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ORIGINAL PAPERS

The Distribution of Chlorophyll *a* in the Bottom Sediments of Aniva Bay (Sea of Okhotsk)

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Abstract—This paper reports the first data on the content of plant pigments in the upper bottom sediment layer of Aniva Bay (Sea of Okhotsk) located in the temperate-monsoon climatic zone. A positive relationship was found between the concentration of sedimentary chlorophyll *a* and its total content in the water column, which reflects a prevalent role of phytoplankton in the formation of the sedimentary pigment complex. A significant variability of the spatial distribution of the pigments in the bay is shown to be caused by the hydrological—hydrochemical parameters and characteristics of the bottom sediments. The contents of chlorophyll *a* and phaeopigments in sediments showed values of the oligotrophic category and averaged 6.5 ± 0.7 μg/g of dry sediment or 0.47 ± 0.06 mg/g of organic matter.

Keywords: plant pigments, bottom sediments, Aniva Bay

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INTRODUCTION

The relationship between chlorophyll *a* content in phytoplankton and phytoplankton productivity allows the use of the main pigment of the microalgae photosynthetic apparatus as a marker of the productivity of marine and freshwater ecosystems [2, 9, 16, 25, 27, 28, 35]. Pigments enter the bottom sediments (BSs) from the water column during sedimentation of suspended autochthonous and allochthonous organic matter (OM). The content of pigments preserved in sediments is associated with biotic and abiotic factors that influence the value of primary production; therefore, characteristics of pigments are used to assess the ecological status of water bodies and the long-term dynamics of phytoplankton biomass and composition [26, 31–34, 37].

Aniva Bay (the Sea of Okhotsk) is one of the most productive areas of southern Sakhalin. The construction of a natural gas liquefaction plant in the coastal zone and its launch in 2009 created the risk of a negative impact on valuable fishing grounds. Hence, it is important to study the dynamics of the status of bay's ecosystem components that are experiencing anthropogenic impacts using rapid indicators such as the characteristics of pigments. Most of the studies of plant pigments in Aniva Bay were performed on phytoplankton [3, 10, 11, 19]. Sedimentary pigments, which are of particular importance for the characterization of the productivity properties of the benthic area, have virtually not been studied.

The purpose of this research is to assess the content of plant pigments in the bottom sediments of Aniva Bay and to identify the factors that control their distribution. To this end, it is necessary to investigate the spatial distribution of sedimentary plant pigments in relation to the physico-chemical properties of bottom sediments (particle size distribution, moisture, and organic matter content) and characteristics of water (depth, temperature, pH, and dissolved oxygen).

MATERIALS AND METHODS

Aniva Bay is located in the southern part of Sakhalin Island between Cape Crillon (45°54′ N, 142°05′ E) and Cape Aniva (46°01′ N, 142°25′ E). Its area is 5809 km^2; the volume of water is 306.2 km^3 [13]; the axial length is 80 to 110 km; and the length of the coastline is approximately 270 km. The average depth of the bay is 63 m, the shallowest depths (10—40 m) are found in the northern part of the bay and the greatest depths (100—110 m) are in the central part [14]. The bottom relief is not very variable. The climate in the bay area is moderately monsoonal, with active cyclonic activity and a large amount of precipitation (approximately 800 mm per year). In the bay, water exchange occurs between the Sea of Japan and the Sea of Okhotsk. Depending on the spread of a branch the Soya Cur-

Table 1. The characteristics of stations (1–24) of bottom sediment sampling in Aniva Bay

Section	Station	Depth, m	Content of dissolved oxygen near bottom, % saturation		Bottom sediment type	
			2005	2013	2005	2013
I	1	16	–	98.6	–	2
	2	41	–	97.7	–	2
	3	35	–	98.1	–	3
	4	40	84.4	98.3	2	1
	5	24	96.2	99.4	1	1
II	6	16	–	98.2	–	2
	7	48	–	96.7	–	2
	8	62	–	70.3	–	1
	9	71	80.7	73.4	3	1
	10	65	–	82.2	–	1
	11	33	93.3	97.1	2	2
III	12	60	87.9	94.1	2	1
	13	80	–	–	–	–
	14	84	84.1	65.9	3	1
	15	71	–	76.2	–	3
	16	56	–	97.7	–	4
	17	28	95.8	96.3	5	3
IV	18	28	92.8	97.0	5	3
	19	77	–	79.5	–	1
	20	87	–	76.5	–	2
	21	97	77.3	71.4	1	1
	22	101	–	61.1	–	2
	23	97	87.6	–	2	–
	24	72	87.9	80.5	3	2

Bottom sediments: 1, aleurites and pelites; 2, aleurites and pelites with an admixture of sand; 3, silty sand; 4, pebbles and gravel with an admixture of silt; 5, pebbles and gravel; "–," no data.

rent, the water transparency in the bay can vary from 2 m in May to 18 m in July.

The material was collected from the R/V *Dmitry Peskov* during complex expeditions on May 25–26, 2005 and from October 29 to November 1, 2013 on four standard oceanographic sections (Fig. 1; Table 1) oriented in the latitudinal direction [18].

At each station, sea water samples were taken at standard depths (0, 10, 20, 30, 50, 75 m, bottom) using a rosette water sampler; temperature and salinity were measured with an FSI ICTD profiler no. 1356. The pH value was determined using a portable MA130 pH meter–ion meter (Mettler Toledo); the percentage of oxygen saturation of seawater was calculated according to the Green–Carritt tables after the dissolved oxygen concentration had been measured by the Winkler method [17].

Bottom sediments were collected using a van Veen bottom grab (stainless steel, sample volume 30 L, and a sampling area of 0.2 m^2). After removing water, samples of the upper 5-cm sediment layer were averaged by the quartering method, packed in plastic bags, and stored for no more than 1 month at a temperature of –20°C. The samples were then thawed, homogenized for 1 min, and analyzed in two replicates. Ten mL of 90% acetone were added to tight-cap tubes with samples, mixed thoroughly with a glass rod, and placed in a refrigerator for 1 day. The suspension was precipitated using an OPN-VUKhL 4.2 centrifuge at 8000 rpm for 15 min. For complete extraction, pigments were re-extracted by keeping the precipitate in a fresh portion of the solvent for 1 h. The optical density of the acetone extracts (before and after acidification) was measured on a UV-3600 spectrophotometer (Shimadzu) at wavelengths of 665 and 750 nm. The concentrations of chlorophyll *a* (Chl + Ph) and phaeophytin *a* (Ph) in

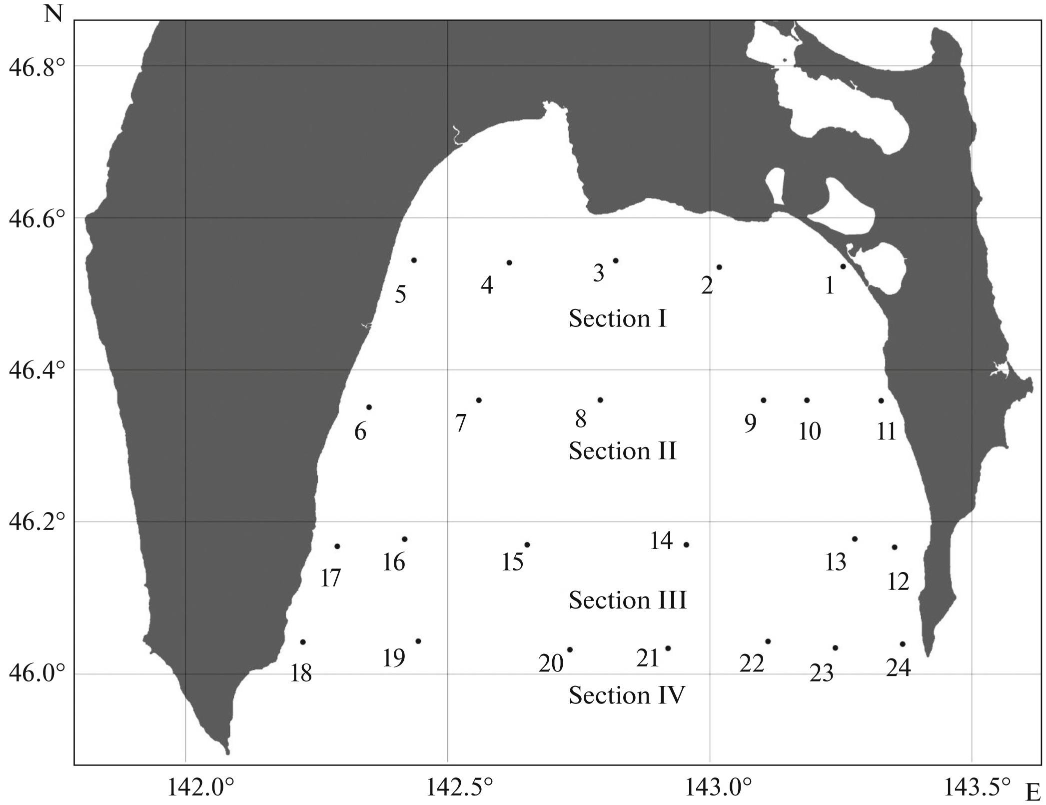

Fig. 1. A schematic map of the sections and sampling stations in Aniva Bay, Sea of Okhotsk.

the samples were calculated using the Lorenzen formulas [29]. The pigment content was calculated in micrograms per gram of dry sediment and in milligrams per gram of organic matter [20].

The moisture content of the BS was evaluated based on the difference between the mass of samples before and after their drying at a temperature of 105°C. The OM content was determined by the photometric method [5]. Prior to analysis, the sediment was washed with distilled water so that the proportion of chlorides would not exceed 0.6%. The particle size composition of sediment was determined by sieve analysis and areometric methods [7]. Bottom sediment type was determined from the particle size fraction: pebbles and gravel, 1 to >10 mm; sand, 1 to 0.1 mm; aleurite and pelite, 0.1 to <0.005 mm [6].

The trophic status of the benthic area was assessed from the concentration of Chl + Ph per gram of dry sediment: oligotrophic, <13 μg/g; mesotrophic, 13–60; eutrophic, 60–120; hypertrophic >120 [30]. Statistical analysis and interpretation of the data were performed using the Excel and STATISTICA software packages and formulas [8, 12, 36].

RESULTS

The abiotic conditions during surveys in the spring of 2005 and in the fall of 2013 differed. This caused the uneven temporal distribution of plant pigments in the bottom sediments of Aniva Bay. In the spring of 2005, salinity and oxygen concentration in the water column were higher than in the fall of 2013 and the temperature decreased to negative values (Table 2). The oxygen content at the surface and near the bottom at deep-sea stations did not reach saturation almost anywhere (77–96%). In the fall, due to a temperature leap in the 6–15 m thermocline layer, microalgae productivity was highest in the subsurface layer (10 m). This caused oxygen stratification, viz., an increase in the dissolved oxygen concentration in surface water (101–126% saturation) and its decrease (61–81% saturation) near the bottom at deep-sea stations 20–24.

The structure of the sediment complex is one of the factors influencing the pigment distribution in sediments. In Aniva Bay, the sediment type differed between years and between stations. Compared to the fall of 2005, in the spring of 2013 the percentage of fine fractions markedly increased in the deepwater part of the bay, while in the shallow northern coastal area the sediment type was unchanged and was mainly represented by sandy-aleurite silts. In the spring of 2013, aleurites and pelites with an admixture of sand were predominant in the southern open part (stations 21, 23, 24) and in the eastern coastal part of Aniva Bay (stations 11 and 12), while sand and gravel predominated in the central part (stations 9 and 14) and the western coastal area (stations 17 and 18) (Table 1). The

Table 2. Abiotic conditions in Aniva Bay

Parameter	2005		2013	
	near bottom	in water column	near bottom	in water column
Temperature, °C	–1.6–0.8 / –0.9 ± 0.3	–1.0–4.3 / 1.4 ± 0.3	0.1–9.1 / 4.9 ± 0.8	0.1–9.6 / 7.6 ± 0.2
Salinity, ‰	32.2–33.0 / 32.7 ± 0.1	30.6–32.7 / 31.9 ± 0.1	30.3–33.0 / 31.5 ± 0.2	30.2–32.9 / 31.2 ± 0.1
pH	7.46–7.93 / 7.63 ± 0.05	7.33–8.09 / 7.82 ± 0.03	7.63–8.14 / 7.95 ± 0.02	7.91–8.15 / 8.08 ± 0.01
Dissolved oxygen, mg/dm^3	9.28–12.03 / 10.35 ± 0.25	9.96–12.47 / 11.17 ± 0.12	7.13–9.55 / 9.05 ± 0.16	8.90–12.37 / 9.54 ± 0.05
Dissolved oxygen, % saturation	77.3–96.2 / 88.0 ± 1.8	85.4–113.1 / 97.6 ± 1.3	61.1–99.4 / 91.8 ± 3.8	79.2–125.8 / 97.8 ± 0.6

Here and in Table 3, the numerator gives the range of values and the denominator gives the mean and error.

sediments in the central (stations 8–10, 14, 15), southern deepwater (stations 19–24), and eastern coastal (stations 11 and 12) parts of the bay were represented by aleurites and pelites with an admixture of sand, and in the western coastal part (stations 16–18) were pebbles and gravel with silt.

Concentrations of plant pigments were distributed according to the quantitative characteristics of bottom sediments. Thus, with an increase in the percentage of fine particles in the sediment structure there was an increase in the natural moisture content of the sediment and in the OM concentration (Figs. 2a, 2b). Increased concentrations of Chl + Ph and Ph corresponded to aleurite-pelite silts with high (for the bay) moisture contents and the maximum OM content (Fig. 2c); decreased concentrations of Chl + Ph and Ph corresponded to sands and coarse-grained sediments with low moisture contents and minimal OM. Phaeopigments made up the bulk (78–87%) of the total plant pigment content (Table 3). The contribution of Ph was higher in the fall than in the spring, which is in accordance with the view that pigment degradation prevails over pigment synthesis at the end of the vegetation season. Analysis of the data by the Student's test indicated significant differences in the average values of Chl + Ph and Ph in the bottom sediments of the bay in the spring of 2005 and in the fall of 2013 (significance level $p < 0.01$).

The concentrations of Chl + Ph in bottom sediment OM, as well as the Chl + Ph content calculated per gram of dry sediment, generally increased with an increase in the fine-particle fraction of sediment in the bay (Fig. 3). In both periods of observation, the contents of small-grain fractions in sediments decreased in the direction from the northern coastal part (section I) to the middle of the bay (sections II and III) and somewhat increased in its southern open part (section IV) (Figs. 4a, 4b). The variability of pigment concentration on sections coincided on average with the spatial dynamics of sediment particle size composition (Figs. 4c–4e). Thus, the content of Chl + Ph in sediments and in OM at stations of the northern and southern sections was higher than at stations of central sections. The maximum chlorophyll content was recorded at stations of the northern coastal section, which is associated with increased phytoplankton productivity under eutrophication conditions. The high concentrations of pigments in sediments at stations of the southern section were also due to the increased primary production, as indicated by the chlorophyll content in the water column (42–44 mg/m^2). The photosynthetic activity of phytoplankton depends on nutrient availability as a result of intensive water exchange with the open part of the La Perouse Strait and on the influence of waters of the Sea of Okhotsk and upwelling. Suspended organic matter containing pigments accumulates in the water column and is deposited in the deepwater part of the bay.

DISCUSSION

The study of the distribution patterns of plant pigments in the upper sediment layer of Aniva Bay in relation to biotic and abiotic factors of productivity showed that the pigment content in sediments increased with an increase in station depth, sediment moisture content, and OM concentration (Table 4). The relationship between sedimentary pigment content and phytoplankton production was reflected in a positive correlation between the chlorophyll *a* concentration in sediments and in the water column below 1 m^2; some decrease in the relationship in 2013 was due to a decrease in the microalgae productivity in the fall. The phytoplankton origin of OM was confirmed by the presence of a relationship between the organic matter content and the depth of station ($r = 0.58$ in

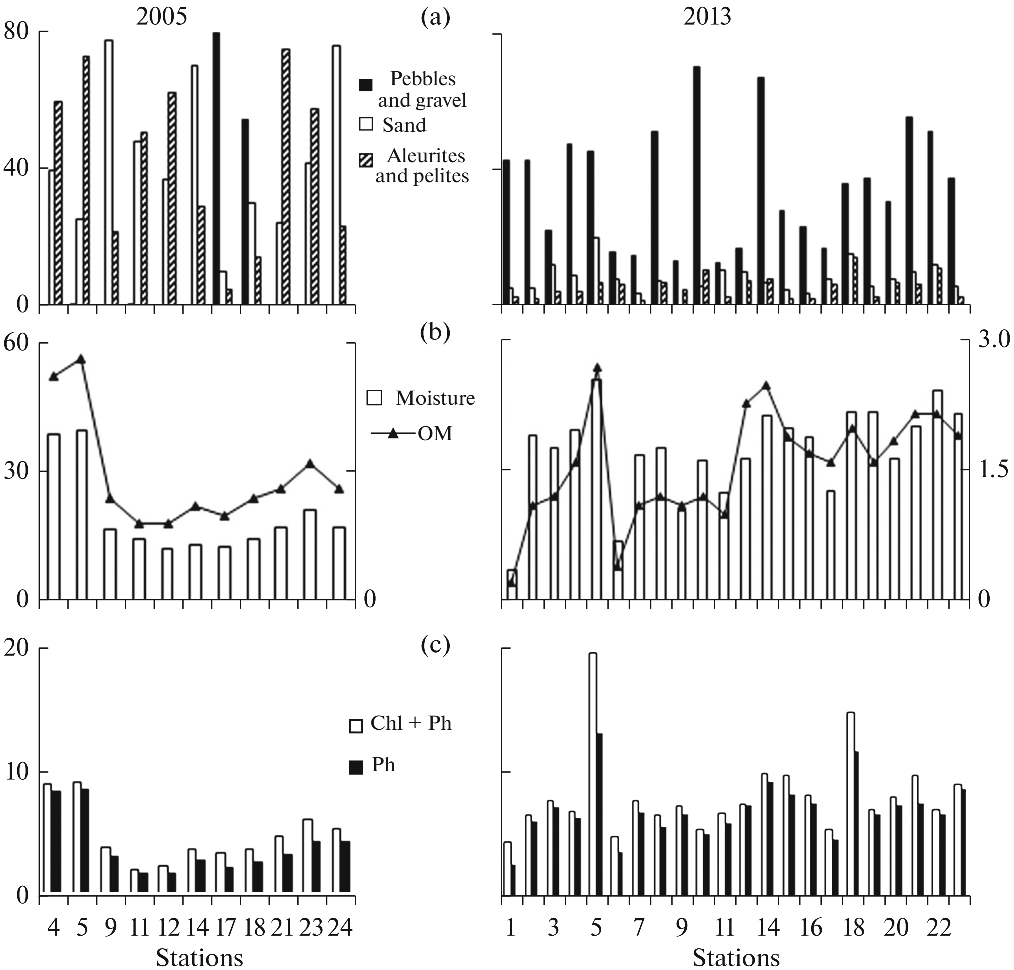

Fig. 2. The content of particle size fraction (a), organic matter and moisture (b), and plant pigments (c) in the bottom sediments of Aniva Bay at different stations. The abscissa gives the numbers of stations; the ordinate gives (a) particle-size fraction content, % dry sediment; (b) moisture (left: percent water of wet mass) and organic matter content (right: percent dry sediment); (c) pigment concentration, μg/g of dry sediment. Designations: OM, organic matter; Chl, chlorophyll *a*; Ph, phaeophytin *a*.

2005 and $r = 0.67$ in 2013, $p < 0.05$). The correlation between pigment content and sediment properties was not observed at stations 4, 5, and 18 in the zone influenced by river runoff, where small depths (24–40 m) and a high percentage of oxygen saturation of near-bottom layers (97–99%) contributed to the rapid destruction of chlorophyll, which was enhanced in shallow water under the action of sunlight. The maximum OM content (2.0–2.8%) and increased moisture content of the sediments (39.5–51.1%) in these areas are associated with an abundant development of benthic algae at increased nutrient concentrations. The latter was due to natural (river runoff and spawning of salmon) and anthropogenic (the large sea trading port of Korsakov and the construction and launch of a liquefied gas production plant) impacts on the shallow area of the bay [10, 13].

The relationship between pigment content and hydrological–hydrochemical parameters was less pronounced. In the spring of 2005, an increase in temperature from –1.6 to 4.3°C was accompanied by an increase in sedimentary pigment content (Table 5). In the fall of 2013, the concentrations of Chl + Ph and Ph increased with a pH decrease from 8.15 to 7.63 with increase in station depth.

A factor analysis revealed the two most significant factors that in the spring of 2005 accounted for 67–71% of the total variability of the studied parameters (Table 5). The first factor, with a contribution of 38% to the total dispersion, most significantly determined the variability of productivity characteristics (the content of Chl + Ph and Ph) and the physicochemical parameters of sediments (moisture content and the contents of OM and fine particle size fractions). Interpretation of the factor loads allowed identification of this factor as biotic. The second factor (33% of the total dispersion) positively correlated with station depth, but negatively correlated with temperature, pH, and dissolved oxygen. This factor is evidently hydrological–hydrochemical.

Table 3. The characteristics of bottom sediments in Aniva Bay

Parameter	2005	2013
Moisture content, %	12.0–39.5 / 20.0 ± 2.9	7.0–51.5 / 36.0 ± 2.9
Particle size d >10–1 mm, %	0.0–85.4 / 12.9 ± 8.8	0.0–45.6 / 2.3 ± 2.1
Particle size d = 1–0.1 mm, %	0.0–78.1 / 43.9 ± 6.8	8.4–71.3 / 36.8 ± 4.4
Particle size d = 0.1–<0.005 mm, %	0.0–75.7 / 43.2 ± 7.5	28.5–91.7 / 60.9 ± 4.5
Organic matter content, %	0.9–2.8 / 1.4 ± 0.2	0.2–2.7 / 1.6 ± 0.2
Chl + Ph, μg/g of dry sediment	1.9–9.0 / 4.7 ± 0.7	4.4–19.5 / 8.2 ± 0.7
Chl + Ph, mg/g of organic matter	0.21–0.40 / 0.32 ± 0.02	0.32–2.2 / 0.62 ± 0.09
Ph, % of total pigment content	63.7–93.1 / 77.6 ± 3.0	59.9–100.0 / 86.9 ± 2.1

Here and in Tables 4 and 5: Chl, chlorophyll *a*; Ph, phaeophytin *a*.

Table 4. The coefficients of correlation between the concentration of sedimentary plant pigments and the biotic and abiotic parameters of water and bottom sediments in Aniva Bay ($p < 0.05$)

Parameter	Chl + Ph, μg/g		Ph, μg/g	
	2005	2013	2005	2013
Depth, m	+0.58	+0.58	+0.47	+0.63
Temperature, °C	+0.40	−0.48	+0.40	–
pH	–	−0.68	–	−0.73
Moisture content, %	+0.95	+0.63	+0.98	+0.76
Organic matter content, %	+0.97	+0.68	+0.99	+0.80
Chl + Ph, mg/g of organic matter	+0.57	+0.68	+0.45	+0.49
Chl + Ph in water column, mg/m^2	+0.58	+0.50	–	+0.62

"–", no statistically significant relationships.

In the fall of 2013, the dominant factor, which accounted for 50% of the variability of most of the studied parameters, was the peculiarities of the water regime. Upwelling and the East Sakhalin Current, which enrich the surface water of the bay with nutrients during this period [13, 22], contributed to the increased phytoplankton productivity. The contribution of the second factor that influenced the content of silt fractions was 17%. Since the sediment genesis processes of pelites and aleurites are different (pelites are transferred over farther distances than aleurites), the placement of fine silty particles into a single group is apparently due to the morphometric characteristics of the bay (depth) and is common to accumulation zones.

Aniva Bay can be considered oligotrophic by virtue of the average content of chlorophyll and derivatives in sediments [30], which was 6.5 ± 0.7 μg/g of dry sediment (0.47 ± 0.06 mg/g OM). According to the chlorophyll *a* content in plankton, a similar trophic state of the bay was determined in the summer–fall period [10] according to the classification of productivity of freshwater ecosystems [1]. At the same time, according to the classifications of productivity of waters of the World Ocean based on surface chlorophyll concentration [2, 16, 24], Aniva Bay in its different areas falls into the range from eutrophic to mesotrophic in

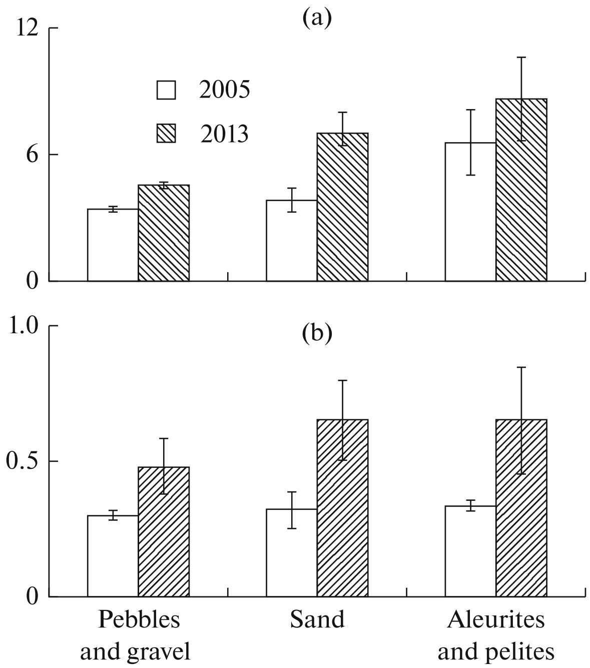

Fig. 3. The content of plant pigments in different-type bottom sediments of Aniva Bay in different years: (a) in dry sediment, μg/g; (b) in organic matter, mg/g.

the spring and from mesotrophic to oligotrophic in summer and fall.

The main reasons for the low content of Chl + Ph in the sediments of Aniva Bay are probably the specific features of the hydrodynamic regime with intense cyclonic activity and the structure of the sediment complex. These determine the conditions of distribution and transformation of pigments. The peculiarities of the relationship between pigment content and environmental factors reflect the specific features of the marine ecosystem with depths of 16 to 101 m and high water transparency (10–15 m), as well as relatively low temperature (–1.6 to 9.6°C), characteristic salinity 30.2–33.0‰, pH values in the range of 7.33–8.15, and a dissolved oxygen content of 61–126% saturation. The Chl + Ph content in bottom sediments of Aniva Bay in the Sea of Okhotsk (1.9–19.5 μg/g) is similar to the concentration of sedimentary plant pigments in Amurskiy Bay of the Sea of Japan (3.0–19.0 μg/g) [15]. The distribution patterns of pigments in the sediments of Aniva Bay are consistent with those in marine and freshwater ecosystems [4, 20, 21, 23, 35].

In conclusion, we obtained the first data on the plant pigment content in the bottom sediments of Aniva Bay (Sea of Okhotsk) located in the temperate monsoon climate zone. The concentration of sedimentary plant pigments was low, indicating the oligotrophic state of the benthic area and its similarity to that of the pelagic area. The amount of Chl + Ph varied depending on the bottom sediments type and physicochemical characteristics, as well as the total chlorophyll content in the water column, which reflects the prevailing influence of phytoplankton productivity on the formation of the sedimentary pigment complex. The temporal variability of the pigment content in the bottom sediments of the bay is caused by different factors: in the spring, the hydrological and hydrochemical characteristics (depth, temperature, pH, dissolved oxygen, etc.) and the properties of the bottom sediments (sediment complex structure, mois-

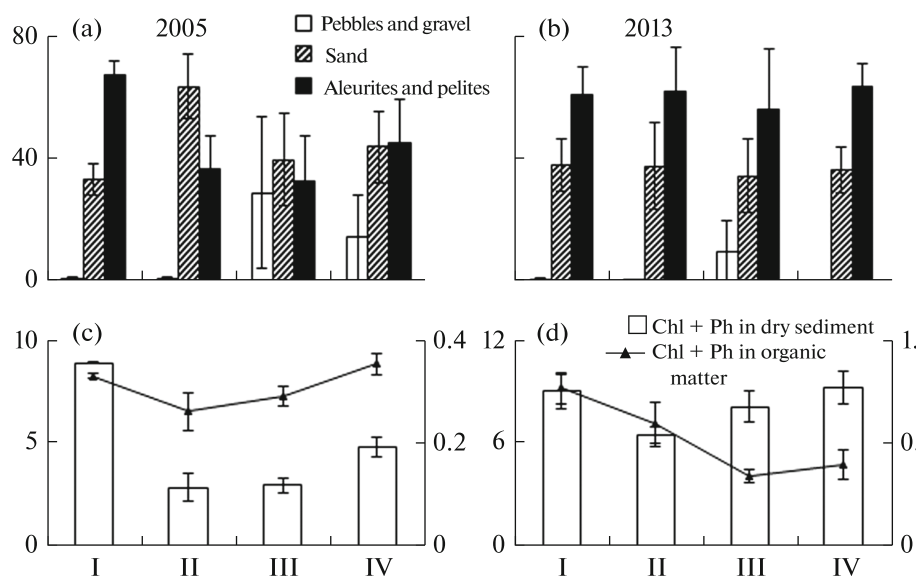

Fig. 4. The content of particle size fractions, % (a, b); chlorophyll *a* and phaeophytin *a* in dry sediment, μg/g (c) and in organic matter, mg/g (d) in the bottom sediments of Aniva Bay on standard sections I–IV in 2005 and 2013. Designations: Chl, chlorophyll *a*; Ph, phaeophytin *a*.

Table 5. Factor loadings for the studied parameters of water and bottom sediments in Aniva Bay ($p < 0.05$)

Parameter	2005		2013	
	factor 1	factor 2	factor 1	factor 2
Depth, m	−0.07	**0.93**	**0.91**	0.13
Temperature, °C	0.29	**−0.88**	**−0.71**	−0.31
pH	−0.21	**−0.71**	**−0.87**	−0.01
Dissolved oxygen, mg/dm^3	−0.46	**−0.77**	−0.64	−0.50
Total Chl + Ph in water column, mg/m^2	−0.17	0.62	0.20	−0.45
Moisture content, %	**0.97**	−0.22	**0.81**	−0.25
Organic matter content, %	**0.98**	−0.20	**0.83**	−0.14
Chl + Ph, µg/g of dry sediment	**0.97**	−0.08	**0.92**	−0.36
Chl + Ph, mg/g of organic matter	0.44	0.40	−0.20	0.00
Ph, µg/g of dry sediment	**0.98**	−0.13	**0.95**	−0.34
Particle size d = >10–1 mm, %	−0.43	−0.68	0.31	−0.46
Particle size d = 1–0.1 mm, %	−0.09	0.63	**0.78**	−0.65
Particle size d = 0.1–<0.005 мм, %	0.58	0.22	**0.89**	**0.85**
Contribution of a factor to total variance, %	38	33	50	17

The bolded values are significant loadings.

ture, and OM content); in the fall, the peculiarities of the water regime (upwelling, influence of water masses of the Sea of Okhotsk), which contribute to a rapid change in abiotic conditions, increasing the productivity of phytoplankton.

The data obtained for Aniva Bay are consistent with the results of studies of the plant pigment distribution in the bottom sediments of marine and freshwater water bodies and reflect the environmental zonality and unified patterns of functioning of aquatic ecosystems.

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COMPLIANCE WITH ETHICAL STANDARDS

The authors declare that they have no conflict of interest. This article does not contain any studies involving animals or human participants performed by any of the authors.

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