Biohydrochemical Studies of the Intra-Annual Nutrient Dynamics in the Northeastern Shelf Waters of the Sakhalin Island

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Abstract. The transformation of nutrients in marine environments of the northeastern part of the Sakhalin shelf was studied. Based on the data on the status of the thermohaline parameters of sea water, the dynamic ocean model and the hydroecological model, the seasonal dynamics of concentrations of organic and mineral substances for growth biomass aquatic organisms are presented.

1. Introduction
Many marine areas of the Russian Far East are subject to significant anthropogenic impact [1,2]. Evaluation of the sustainability of oppressed marine ecosystems and their self-healing potential is based on the analysis of the circulation of organic matter, nutrients and primary production [3,4,5]. Methods of mathematical modeling are widely used for these purposes [6,7,8]. The dynamics of nutrients, their chemical and biological transformation, biological productivity of water bodies are studied depending on the impact of environmental factors on the ecosystem: temperature and transparency of water, light intensity, nutritional load. The Northeast Sakhalin Shelf (NESS) is an area of active oil and gas production and is potentially dangerous for pollution. Therefore, the assessment of the current state and the recovery potential of the water area is of great scientific and practical importance. The calculations for the NESS were carried out using long-term hydrological data [9], the hydrodynamic model of the ocean of the Bergen University (BOM) [10], and the hydroecological model CNPSi of the transformation of biogenic substances [11,12]. These instruments have proven themselves in studying the characteristics of hydrodynamics and biohydrochemistry of waters in various regions.

2. Object and methods of research
The entire water area of the NESS is divided into Regions 1–4 (Fig. 1). The morphometric parameters of these regions are presented in Table 1. In addition to the morphometric parameters, biogenic substance (BS) concentrations in tributaries and adjacent water areas, mean monthly water
temperature ($T_w$), light intensity and water transparency, as well as water exchange volumes between Regions 1–4 and the open part Sea of Okhotsk are also presented in Tables 2–4. Water exchange parameters were calculated on the basis of current indicators for the water areas of the NESS based on the ocean model BOM for long-term observations of $T_w$ and salinity ($S_w$) of the sea waters of the

| Characteristic dimension | Regions of NESS |
|-------------------------|-----------------|
| Mean depth, m           | 640 1520 300 730 |
| Water area, thou. km$^2$| 48 15 35 19  |
| Water volume, thou. km$^3$| 30.7 22.8 10.5 13.7 |

NESS region. The methodology for preparing the initial data for calculations using the CNPSIm model is described in [13].

The main seasonal features in changes of thermohaline parameters in the Regions 1–4 of the NESS are singled out. The water column is divided into two layers during the year [13]: in the cold period, this is due to the development of winter vertical water circulation processes, and in warm weather - with the warming of the surface layer (Table 2).

**Figure 1.** Map-scheme of the area of NESS.

Calculations of changes in the concentrations of substances were carried out for two years. Estimates of the values of biohydrochemical parameters at the end of the first year are considered average long-term environmental parameters. They are taken as initial concentrations, in the second year of calculations, in order to present the seasonal dynamics of concentrations of substances, biomass of organisms, fluxes of internal / external substances for the biohydrochemical characteristic of the behavior of marine ecosystems depending on environmental conditions and anthropogenic impact. The values of total flow rates calculated using the specification (Table 3) determine the pronounced two-way exchange of water across the boundaries between Regions 1-4 and with the waters of the Sea of Okhotsk.
Table 2. Long-term values of marine characteristics by month for Regions 1–4 of NESS.

| Region | Month | Depth of vertical mixing of water (XI–V) and termocline position (VI–X), m | Water temperature, °C | Light intensity, cal/(sm² *day) | Precipitation, km³ | Secchi depth, m |
|--------|-------|---------------------------------------------------------------------|---------------------|-----------------------------|-------------------|-----------------|
| I–IV   |       |                                                                     |                     |                             |                   |                 |
| 1-4    |       | 150 150 150 150 150 20 30 40 50 60 75 100                           | -0.8 -1.2 -1.3 -1.4 -1.1 1.7 4.6 5.4 6.2 3.7 1.1 0.0 | 90 114 168 213 219 240 219 206 200 129 120 90 | 0.32 0.39 0.48 0.60 0.66 0.71 0.69 0.62 0.54 0.48 0.34 0.32 | 1.11 0.89 0.98 1.49 1.96 1.83 2.76 3.19 3.58 2.70 1.69 1.61 | 1.83 1.96 2.76 3.19 3.58 2.70 1.69 1.61 |
| 1      |       | 1.5 1.0 1.0 1.0 1.4 0.6 1.0 0.5 1.0 0.6 1.0 0.8       | 1.1 1.4 1.4 1.4 1.4 1.4 1.1 2.4 4.8 5.5 6.1 4.0 | 0.2 0.2 0.6 0.7 0.6 0.7 0.6 0.7 0.3 0.2 0.4 0.5 0.2 | 1.5 1.4 1.3 1.3 0.9 3.0 5.7 6.0 6.3 4.3 2.0 0.3 | 0.8 0.6 0.5 0.5 0.5 0.5 0.5 0.5 0.4 0.3 0.4 0.6 0.8 0.8 |
| 2      |       | -0.6 -1.0 -1.2 -1.2 -0.9 3.1 6.5 6.7 6.9 4.1 1.2 0.1     | 1.4 1.4 1.4 1.4 1.4 1.4 1.4 0.8 1.0 1.0 1.0 1.3 | 0.2 0.1 0.4 0.3 0.2 0.3 0.3 0.4 0.5 0.2 0.5 0.2 | 0.4 0.6 0.5 0.5 0.5 0.5 0.5 0.5 0.4 0.3 0.4 0.6 0.8 0.8 |
| 3      |       | -0.6 -1.2 -1.4 -1.4 -1.1 2.4 4.8 5.5 6.1 4.0 1.9 0.2     | 0.2 0.2 0.6 0.7 0.6 0.7 0.6 0.7 0.3 0.2 0.4 0.5 0.2 | 0.2 0.1 0.4 0.3 0.2 0.3 0.3 0.4 0.5 0.2 0.5 0.2 | 0.4 0.6 0.5 0.5 0.5 0.5 0.5 0.5 0.4 0.3 0.4 0.6 0.8 0.8 |
| 4      |       | -0.4 -1.1 -1.3 -1.3 -0.9 3.0 5.7 6.0 6.3 4.3 2.0 0.3     | 0.2 0.1 0.4 0.3 0.2 0.3 0.3 0.4 0.5 0.2 0.5 0.2 | 0.2 0.1 0.4 0.3 0.2 0.3 0.3 0.4 0.5 0.2 0.5 0.2 | 0.4 0.6 0.5 0.5 0.5 0.5 0.5 0.5 0.4 0.3 0.4 0.6 0.8 0.8 |
| 1-4    |       | 0.8 0.6 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.4 0.3 0.2 0.1 0.1 | 0.2 0.1 0.4 0.3 0.2 0.3 0.3 0.4 0.5 0.2 0.5 0.2 | 0.2 0.1 0.4 0.3 0.2 0.3 0.3 0.4 0.5 0.2 0.5 0.2 | 0.4 0.6 0.5 0.5 0.5 0.5 0.5 0.5 0.4 0.3 0.4 0.6 0.8 0.8 |
| 1      |       | 1.1 0.89 0.98 1.49 1.96 1.83 2.76 3.19 3.58 2.70 1.69 1.61 | 1.58 1.14 1.13 1.25 1.61 1.52 2.27 2.38 2.64 2.26 2.16 2.06 | 1.2 1.3 1.0 0-1 3-8 6-8 7-8 7-8 7-8 8-10 9-11 8-12 | 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2.0 2.1 | 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2.0 2.1 |

The range of values of water flow varies from one to three orders of magnitude, taking into account variations in the thickness of the separated upper and lower layers of water in different months. The inflow of water from the Tym River varies between 0.035-0.935 km³/month.

During the year, there is a bilateral water exchange across the borders of the NESS regions with an open water area of the Sea of Okhotsk. The calculations took into account the values of water flow rates estimated using specifications that determine the exchange of water in the north (in Region 1), in the north and east (in Region 2), in the east and south (with Region 4). The introduction of BS into the water area occurs with the flow of the Tym River (in Region 3), from the open areas of the Sea of Okhotsk (in Regions 2 and 4), as well as from neighboring waters and with precipitation (in Regions 1-4).

3. Results and discussion

The results of intra-annual changes in calculated concentrations of basic substances N, P, Si for the second settlement year are presented and discussed. The following abbreviations have been introduced: DOC, DON, and DOP — concentrations of dissolved organic carbon, nitrogen, and phosphorus, respectively; ND and PD are weighted components of detritus containing nitrogen and phosphorus; DIP and DISi are concentrations of dissolved mineral forms of phosphorus and silicon.

BS transfer occurs during bilateral water exchange between Regions 1-4. Table 4 shows the results of calculating the inputs of BS in each region during the exchange of water across the boundaries between Regions 1–4, namely: the amplitude ranges of the monthly transmission, the final annual and “clean” transfer (taking into account the BS removal losses with water flow).

The transfer of BS in bilateral water exchange between the open waters of the Sea of Okhotsk and Areas 1-4 were taken as a result of previous calculations [15].
The dynamics of changes in the concentrations of various forms of N and P during the year is presented in Fig. 2. Intra-annual changes in the content of N and P in the dissolved (N_{dis}, P_{dis}) and suspended (N_{par}, P_{par}) fractions, as well as the total content of N and P (N_{tot}, P_{tot}) are presented in Fig. 3.

**Table 3.** Long-term monthly values of flow rates at the boundary of Regions NESS, exchange with outer waters of the Sea of Okhotsk, vertical transport (km$^3$/month).

| Transport from | I   | II  | III | IV  | V   | VI  | VII | VIII | IX  | X   | XI | XII |
|----------------|-----|-----|-----|-----|-----|-----|-----|------|-----|-----|----|-----|
| 1-N            | 388 | 361 | 354 | 376 | 493 | 74  | 265 | 284  | 175 | 155 | 302| 340 |
| 1-2            | 377 | 313 | 356 | 305 | 193 | 6   | 1   | 11   | 200 | 254 | 419| 285 |
| 2-1            | 1607| 1740| 1836| 1773| 2087| 2126| 1886| 1795 | 1222| 1305| 1565| 1450|
| 3-1            | 88  | 89  | 129 | 133 | 138 | 52  | 124 | 98   | 49  | 55  | 52 | 84  |
| 1-3            | 9.0 | 0.3 | 0.2 | 0.7 | 0.2 | 144 | 130 | 113  | 149 | 307 | 210| 118 |
| 4-2            | 244 | 277 | 340 | 323 | 308 | 34  | 29  | 129  | 111 | 17  | 61 | 113 |
| 2-4            | 31  | 14  | 8   | 7   | 17  | 5   | 69  | 0    | 5   | 89  | 41 | 26  |
| 3-4            | 236 | 262 | 346 | 372 | 698 | 175 | 62  | 148  | 204 | 299 | 412| 265 |
| 3-3            | 311 | 179 | 153 | 149 | 109 | 533 | 426 | 515  | 516 | 638 | 717| 636 |
| 4-3            | 226 | 114 | 107 | 105 | 89  | 12  | 61  | 58   | 131 | 203 | 301| 435 |
| 265            | 234 | 278 | 304 | 458 | 676 | 461 | 645 | 626  | 724 | 732 | 405| 405 |

Exchange with outer water area - from the Sea of Okhotsk:

| Transport from | I   | II  | III | IV  | V   | VI  | VII | VIII | IX  | X   | XI | XII |
|----------------|-----|-----|-----|-----|-----|-----|-----|------|-----|-----|----|-----|
| 1-N            | 388 | 361 | 354 | 376 | 493 | 74  | 265 | 284  | 175 | 155 | 302| 340 |
| 1-2            | 377 | 313 | 356 | 305 | 193 | 6   | 1   | 11   | 200 | 254 | 419| 285 |
| 2-1            | 1607| 1740| 1836| 1773| 2087| 2126| 1886| 1795 | 1222| 1305| 1565| 1450|
| 3-1            | 88  | 89  | 129 | 133 | 138 | 52  | 124 | 98   | 49  | 55  | 52 | 84  |
| 1-3            | 9.0 | 0.3 | 0.2 | 0.7 | 0.2 | 144 | 130 | 113  | 149 | 307 | 210| 118 |
| 4-2            | 244 | 277 | 340 | 323 | 308 | 34  | 29  | 129  | 111 | 17  | 61 | 113 |
| 2-4            | 31  | 14  | 8   | 7   | 17  | 5   | 69  | 0    | 5   | 89  | 41 | 26  |
| 3-4            | 236 | 262 | 346 | 372 | 698 | 175 | 62  | 148  | 204 | 299 | 412| 265 |
| 3-3            | 311 | 179 | 153 | 149 | 109 | 533 | 426 | 515  | 516 | 638 | 717| 636 |
| 4-3            | 226 | 114 | 107 | 105 | 89  | 12  | 61  | 58   | 131 | 203 | 301| 435 |
| 265            | 234 | 278 | 304 | 458 | 676 | 461 | 645 | 626  | 724 | 732 | 405| 405 |

Vertical transport in water area: (↑↑) means upward, (↑↓) means downward.

In the first part of a year, the dynamics of the total mineral N (N_{min}) concentrations in the waters oscillates synchronously with changes in the NO$_3$ concentrations as the dominant fraction of N_{min}. In the middle of a year, expressed maxima of N_{min} contents were noted, which is a consequence of the increased concentrations of NH$_4$ and NO$_3$, fixed in almost the same periods of time. In the last third of a year, the dynamics of N_{min} concentrations coincides practically with the NO$_3$ dynamics since the
content of NH$_4$ and NO$_2$ remains low in the second half of a year and does not significantly affect the total N$_{\text{min}}$ content in different regions of the sea. In the waters of coastal Regions, the concentration of DON is higher when in remoted from the coast Regions for most part of a year.

Comparison of the values of the ratios of the components N and P shows that:

- in the waters of all regions, the range of changes in the proportions of the weighed components of N$_{\text{par}}$: P$_{\text{par}}$ is usually lower than the ratio of the concentrations of their dissolved and total components (N$_{\text{dis}}$: P$_{\text{dis}}$);

- the waters of Region 3, into which the river flow enters, have smaller ranges of variability in the ratios of suspended fractions N$_{\text{par}}$: P$_{\text{par}}$ in higher ranges of the ratios of their dissolved and total concentrations (N$_{\text{dis}}$: P$_{\text{dis}}$);

- there are differences in the ratios of the N: P components depending on the location of the regions: in coastal Regions 1 and 3 in general, the variability ranges of the ratios of dissolved and total N: P concentrations are higher than in regions 2 and 4 remote from the coast. The dynamics of BS content was used in the calculation of the primary production (table 4).

The development season of phytoplankton F1N (a), heterotrophic bacteria B1N (d) and both zooplankton groups Z1N (e), Z2N (f) begins synchronously with the onset of the calendar summer in early June and lasts until the end of October. During the first month, the productivity reaches a maximum, then the limitation of nutrients begins to affect, productivity decreases by 2-3 times. Another peak in productivity is at the end of the season.

The beginning of the productive season for the two groups of phytoplankton F2N (b) and F3N (c) is shifted to mid-August. During August-December, 3-4 biomass maxima are observed due to cyclic processes of development of organisms and circulation of water masses.

Table 4. Estimated number of BS entering the upper water layer monthly and per year (thousand tons) into waters of regions NESS at the bilateral water exchange across the boundaries between regions.

| Parameter | Region 1 | Region 2 | Region 3 | Region 4 |
|-----------|----------|----------|----------|----------|
| DOC       | 1258     | 7248     | 6771     | 694      | 3633     | 3577     | 514      | 1843     | 700      | 269      | 1252     | 3740     |
| DON       | 171      | 644      | 238      | 180      | 1253     | 871      | 125      | 350      | 1074     | 253      | 1158     | 37       |
| ND        | 13       | 74       | 64       | 13       | 26       | 54       | 8        | 40       | 38       | 4        | 8        | 48       |
| PD        | 2        | 4        | 3 <1     | 1        | 4        | 1        | 2        | 1        | 1        | 1 <1     | 1        | 1        |
| DOP       | 4        | 11       | 8        | 4        | 18       | 7        | 2        | 4        | 11       | 2        | 18       | 8        |
| NH$_4$    | 1        | 6        | 5        | 1        | 2        | 3 <1     | 2        | 1 <1     | 1        | 1 <1     | 1        | 1 <1     |
| NO$_2$    | 1        | 3        | 2 <1     | 1        | 1        | 1        | 2        | 1 <1     | 1        | 1 <1     | 1        | 1 <1     |
| NO$_3$    | 27       | 75       | 68       | 17       | 62       | 4 <2     | 5        | 16       | 59       | 15       | 55       | 7        |
| DIP       | 11       | 48       | 35       | 8        | 40       | 9        | 11       | 40       | 32       | 3        | 9        | 54       |
| DIS$_i$   | 29       | 78       | 8        | 57       | 241      | 212      | 25       | 62       | 248      | 57       | 203      | 47       |

1* - maximum input per month;  
2* - the annual input;  
3* - the «net» input per year or the difference between the input and output by water flow to the neighboring areas.
**Figure 2.** Dynamics of the N (a-f) & P (g-k) form concentrations for the second calculated year in the waters of Regions 1–4 NESS.

**Figure 3.** Dynamics of the concentration of P forms for the second calculated year: DIP (a), DOP (b), PD (c) in the waters of Regions 1–4 NESS.
4. Conclusion
The use of the CNPSi model and long-term data on the state of the natural environment makes it possible to adequately describe the dynamics of changes in the concentrations of biogenic substances in the marine environment during the year.

The steady trend of “compliance” of the concentrations of substances at the beginning and at the end of the year confirms the balance of these processes for the average long-term conditions in the ecosystem of the study area.

The calculated values of biomass, the specific growth rate of bioproducts are in good agreement with the ideas about the life cycles of organisms and can be used to characterize the processes of transformation of a substance into NESS.

5. References
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Acknowledgments
This study was supported in the Shirshov Institute of Oceanology (Russian Academy of Science) by the State Task on the Topic № 0149–2018–0015, SakhGU Topic № 5.9510.2017/8.9.