Southern Caspian Sea varied from 0.4 to 0.8 mg/L, i.e. within the limits of August–September 2013, but significantly differed from the data of May–June 2013, when it was greater (0.8 mg/L) and evenly distributed [1, 7].

In Spring–Summer 2012, the concentration of SPM became higher as a result of a rise in phytoplankton biomass (the bloom peak) and of the inflow of flood river water rich in terrigenous OM.

The chl *a* concentration and phytoplankton biomass were regarded as the markers of the abundance of autochthonous OM in the water column [7].

In May–June 2012, the chl *a* concentration was high (0.6–2.3 μg/L) in the layers from ≥15–60 m deep (unlike the concentration of SPM) and was allocated to the depth of the seasonal thermocline layer [7]. The cold-water community was usually dominated by diatomic algae (*Pseudo-nitzschia seriata* and *Dactyliosolen fragilissimus*) in the open sea and by dinoflagellates (mainly by *Prorocentrum cordatum*, as well as by *Gonyaulax polygramma*, *Prorocentrum micans*, and *Diplopsalis lenticula*) in the zone of the beginning seasonal upwelling near the eastern seashore [14]. These microalgae were abundant and bloomed in the thermocline layer.

In June 2010, almost the entire photic layer in the Middle and Southern Caspian Sea was dominated by diatoms (to 99.8% of the biomass). They were only sometimes replaced by dinoflagellates. High chl *a* concentrations were as usually allocated to the thermocline layer to the depths of 10–45 m. The highest chl *a* concentrations (7.6–4.6 μg/L) in the Derbent Depression (station 3503, the depth 749 m) were related to the large phytoplankton biomass (to 1 g C/m^3) dominated by dinoflagellate alga *Gonyaulax polygramma* [15]. In the upwelling zone on the eastern seacoast, the chl *a* concentration in that season was 2.8 μg/L in the 40 m layer under the thermocline zone (station 3532, 41 m). The algae population there was dominated by *Pseudosolenia calcar-avis*, a large diatom (289 mg C/m^3).

In August–September 2013, the chl *a* concentration in the surface (0–1 m deep) water layer was as usual the highest in the Northern Caspian Sea (to 29.5 μg/L within the 2–7 PSU isohalines). A reliable linear correlation was revealed between the concentrations of SPM and chl *a* in the surface waters of the Northern Caspian Sea: $y = 2.11x$, $R^2 = 0.95$, $n = 7$. An in-phase distribution of these two parameters was revealed in the Northern Caspian Sea in early summer [7]. The chl *a* concentration dropped about three times with an increase in water salinity to 9.5 PSU. At an ordinary water salinity of 11.3 PSU, it usually did not exceed 0.5 μg/L in the Middle Caspian Sea and rose to 1 μg/L at the northwestern slope of the Derbent Depression.

In the Southern Caspian Sea, the chl *a* concentration in the surface layer was greater and varied from 0.5 to 1.2 μg/L. It was the highest in shallow waters in the eastern sea (station 1334 near Ogurchinskii Island), not far from the Apsheron Sill. These areas of increased chl *a* concentration were probably formed by mesoscale eddies, but their role is poorly studied [9].

In August–September 2013, the distribution pattern of chl *a* was in general nonuniform in contrast to early summer [7], which is well reflected in satellite images of the surface water layer (according to MODIS-Aqua satellite color scanner data). The phytoplankton in the surface (from 0–1 m deep) layer in that period was formed by warm-water species, also typical of early summer: *Coscinodiscus perforatus*, *Prorocentrum cordatum*, and *Gonyaulax polygramma* [14, 15]. Spots with increased chl *a* concentration in satellite images corresponded to another phytocenosis dominated by the cyanobacteria *Lyngbya limnetica* and *Phormidium* sp. and the dinoflagellate *Prorocentrum cordatum* in the Middle Caspian Sea, and the green alga *Binuclearia lauterbornii* var. *lauterbornii* in the Southern Caspian Sea.

The highest chl *a* concentrations (from 1 to 5.7 μg/L) in the Middle and Southern Caspian Sea in August–September 2013 were typical of the seasonal thermocline layer. Its phytocenosis was dominated by the dinoflagellate *Gonyaulax polygramma* [14, 15]. The pronouncedly stratified water column was specified into two areas of increased chl *a* concentration: the seasonal upwelling zone near the eastern shore of the Middle Caspian Sea (2.2–5.3 μg/L in the 17–19 m layer) and the southern edge of the Derbent Depression (2.1 μg/L, the 27 m layer). These areas are significantly deeper than the layer seen from satellites, which resulted in incorrect data on the chl *a* concentration in the upwelling zone [9]. The analysis of phytoplankton samples confirms the accumulation of this pigment in the 17–100 m layer, including the thermocline, with abundant dinoflagellates *Gonyaulax polygramma* (up to 3.5×10^5 cells/L, 15–16 g/m^3, 1.6–1.7 g C/m^3). The share of this species in the total phytoplankton biomass in late summer was 99%.

The distribution pattern of chl *a* in the intermediate and bottom layers is similar to that of SPM. Its concentration averaged 0.13 μg/L and varied from traces in the deep-water depression to 0.9–1.5 μg/L at a depth of 87 m in the upwelling zone of the Middle Caspian Sea and near Ogurchinskii Island in the Southern Caspian Basin (station 1334, 12 m layer). Almost all areas with the bottom nepheloid layer were characterized by a higher chl *a* concentration in comparison with the above layers.

In October 2012, the chl *a* concentration in the 0–1 m layer varied from 2 to 34 μg/L in the Northern, within 0.9–1.9 μg/L in the Middle, and within 0.7–1.1 μg/L in the Southern Caspian Sea. These data were significantly higher than those for early summer 2012 and late summer 2013 [7]. In the Middle Caspian Sea, the chl *a* concentration was about twice as high in autumn than in early and late summer. It should be mentioned that this parameter in the thermocline layer was not usually increased. Its variations in the TQL (30–50 m layer) were similar to those in the 0–1 m layer over the entire sea area (from 0.5 to 1.9 μg/L). This leveling of the chl *a* concentration in the TQL in late autumn was obviously related to water mixing by wind during frequent storms, to slighter stratification, and to certain other factors.

The distribution pattern of phytoplankton in the TQL in October–November 2012 was relatively even: large accumulations and blooming were absent. Its biomass varied from 9.1 to 70.3 mg/m^3 or from 1.0 to 44.5 mg C/m^3 (for the Middle and Southern Caspian Sea). Phytoplankton was dominated by diatoms *Chaetoceros peruvianus* (which often accumulated) and *Thalassionema nitzschioides*; green alga *Binuclearia lauterbornii* var. *lauterbornii*; and dinoflagellates *Prorocentrum micans, Prorocentrum cordatum*, and *Gonyaulax polygramma* [16]. Cells of all predominant species were filled with chromatophores. Under conditions of high sun light in summer, such cells were only seen to depths corresponding to the lower boundary of the seasonal thermocline, i.e., to the lower limit of photosynthetic available radiation. In autumn, when algae adapt to relatively low sun light, the specific mass of phytopigments in cells increases. Hence, the saturation of cells with chromatophores, participation of green algae (chlorophyll in their chromatophores dominates over other pigments) in the dominant complex, and detritus accumulation result in a rise in the integral chl *a* concentration in the surface water layer in autumn as compared to summer.

The studied samples taken in October–November 2012 were also distinguished by a large amount of microzooplankton (infusoria and nauplius) and detritus (fragments of mesozooplankton bodies (barbells, limbs of small crustaceans, etc.) and macrophytes).

In the intermediate and bottom layers, the distribution pattern of the chl *a* concentration in October 2012 corresponded to the summer patterns [7, 14].

In November 2008, the distribution pattern of chl *a* in the TQL of the Middle Caspian Sea was similar to that in October–November 2012, and its concentration varied from 1.3 to 4.3 μg/L. The phytoplankton community was usually dominated by diatoms (*Chaetoceros peruvianus*, *Thalassionema nitzschioides*, *Skeletonema costatum*, *Fragilaria* sp., etc.). Their biomass comprised up to 81% of the total biomass [16]. Dinoflagellates were dominated by *Prorocentrum micans*. The amount of zooflagellate *Ebria tripartita* was also increased.

The POC content in the surface (from 0–1 m deep) layer in August–September 2013 varied from 14.8% (station 1337) to 20.0% (station 1344) of the total concentration of SPM in the water layer over the shelf to a depth of 100 m in the Middle Caspian Sea. In water above the deep Derbent and Southern Caspian Depressions, this parameter for surface layers was similar (18.1 and 18.6%).

Over the shelf of the Apsheron Sill (shallow-water stations 1337 and 1338), the POC content in the surface layer was significantly lower (14.8 and 10.9%, respectively). It was the highest in the subsurface (18–36 m) layers and was allocated to the top boundary of the seasonal thermocline. In all other studied water columns, the POC content was the greatest in the 0–1 m layer and dropped irregularly with depth to the sea bottom (Fig. 2). For example, at stations 1326 and 1327 in the Derbent Depression and stations 1330 and 1331 in the Southern Caspian Depression, the POC content dropped to zero in some layers and increased in deeper water layers (stations 1326 and 1327), obviously as a result of lateral water movement. At other stations (1339 and 1331), POC was absent in deep water layers to the bottom surface. This kind of POC distribution pattern in the Caspian Sea was not seen in early summer [20].

In October 2012, the POC content in the TQL (0–40 m) varied from 21 to 47% and averaged to 34%. It should be mentioned that its vertical and spatial distribution patterns in that period were comparatively even in contrast to summer. This is confirmed by the above data of the microscopic study of phytoplankton.

In November 2008, the highest POC content (from 2.4 to 47%) in the Middle Caspian Sea was seen in the TQL [10]. These data obviously correspond to water of the Northern Caspian Sea transported by the constant lateral current along the western shore and by periodic eddies. In the deep water mass under the seasonal thermocline layer, the POC content usually dropped two or more times. Nevertheless, at station 14 in the Northern Depression (at the northeastern edge of the Derbent Depression), the POC content increased in

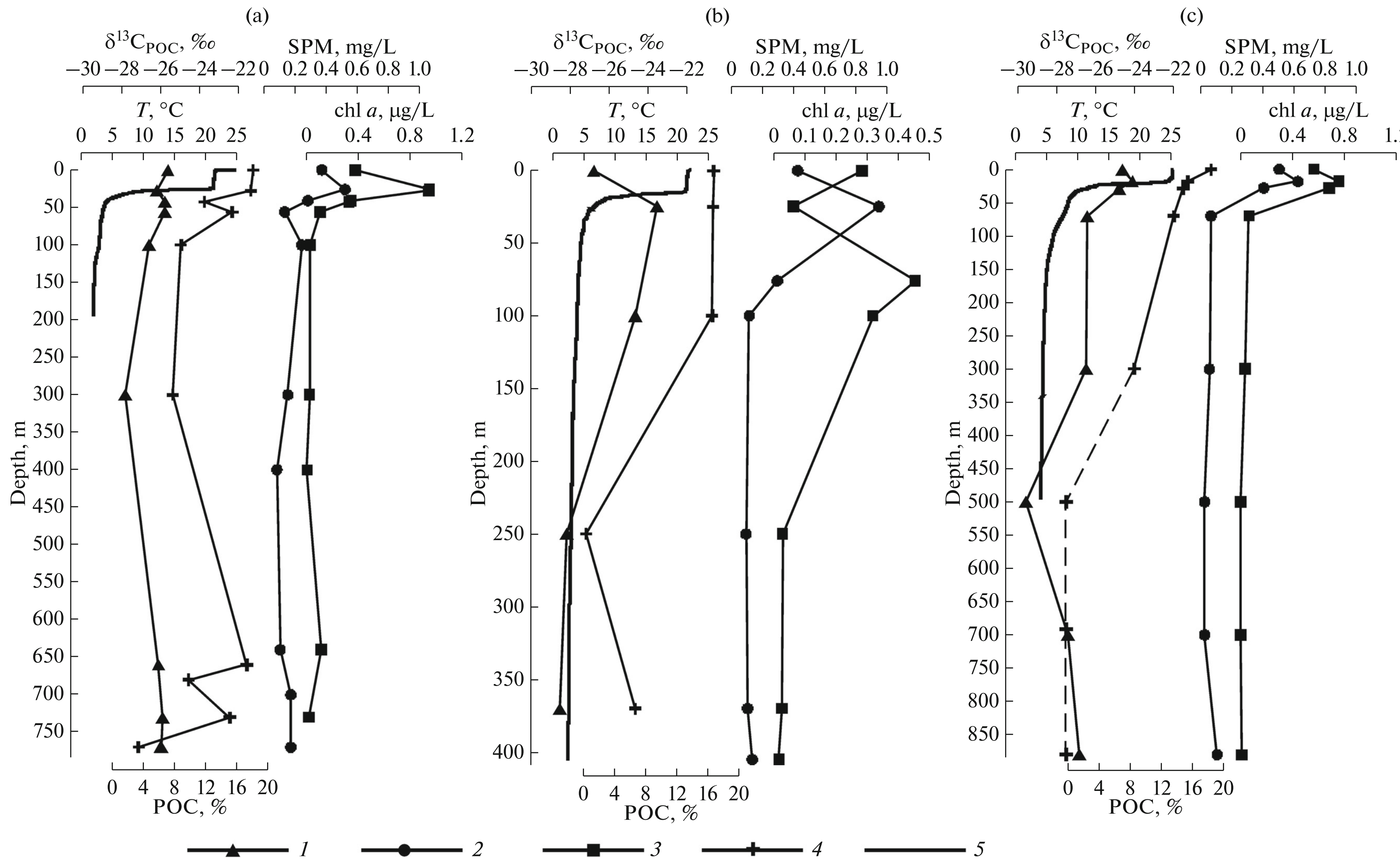
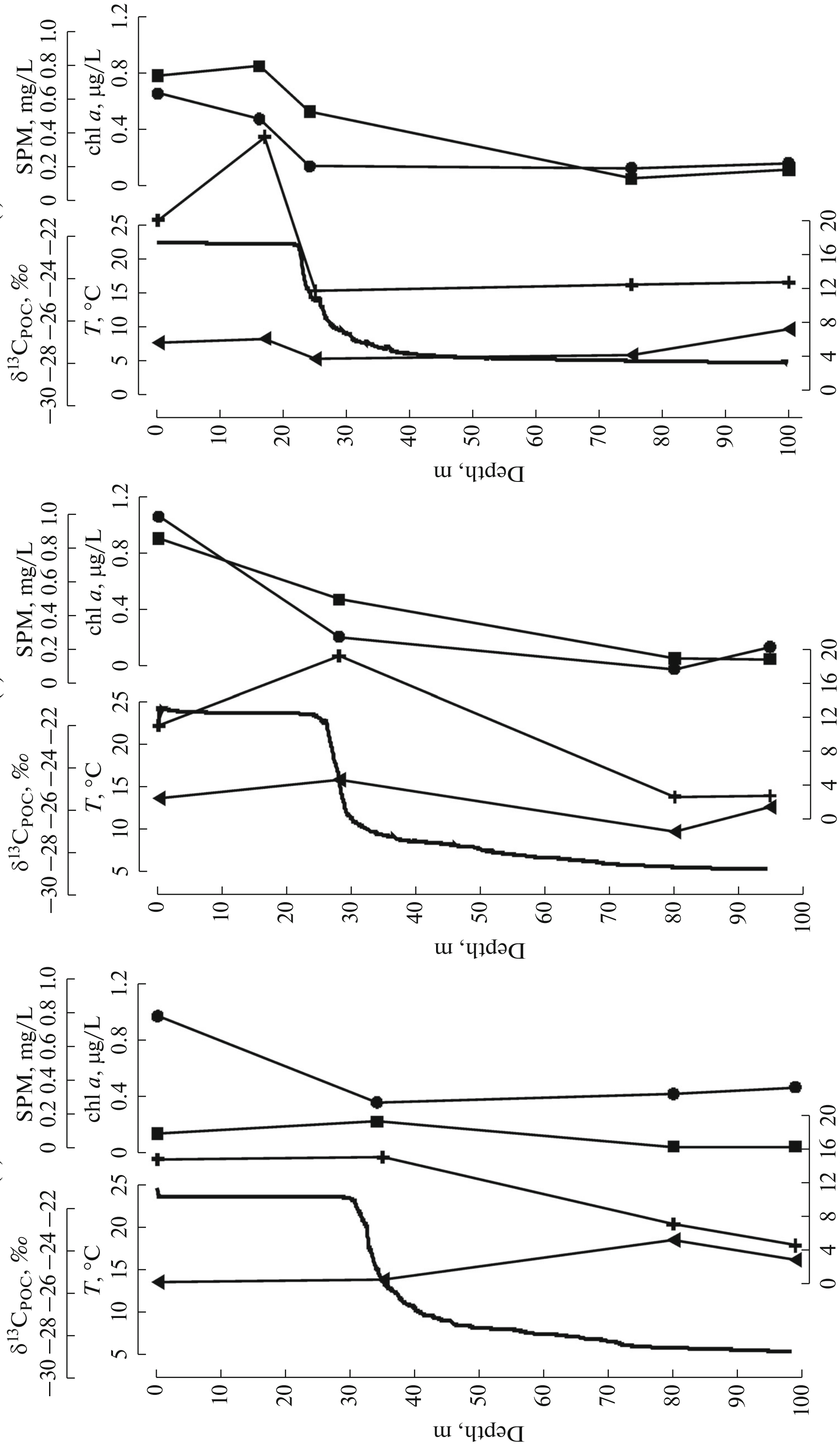


Fig. 2. (*1*) Vertical distribution of $\delta^{13}C_{POC}$, (*2*) concentration of SPM, (*3*) chl *a*, (*4*) POC content, and (*5*) temperature in water column of the Middle and Southern Caspian Sea in August–September 2013 (a–f) and in October–November 2012. (g–i): (a) station 1326, 41°50.11′ N and 50°05.93′ E, depth 788 m; (b) station 1327, 41°16.37′ N and 50°12.07′ E, 420 m; (c) station 1331, 38°18.80′ N and 50°46.43′ E, 890 m; (d) station 1337, 39°55.26′ N and 51°38.51′ E, 100 m; (e) station 1338, 40°16.46′ N and 51°42.47′ E, 100 m; (f) station 1344, 43°33.21′ N and 49°26.74′ E, 102 m; (g) station 4106, 41°32.58′ N and 50°34.62′ E, 690 m; (h) station 4113, 38°58.84′ N and 50°44.44′ E, 1005 m; (i) station 4118, 42°40.41′ N and 50°50.74′ E, 302 m. Locations of stations given in Fig. 1.



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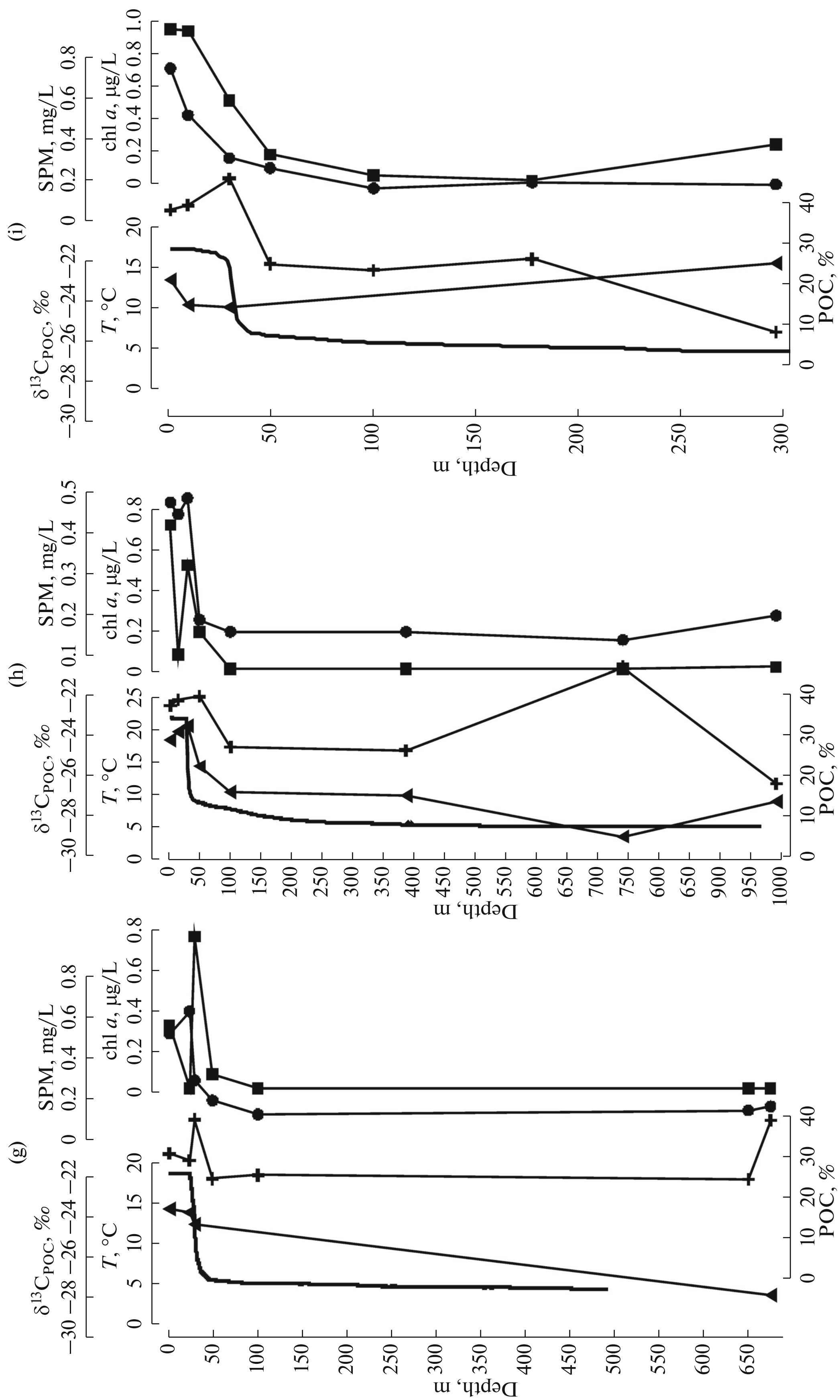

Fig. 2. (Contd.)

Table 2. Mean values and variation limits of $\delta^{13}C_{POC}$ in different seasons in top 0–40 m water layer of the Caspian Sea according to our new and previous data [7, 10, 11, 20]

Seasons	November 2008	June 2010	May–June 2012		October 2012		August–September 2013		
region	Middle	Middle	Middle	Southern	Middle	Southern	Northern	Middle	Southern
number of samples	6	11	17	5	8	5	2	10	6
$\delta^{13}C_{POC}$, ‰	–24.0... –21.8	–25.6... –20.9	–25.6... –23.0	–23.7... –23.0	–24.4... –23.0	–24.2... –23.8	–26.2... –25.7	–27.8... –23.5	–25.5... –20.5
	–22.8	–23.5	–24.34	–23.1	–23.8	–23.8	–26.0	–26.0	–24.1

the intermediate 120 m layer and then dropped towards the bottom. It can be assumed that lateral transport of matter is seen not only in the surface sea water, but also in deep layers [12]. It was already pointed out that the currents above the Caspian Sea depressions significantly differ in autumn [1].

Distribution of $\delta^{13}C_{POC}$. In June 2010, the surface (0–1 m) layer above the shallow-water shelf of the Caspian Sea was characterized by a correlation between $\delta^{13}C_{POC}$ and distance from the coast: in water over the shelf <50 m deep, part of the light-isotope POC mainly transported from land by rivers was the highest [11].

In May–June 2012, $\delta^{13}C_{POC}$ in water column of the Middle and Southern Caspian Sea varied from –29.9 to –21.9‰. Isotopes of $\delta^{13}C_{POC}$ were lighter in the Derbent Depression and at its northern edge in comparison with more southern water areas [7, 20].

In August–September 2013, $\delta^{13}C_{POC}$ in the surface (0–1 m) layers of the Middle and Northern Caspian Sea were similar (–25.9‰, n = 12, Table 2) and became heavier southward: to –25.1‰ at the Apsheron Sill (station 1337) and to –24.6‰ in the Southern Caspian Depression. The amount of light-isotope terrigenous component of SPM brought by large rivers to the Northern Caspian Sea dropped from north to south along the Trans-Caspian axial transect. In the Southern Caspian Basin, including the slopes of the Apsheron Sill, the POC isotopic composition was 1.5–3.0‰ heavier compared to the Northern Caspian Sea and northern part of the Middle Caspian Sea. A similar pattern was revealed for early summer [7, 20]. For example, in May–June 2012, the input of allochthonous OM by the Volga River and deficit of mineral forms of nutrients in the surface water layer, limiting the development of phytoplankton, resulted in a lighter isotopic composition of POC in the Derbent Depression and at its northern periphery than in the Southern Caspian Sea.

The content of terrigenous POC in the surface water layer of the Derbent Depression significantly dropped in August–September 2013 (–25.7‰). Terrigenous matter dominated in OM (–26.8‰) at its southern slope (station 1327 420 m deep) were obviously washed from the slope and/or input with the contour current. It can be assumed that the flows directed along the western coast and containing river SPM (from the Volga River and rivers of the Northern Caucasus) penetrate the southern water area of the Derbent Depression [1, 7, 12, 18]. The isotopic composition of POC became significantly heavier (by 3.3‰) at the top boundary of the seasonal thermocline (station 1327) in comparison with the subsurface layer. It was –23.5‰ in the 27 m layer, which corresponded to the accumulation area of warm-water phytoplankton.

Hence,–27‰ (station 1344) may be taken as the reference point of terrigenous OM in the Caspian Sea in late summer, and –20.5‰ (shallow-water station 1334 on the shelf near Ogurchinskii Island) may be considered a reference point of planktonogenic OM. The latter is heavier than the reference point determined near the thermocline layer in the Southern Caspian Depression and in the upwelling zone in the Middle Caspian Sea in early summer 2012 ($\delta^{13}C_{POC}$ is from –21.9 to –22.4‰) [7, 20] characterized by accumulation of dinoflagellates and diatoms. Nevertheless it is similar to the parameter measured in the Derbent Depression in the seasonal thermocline layer (16 and 40 m layers, station 1003, sea depth of 749 m) in June 2010 ($\delta^{13}C_{POC}$ = –20.9‰), when the blooming of dinoflagellates was seen [11, 15]. Large accumulations of phytoplankton were often revealed in the seasonal thermocline layer in summer.

The distribution pattern of $\delta^{13}C_{POC}$ in water columns of the Middle Caspian Sea in August–September was rather even. In the 0–1 m layer, OM was enriched with isotope-light terrigenous C_{org} (from –27.8 to –27.6‰). In the thermocline layer, the portion of planktonogenic OM became slightly greater, which corresponded to the vertical distribution pattern of phytoplankton.

In the surface water layer of the Derbent Depression, $\delta^{13}C_{POC}$ varied slightly to the 60 m layer (from –25.7 to –28.0‰). With the decrease in POC content at a depth of 100–400 m, the share of terrigenous material in OM rose ($\delta^{13}C_{POC}$ was from –26.0 to –27.9‰). At the 660 m layer, near the top boundary of hydrogen sulfide contamination, the C_{org} content obviously increased due to the death of aerobic organisms, and OM was still dominated by terrigenous C_{org} with $\delta^{13}C_{POC}$ from –25.9 to –26.1‰.

The maximal OM content in the Southern Caspian Depression in August–September 2013 was seen in the surface 30 m water layer (POC = 15.0–18.6%), where the isotopic composition of POC was heavier (from –24.1 to –24.8‰) and enrichment in autochthonous matter was greater than in the Derbent Depression.

In the anaerobic conditions of deep-water depressions, the concentration of SPM was usually small and the POC content dropped to traces (Table 2, Fig. 2). For example, in the anaerobic water layer with hydrogen sulfide and methane (at a depth greater than 660 m), $\delta^{13}C_{POC}$ varied from –26 to –29‰. This isotopic composition of SPM can be explained by biogeochemical processes [20] or it may be a laboratory artifact related to the low C_{org} content in samples, which decreases the measurement accuracy. Further researches of the isotopic carbon composition in deep-water layers will obviously lead to a definite conclusion.

Hence, in late summer, the highest POC contents in the top water layers, including the thermocline, coincided with the maxima of POC with a heavier isotopic composition as a result of the corresponding phytoplankton distribution.

In October 2012, $\delta^{13}C_{POC}$ in the surface water layer and in the thermocline above the Derbent Depression varied from –23.0 to –23.8‰ (stations 4118, 4106, and 4107), which testifies to the dominance of planktonic OM. The isotopic composition here in October was heavier than in summer, which was mainly related to abundant detritus and microzooplankton in the TQL. For example, in May–June 2012, $\delta^{13}C_{POC}$ in the surface (0–1 m) water layer was –25.7‰ in the Middle and –23.2‰ in the Southern Caspian Sea. In early summer, the content of planktonogenic POC in the zone of the seasonal thermocline of the Middle Caspian Sea was greater compared to the surface layer ($\delta^{13}C$ = –24.5‰, n = 9), and POC in the TQL in the Southern Caspian Sea remained mainly planktonogenic ($\delta^{13}C_{POC}$ = –23.0‰, n = 4). This isotopic composition completely reflected the distribution pattern of phytoplankton in that season.

In autumn, the content of terrigenous POC in the top 22 m water layer over the shelf near the Apsheron Sill (station 4109) was higher (–24.2‰, n = 3, Fig. 2) compared to the Middle Caspian Sea (–23.8‰, Table 2). This $\delta^{13}C_{POC}$ value (–24.2‰) was also typical of the surface (0–1 m) layer at station 4113 in the Southern Caspian Depression. In deeper water, towards the seasonal thermocline, the isotopic composition of POC became heavier (to –23.5‰ in the 30 m layer), which was obviously related to a greater share of detritus in SPM. In the surface and thermocline layers, it was dominated by autochthonous OM characterized by $\delta^{13}C_{POC}$ = –23.8‰ at the eastern slope of the depression (station 4115, Fig. 2) and became maximal (–20.5‰) at the eastern shelf of the Southern Caspian Sea (station 1334).

The data show that in October–November 2012, when the share of terrigenous OM in SPM in rivers was significantly lower when compared to the flood period (May) and the abundance of detritus and microzooplankton in river and sea SPM was strongly higher, the values of $\delta^{13}C_{POC}$ in the TQL of the Middle and Southern Caspian Sea were similar, and the isotopic composition of SPM was heavier than in summer (Table 2). Seasonal variations in POC composition were obviously determined by phytoplankton blooming, the intensity of mixing of the top water layer by wind, and the amount of input terrigenous OM. In autumn, the isotopic composition of POC became similar to that of C_{org} of plankton.

In November 2008, OM in the Middle Caspian Sea was mainly planktonogenic (to –21.8‰ [10]); i.e., $\delta^{13}C_{POC}$ was close to that in October–November 2012 (Table 2). It may be assumed that the composition of SPM becomes more even as a result of water mixing by wind in autumn. The mean data on $\delta^{13}C_{POC}$ in the TQL pointed to the dominance of planktonogenic particulate OM.

So, $\delta^{13}C_{POC}$ of the Caspian Sea in summer and autumn varied from –27.8 to –20.5‰ and was related to the participation of terrigenous OM of light isotopic composition and autochthonous OM of heavy isotopic composition (enriched in ^{13}C isotope) in SPM. The interval of $\delta^{13}C_{POC}$ from –22 to –20‰ mainly corresponded to the isotopic composition of POC of sea plankton (autochthonous OM), while $\delta^{13}C_{POC}$ from –27.8 to –26‰ was corresponded to POC brought in by the Volga River. The difficulties in specifying the isotopic composition of allochthonous and autochthonous POC are related to the fact that the greatest share of SPM in the Volga River is formed by freshwater phytoplankton (diatoms, cyanobacteria, green algae, etc.) and their detritus [8]. Similar freshwater algae species are widespread in the Northern Caspian Sea. Their isotopic composition is similar to that of sea phytoplankton in the Middle and Southern Caspian basins.

CONCLUSIONS

We have studied the genesis of SPM in water column of the Caspian Sea in different seasons: early and late summer and autumn. The values $\delta^{13}C_{POC}$ = –27‰ and $\delta^{13}C_{POC}$ = –20.5‰ have been taken as the reference points of terrigenous and planktonogenic OM, respectively. The seasonal variations in the composition of SPM in the top (~0–40 m) water layer of the Middle and Southern Caspian Sea have been revealed. The POC composition reflects the specific features of these changes.

In all the studied seasons, the isotopic composition of POC in the Northern Caspian Sea was usually light and the distributions of the SPM and chl *a* concentrations were in-phase.

In summer, the share of the particulate terrigenous matter with a light isotopic composition brought to the Northern Caspian Sea by large rivers dropped from north to south along the Trans-Caspian axial transect. For example, the isotopic composition of POC was 1.5–3.0‰ heavier in the Southern than in the Northern Caspian Sea. In the Middle Caspian Sea, the abundant phytoplankton (blooming), representing autochthonous OM of heavy isotopic composition, was allocated to the thermocline layer. The leading factors of formation of SPM were changed from May till September.

In early summer, POC of the Middle Caspian Sea included phytoplanktonogenic OM (mainly represented by the cold-water community composed of the remainders of the winter–spring bloomimg) and terrigenous OM (brought in by rivers during the spring–summer floods). In the Southern Caspian Sea, the share of terrigenous OM in SPM in that period was considerably lower than that of phytoplanktonogenic OM, because smaller amounts of riverine particles reached it. For example, the isotopic composition of POC in the Derbent Depression was lighter compared to water areas south of it.

In late summer (August–September), SPM of the open sea was dominated by terrigenous POC, while planktonogenic matter had already been consumed by microorganisms and had partially sunk to deeper water layers [20]. The bloom of the warm-water phytoplankton community in the Middle and Southern Caspian Sea was seen at a depth of the seasonal thermocline layer and was allocated to seasonal upwelling near the eastern coast or to mesoscale eddies [14].

In autumn (October–November), in the period of strong storms, the top water layers were mixed and the concentration and isotopic composition of POC in the Middle and Southern Caspian Sea became leveled ($\delta^{13}C_{POC} = -23.8$‰ and $\delta^{13}C_{POC} = -23.8$‰, respectively). The OM that had earlier sunk to deeper water layers was able to rise to the 0–40 m layer. It was revealed that POC was deposited in the TQL in autumn. It mainly accumulated in biogenic OM formed by microzooplankton, phytoplankton, and detritus (remains of summer blooms and fragments of macrophytes and bodies of mesoplankton). The sinking of POC that accumulated in the TQL was obviously prevented by the seasonal thermo- and pycnocline. In October–November, the distribution of phytoplankton in the TQL was rather even and mass accumulations and blooms were absent. Nevertheless, the saturation of cells with chromatophores (adaptation to relatively low sun light), participation of green algae in the dominant algae composition, and detritus accumulation in the TQL favored a rise in the integral chl *a* concentration in autumn compared to summer.

This was a specific phenomenon, when the isotopic composition of particulate OM became heavier in autumn, in the period of a smaller phytoplankton bloom, in comparison with summer, when mass accumulations and extraordinary phytoplankton blooms were seen in the thermocline layer. This phenomenon is typical of the Middle and, obviously, Southern Caspian Sea (the latter requires more actual data).

The conclusions about seasonal variations in POC composition in the ~0–40 m water layer require further research and confirmation based on other biogeochemical proxies.

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