FORMATION OF HYDROGEN SULFIDE IN ISOLATED BASINS AT THE KARELIAN WHITE SEA COAST

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ABSTRACT

The results of a study of the formation of hydrogen sulfide in isolated basins, which are at different stages of isolation in Kandalaksha Bay of the White Sea, are presented. It has been demonstrated that hydrogen sulfide has developed in higher degrees in a basin mostly isolated from the sea. This basin shows pronounced features of meromixis. Accumulation of hydrogen sulfide in lakes, where the salt water periodically flows in from the sea, is connected with the development of seasonal stratification and anaerobic conditions in the bottom waters. The concentration of hydrogen sulfide increases from the surface to the near-bottom layer, where the highest concentrations of H_2S were determined in all basins.

INTRODUCTION

On the Karelian coast of the White Sea, the part of the waterside zone has been rising rapidly after the last glacier retreats (1,2). That's why some of the water basins gradually lose their connection with the sea and turn into lakes. Unique hydrochemical and hydrobiological conditions are formed in these basins (3,4,5). Therefore, investigation of these basins (lakes) is interesting for studying biogeochemical processes which occur in the reservoir during the transformation of the marine ecosystem.

During the research expeditions which started in March 2012, several water basins at different stages of isolation from the sea were examined in the vicinity of the Nikolai Pertsov White Sea Biological Station of Lomonosov Moscow State University (Figure 1).

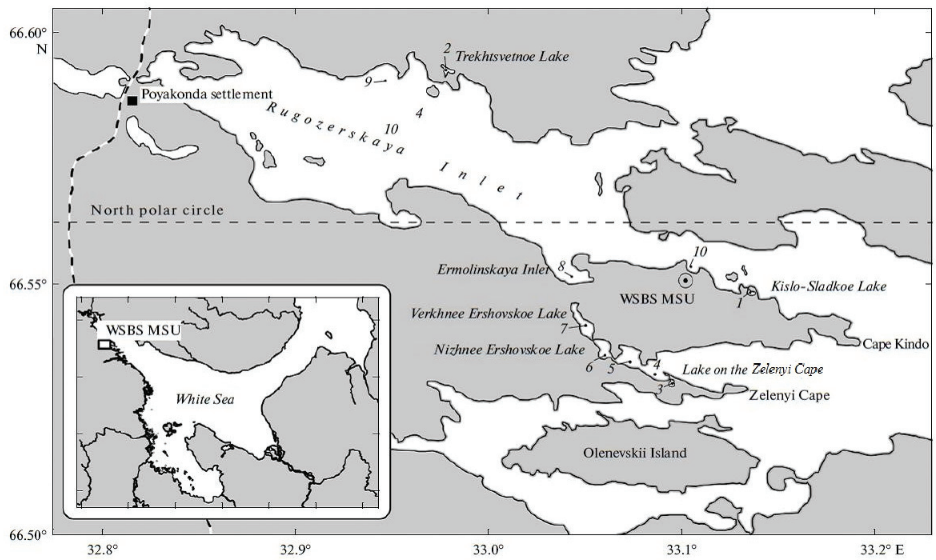

Figure 1: The area of the field work.

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Development of hypoxia in stratified salt waters of these lakes creates favourable conditions for strengthening the process of sulfate reduction and accumulation of hydrogen sulfide in the water column in three studied lakes (Kislo-Sladkoe, Trekhtsvetnoe and the lagoon on the Zelenyi Cape). The formation of hydrogen sulfide in lakes that were at different stages of separation from the sea was monitored in the course of these studies. These studies were especially interesting, because large amounts of seawater entered these lakes practically isolated from the sea as a result of storm surge in autumn 2011, which led to significant changes in their hydrological structure. Flooding cleaned these basins and returned them to an earlier level of hydrogen sulfide. A new reference point for observations on the restoration of stratification and the formation of hydrogen sulfide in these basins (lakes) was assigned.

METHODS

Water from different depths was sampled with a Mini Purger WP 4012 submersible pump. The hydrogen sulfide was determined using a photometer Expert-003 and a iodometric method according to (6). Water samples with high concentrations of hydrogen sulfide were diluted by distilled water and analysed with both methods. Salinity was measured using a CastAway conductometer, pH was determined using a pH-meter model WaterLiner WMM-73.

RESULTS

Lake Kislo-Sladkoe

This lake (66°32.87'N; 33°08.14'E) is located 1.5 km from the biological station. It is a small lake (170 m long, 90 m wide) with an average depth of 1.5 m and a maximum depth of 4.7 m. Seawater enters into this basin during spring tides. Wind mixing, desalination from snow melting, inflow of a small stream and precipitation affect only the top metre depth.

In March 2012, after fall washing by sea-water, salinity of the surface layer was 26.2 psu (Figure 2) and remained practically unchanged with depth. In September 2013, as a consequence of seawater inflow during particularly high fall tides, salinity was evenly distributed with depth (21.9-23.8 psu). In all other cases, there is desalination of the surface layer mainly due to rainfalls and snowmelt (3).

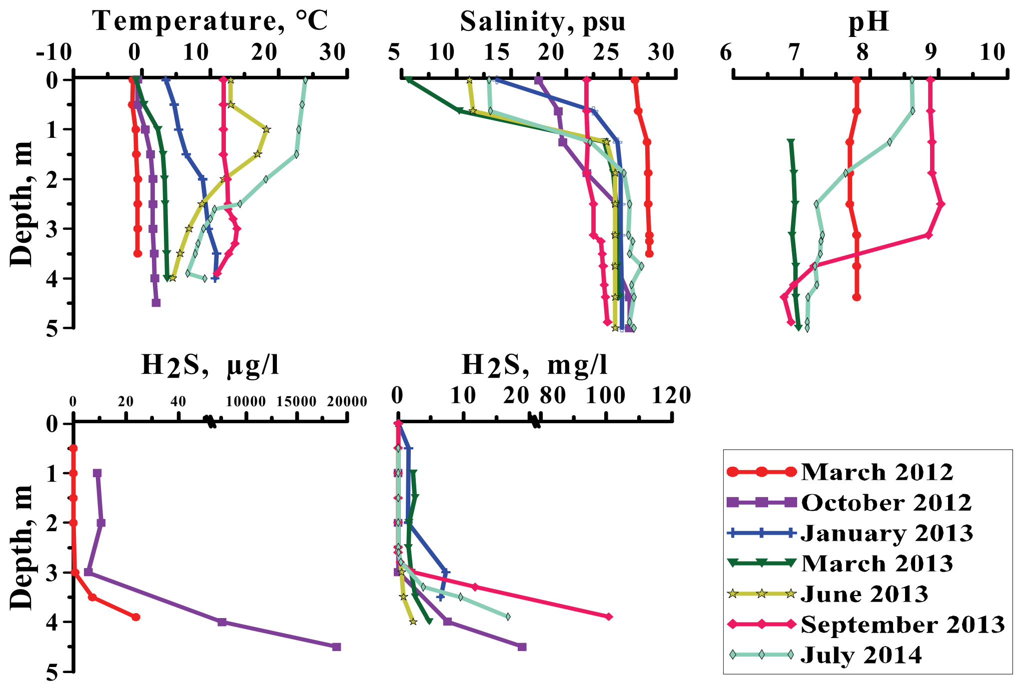

Figure 2: Vertical distribution profile of temperature, salinity, pH, and hydrogen sulfide (H_2S) concentration in Lake Kislo-Sladkoe.

The temperature distribution in the lake water is in good agreement with the corresponding climatic seasons (Figure 2). An increase in temperature in the subsurface layer of 0.5 - 1.5 m in June 2013 is typical of this basin during the summer season (3,7) and due to the absorption of solar radiation by dark bottom sediments and the density barrier between warmed layer and overlying freshened layer of water, which serves as a sort of "greenhouse roof".

During the ice period (March 2012 and 2013), pH varied little with depth (Figure 2). Its shift to the alkaline area (pH = 8.8) was distinguished in September 2013 and July 2014 in the upper layers of the water column (3 m). It can be a consequence of an active process of photosynthesis. A subsequent abrupt decrease in the index (pH = 6.8) (to a depth of 3.5 m), is probably connected with the activity of bacteria producing hydrogen sulfide and carbon dioxide.

Significant hydrological changes in the water column of the Kislo-Sladkoe lake were observed as a result of seawater inflow during the autumn surge in 2011 and 2013. After the first autumn washing by seawater, hydrogen sulfide was detected in March 2012 in small amount (28.3 µg/l) only in the near-bottom layer (Figure 2). In October 2012, hydrogen sulfide was determined throughout the water column with a maximum of 19 mg/l near the bottom which indicates the ongoing intense processes of sulfate reduction in the basin. This pattern of hydrogen sulfide distribution remained the same in the lake in the subsequent cold period (January and March 2013). Hydrogen sulfide concentration in the upper layers of the lake was 1.5-2.5 mg/l, reaching a maximum in the near-bottom layer (7.3 mg/l in January and 4.8 mg/l in March). In the summer and autumn of 2013 and the summer of 2014, hydrogen sulfide remained only in the deep water layers (below 2.5 m). In the summer months, its concentration below 2.5 m was 2.3-16.7 mg/l; in September it increased to 100.7 mg/l. Formation of so significant amounts of hydrogen sulfide in autumn is connected with the development of favourable conditions for the process of sulfate reduction (a combination of anoxic conditions supplying the near-bottom water layer with organic matter formed by photosynthesis during the warm season).

The Cape Zelenyi lagoon

The lagoon (lake) is located at the base of Cape Zelenyi and connected with the Kislaya Inlet (66°31.80'N, 33°05.55'E). It has a rounded shape with a width and a length of 120 m, the area is 12,840 m^2; the average and maximum depth is 2 m and 6.5 m, respectively. The lagoon keeps connection with the sea over a small threshold and the sea water enters inside through it during each flood tide.

The bottom water in the lagoon is colder and saltier than the bottom layer of Lake Kislo-Sladkoe (Figure 3). Moreover, its salinity is higher than that of the adjacent sea area, which is due to the small watershed and exiguity of freshwater runoff from the shore as well as to the outflow of brine during seawater freezing (7,8).

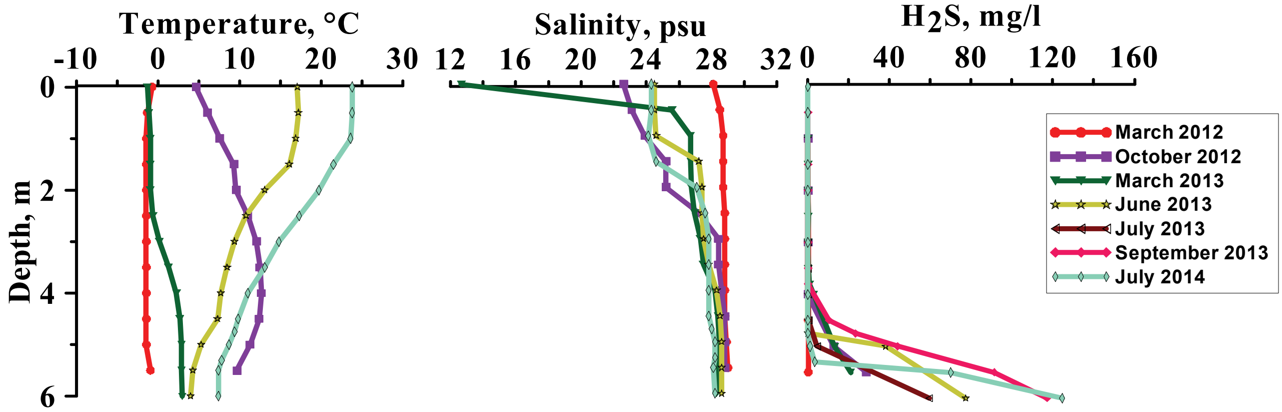

Figure 3: Vertical distribution profile of temperature, salinity and concentration of hydrogen sulfide in the lake at Cape Zelenyi.

Vertical stratification in the lagoon at Cape Zelenyi, as well as in Lake Kislo-Sladkoe, in winter depends on the height of autumn spring tides affecting the degree of reservoir flushing and, as a consequence, the distribution of hydrogen sulfide.

After washing of the basin at high tide in autumn 2011, hydrogen sulfide concentration in the water did not exceed 200 µg/l (9) in March 2012; even near the bottom, it was significantly lower than the concentration which was recorded by S.I. Shaporenko in summer in 2001-2002 (3). In October 2012, its concentration in the near-bottom layers increased to 12.6 mg/l at a depth of 5 m and to 28.7 mg/l in the near-bottom waters (5.5 m), which is only three times less than the previously recorded maximum (90 mg/l). By the fall of 2013, the hydrogen sulfide concentration in the near-bottom water was 117 mg/l, and in July 2014 it was 125 mg/l. High concentrations of hydrogen sulfide, typical of the near-bottom waters of the basin, according to (3) is due to the massive development of filamentous algae in the lagoon, whose rot off collect at the bottom and serve as a substrate for sulfate-reducing bacteria. In general, the Cape Zelenyi lagoon as well as Lake Kislo-Sladkoe are characterized by an increase in the concentration of hydrogen sulfide in the near-bottom layer during the growing season of the year with a maximum value in the fall.

Lake Trekhtsvetnoe

Lake Trekhtsvetnoe (Tricolor) is located in the Pekkelinskaya Inlet (66°35.53'N, 32°59.97'E). The size of this basin is 340 m × 150 m with a maximum depth of 7.5 m. The lake lost its connection with the sea a long time ago. Therefore, there are no regular tide inflows.

The lake has a distinct vertical stratification of the water column throughout the year, a freshened top layer of 1 m, and a sharp increase in salinity to ~20 psu near 2 m depth. Salinity increases smoothly to 22 psu in the near-bottom layer. Seasonal temperature changes occur only in the upper layers, while the temperature remains constant in the near-bottom layer (5.2 ± 0.4°C). The pH values show seasonal changes in the upper 2 m; below 2 m, the pH is about 7 and does not change with the season (Figure 4).

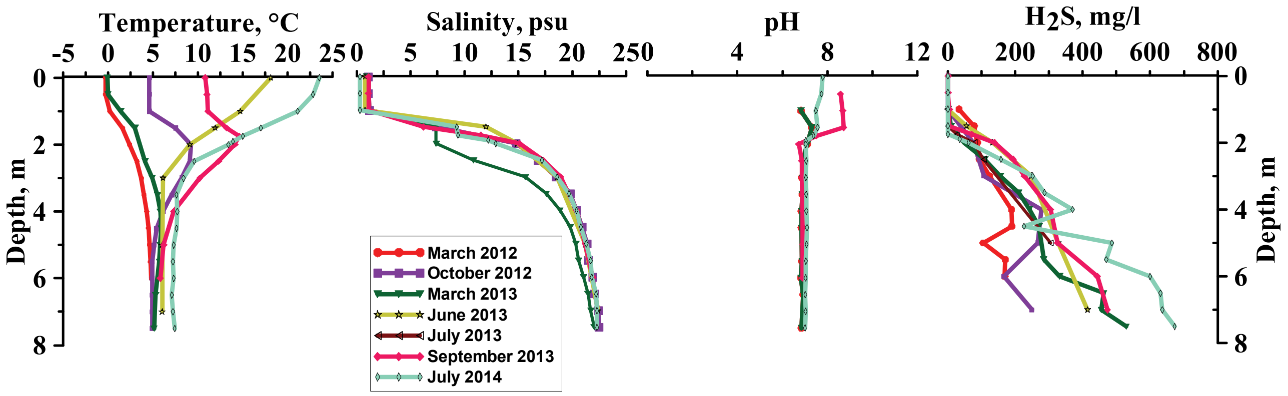

Figure 4: Vertical distribution of temperature, salinity, pH and hydrogen sulfide concentration in Lake Trekhtsvetnoe.

Analysis of obtained data demonstrates the stability in the vertical distribution and in the level of H_2S concentrations for anaerobic waters of Trekhtsvetnoe Lake, which suggests that it is a prevalent meromictic lake. The meromictic structure facilitates the accumulation of significant amounts of organic matter in the salt waters of the monimolimnion, it significantly stimulates the activity of sulfate-reducing bacteria and contributes to the accumulation of significant amounts of hydrogen sulfide. The concentration of hydrogen sulfide in the monimolimnion increases towards the near-bottom layer, where it reached maximum concentrations of 470 mg/l in September 2013 and of 673 mg/l in July 2014. It can be noted that these hydrogen sulfide concentrations are significantly higher than the concentrations found in the Black Sea anaerobic waters (9.6 mg/l) (10) and in the Norwegian Framvaren Fjord (204 mg/l) (11,12).

CONCLUSIONS

A unique hydrochemical structure has formed in basins isolated from the Kandalaksha Bay of the White Sea. These basins (lakes) differ from each other in the degree of hydrogen sulfide, because they are at different stages of isolation from the sea.

Lake Trekhtsvetnoe has lost its connection with the sea; it has the steadiest meromictic structure and the highest concentration of hydrogen sulfide in monimolimnion (up to 673 mg/l). This value significantly exceeds the concentration of hydrogen sulfide in other bodies of water with anaerobic conditions (the Black Sea, Framvaren Fjord).

In the Zelenyi Cape lagoon, which still retains connection with the sea, fluctuations in hydrogen sulfide concentrations in the anoxic water layer are significant and can change with the arrival of fresh portions of seawater. Instability of anaerobic conditions is confirmed by current data. A long-term trend of increase in the H_2S concentration in the bottom layer is noticed. The amount of H_2S in the bottom layer (~ 120 mg/l) is 5 times higher than it was in the winter of 2013.

In Lake Kislo-Sladkoe, connected with the sea only during spring tides, seasonal changes of hydrogen sulfide concentrations in the bottom layer were registered. The concentrations in September 2012 and October 2013 were significantly (20 times) higher than the values recorded in the other seasons. Intensification of sulfate reduction in this case is caused by "volley" receipt of labile organic matter as a result of mass dieback of summer plankton.

As a result, a unique hydrological structure was formed in these lakes allowing us to trace the development of anoxic conditions in the process of their isolation from seawater. The presence of favourable conditions for sulfate reduction and development of hydrogen sulfide in the studied basins is demonstrated, which confirms the topicality of these studies and the necessity of continuing them in future.

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