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Seasonal Variability of Dissolved Methane in the Shallow Coastal Zone: The Case Study of the Golubaya Bay, Northeastern Part of the Black Sea

Elena S. Izhitskaya *, Alexander V. Egorov and Peter O. Zavialov

Shirshov Institute of Oceanology, Russian Academy of Sciences, 36 Nakhimovsky Prosp., Moscow 117997, Russia
* Correspondence: kovaleva_es@ocean.ru

Abstract: The variability of the dissolved methane content in coastal zones is an important component of the biogeochemical cycle in the marine ecosystem. The objective of this study is to investigate the seasonal variability of dissolved methane distribution in the aerobic shallow coastal zone through the example of the small bay in the northeastern Black Sea. This study is based on the direct observations carried out during a long-term monitoring program conducted in the bay from 1999 to 2016. The seasonal and inter-annual variability of the dissolved methane pattern is considered under the climatic conditions as well as under the influence of extreme flood. The seasonal range of the dissolved methane content variability in the shallow part of the northeastern Black Sea is 1–2 orders of magnitude higher compared with the areas remote from the coast. The dissolved methane content in Golubaya Bay in summer is an order of magnitude higher than the winter values. In particular, local methane maxima located near the river and stream mouths and in the central bottom part of the bay have a well-shown seasonal cycle. The extreme flood conditions observed in July 2012 resulted in high methane concentrations 2 months after the flood event, when the surface concentrations of the dissolved CH_4 exceeded the equilibrium with the atmospheric values by a factor of 400. The obtained results provide a unique opportunity to estimate the scale of the biogeochemical processes in marine coastal environments under the influence of climatic and extreme conditions.

Keywords: methane production; coastal waters; extreme flood; biogeochemical cycle; methane paradox; aerobic conditions; sea shelf; the Black Sea

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1. Introduction

The study of dissolved methane in natural waters is one of the most important tasks of modern biogeochemistry, since methane is a significant actor in the global carbon cycle [1]. This gas has wide practical application as a fuel. At last, methane emissions into the atmosphere enhance the greenhouse effect, exceeding the activity of the carbon dioxide [2,3].

The formation of biogenic methane occurs during one of the final stages of organic matter decay under anaerobic conditions. Nevertheless, an excess of methane concentrations in aerobic oceanic waters above the equilibrium values with the atmospheric air is observed. This phenomenon is referred to in the literature as the ocean methane paradox [4]. Despite the fact that studies and discussions on methane formation in the aerobic layer have been ongoing for decades, at present, there is no complete understanding of the process that would allow us to identify the factors that govern and sustain methane production. The most plausible explanation for methane formation in aerobic waters is the existence of anaerobic microenvironments in the intestinal tracts of zooplankton, fecal pellets, and suspended particles in the water column [5], as well as specific biogeochemical pathways such as the bacterial decomposition of methylphosphonates [6–9], the degradation of dimethylsulfoniopropionate (DMSP) [10], and the activity of potentially methanogenic Archaea attached to photoautotrophs [11]. The methane paradox is the focus of studies in numerous marine and lake environments [12–16], including the Black Sea.

Meanwhile, the Black Sea is known as the largest meromictic [17] and methane-containing [18] water body on the Earth due to the presence of permanent vertical density stratification, preventing deep-water ventilation in the water column of the sea [19,20]. Thus, huge volumes of dissolved methane and hydrogen sulfide are concentrated in the anaerobic zone of the Black Sea beneath the cold intermediate layer [21]. At the same time, many studies of the methane content in the upper aerobic zone of the Black Sea indicate an increased gas content above the equilibrium value with the atmospheric air [22,23]. The main reason for the methane paradox in the Black Sea is the decomposition of methane in the anaerobic microenvironments mentioned above. The study by Rusanov et al., 2014 [24], showed that the highest intensity of methane microbial formation coincided with the maximum fluorescence and hence the maximum concentration of phytoplankton, while rates of methane oxidation on observed profiles were an order of magnitude lower than the rates of methane formation. The coastal areas of the Black Sea are exposed to additional indirect sources of methane. First of all, those include the continental runoffs [25] and release of methane from bottom sediments in shallow areas [26,27]. In addition, the observed anthropogenic impacts result in the pollution of coastal waters with organic matter, which also contains methane. Thus, the formation of dissolved methane maxima in the surface layer of the water column caused by the continental runoff was observed on the shallow Black Sea shelf in the region of Sochi and the Kerch Strait [23]. Vertical gradients of dissolved methane content towards the bottom were observed in the regions adjoining the Feodosia Bay and were associated with water–sediment interactions and gas emissions from the seafloor [23].

However, the spatial patterns of methane distribution in many cases can be masked by the influence of temporal variability. According to observations at stations with a depth over 100 m in the northeastern Black Sea, the CH_4 maximum in aerobic waters has effectively shown seasonal dependence [24,28]. The latter could be connected to the seasonal dynamics of the biological communities of the northeastern Black Sea [29]. Moreover, the temporal dynamics of dissolved methane concentrations in the coastal zones of the northeastern Black Sea is significantly affected by rapid and short-term increases in continental runoff occurring during flood conditions [30], while the continental runoff is among the sources of suspended matter, anthropogenic pollution and dissolved methane in the region [31,32].

The shallow coastal regions and lakes are generally in the focus of recent studies as potential methane sources for the atmosphere [33–36]. Moreover, local conditions in coastal regions are of great importance in controlling CH_4 emissions, because the variability explained by the more commonly studied abiotic factors is low worldwide [37]. Thus, a more profound insight into the seasonal dynamics of the dissolved methane as an integral part of the biogeochemical cycle is important for understanding the state of the aerobic coastal ecosystem of the Black Sea, and the lack of available direct observations only enhances the significance of the problem. The objective of this study is to investigate the seasonal variability of dissolved methane distribution in the aerobic shallow coastal zone in the northeastern Black Sea. Such zones are characterized by stronger climatic signals, and the increased mixing and enhanced intensity of hydrobiological processes as well as the influence of continental runoff. The study is based on the direct observations carried out during a long-term program in the Golubaya Bay of the northeastern Black Sea coast. The seasonal and inter-annual variability of the dissolved methane pattern in the bay is considered under the climatic conditions as well as under the influence of extreme flood.

2. Materials and Methods

2.1. Study Site

The Golubaya Bay is located in the northeastern shelf of the Black Sea to the west of Gelendzhik Bay (Figure 1). The coastline length of the bay is about 1700 m. In a cross-section, the bottom of the bay is a morphologically distinct depression [38]. The maximum depths within the bay reach 12 m. The bay is fed by the small Ashamba River; however, the water salinity is usually about 17–18 psu that is similar to the open-sea

conditions. According to Roshydromet, the maximum daily precipitation at the Gelendzhik meteorological station used to be 105 mm; the probability of exceeding this indicator was estimated as once in 100 years. The typical factors that determine the dissolved methane pattern, such as phytoplankton biomass and water exchange in the river-coast-open sea zone, change dramatically during a catastrophic flood [39]. During the day, from 6 July to 7 July 2012 311 mm of precipitation was observed in Gelendzhik [40]. The fall of an almost six-month amount of precipitation in less than a day caused a catastrophic rise in the water level in rivers and small streams. In a short time, this led to the discharge of solid and suspended matter to the bay in volumes comparable to amounts worth several years under usual conditions. The salinity of the coastal water dropped to 2‰ [41]. Overall, during the catastrophic flood conditions, the Ashamba river carried out to the bay at least 130,000 tons (of 65 thousand m^3) of suspended matter [40]. The subsequent sedimentation of the matter changed the usual conditions of the biogeochemical cycle of the bay and became a potential source for methanogenesis.

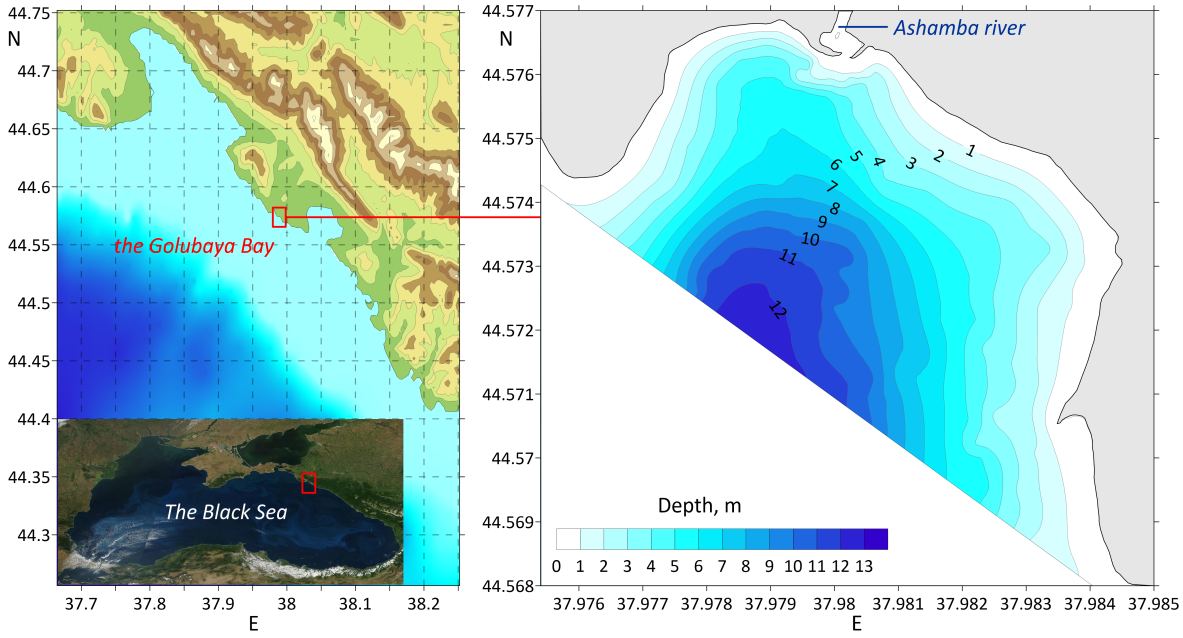

Figure 1. Study region: location of Golubaya Bay in the northeastern part of the Black Sea shore and an approximate bathymetric map of the bay.

2.2. Water Sampling Design

This study is based on the field observations of dissolved methane concentrations in Golubaya Bay. The time frame of the analyzed data spans from 1999 to 2016 (Figure 2). For the first time, water samples for the dissolved CH_4 in Golubaya Bay were taken in the surface layer in the summer of 1999. This was followed by several episodic measurements in 2001 and 2008, as well as by the first estimations of the methane content in the Ashamba River bed. Subsequently, the annual monitoring of dissolved methane concentrations was conducted in the bay since 2011, encompassing measurements in both the surface and bottom layers of the water column, as well as in the Ashamba River channel. Measurements were taken during the summer and winter seasons, with some exceptions in certain years when measurements were conducted in the autumn. Overall, in this study, we consider the data from the summer of 1999 to the autumn of 2016, including the measurements that took place in 2012 after the extreme flood.

Water samples were collected using a boat during cruises of several hour cruises. Sampling stations were evenly distributed across the research area. Water samples from the Ashamba River bed were collected on the same day just after the marine part of the survey.

River bed sampling stations started from the river mouth and continued up to more than 2500 m upstream, their frequency increased with approach to the mouth (Figures 3–5).

2.3. Laboratory Analysis

Water sampling was carried out by a bucket from the sea surface of the bay and the Ashamba River, and by a 3 L Niskin bottle from the bottom horizon of the water column. At each station, the samples were collected into glass flasks with narrow necks (30 mL volume). The sampling procedure was as follows: a flask was filled with water with the overflow of one volume to avoid blistering inside; the gas phase was formed by the displacement of a water portion with a syringe. The flask was closed by a cap with a rubber insertion and stored under cool conditions and in position when the gas phase inside had no contact with the cap to avoid a gas exchange between the sample and the atmospheric air. A headspace analysis procedure, described in detail in [42,43], was applied during the laboratory processing of the obtained samples. The methane concentrations were then determined by injecting 0.5 mL of headspace gas into the gas chromatograph HPM-2 equipped with a flame ionization detector. Additionally, the measurement error was assessed during the field surveys using the following procedure: a series of parallel detections was conducted for single samples at different sites, encompassing both low and high values of dissolved CH_4. According to obtained estimation, the average scatter on parallel measurements reached a value of about 4%. The method has been already tested and implemented before for the Black Sea conditions [23] and has been adapted for a wide range of salinity conditions from brackish to hypersaline environments [44]. Atmospheric equilibrium concentrations of methane in water were calculated from the equation suggested by [45] using the temperature and salinity data.

3. Results

According to the results of measurements in the waters of the Golubaya Bay, almost all the values of dissolved methane concentrations, regardless of the season, exceed the equilibrium value with atmospheric air, which is about 2 nM [45] (Figure 2). The distribution of the measured concentrations by months shows that the lowest values were registered in the winter season (2–43 nM). The absolute values, as well as their range, were the highest in summer months (from 5 to 1400 nM). The series of spring and autumn methane concentrations are in the intermediate range (5–140 nM). One exception is a series of concentrations in September 2012, measured 2 months after the catastrophic flood and yielding the values from 14 to 820 nM (Figure 3g,j).

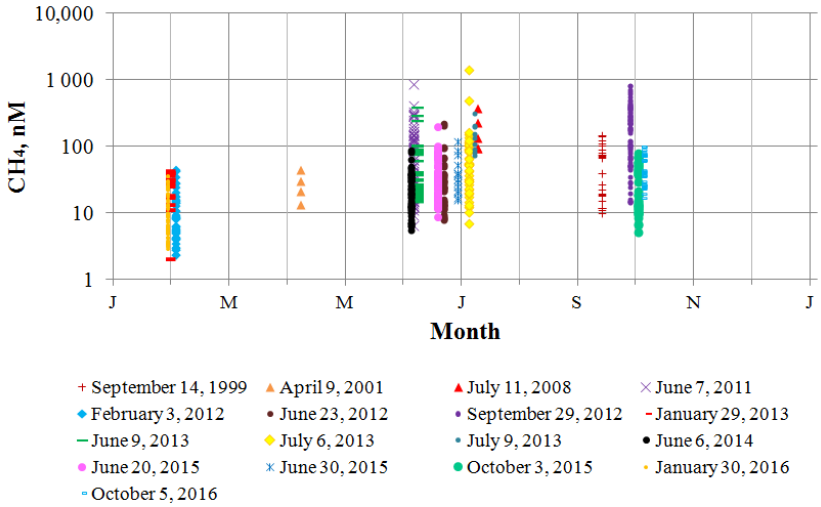

Figure 2. Dissolved methane content in the waters of Golubaya Bay during the period of observations from 1999 to 2016.

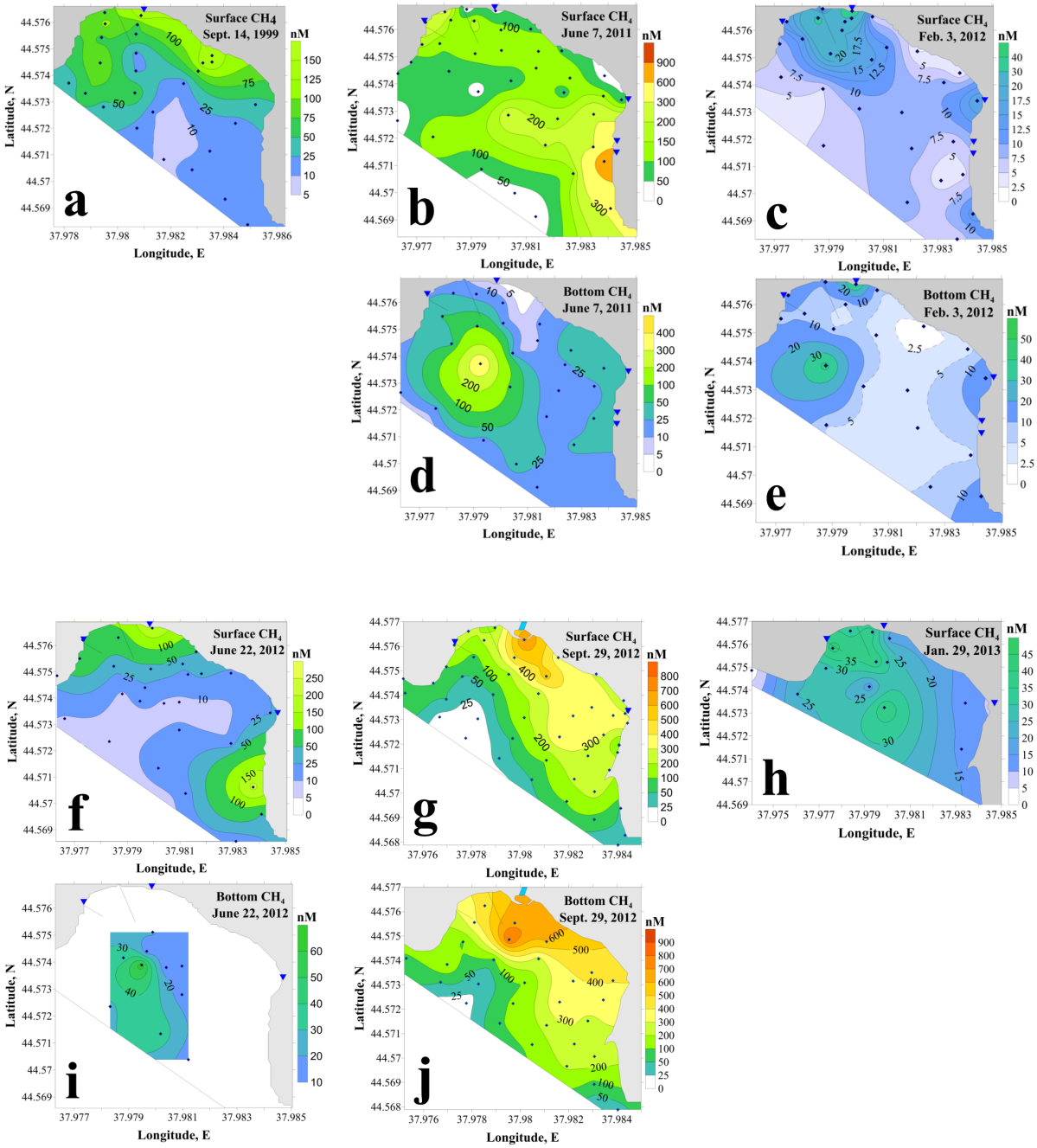

Figure 3. Dissolved methane distribution in the water layers of Golubaya Bay in September 1999 ((**a**)—surface), June 2011 ((**b**)—surface, (**d**)—bottom), February 2012 ((**c**)—surface, (**e**)—bottom), June 2012 ((**f**)—surface, (**i**)—bottom), September 2012 ((**g**)—surface, (**j**)—bottom) and January 2013 ((**h**)—surface). Water sampling stations are indicated by dark blue rhombuses. The mouths of the watercourses are marked with blue triangles.

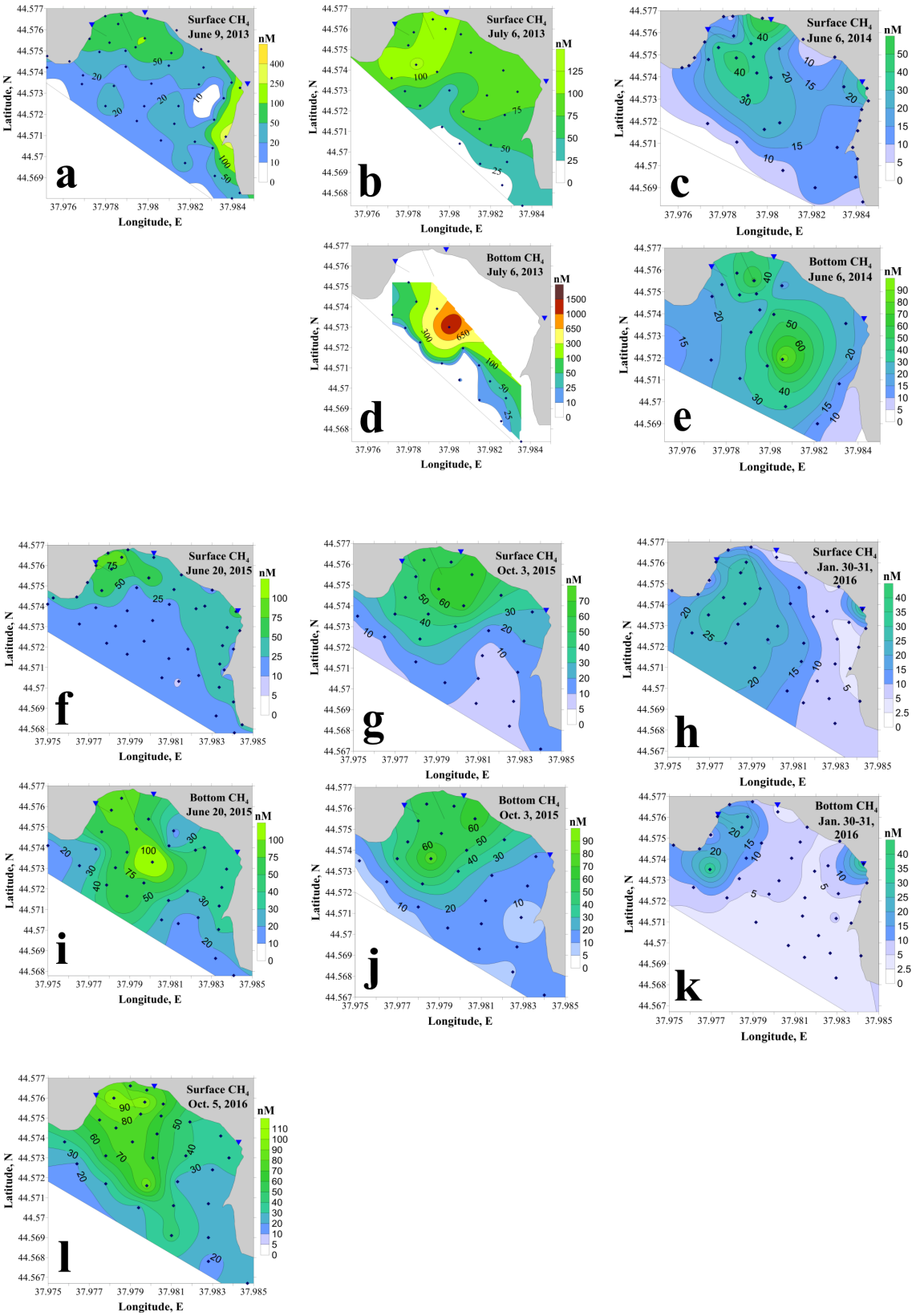

Figure 4. Dissolved methane distribution in the water layers of Golubaya Bay in June 2013 ((**a**)—surface), July 2013 ((**b**)—surface, (**d**)—bottom), June 2014 ((**c**)—surface, (**e**)—bottom), June 2015 ((**f**)—surface, (**i**)—bottom), October 2015 ((**g**)—surface, (**j**)—bottom), January 2016 ((**h**)—surface, (**k**)—bottom) and October 2016 ((**l**)—surface). Water sampling stations are indicated by dark blue rhombuses. The mouths of the watercourses are marked with blue triangles.

For the simple estimation of the seasonal variability of methane content in the waters of Golubaya Bay, we note that the main areas of methane accumulation here are the plumes of the Ashamba River (in the north of the Bay) and other inflowing streams (in the northwest and east), as well as the central deep section of the bay (bottom source). The methane concentration ranges in these main zones are presented in Table 1. A more detailed description of these sources is given in the Discussion section.

Table 1. Dissolved methane content in the different parts of Golubaya Bay in various seasons.

Season	Minimum, Nm	Maxima, Nm			
		Ashamba Plume	Northwestern Part	Eastern Part	Central Part
Winter	2	40	40	35	35
Spring		45			
Summer	5	200	75	75	1400
Autumn	5	150	100	40	70
Flood	14	820			

The methane content in the Ashamba river bed varied from 1 to 98 nM in winter, while it reached 59 nM in spring. The concentration range in summer was 3–2500 nM and 50–920 nM in autumn, i.e., 2 months after the flood (Figure 5). Methane concentrations in all seasons grew exponentially towards the mouth (note the logarithmic concentration scale on Figure 5), starting from about 500 m upstream. High methane concentrations after the flood were registered already at a distance of 1500 m upstream from the mouth.

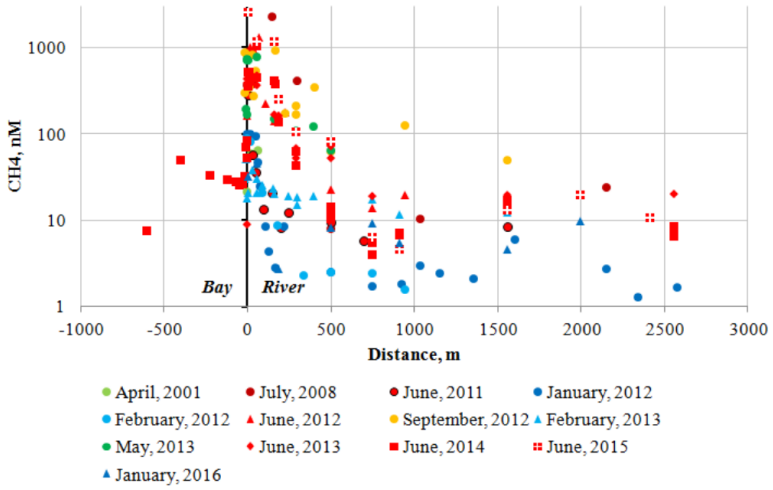

Figure 5. Dissolved methane concentrations in the waters of Ashamba River (2001–2016) and at the section from the Ashamba River mouth to the open sea (June 2014).

4. Discussion

The functioning mechanisms of the biogeochemical system within Golubaya Bay's waters can be determined by analyzing the spatial and temporal distribution of methane concentrations. Through years of monitoring, specific zones have been identified where an increased methane content was observed compared to the general background values in the bay. These areas include the surface layer—the river plume located in the northern part of the bay near the mouth of the Ashamba River, along with plumes in the northwest and east areas of the bay near inflowing streams. It is known that fresh watercourses are often characterized by an increased methane content in the estuarine zones [23,46–48]. Continental waters carry a significant amount of suspended solids that accumulate in these zones. The interaction area of the sea and river waters is characterized by a high vital activity of phyto- and zooplankton, which in turn lead to an increase in the methane released into the water [49,50]. The intestinal tracts and fecal pellets of the zooplankton as anaerobic

micro-environments in the water column are one of the likely sources of methane [5]. The allochthonous organic matter coming within river flows from estuarine areas and deposited on the bottom is an additional contributor to the increased methane concentrations [26]. Such a bottom source apparently causes the increase in methane content in the shallow (up to 1 m) southeastern part of the bay in some months (Figures 3b,f and 4a).

In addition, the maps of dissolved methane distribution in the bottom layer of the bay revealed an almost permanent source of increased methane concentrations in the bay, located in its central, deepest part (Figures 3d,e,i and 4d,e,i). The bottom at this site is composed of clay [51]. Anaerobic conditions favorable for methane generation are formed in the thin upper layer of bottom sediments [52,53]. Such a bottom source was also recorded once during the first detailed survey of methane of the bay (in its northern part) in September 1999 (Figure 3a). The depths in that part of the bay do not exceed 1 m, so the effect of the source was clearly visible at the water surface. Direct underwater sampling showed that the bottom surface was covered with a thin layer of bacterial mat.

The lowest methane concentrations in the waters of the bay, typical for the winter period, were close to the equilibrium value with atmospheric air (Table 1). This points on the absence of methane generation sources in the waters. However, the methane content in the plumes and bottom source of the bay exceeds the equilibrium one by a factor of 18–20 times on average in winter months due to the accumulation of phyto- and zooplankton and organic matter decomposition in these areas. With increasing water temperature, the biomass of zooplankton in water of the bay also grows by summer [54]. As a result, even the minimum concentrations of methane in the warm period exceed the equilibrium value with atmospheric air by a factor of 2.5, while the maximum concentrations of methane in the warm period exceed the equilibrium value with atmospheric air by a factor of up to 700 (1400 nM). At the same time, the maximum values recorded in the water column of the northeastern Black Sea in summer reach 63 nM at offshore stations with depths of over 50 m [24,28]. In autumn, the methane content in the plumes of Ashamba River and the eastern stream as well as in the bottom source area gradually decrease (to 150, 40, and 70 nM, respectively); however, the background concentrations are still relatively high (5 nM), while higher values than in summer are observed in the plume of the northwestern stream (100 nM). The cause of this process is probably the high level of vital activity of plankton in shallow waters. Dissolved methane concentrations at deeper stations in the northeastern Black Sea observed by [24,28] in autumn are significantly lower than in the shallow bay, as they ranged from 9 to 27 nM.

A similar increase in the summer concentrations compared to those of winter was recorded in one of the main sources of methane in the bay—Ashamba River. A biogeochemical barrier is formed at the border of the river and the bay throughout the year. In summer, the warming of the water likely leads to an intensification of methane formation in anaerobic microenvironments and the upper layer of the bottom sediments.

However, the most interesting situation was observed in the autumn of 2012 (Figure 3g,j). As a result of heavy rainfalls in the region, a catastrophic flood caused severe damage in July 2012. As a result of the flood, the depth of the Ashamba River riverbed increased on average by 2–2.5 m, whilst its width increased by 8–10 m. Tree-shrub cover, dozens of destroyed buildings, and several cars were washed away from the catchment of the river. According to the estimates [38], the solid discharge of the Ashamba River for 6 July 2012 amounted to about 520,000 m^3. The vertical profiles of temperature and salinity in the bay during the flood period illustrate significant changes in the hydrological structure of the waters [55]. Due to the strong and prolonged cold rain and consequently the increased runoff of Ashamba River to Golubaya Bay, the temperature in the upper 2–3 m was lower than the temperature of the rest of the water column. Strong water freshening was also recorded; in some cases, the surface salinity reached 2 psu, while during June and early July, it usually did not fall below 16 psu. Right after the flood, the productivity of phytoplankton in the waters of Golubaya Bay decreased; however, a large amount of nutrients from the flood could have led to an increase in the vital activity of phyto- and zooplankton [55,56].

Pautova et al., 2018 [39], registered a significant increase in the abundance and biomass of existing phytoplankton dominants and did not exclude the possibility of the occurrence of extinction phenomena during the decomposition of phytoplankton biomass, potentially formed after the flood in the absence of the mixing of coastal and open sea waters.

The first measurements of methane content in Golubaya Bay after the flood were carried out in September 2012. The methane distribution pattern in the surface and bottom water layers demonstrated that the area of influence of the Ashamba River flow covered almost the entire bay at that time, with the exception of its central part. The dissolved methane content reached 800 nM at the sea surface and 900 nM near the bottom. Moreover, gas bubbles were visually observed to rise to the surface of the water, which makes it possible to consider both the diffusion and ebullition of methane from the bottom of the bay. Even 2 months after the disaster, the increased intensity of biogeochemical processes was visible.

In January 2013, a seasonal decrease in methane concentrations in the surface waters of Golubaya Bay was observed due to the weakening of the zooplankton activity (Figure 3h). The maximum CH_4 concentrations were 45 nM at that time. The area of relatively high methane content covered not only the zone nearest to the river mouth, but also the central part of the bay, in contrast to the data from the previous winter (February 2012), where river and stream plumes were localized near the coast (Figure 3c,e). The surface methane concentrations in June 2013 (almost a year after the flood) were generally similar to the summer values before the flood; the methane content reaches 100 nM in the river plume and 400 nM in the shallow eastern part of the bay (Figure 4a). Thus, the gradual return of the biogeochemical state of the bay system to normal conditions can be observed.

The relatively wide period of the considered observations also provides an opportunity to identify the annual variability of CH_4 concentrations in Golubaya Bay (Figure 6). The presented line of the temporal methane fluctuations make it possible to trace the more pronounced seasonal CH_4 course compared with the less noticeable annual one in the investigated coastal area. Notably, a significant increase in methane was detected in the summer of the year following the catastrophic flood. On the one hand, this pattern is well demonstrated due to the frequent observations in 2013. Similarly, the high mean methane content was recorded only once earlier, in the summer of 2008. Meanwhile, this can be explained by the limited sampling area in this year which was adjusted to the methane-saturated zone near the river mouth.

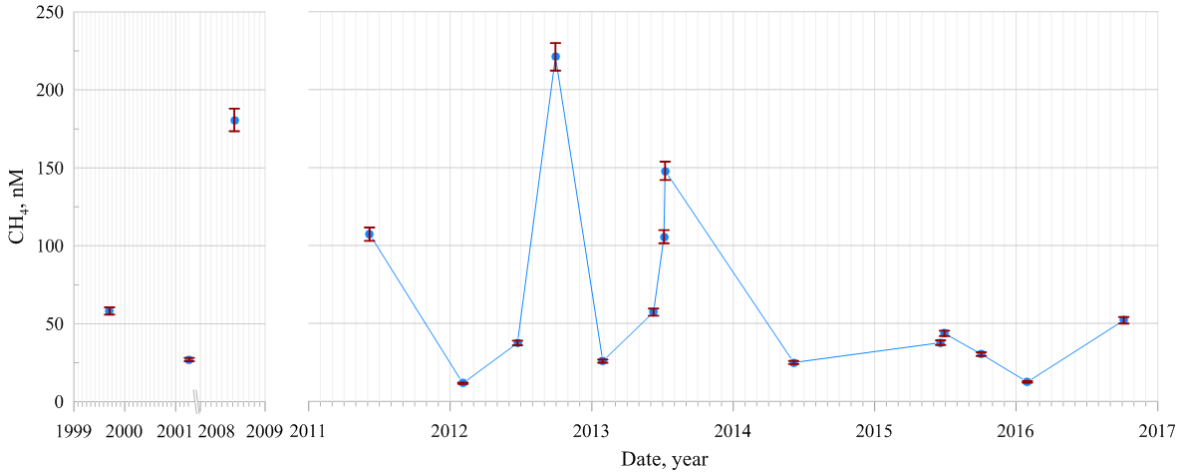

Figure 6. Mean concentrations of dissolved methane for each of the surveys (blue points) depending on the time (1999–2016) in Golubaya Bay. The error bars of the datasets are shown by dark-red lines.

The results of this study, based on the analysis of a long series of data, make it possible to trace the pronounced seasonal course of the dissolved methane in coastal waters. Comparison of the obtained results with similar long-term studies in other marine areas

allows us to conclude that the range of methane content fluctuations during the year in Golubaya Bay is an order of magnitude higher than in the coastal areas of the Balearic Sea [16]. A similar range of dissolved methane concentrations in different seasons were observed in the shallow coastal waters of the Baltic Sea [57,58]. Such an oversaturation of waters with methane in the studied area indicates its significant contribution to the methane budget of coastal waters. This is an important result in terms of the fact that coastal seas supply about three-quarters of the total marine methane emissions [59,60].

Based on these, observations, we suggest that the methane mass balance for Golubaya Bay in its general form includes the following major components: input (in situ CH_4 production, freshwater inflow, bottom supply) and output ones (CH_4 oxidation, and emission into the atmosphere). Actually, most of the terms depend on biological conditions and processes in marine and fresh waters. Meanwhile, the abiotic factors such as temperature, salinity, and wind speed affect the methane emission [45,61] and the biological activity in water environments. Generally, the seasonal CH_4 fluctuations follow the annual temperature course within the investigated area. The slight seasonal variations in water salinity values have a commonly low impact on methane concentrations in the bay, with the exception of the short-term events of substantial salinity changes such as the catastrophic flood case mentioned above.

5. Conclusions

The direct measurements of dissolved methane concentrations in coastal waters conducted over 17 years in various seasons allowed the identification of the peculiarities of the seasonal dynamics of the CH_4 spatial pattern. The case study of Golubaya Bay shows that the seasonal range of the dissolved methane content variability in the shallow part of the northeastern Black Sea is 1–2 orders of magnitude higher compared with the areas remote from the coast. The increased biological productivity and the decomposition of organic matter at low depths cause this pattern. Direct observations show that the dissolved methane content in Golubaya Bay in summer is an order of magnitude higher than the winter values. In particular, local methane maxima located near the river mouth and in the central bottom part of the Bay have a well-shown seasonal cycle. The observed magnitudes of seasonal variations in the methane content were significantly more pronounced than the interannual trend. In addition, the extremely high methane concentrations in the bay were recorded 2 months after the extreme flood. Surface concentrations of the dissolved CH_4 exceeded the equilibrium with the atmosphere values by a factor of 400. The obtained results provide a unique opportunity to estimate the scale of the biogeochemical processes in marine coastal environments under the influence of extreme flood conditions.

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