Bottom sediments as indicators of water resources state within the town boundaries of Cherepovets, Vologda region

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Abstract. The article considers the research of the plant pigments content in the upper layer of the bottom sediments in the rivers (the Serovka, the Yagorba, the Sheksna), which are affected by communal and industrial wastewater in Cherepovets. The average content of pigments in the bottom sediments of the Serovka and the Yagorba rivers was higher than in the Sheksna river during the observation period (July 2015 – December 2016). According to the indices $E_{480}/E_{665}$, $E_{480}/(1.7E_{665k})$ and the ratio of chlorophyll to pheophytin, the pigmentary fund of benthic algocenoses is mainly in a degraded state. In terms of chlorophyll and pheopigments (calculated on dry soil) amount, the bottom sediments of the Serovka river are characterized by the mesotrophic category values, while the ones of the Yagorba and the Sheksna rivers – by oligotrophic values.

1. Introduction
The rivers flowing in the town are used to provide drinking water, irrigation of agricultural land, industrial and municipal water supply and wastewater discharge, navigation, fishing and recreation. River water quality largely depends on the bottom sediments state. Annually a huge amount of industrial and communal wastewater is discharged into reservoirs. It leads to the accumulation of various substances in the bottom sediments, and affects the processes in the reservoirs. Sewage can lead to eutrophication of water bodies. At present water bodies eutrophication is global in scope. The main indicator of eutrophication is primary production. To determine water bodies productivity various indicators are used. They include the content of chlorophyll, pheophytin, carotenoids, and pigment indices [1–4]. Bottom sediments are considered the best indicators of eutrophication, since they are sources of internal nutrient loading, which largely determines reservoir productivity [5–7]. Determination of the plant pigments content in the bottom sediments makes it possible to assess the ecological state of water bodies, and to predict their ecological state for the future.

The research is aimed at estimating of the rivers ecological state within the boundaries of Cherepovets, Vologda region, on the basis of pigment characteristics of the bottom sediments. Cherepovets is the largest town in Vologda region, the administrative center of Cherepovets district. It is located on the Sheksna river, on the left tributary of the Volga, at the mouth of the Yagorba river. The Sheksna, the Yagorba, the Serovka, the Nelaž, the Torovka, and the Koshta rivers flow in the town and its surrounding areas [8]. Characteristic feature of all the rivers in the Cherepovets area is their regulation by a backwater from the Rybinsk reservoir, resulting in the formation of deep-water bays in the mouths of the rivers. The entire water area of the northern part of the Sheksna and the small rivers of this region are under the powerful influence of Cherepovets. It receives heated urban water, a large number of organic compounds of domestic and industrial origin. Urban sewage spreads over a distance of more than 11 kilometers along the Sheksna River, and the effect of sewage in the plume manifests itself at a distance up to 25-55 kilometers. Severe contamination with phenols, naphthalene derivatives, petroleum products, fecal discharges leads to a sharp increase in the number of bacteria. The Koshta, the Sheksna, the Serovka rivers, the mouth of the Yagorba river are severely polluted. The Sheksna river undercurrent has a significant influence on the water formation of the northern part of the Sheksna reach in the Rybinsk Reservoir, and is strongly affected by the tributaries and upper areas of the Sheksna reservoir [9]. The greatest anthropogenic load is on the water objects, on the banks of which there are large industrial hubs, including Cherepovets (the Koshta, the Yagorba,
the Serovka rivers) [10]. On the banks of all these rivers there are industrial enterprises: JSC "Cherepovets Port", JSC "Severstal-Invest", CJSC "Cherepovets Plywood and Furniture Factory", the river berths for the country passenger ships, JSC "Cherepovets Match Factory FESKO", JSC "Cherepovets Shipbuilding and Shiprepairing Plant", cattle-breeding complex (CJSC "Botovo") and summer cottages.

2. Methods
The research samples were selected on the territory of Cherepovets town from July 2015 to December 2016 in the Sheksna, the Yagorba and the Serovka rivers by the GR91 bottom-grab from the upper layer of the bottom sediments (0−5 cm) in the shallow areas, two meters from the water edge (at the depth of 1−1.5 m), one time per month during the year. Plant pigments in the bottom sediments were determined by spectrophotometric method on the PE-5400uf spectrophotometer in acetone extract, the calculations were carried out according to the Lorentz equations, generally accepted for phytoplankton, with some modifications [11, 12]. The indicator of the pigmentary stock degradation degree (the ratio of carotenoids and chlorophyll concentrations) was estimated from the extract optical densities at wavelengths of 480, 665 nm before and after acidification by the E480 / E665 and E480 / 1.7 * E665k indices [11]. The soil moisture content and the amount of organic substance were determined by traditional methods [13]. The river trophic state estimate was computed on the basis of the sum of chlorophyll and phenopigments calculated on dry soil: <13 μg / g oligotrophic, 13−60 μg/g mesotrophic, 60−120 μg / g eutrophic, > 120 μg/g hypertrophic [14].

3. Results and Discussion
The bottom sediments of the rivers under study differed significantly in the content of photosynthetic pigments, organic substance and humidity. The chlorophyll content in the bottom sediments of the Serov river ranges from 0.83 to 29.5 μg/g, pheophytin – from 0.78 to 34.4 μg/g, carotenoids – from to 8.7 to 48.4 μg/g. The chlorophyll content in the bottom sediments of the Yagorby river ranges from 0.3 to 20.9 μg/g, pheophytin – from 0.1 to 31.8 μg/g, carotenoids – from 1.5 to 46.6 μg/g. The chlorophyll content in the bottom sediments of the Sheksna River fluctuates from 0.21 to 5.5 μg/g, pheophytin from 0.29 to 7.2 μg/g, carotenoids from 1.5 to 9.3 μg/g. The content of carotenoids in the of river bottom sediments considerably exceeds the content of chlorophyll, which may be a consequence of stratification leading to changes in destructive processes [11], different rates of plant pigments destruction: carotenoids are destroyed more slowly. The average content of chlorophyll with pheophytin (Ch + F) in the upper layer of the Serovka (17.8±3.1 μg/g) and the Yagorba (12.9±2.9 μg/g) bottom sediments was characterized by higher values than in the Sheksna river 5.0±0.55 μg/g). The greater pigment content over the period under study was observed in the Serovka river (figure 1) than in the Yagorba and the Sheksna rivers. The intake of phytoplankton organic substance in the bottom sediments depends on the flow speed and on the anthropogenic influence – the inputs of nutrients due to sewage from the industrial enterprises and from local settlements situated on the banks of the rivers. The River Sekovka differs from the Yagorba and the Sheksna rivers by a lower flow rate. It increases the nutrient content in the water and, in combination with the weak hydrodynamic regime, affects the siltation of the reservoir.
Figure 1. The average content of pigments in the bottom sediments of the Cherepovets rivers (from July 2015 to December 2016).

By soil type: the Serovka river – gray silt; the Yagorba river – silty sand; the Sheksna – sand. The content of water (humidity) in soils is directly dependent on the soil type. Large and medium-grained sand is characterized by low humidity (11–24%). The highest moisture content is typical for silts (15–55%). Silty sands keep an intermediate position (19–31%).

The average pigment content clearly increased in the series: sand (the Sheksna river) → silty sand (the Yagorba river) → gray silt (the Serovka river) (figure 2). According to the analysis of the plant pigments content, organic substance and moisture, the investigated rivers can be arranged in the following order: the Serovka river > the Yagorba river > the Sheksna river.

Figure 2. Humidity and organic substance (OV) content in the bottom sediments of the Cherepovets rivers (from July 2015 to December 2016).
The plant pigments ratio in the water and bottom sediments reflects the result of the synthesis and destruction of the newly formed organic substance, the result of the photosynthetic apparatus of algae and their pigments transformation [15] (Table 1). Chlorophyll in the river bottom sediments is represented mainly by the products of destruction − from 60 to 98% of their total amount with chlorophyll.

| N | Pigmentary indices | The Serovka river | The Yagorba river | The Sheksna river |
|---|--------------------|-------------------|-------------------|------------------|
| 1 | E$_{480}$/E$_{665}$ | 3.08              | 2.60              | 2.60             |
| 2 | E$_{480}$(1.7E$_{665}$) | 2.40              | 1.69              | 1.61             |
| 3 | Chl/Ph             | 0.59              | 0.49              | 0.55             |

In the river bottom sediments, the index E$_{480}$/E$_{665}$ changed in the Serovka river from 1.17 to 9.33, in the Yagorba river from 1.07 to 4.58, and in the Sheksna river – from 1.04 to 3.83 at different observation time. Clear seasonal dynamics of the index values were not revealed. The average values of the yellow and green pigments ratios (E$_{480}$/E$_{665}$) (Table 1) exceed the values for the functioning phytoplankton. The correction for the presence of chlorophyll derivatives leads to a slight decrease in the concentration ratio of yellow and green pigments (E$_{480}$/ (1.7E$_{665}$k)) (Table 1), but this index does not reach the values characteristic of phytoplankton. Perhaps this is due to the predominant degradation and discoloration of chlorophyll, the accumulation of transformed organic substance. The ratio of chlorophyll pigments to pheophytin (Chl/Ph) is less than one, indicating the extinction and decomposition of algae [16–18]. The obtained physiological state indices determine the ecological state of phytoplankton as altered, functionally impaired. The rivers under study experience long-term impact of communal and industrial wastewater, as a result of which, in excess amount, various compounds enter the water of these rivers, which adversely affects the structure and functioning of plankton and benthic communities [19], as well as the bottom sediments composition. The qualitative composition of the bottom sediments is the most important factor of the environmental state, since it determines the amount of pollutants deposition, the scale and rate of their entry into the water masses and biota [20].

According to the results of the study, it is possible to estimate the trophic state of the rivers by sedimentary pigments: the Serovka river can be referred to mesotrophic, the Yagorba and the Sheksna rivers − to oligotrophic reservoirs. Of the rivers under investigation, the Serovka river is the most productive in comparison with the Sheksna and the Yagorba rivers, but in all these rivers destructive processes predominate, which determines the ecological state of water bodies as altered, functionally impaired.

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