# EXPERIMENTAL AND FIELD RESEARCH

# BUDGET AND FLUXES OF PARTICULATE ORGANIC CARBON AND NITROGEN ACCORDING TO THE DATA ON THEIR VERTICAL DISTRIBUTION IN THE DEEP PART OF THE BLACK SEA

## Z. P. Burlakova, L. V. Eremeeva, and S. K. Konovalov

UDC 551.464 (262.5)

On the basis of the analysis of the many-year data on the vertical distributions of particulate organic carbon and nitrogen, we compute their annual average amounts for three typical layers of water in the deep part of the Black Sea: for a layer located above the oxycline and characterized by the formation of new portions of particulate organic matter in the course of photosynthesis, inside the oxycline, where the major part of oxygen is consumed and the major part of the flux of particulate organic matter is oxidized, and for the upper part of the anoxic zone characterized by the most active microbiological processes of oxidation of the organic substances and production of sulfides. The available literature data on sedimentation traps are used to study the downward annual average fluxes of particulate organic matter from the euphotic zone into the oxycline and into the anaerobic zone. The seasonal variability of the amounts and fluxes of particulate carbon and nitrogen is revealed.

The investigation of the vertical distribution of particulate organic matter (POM) is required for the quantitative evaluation of the fluxes of organic matter and the analysis of circulation of basic biogenic elements because "the organic matter and all processes affecting its transformations in the sea are the principal factors determining the distinctive features of the chemical composition of waters in the Black Sea" [1].

The vertical distribution of POM was studied in [2–5]. However, all these investigations (except [5]) were carried out inside the aerobic zone, devoted to the analysis only of particulate organic carbon, and irregular. Note that, at present, the processes of transformation of the POM in the zones of interaction of aerobic and anaerobic waters are studied quite poorly. At the same time, these processes strongly affect the vertical distribution of the surface productive layer. Hence, the data accumulated in analyzing these processes can serve as a basis for the description and numerical simulation of the biogeochemical cycles of the most important biogenic elements (e.g., of nitrogen).

The aim of the present work is to give a quantitative description of the seasonal variability of the amounts of  $C_{POM}$  and  $N_{POM}$  for the following three typical vertical layers:

- the layer of water located above the oxycline, where the process of photosynthesis is realized;
- the layer of oxycline, where the major part of oxygen is consumed and the major part of the flux of POM is oxidized;
- the upper part of the hydrogen-sulfide zone (up to  $\sigma_t = 16.5$ ), characterized by the most active microbiological processes of oxidation of the organic substances and production of sulfides.

Marine Hydrophysical Institute, Ukrainian Academy of Sciences, Sevastopol. Translated from Morskoi Gidrofizicheskii Zhurnal, No. 3, pp. 34–49, May–June, 2003. Original article submitted January 18, 2002; revision submitted April 11, 2002.

We also present estimates of the fluxes of POM  $(C_{POM} \text{ and } N_{POM})$  from the euphotic zone into the oxycline and into the anaerobic zone.

#### **Results and Discussion**

Regular investigations of the POM in the Black Sea were carried out within the period since December 1987 till April 1994. A detailed description of the procedures of sampling and evaluation of the amounts of particulate organic carbon and nitrogen in the aerobic zone can be found in [6]. To obtain more correct estimates of the amount of POM and eliminate the influence of elemental sulfur in samples of water from the suboxic and hydrogen-sulfide zones, we took samples in the atmosphere of argon. The accuracy of evaluation of  $C_{POM}$  was equal to 1% and the accuracy of evaluation of N<sub>POM</sub> to 0.3%. As a result, we constructed (for the first time) the detailed vertical profiles and maps of the space distribution of the elements of POM (carbon, nitrogen, and phosphorus) for different seasons and parts of the sea. These results were partially published in [6, 7].

To calculate the amounts of  $C_{POM}$  and  $N_{POM}$  in different vertical layers and find their fluxes, we use the detailed vertical profiles obtained for these elements at 52 stations performed in the course of nine cruises for different seasons, mainly in the west and central parts of the abyssal zone of the Black Sea. Moreover, to determine the ratio of intensities of the production and destruction processes, we use the so-called carbon-to-nitrogen ratio (C:N) in POM. On the average, this quantity is equal to 106:16 (6.7) for newly formed particulate organic substances and increases in the course of destruction processes.

In Table 1, we summarize the data on the amounts of C<sub>POM</sub> and N<sub>POM</sub> obtained as a result of averaging of the *in-situ* data on the amounts of these elements in 5–20-m-thick layers for the groups of stations corresponding to each season and region of investigations (cyclonic circulation and periphery). In all seasons, the boundary of the oxycline was recorded, as a rule, at depths of 30–45 m and specific densities  $\sigma_t = 14.3-15.0$  inside the cyclonic circulation and at depths of 50–80 m for  $\sigma_t = 14.3-14.7$  in the peripheral regions. The boundary of the H<sub>2</sub>S-zone was located at depths of 75–100 m ( $\sigma_t = 16.0-16.2$ ) inside the cyclonic circulation and at depths of 120–160 m ( $\sigma_t = 16.0-16.28$ ) in the peripheral regions.

*Winter.* The investigations of the distribution of POM were carried out in the first half of January 1988 and covered the entire region of the west cyclonic circulation. The hydrological and weather conditions at the beginning of this winter (1987–1988) were especially favorable for the development of convection in the surface layer of waters in the central part of the sea [8]. The average amounts of  $C_{POM}$  and  $N_{POM}$  above the oxycline were equal to  $382.4 \pm 94$  mg-atom C/m<sup>2</sup> and  $44.4 \pm 11$  mg-atom N/m<sup>2</sup>, respectively The behavior of these quantities can be explained by the space and time variations of the rate of formation of new POM in the euphotic layer. The measured values of the rate of formation of new POM varied from 402 to  $610 \text{ mgC/(m^2 \cdot day)}$  at different stations [9].

In winter, intense hydrodynamic processes restrict, as a rule, the accumulation of POM (both living and dead) in the layer located above the oxycline. The computed value of the ratio C : N in the POM averaged over this layer was equal to  $8.9 \pm 2.3$ , which means that the processes of destruction of the POM in low-temperature water are weak.

The average amounts of  $C_{POM}$  and  $N_{POM}$  inside the oxycline were equal to 220.5 ± 82.6 mg-atom C/m<sup>2</sup> and 27.2 ± 10.4 mg-atom N/m<sup>2</sup>, respectively, and the ratio C : N for this layer was equal to 8.2 ± 1.8. Below the boundary of the H<sub>2</sub>S-zone, the average amounts of C<sub>POM</sub> and N<sub>POM</sub> were equal to 76.8 ± 12.3 mg-atom C/m<sup>2</sup> and 11.0 ± 1.2 mg-atom N/m<sup>2</sup>, respectively, and the ratio C : N was equal to 7.0 ± 1.2.

	of the	C:N	11		7.7	I	7.6	5.2	7.7	I	Ι	I	I	I	I	I	Ι	7.0	1.2	
	boundary $\sigma_t = 16.5$																			
ea	below the upper H <sub>2</sub> S zone up to	Z	10		12	Ι	10	12	10	Ι	Ι	Ι	I	I	I	Ι	Ι	11.0	1.2	
f the Black S	Layer below the upper boundary of the $H_2S$ zone up to $\sigma_t = 16.5$	С	6		92	I	76	62	LL	I	I	Ι	I	Ι	I	I	I	76.8	12.3	
eep Part of		C:N	8	Ş	7.4	8.0	7.9	5.6	7.0	7.4	13.0	9.3	8.9	8.3	T.T	6.8	9.1	8.2	1.8	
m <sup>2</sup> ) in the D	Oxycline	N	7	itskii, Cruise 2:	43	39	17	14	24	22	20	17	23	24	28	44	39	27.2	10.4	sov, Cruise 49
of $C_{POM}$ and $N_{POM}$ (mg-atom/m^2) in the Deep Part of the Black Sea		С	6	January 1988, R/V Professor Vodyanitskii, Cruise 25 Cyclonic circulation	320	312	134	79	169	163	260	158	204	200	215	299	354	220.5	82.6	March 1988, R/V Mikhail Lomonosov, Cruise 49 Cyclonic circulation
M and NPO	e the oxycline	C:N	5	y 1988, R/V <i>P</i> i Cycle	9.4	10.5	7.8	5.6	8.4	7.4	12.6	11.1	11.0	7.8	4.5	9.4	10.4	8.9	2.3	ch 1988, R/V A Cyclo
ints of C <sub>PC</sub>	Layer above the o	Ν	4	Januar	31	27	45	67	38	43	39	45	41	59	53	38	51	44.4	11.0	Mar
Table 1. Amounts o	Laye	С	3		290	284	351	376	320	318	492	499	451	462	241	357	530	382.4	94.1	
Tal	Coordinates	(IN, E)	2		42°31′, 30°00′	43°20′, 32°30′	44°00′, 31°39′	44°30′, 31°40′	42°30′, 31°40′	43°15′, 34°11′	43°20′, 31°30′	43°00′, 30°01′	43°30′, 31°42′	43°30′, 33°20′	44°00′, 35°20′	42°00′, 31°40′	42°00′, 31°40′			
	No.	OI STAUON	1		3622	3654	3671	3678	3624	3652	3655	3657	3662	3664	3667	3617	3620	Average	Standard deviation	

## BUDGET AND FLUXES OF PARTICULATE ORGANIC CARBON AND NITROGEN

159

I

I

I

8.1

69

558

8.9

74

655

43°30', 32°15'

5783

11	I	I	I	I	I				I	I	Ι				8.3	8.9	5.2	4.9	6.8
10	I	Ι	I	Ι	I				I	Ι	I				63	37	62	82	61.0
6	I	Ι	Ι	I	Ι				I	Ι	Ι				523	329	322	405	3048
∞	6.3	5.5	9.8	7.8	8.0	7.6	1.5		11.5	11.1	8.1	10.2	1.9	Cruise 18	8.9	8.5	5.5	6.5	ΥL
7	58	61	37	47	43	52.5	12.1	the sea	39	45	35	39.7	5.0	or Kolesnikov,	40	50	85	88	62 0
9	367	333	364	367	344	389.8	84.0	Periphery of the deep part of the sea	447	498	282	409.0	112.9	April 1988, after a mild winter, R/V <i>Professor Kolesnikov</i> , Cruise 18 Cyclonic circulation	354	425	471	576	7565
5	7.2	6.2	9.4	6.7	9.0	7.9	1.4	Periphery of	8.7	13.5	7.1	9.8	3.3	ter a mild win Cyc	15.2	11.4	12.4	4.8	11.0
4	102	124	88	126	86	100.0	21.3		80	45	127	84.0	41.1	April 1988, af	21	42	41	09	11.0
3	732	0LL	827	848	775	767.8	69.3		969	609	906	737.0	152.7		320	480	508	290	300 5
2	43°30′, 32°45′	43°30', 33°15'	43°30′, 33°45′	43°30′, 34°15′	43°15′, 33°15′				43°30′, 31°15′	43°30′, 30°45′	43°30′, 31°45′				43°30′, 33°00′	43°30′, 32°00′	43°30′, 31°00′	42°20′, 30°00′	
1	5784	5785	5786	5787	5834	Average	Standard deviation		5806	5807	5782	Average	Standard deviation		3236	3238	3240	3317	Average

160

Table 1 (continued)	8 9 10 11	.3 1.6 93.4 18.5 2.1		7.0 96 15	6.4 220 19 1	5.7 123 19			.4 6.8 180.5 23.5 7.8	.2 0.7 86.6 11.8 2.5	June 1989, after a mild winter, R/V <i>Professor Vodyanitskii</i> , Cruise 28 Cyclonic circulation		2 7.7 108 19 5.7		10.1 192 9 2	9 4.6 51 10 5.1	0.0 6.6 118.2 16.2 8.7	
L				15	19	19	I	41				25	19	18	0,	10		1
	6	93.		96	220	123	Ι	283	180.	86.		117	108	123	192	51	118.	
	∞	1.6		7.0	6.4	5.7	7.6	7.1	6.8	0.7	i, Cruise 28	4.7	7.7	5.7	10.1	4.6	6.6	
	2	24.3	of the sea	91	98	88	158	187	124.4	45.2	or Vodyanitski n	43	42	22	14	29	30.0	
	9	93.1	Periphery of the deep part of the sea	641	632	504	1201	1330	861.6	375.4	vinter, R/V <i>Professor</i> Cyclonic circulation	203	323	126	142	133	185.4	
	S	4.4	Periphery of	7.9	8.5	6.0	7.8	6.7	7.4	1.0	ter a mild winte Cyc	6.7	5.6	6.5	8.4	6.0	6.6	
	4	15.9		55	59	102	54	135	81.0	36.2	June 1989, aff	47	54	53	45	76	55.0	
	3	110.4		435	499	608	423	902	573.4	197.8		314	304	343	376	455	358.4	
	2			43°30', 30°00'	44°00′, 31°00′	44°00′, 31°30′	44°16′, 30°57′	44°07′, 33°35′				41°30', 31°10'	41°50′, 30°36′	42°03′, 30°26′	42°10′, 30°18′	42°17′, 30°07′		
		Standard deviation		3242	3243	3376	3377	3397	Average	Standard deviation		4052	4054	4055	4056	4057	Average	Standard

## BUDGET AND FLUXES OF PARTICULATE ORGANIC CARBON AND NITROGEN

Table 1 (continued)	11		8.3				5.8		I	I	I	Ι				7.3	I	6.3	
$T_{2}$	10		36	45			12		I	Ι	I	Ι				8	I	15	
	6		300	348			70		I	Ι	Ι	Ι				58	I	95	Ĭ
	∞	w, Cruise 51	11.1	7.2	, Cruise 41	6.2	5.9	6.1	19.1	15.5	6.6	9.1	12.6	5.7		6.0	5.6	5.3	1
	L	hail Lomonosc	25	59	<i>r Vodyanitskii</i> Cruise 30	52	31	41.5	14	17	72	41	36.0	26.9	V Gidrooptik	39	35	48	
	6	November 1989, after a mild winter, R/V Mikhail Lomonosov, Cruise 51	277	422	April 1993, after a cold winter, R/V <i>Professor Vodyanitskii</i> , Cruise 41 and R/V <i>Professor Kolesnikov</i> , Cruise 30 Cyclonic circulation	323	182	252.5	268	264	472	374	344.5	99.1	May 1994, after a cold winter, R/V Gidrooptik	235	196	252	
	5	, after a mild v	9.1	5.6	er a cold wint and R/V <i>Profe</i> Cyc	8.5	5.2	6.9	9.1	7.0	9.9	7.0	8.2	1.5	ıy 1994, after a	6.2	6.1	4.8	
	4	ovember 1989	45	78	April 1993, aft	35	72	53.5	67	118	99	78	89.7	22.8	$M_{a}$	49	76	06	
	3	Ž	408	434	7	296	373	334.5	887	831	653	546	729.2	157.7		304	464	435	
	2		43°41′, 34°12′	42°07′, 37°49′		43°50′, 32°20′	43°30′, 32°20′		43°30′, 32°50′	43°30′, 33°20′	43°50′, 34°25′	43°50′, 36°25′				43°30′, 32°15′	44°10′, 32°15′	44°50′, 32°15′	
	-		6124	6115		5124	5125	Average	5126	5133	5558	5577	Average	Standard deviation		33	37	44	

162

2	3	4	5	9	7	8	6	10	11
	85.2	20.8	0.8	28.7	6.7	0.4	26.2	4.9	0.7
		July	y 1992, R/V <i>P</i> . Cy	July 1992, R/V Professor Vodyanitskii, Cruise 37 Cyclonic circulation	<i>tskii</i> , Cruise 37				
44°00′, 32°13′	13′ 543	67	8.1	324	40	8.1	I	I	I
43°37′, 32°15′	15' 1608	273	5.9	438	67	6.5	I	I	I
43°30′, 33°20′	20' 980	148	6.6	393	54	7.3	I	Ι	I
42°55′, 39°12′	12′ 906	210	4.3	292	53	5.5	I	I	I
	1009	174.5	6.2	362	53.5	6.9			
Standard deviation	442.5	88.0	1.6	66.0	11.0	1.1			
		Augu	ıst 1992, R/V	August 1992, R/V Professor Vodyanitskii, Cruise 38	<i>vitskii</i> , Cruise 3	8			
43°25′, 32°10′	10′ 621	54	11.5	446	42	10.7	158	18	8.8
		Annual avera	age amounts oi Cy	Annual average amounts of CpOM and NpOM after a warm winter Cyclonic circulation	om after a wai 1	rm winter			
	460.3	58.0	8.5	288.4	38.9	<i>T.T</i>	208.3	30.0	7.7
Standard deviation	176.0	26.2	2.6	128.0	19.7	1.9	149.6	23.5	4.0
Ar	Annual average amounts of		I and NPOM Cyv	CPOM and NPOM with regard for April after the cold winter and summer of 1992 Cyclonic circulation	pril after the co	old winter and	1 summer of 19	92	
Average	528.6	72.1	8.1	298.0	40.3	8.1	184.5	26.5	7.5
Standard deviation	261.3	47.3	2.5	117.9	18.6	2.9	141.4	21.9	3.6

*Transition from Winter to Spring (March).* The period of intense bloom of diatoms in the deep part of the sea is accompanied by a multifold increase in the amount of POM above the oxycline. Thus, on the average, the amounts of  $C_{POM}$  and  $N_{POM}$  in this layer were 768 ± 69 mg-atom C/m<sup>2</sup> and 100 ± 21.3 mg-atom N/m<sup>2</sup>, respectively, inside the cyclonic circulation, and the ratio C : N in the POM was equal to 7.9 ± 1.4. The indicated low value of C : N is explained by the fact that 74% of the POM belongs to plankton and the predominant role in its formation (67%) is played by phytoplankton [7]. Moreover, the conditions of supply of the population of phytoplankton with mineral nitrogen were optimal. In the peripheral regions characterized by the downwelling of waters, the amounts of the POM in the layer located above the oxycline were practically equal to the amounts attained inside the cyclonic circulation (737 ± 153 mg-atom C/m<sup>2</sup> and 84.0 ± 41 mg-atom N/m<sup>2</sup>). If the generally accepted hypothesis that the productivity of the peripheral regions in the deep part of the sea is correct, then the observed picture can appear as a result of the passive drift of the POM from the region of intense bloom of the algae into the zone of downwelling. In this case, the observed value of the ratio C : N (9.8 ± 3.3) can, most likely be explained by a bad physiological state of phytoplankton under the conditions of insufficient supply of biogenic elements and the onset of destructive fractionation of the POM.

Inside the cyclonic circulation, the average amounts of POM in the oxycline were equal to  $390 \pm 84$  mgatom C/m<sup>2</sup> and  $52.5 \pm 12.1$  mg-atom N/m<sup>2</sup>, i.e., about half as large as in the upper layer. The ratio C:N was practically equal to its value in the upper layer (7.6 ± 1.5). In the zone of downwelling, the amounts of POM in the oxycline were also about half as large as in the upper layer. The ratio C:N was equal to  $10 \pm 1.9$ , which means that the POM undergoes intense mineralization.

It is worth noting that the distribution of POM and its relative chemical composition in April and May strongly depend on the weather conditions of the preceding winter. Thus, after a mild winter, e.g., in 1987–1988, the rate of formation of new POM decreased under the conditions of a relatively small supply of biogenic substances (formed as a result of weakening of the dynamic activity of waters and early formation of the seasonal thermocline). The average amounts of  $C_{POM}$  and  $N_{POM}$  in the west cyclonic circulation above the oxycline became half as large as in March and equal to  $400 \pm 110$  mg-atom  $C/m^2$  and  $41 \pm 16$  mg-atom  $N/m^2$ , respectively. The value of the ratio C : N in the particulate organic matter was relatively large  $(11 \pm 4.0)$ . This is explained by the degradation of the diatomaceous complex of phytoplankton and the accumulation of detritus above the seasonal thermocline. In this period, the living fraction of POM was as large as 14% of the average amount of  $C_{POM}$  in the zone of photosynthesis [7]. Note that, in the peripheral regions (over the drop of depths), the amounts of  $C_{POM}$  and  $N_{POM}$  in the layer located above the oxycline were larger and equal to  $573.4 \pm 197.8$  mg-atom  $C/m^2$  and  $81 \pm 36.2$  mg-atom  $N/m^2$ , respectively. On the contrary, the value of the ratio C : N was lower than inside the cyclonic circulation ( $7.4 \pm 1$ ). This can be explained by the onset of the intense development of phytoplankton in the shelf zone and the appearance of newly formed POM in the region of the drop of depths [7].

In this period, the amounts of  $C_{POM}$  and  $N_{POM}$  in the oxycline were somewhat larger than in the upper layer and equal to  $456 \pm 93$  mg-atom C/m<sup>2</sup> and  $65.8 \pm 24$  mg-atom N/m<sup>2</sup>, respectively. The ratio C:N averaged over this layer was equal to  $7.4 \pm 1.6$ . This can be explained by the accumulation of the POM caused by the growth of the biomass of diatoms appearing under the pycnocline in the course of the early-spring bloom. Thus, according to [10], only 4–8% of the total amount of cells of big diatoms were concentrated in this part of the biotope at the beginning of March. At the same time, in mid-April (in the course of our investigations), this parameter became as large as 37-56%. Moreover, this period is characterized by the formation of the maximum number of low-temperature diatoms of *Nitzschia* in the upper part of the oxycline [11]. In its lower part, where the content of oxygen decreases to 0.55-0.22 ml/liter ( $25-10\mu$ M), we observe the formation of dense accumulations of mesozooplankton. Note that the maximum concentrations of the bacterial plankton and protozoa are practically always connected with these accumulations in late spring [12, 13]. Moreover, the accumulation of organic substances can sometimes occur in this layer as a result of bacterial photosynthesis [14]. In the peripheral regions (in the zone of downwelling), large amounts of the POM ( $861.6 \pm 375.4$  mg-atom C/m<sup>2</sup> and  $124.4 \pm 45.2$  mg-atom N/m<sup>2</sup>) and low values of C : N ( $6.8 \pm 0.7$ ) detected in the oxycline can, most likely, be explained by the drift and sinking of the fresh detritus from the shelf zone.

Note that, inside the cyclonic circulation, the maximum (in the annual cycle) amounts of  $C_{POM}$  and  $N_{POM}$  in the upper layer of the anaerobic zone (395 ± 93 mg-atom C/m<sup>2</sup> and 61.0 ± 18.5 mg-atom N/m<sup>2</sup>) were detected in April after a mild winter of 1987–1988. The average value of the ratio C : N for this layer was equal to  $6.8 \pm 2.1$ . The observed changes in the composition and morphological characteristics of the POM can serve as a possible explanation of the seasonal and annual variability of the maximum values in the vertical distributions of particulate organic carbon and nitrogen. Thus, the diatomaceous detritus with high-density silicon frustules 0.008-1 mm in size precipitates with a velocity of up to 280 m/day. This observation is confirmed by the maximum fluxes of carbon and nitrogen from the surface layer into the oxycline and from the oxycline into the anaerobic zone typical of the analyzed period (see Table 2). At the same time, it may happen that the growth of the mass of bacteria as a result of chemosynthesis (which decreases the observed value of the ratio C : N) is an additional important source of the POM in the upper part of the anaerobic zone. For the period of our investigations, the intensity of chemosynthesis in this layer (averaged over four stations) was equal to 240 mg C/m<sup>2</sup> per day [15], i.e., about a half of the primary production recorded in this part of the sea.

*Summer*. In summer, the process of formation of the seasonal thermocline and the corresponding zone of high-density gradients plays the role of the principal factor determining the distribution of POM. In the southwest part of the cyclonic circulation, the amounts of  $C_{POM}$  and  $N_{POM}$  above the oxycline in summer 1989 (after a mild winter) were as follows:  $358.4 \pm 61.0 \text{ mg-atom C/m}^2$  and  $55.0 \pm 12.0 \text{ mg-atom N/m}^2$ . The ratio C : N was equal to  $6.6 \pm 1$ . The indicated relatively low values of the quantities  $C_{POM}$  and  $N_{POM}$  and the ratio C : N can probably be explained by the predominance of small-celled peridial and yellow-green algae at that time [17].

In the oxycline, the amounts of  $C_{POM}$  and  $N_{POM}$  were about half as large as in the upper layer and equal to  $185.4 \pm 82.8 \text{ mg-atom C/m}^2$  and  $30 \pm 12.6 \text{ mg-atom N/m}^2$ , respectively. The ratio C:N was equal to  $6.6 \pm 2.3$ . The indicated low values of C:N can possibly be explained by the fact that the main mass of the POM is formed in the upper part of the oxycline by the biomass of eukaryotic picoalgae and cyanobacteria [18]. The latter are characterized by low values of the ratio C:N because the fraction of protein in these algae is higher than in algae of other groups. In the lower part of the oxycline, rich bacterial plankton develops in this period within the limits of the suboxide zone due to the presence of organic substances produced by meso- and microzooplankton.

In the layer located below the boundary of the H<sub>2</sub>S-zone, the amounts of  $C_{POM}$  and  $N_{POM}$  were equal to 118.2 ± 50.2 mg-atom C/m<sup>2</sup> and 16.2 ± 6.7 mg-atom N/m<sup>2</sup>, respectively. The ratio C : N was equal to 8.7 ± 7.1. The decrease in the amounts of  $C_{POM}$  and  $N_{POM}$  in June as compared with spring can be explained by the lowest, in the seasonal cycle, intensity of chemosynthesis in summer [15].

Autumn. In this period, we computed the amounts of POM for two stations made in the central part and in the peripheral regions of the southeast part of the sea. We believe that the principal physical factors determining the vertical distribution of POM in autumn are the destruction of the seasonal thermocline and the decreasing stability of waters. As a result, the POM is intensely transported into deeper layers of water. In the central part of the sea, the ratio C:N in the POM varied from 9.1 in the layer located above the oxycline to 11.1 inside the oxycline, which means that the POM inside the oxycline is highly mineralized.

The increase in the amounts of both components of the suspension in the upper part of the anaerobic zone by about a factor of 2.5 as compared with summer can, most likely, be explained by the seasonal maximum in the intensity of chemosynthesis recorded in autumn in a layer located below the boundary of the H<sub>2</sub>S-zone by 20–30 m [15]. As an additional source of POM in this zone, one can mention the inflow of fresh detritus from

the layer of accumulation of zooplankton in the lower part of the oxycline. The ratio C:N was, in this case, equal to 8.3. In the peripheral regions, the values of the ratio C:N varied from 5.6 above the oxycline to 7.2 inside the oxycline and 7.7 below the boundary of the H<sub>2</sub>S-zone.

After cold winter (April 1993). The amounts of POM and their distribution between the layers were close to those observed in winter. The average amounts of POM were 334.5 mg-atom  $C/m^2$  and 53.5 mg-atom  $N/m^2$  above the oxycline, 252.5 mg-atom  $C/m^2$  and 41.5 mg-atom  $N/m^2$  inside the oxycline, and 70 mg-atom  $C/m^2$  and 12 mg-atom  $N/m^2$  below the boundary of the H<sub>2</sub>S-zone. The averaged values of the ratio C:N were equal to 6–7 for the entire water column.

At the stations made after the onset of the formation of seasonal thermocline, the amounts of POM in the layer lying above the oxycline were equal to  $792.2 \pm 158$  mg-atom C/m<sup>2</sup> and  $89.7 \pm 22.8$  mg-atom N/m<sup>2</sup>. The ratio C:N in the POM was equal to  $8.2 \pm 1.5$ . In these regions, the process of dying of big diatoms (up to 50% of cells are destroyed, the concentration of spores is high) [19] is accompanied by the intense development of smaller forms consuming mainly (76%) the regenerated form of mineral nitrogen (in particular, ammonium) [20].

It is worth noting that the amounts of POM above the oxycline in April 1993 (after cold winter) were 1.5-2 times larger than in April 1988 (after warm winter). This phenomenon can, most likely, be explained by different intensities of the process of winter convective ventilation of waters and, hence, different amounts of biogenic substances appearing in the euphotic layer. As a result, after cold winters, the rate of formation of new organic substances is higher [19].

The amounts of POM in the oxycline were equal to  $344.5 \pm 99 \text{ mg-atom C/m}^2$  and  $36.0 \pm 27 \text{ mg-atom N/m}^2$ . The ratio C : N was equal to  $12.6 \pm 5.7$ . The maximum values of this ratio (15.5-19.1) were recorded at the stations where the amount of nitrogen in the POM was close to the lower bound of detectability in the sub-oxic zone and below the boundary of the H<sub>2</sub>S-zone. This may happen either as a result of intense additional destruction of the POM coming from the surface layer in the upper part of the oxycline or in the case where the velocity of sedimentation of the POM of diatomaceous origin is high and, hence, it is not accumulated in the analyzed layer.

Late spring after cold winter (May 1994). The amounts of POM in the deep part of the sea were lower than in April and equal to  $401 \pm 85.2 \text{ mg-atom C/m}^2$  and  $71.7 \pm 20.8 \text{ mg-atom N/m}^2$  above the oxycline,  $227.7 \pm 28.7 \text{ mg-atom C/m}^2$  and  $41.0 \pm 6.7 \text{ mg-atom N/m}^2$  inside the oxycline, and  $76.5 \pm 26.2 \text{ mg-atom C/m}^2$  and  $11.5 \pm 4.9 \text{ mg-atom N/m}^2$  below the boundary of the H<sub>2</sub>S-zone. The values of the ratio C : N averaged over the layers were low (5.5–6.6). Note that the difference between the values of the ratio C : N inside the oxycline in May (5.6) and April (12.6) was quite large. This can be explained by the accumulation of *Nitzschia* diatoms in the cold intermediate layer (upper part of the oxycline). In late spring and at the beginning of summer, the biomass of these algae can be as large as several grams per cubic meter [11]. In this period, a layer characterized by the accumulation of mesozooplankton (and, hence, of bacterial plankton and cyanobacteria correlated with it) is formed in the lower part of the oxycline [21].

Some years are characterized by the appearance of local spots of blooming phytoplankton in the open sea in summer. In these cases, the difference between the values of its mass in neighboring areas may be quite large [17]. A situation of this sort was observed in July 1992. The amounts of POM above the oxycline were equal to  $1009.0 \pm 442.5$  mg-atom C/m<sup>2</sup> and  $174 \pm 88.0$  mg-atom N/m<sup>2</sup>. The ratio C : N was equal to  $6.2 \pm 1.6$ . Inside the oxycline, these quantities were equal to  $362 \pm 66$  mg-atom C/m<sup>2</sup>,  $53.5 \pm 11.0$  mg-atom N/m<sup>2</sup>, and  $6.9 \pm 1.1$ , respectively. The processes of subsequent degradation of bloom and destruction of POM strongly affected the vertical distributions of the particulate substances.

ns of $C_{POM}$ and $N_{POM}$ (mg-atom/m <sup>3</sup> ) on the Upper Boundaries of the Oxycline and the $ m H_2S$	$_{\rm I}$ and $~N_{\rm POM}~$ (mg-atom / (m^2 \cdot day)) for Different Seasons in the Deep Part of the Black Sea
Table 2. Average Concentrations of $C_{POM}$	Zone and the Fluxes of C <sub>POM</sub> and N <sub>POI</sub>

		Into	Into the oxycline	e			From the c	oxycline th	rough the be	oundary of t	From the oxycline through the boundary of the H <sub>2</sub> S zone	e	
Season	Upper boundary	CPc	CPOM	$N_{ m P}$	Npom		Upper boundary of the	CPOM	WC	Z	Npom		No. of st
	$\sigma_t$	mg-atom/ m <sup>3</sup>	mg-atom/ (m <sup>2</sup> ·day)	mg-atom/ m <sup>3</sup>	mg-atom/ (m <sup>2</sup> ·day)		$H_2S$ zone, $\sigma_t$	mg-atom/ m <sup>3</sup>	mg-atom/ (m <sup>2</sup> ·day)	mg-atom/ m <sup>3</sup>	mg-atom/ (m <sup>2</sup> ·day)		
January 1988	14.25–15.1	6.45	25.13	0.90	3.50	7.5	15.9–16.2	2.56	1.03	0.34	0.16	7.5	12
March 1988	14.4–15.02	14.62	57.0	2.04	7.97	7.3	16.1–16.24	5.08	2.03	0.70	0.28	7.2	9
April 1988	14.82–14.85	11.9	46.58	1.29	5.02	10.9	16.11–16.18	11.7	4.67	1.97	0.79	6.4	4
June 1989	14.33–14.61	5.55	21.64	1.10	3.56	5.9	16.07–16.22	2.71	1.08	0.42	0.17	8.7	9
November 1989	14.74	5.16	21.11	0.84	3.28	6.2	16.07	4.72	1.89	0.78	0.31	7.7	$\omega$
April-May 1993-1994	14.36-14.88	9.62	37.52	1.32	5.14	8.0	16.06–16.19	4.38	1.75	0.42	0.17	10.3	~
July– August 1992	14.3	12.94	50.50	1.51	5.9	8.7	16.1–16.14	3.97	1.59	0.63	0.25	7.0	$\mathfrak{c}$

Thus, for the analyzed period, the amounts of particulate organic carbon and nitrogen above the oxycline at the stations made in July and August became 2.6 and 5 times smaller, respectively. The ratio C:N increased from 6.0 in July to 11.5 in August.

In August, the amounts of POM in the oxycline were 446 mg-atom  $C/m^2$  and 42.0 mg-atom  $N/m^2$  and the ratio C:N was equal to 10.7. Below the boundary of the H<sub>2</sub>S-zone, these quantities were equal to 158.0 mg-atom  $C/m^2$ , 18.0 mg-atom  $N/m^2$ , and 8.8, respectively.

Thus, the vertical distributions of the POM in July 1992 (period of bloom) and June 1989 (no bloom) were similar but the absolute values recorded during the period of bloom were much higher.

The difference between the annual average amounts of POM for years with absolutely different weather conditions can actually be detected only above the oxycline and is insignificant (~ 15%) (Table 1). This is explained by the fact that the productivity of surface waters depends on the intensity of the processes of vertical exchange of water guaranteeing the inflow of biogenic elements into the euphotic zone. Note that the character of hydrophysical processes running in cyclonic circulations during the cold season is, in general, similar but the intensity of these processes depends on the actual hydrometeorological conditions [8]. Thus, the amounts of POM in the deep part of the sea are determined, to a great extent, by the rate of its production in the surface layer as a result of primary synthesis. At the same time, the vertical distribution and composition of POM in seawater depend not only on the process of primary production but also on the subsequent "processing" of newly formed POM by the consumers, living activity of bacteria, formation of detritus, and velocity of sedimentation. The process of chemosynthesis in the lower part of the oxycline (suboxic zone) and immediately below the boundary of the H<sub>2</sub>S-zone is also an important additional source of POM. Note that the intensity of chemosynthesis is characterized by a well-pronounced seasonal variability with two maxima attained in spring (after warm winter) and November and a minimum attained in summer [15].

In Table 2, we present the intensities of the fluxes of  $C_{POM}$  and  $N_{POM}$  from the surface layer into the oxycline and through the boundary of the H<sub>2</sub>S-zone obtained by multiplying the mean concentration of particulate organic carbon (nitrogen) by the velocity of sedimentation of POM at a given depth. The velocities of sedimentation of suspension were found according to the data obtained by using sedimentation traps [16].

As follows from Table 2, the fluxes of  $C_{POM}$  and  $N_{POM}$  from the surface layer into the oxycline after mild winter varied from 21.11 mg-atom C/(m<sup>2</sup>·day) and 3.28 mg-atom N/(m<sup>2</sup>·day) to 57.0 mg-atom C/(m<sup>2</sup>·day) and 7.97 mg-atom N/(m<sup>2</sup>·day). The maximum fluxes of  $C_{POM}$  and  $N_{POM}$  were recorded in March and April. In winter, summer, and late autumn, they were practically identical. This is directly connected with the productivity of surface waters largely determined by the seasonal variability of the process of primary production. The average atomic values of the ratio C : N for POM in the process of sedimentation vary, as a rule, within the range 5.9–7.5. Only in April, the ratio C : N significantly differs from these values and is equal to 10.9. This is explained by a decrease in the intensity of production and high intensity of destruction observed in April [7].

After mild winters, the fluxes of  $C_{POM}$  and  $N_{POM}$  from the oxycline into the H<sub>2</sub>S-zone sharply decrease and become equal to 1.03–4.67 mg-atom C/(m<sup>2</sup>·day) and 0.16–0.79 mg-atom N/(m<sup>2</sup>·day) with maximum values attained in April. Note that, in spring and autumn, the fluxes of POM from the oxycline into the H<sub>2</sub>S-zone decrease by about an order of magnitude as compared with the fluxes from the surface layer into the oxycline. At the same time, in January, March, and June, they become more than 20 times weaker.

It is of interest that the fluxes of POM into the oxycline observed in April after cold and long winter insignificantly differ from the fluxes observed in April after mild winter. On the contrary, the fluxes of POM from the oxycline into the H<sub>2</sub>S-zone become weaker (by a factor of 2.5 for  $C_{POM}$  and by a factor of 4.5 for  $N_{POM}$ ). This is explained by the fact that the period of our investigations coincided with the onset of rearrangement from the winter to summer structure of waters in the course of which the existing balance in the production-destruction system was violated. High intensities of the fluxes of  $C_{POM}$  and  $N_{POM}$  from the euphotic layer into the oxycline were also observed in July–August 1992 at the time of intense bloom of pyrophytic algae. In this period, the fluxes of  $C_{POM}$  and  $N_{POM}$  below the boundary of the H<sub>2</sub>S-zone became 32 and 24 times weaker, respectively.

The data presented above show that the period of intense autotrophic production is followed by the period of intense vertical redistribution of POM both in early spring and in summer during the period of intense bloom of algae. In this case, the *in-situ* biological processes in the deep part of the Black Sea (including bacterial chemosynthesis) maintain basic amounts of the "export" production from the euphotic zone.

#### CONCLUSIONS

1. For the first time, on the basis of the analysis of detailed vertical profiles of  $C_{POM}$  and  $N_{POM}$ , we determined their monthly and annual average amounts for three layers in the deep part of the Black Sea. After mild winters, the annual average amounts of  $C_{POM}$  and  $N_{POM}$  were as follows:  $460 \pm 176 \text{ mg-atom } C/m^2$  and  $58 \pm 26 \text{ mg-atom } N/m^2$  (in the layer lying above the oxycline and characterized by the formation of new POM in the process of photosynthesis) and  $288 \pm 128 \text{ mg-atom } C/m^2$  and  $39 \pm 19.7 \text{ mg-atom } N/m^2$  (inside the oxycline), respectively. In the layer below the boundary of the hydrogen-sulfide zone (up to a conventional density of 16.5), these quantities were equal to  $208 \pm 150 \text{ mg-atom } C/m^2$  and  $30 \pm 23.5 \text{ mg-atom } N/m^2$ , respectively.

2. We also estimated the downward fluxes of the POM (carbon and nitrogen) from the euphotic zone into the oxycline and below the boundary of the hydrogen-sulfide zone (up to a conditional density of 16.5). The annual average fluxes of  $C_{POM}$  and  $N_{POM}$  from the euphotic zone into the oxycline after mild winters were equal to 34 mg-atom C/(m<sup>2</sup> · day) and 4.7 mg-atom N/(m<sup>2</sup> · day), respectively. Below the boundary of the hydrogen-sulfide zone, they were equal to 2.1 mg-atom C/(m<sup>2</sup> · day) and 0.34 mg-atom N/(m<sup>2</sup> · day), respectively.

3. We also revealed the seasonal and annual variability of the amounts and fluxes of  $C_{POM}$  and  $N_{POM}$  and its dependence on the regional changes in the climate.

The present work was carried out within the framework of the national project of the Ukrainian Academy of Sciences "Interdisciplinary Research into the Fundamental Processes of Formation and Evolution of the Ecological System of the Abyssal Part of the Black Sea under the Conditions of Intense Anthropogenic Loading, Regional Variations and Global Changes in the Climate" and international European Project INTAS No. 99-01710 "Nitrogen Cycling in the Oxic/Anoxic Environments of the Black Sea: Data Analysis and Numerical Simulation."

#### REFERENCES

- 1. B. A. Skopintsev, *Formation of the Current Chemical Composition of Waters in the Black Sea* [in Russian], Gidrometeoizdat, Leningrad (1975).
- 2. V. S. Filippov, "Particulate organic carbon in waters of the aerobic zone of the Black Sea," in: *Ecosystem of the Pelagic Zone of the Black Sea* [in Russian], Nauka, Moscow (1980), pp. 62–64.
- 3. S. V. Vostokov, "particulate organic substances in the open waters of the Black Sea in spring 1984," in: *Contemporary State of the Ecosystem of the Black Sea* [in Russian], Nauka, Moscow (1987), pp. 59–67.
- S. V. Vostokov, "Dynamics of the particulate organic matter in the Black Sea during the period of winter-spring bloom of phytoplankton," in: *Variability of the Ecosystem of the Black Sea: Natural and Anthropogenic Factors* [in Russian], Nauka, Moscow (1991), pp. 262–271.
- 5. S. V. Lyutsarev and S. S. Shanin, "Specific features of the vertical distribution of particulate organic carbon in the Black-Sea waters," *Okeanologiya*, **36**, Issue 4, 538–542 (1996).

- Z. P. Burlakova, L. V. Eremeeva, and S. K. Konovalov, "Particulate organic matter of the Black Sea euphotic zone: seasonal and long-term variation of spatial distribution and composition," in: *NATO ASI Ser., Sensitivity to Change: Black Sea, Baltic Sea and North Sea, NATO ASI Series,* Ser. 2: Environment, Vol. 27, Kluwer, Dordrecht (1997), pp. 223-238.
- Z. P. Burlakova, L. V. Eremeeva, and S. K. Konovalov, "Seasonal and spatial variability of the amount of particulate organic matter in the active layer of the Black Sea," *Morsk. Gidrofiz. Zh.*, No. 5, 30–62 (1998).
- I. M. Ovchinnikov, L. V. Moskalenko, Yu. I. Popov, et al., "Specific features of the hydrological structure of the Black Sea in winter," in: Variability of the Ecosystem of the Black Sea: Natural and Anthropogenic Factors [in Russian], Nauka, Moscow (1991), pp. 8–25.
- Z. Z. Finenko and D. K. Krupatkina, "Primary production in the Black Sea in the winter-spring period," *Okeanologiya*, 33, Issue 1, 94–104 (1993).
- I. N. Sukhanova, S. I. Pogosyan, and V. S. Vshivtsev, "Time dependence of the structure of populations of the mass species of spring bloom," in: *Variability of the Ecosystem of the Black Sea: Natural and Anthropogenic Factors* [in Russian], Nauka, Moscow (1991), pp. 117–127.
- 11. T. N. Rat'kova, "Phytoplankton of the open part of the Black Sea," in: *Structure and Production Characteristics of Plankton Associations of the Black Sea* [in Russian], Nauka, Moscow (1989), pp. 38–52.
- 12. A. I. Kopylov and A. F. Sazhin, "Heterotrophic nanoplankton of the aerobic zone of the Black Sea," in: *Structure and Production Characteristics of Plankton Associations of the Black Sea* [in Russian], Nauka, Moscow (1989), pp. 139–156.
- A. F. Sazhin and A. I. Kopylov, "Bacterial plankton of the oxygenic zone of the open part of the Black Sea," in: *Structure and Production Characteristics of Plankton Associations of the Black Sea* [in Russian], Nauka, Moscow (1989), pp. 122–139.
- 14. D. Y. Repeta, D. J. Simson, B. B. Jorgensen, et al., "Evidence for anoxygenic photosynthesis from the distribution of bacteriochlorophyles in the Black Sea," *Nature*, **342**, 69–72 (1989).
- A. A. Bezborodov, Z. P. Burlakova, M. B. Gulin, et al., "Biochemical processes in the zone of interaction of aerobic and anaerobic waters in the Black Sea," in: *Complex Oceanographic Investigations of the Black Sea* [in Russian], Sevastopol (1990), pp. 148–163.
- D. M. Karl and G. A. Knauer, "Microbial production and particle flux in the upper 350m of the Black Sea," *Deep-Sea Res.*, 38, Suppl. 2, S921–S942 (1991).
- 17. L. V. Georgieva, "Range of species and dynamics of phytocenosis," in: *Plankton of the Black Sea* [in Russian], Naukova Dumka, Kiev (1993), pp. 31–55.
- L. G. Senichkina, L. V. Georgieva, D. A. Nesterova, et al., "Phytoplankton of the Black Sea in summer 1989: biomass and its dependence on hydrological conditions," in: *Variability of the Ecosystem of the Black Sea: Natural and Anthropogenic Factors* [in Russian], Nauka, Moscow (1991), pp. 104–116.
- L. V. Stel'makh, A. V. Ivanov, and L. V. Georgieva, "Primary production and phytoplankton in the Black Sea in spring," in: *Diagnosis of the State of Marine Environments in the Coastal and Shelf Zones of the Black Sea* [in Russian], Marine Hydrophysical Institute, Sevastopol (1996), pp. 67–74.
- O. V. Krivenko and M. V. Kirikova, "Vertical structure of the distribution of nitrates and the processes of consumption of inorganic nitrogen by microplankton in the Black Sea in spring," *Morsk. Gidrofiz. Zh.*, No. 4, 69–80 (2002).
- M. V. Flint, A. I. Kopylov, S. G. Poyarkov, et al., "Vertical distribution of plankton in the lower layers of the oxygenic zone and its correlation with the processes of bacterial chemosynthesis," in: *Structure and Production Characteristics of Plankton Associations of the Black Sea* [in Russian], Nauka, Moscow (1989), pp. 233–246.