# A Case Study Report on Assessment of Eutrophication Status in Peter the Great Bay, Russia

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## I. Executive Summary

Using available data about river runoff and waste waters inputs into PGB, the annual nutrients loading of PGB was assessed. For assessment of eutrophication status of PGB we used following criteria: a) it was set an almost zero nutrient concentrations in photic layer with thick 50 m as reference condition; b) We accept threshold value of DO as 76  $\mu$ M which corresponds hypoxia conditions. Using Redfield ratios in organic matter and DO<sub>th</sub>= 76  $\mu$ M, threshold values of DIN and DIP were calculated. This approach of assessment of eutrophication status and literature data biological degradation of Amursky Bay (Sub-area **A** of PGB) suggest that Sub-area **A** has current eutrophication status as "**High**" and "**Increase**". Most part of Sub-area **B** is considered that it has eutrophication status as a "Low" with non-detectable trend. At present time, most part of Sub-area **C** has a "Low" eutrophication status with non-detectable trend.

## **II. Introduction**

There are many definitions of eutrophication which are extensively discussed in publications (Nixon, 1995; Andersen et al., 2006). Nixon gave own definition of eutrophication: "Eutrophication (noun) – an increasing in the rate of supply of organic matter to an ecosystem". He stressed that this definition is short and simple. He emphasized that eutrophication is process of change in the trophic status on an ecosystem, it is not a trophic status. The cause of the eutrophication may be an increase in the input of inorganic nutrients, a decrease in the turbidity of the water, a change in the hydraulic residence time of the water, a decline in grazing pressure, etc. A variety of other changes may be associated with eutrophication, for example, reducing of biodiversity, hypoxia, fish kills. Nixon's view emphasizes that eutrophication is rather a fundamental change in the energetic base that may propagate through the system in various ways and produce a variety of changes. In further he wrote: "However, I do suggest that all of us, scientists, regulators, politicians, and even the activists need to consider coastal marine eutrophication and oligotrophication as the fundamental ecological processes they are. They are not simple 'pollution problems' but major ecological changes that must be viewed through the macroscope." (Nixon, 2009). In practical sense, Nixon's definition gives clear distinguishes between phenomena (eutrophication), causes (depth penetration of PAR, nutrient enrichment, grazing pressure, residence time of water) and consequences (hypoxia, fish kills, turbidity) (Nixon, 2009). Anderson's definition of eutrophication stressed another reasons and consequences of this phenomenon (Andersen et al., 2006). This definition is: "the enrichment of water by nutrients, especially nitrogen and/or phosphorus and organic matter, causing an increased growth of algae and higher forms of plant life to produce an unacceptable deviation in structure, function and stability of organisms present in the water and to the quality of water concerned, compared to reference conditions" (Andersen et al., 2006).

At present time scientific community recognized that eutrophication is a widespread phenomenon of the world affecting on ecosystems of coastal and deep waters mostly via forming of "excess" biomass that results in catastrophic changes of biodiversity and forming of dead zones (hypoxia and anoxia) (Duarte, 2009). The formation of dead zones has been exacerbated by the increase in primary production and consequent worldwide coastal eutrophication fueled by riverine runoff of fertilizers and the burning of fossil fuels. Enhanced primary production results in an accumulation of particulate organic matter, which encourages microbial activity and the consumption of dissolved oxygen in bottom waters. Dead zones in the coastal oceans have spread exponentially since the 1960s and have serious consequences for ecosystem functioning (Diaz, Rosenberg, 2008).

We assume that eutrophication in local sites of the world is linked with each other via global changes (global warming, burning of fossil fuel, increasing population, urbanization and etc.) and common mechanisms of its development. Therefore sharing information about eutrophic status of different sites of NOWPAP member states produces new knowledge which permits to make decisions in mitigation of expanding eutrophication.

## II.1. Historical Review

There are two organizations which carry out environmental monitoring on Peter the Great Bay (PGB) and keep information about this. These are:

1) Federal State Budgetary Institution Primorskoe Administration for Hydrometeorology and Environmental Monitoring (FSBIPAHEM) was established in 1937. Main goal of the organization is environmental monitoring of atmosphere, hydrosphere and soils.

2) Far Eastern Regional Hydrometeorological Research Institute (FERHRI) was established in 1950. Main goals are development of methods of monitoring systems, modeling for forecasting of environmental changes, carrying out of marine observations.

Both organizations are under umbrella of ROSHYDROMET (FEDERAL SERVICE ON HYDROMETEOROLOGY AND MONITORING OF ENVIRONMENT).

Actually, FSBIPAHEM started monitoring of chemical pollutants of coastal Primorye environment in late 1960s years. First quarter reports of row chemical pollutants data was published in 1968. ROSHYDROMET is under Russian Government. FERHRI and FSBIPAHEM merged together about in 1971 and started ecological monitoring of PGB. In 1980 these organizations were split and they are existing separately again. However they continue ecological monitoring of PGB together. Scheme of monitoring stations is demonstrated on Fig.1 (Lishavskaya et al., 2010).



**Fig. 1.** Scheme of monitoring stations in PGB for ecological observations carried out by FSBIPAHEM/FERHRI during more than 40 years (from 1971 to present time).

Analyses were carried out on following parameters: dissolved oxygen, pH, nitrite, nitrate, ammonium, total nitrogen, phosphates, total phosphorous, silicates, oil hydrocarbons, trace metals (Pb, Cu, Zn, Ni, Cd), pesticides, phenols and detergents. It was planed that each ten days sampling and analyzing should be carried out in warm period of year (from April to November) according to scheme presented on Fig.1. However due to rejecting of budget in late 80-th years this monitoring program was reduced. There are quarter reports of row data from 1968 to 1984 and annual reports from 1985 up to present time. Also there are annual reviews about chemical pollution of coastal marine environment, which published by FSBIPAHEM and FERHRI from 1968 to present time. An

additional problem in reconstruction of historical data regarding to eutrophication of Peter the Great Bay is that, row data of annual reports of these observations and reviews were unavailable in the open access publications at the Soviet time (up to 1991). From 1991 to present time annual reports and reviews of FSBIPAHEM are available but after payment only. Reviews of these annual reports lead to conclusions (Lishavskaya et al., 2010) that Zolotoy Rog Bay is heavily contaminated area that agree with previously investigations (Tkalin et al., 1993; Tkalin et al., 1996; Belan et al., 2007). Amursky Bay and Ussurijsky Bay are characterized as moderate and weak contaminated areas respectively (Lishavskaya et al., 2010). Reviews of annual reports of FSBIPAHEM are partly including into annual reports of the State Oceanographic Institute (SOI) which are available in open access publications (Korshenko et al., 2006; Korshenko et al., 2008a; Korshenko et al., 2008b; Korshenko et al., 2009a; Korshenko et al., 2009b). Annual reviews of FSBIPAHEM are partly including into annual reviews of Goshydromet (Review, 2009; Review, 2010; Review, 2011; Review, 2012). Annual reports of SOI and Reviews of Goshydromet give general information only about contaminations and ecological state of PGB. There is no more detail information than those in publications of the Annual reports of FSBIPAHEM.

There are scientific organizations which carry out ecological investigations of the PGB. These

are:

- 1. Pacific Scientific Research Fisheries Center (TINRO-Centre) was established in 1925;
- 2. Far Eastern Federal University (FEFU) was established in 1899;
- 3. Pacific Geographical Institute Far Eastern Branch of Russian Academy of Sciences (PGI) was established in 1971;
- 4. A.V. Zhirmunsky Institute of Marine Biology Far Eastern Branch of Russian Academy of Sciences (IMB) was established in 1970
- 5. V.I.Il`ichev Pacific Oceanological Institute Far Eastern Branch of Russian Academy of Sciences (POI) was established in 1973.

Some institutes contain monitoring centers/laboratory inside itself. These are Harmful Algal Monitoring Center established in 2007 (IBM FEB RAS), Pollution Monitoring Regional Activity Center formed in 1999 (PGI FEB RAS). However main goal of these five organizations is scientific research. These organizations published some books which are very important for undeserving of how ecosystem of PGB is going.

## II.1.1. Early oceanography study of PGB

Geographical descriptions, first oceanographic measurements (depths, currents, tidal currents), climate of PGB and adjacent basins were given in the second half of the 19-th century by Russian officers of the Russian Fleet. Review of publications concerning this period investigation of PGB recently was given by Khristoforova (2012). In 1925 outstanding Russian scientist, professor K.M. Derugin formed Pacific Scientific Fisheries Station (TONS) which later became TINRO-CENTER. Review of main stages of oceanographic studies carried out by TINRO-Center and their results obtained since 1925 till 2005 was given by Khen and Moroz (2005). Most important of publication of early period is hydrological essay about Amursky Bay and estuary Suyphun (Razdolnaya) River (Gomoyunov, 1927). The zoobenthos and planktonic studies including PGB area are carried out by TINRO-Center since 1925 till present day 2005. Reviews of these studies were given elsewhere (Nadtochy and Koblikov, 2005; Dolganova, 2005; Nadtochy, Galysheva, 2012). Professor K.M. Derugin organized hydrochemical observations in PGB (Amursky Bay and Ussuriisky Bay) from 1931 till 1935. Observations were implemented on hydrological parameters (temperature, salinity, depth) and following hydrochemical parameters: dissolved oxygen, pH, total alkalinity, nitrite, nitrate, phosphates, and silicates. Voronkov considered and discussed of these observations (1941a; 1941b). He noted that seasonal variation of dissolved oxygen concentration, with minimum in bottom waters in late summer-beginning September. Minimal concentration was about 68 % from saturation. Phosphate concentrations in PGB vary at summer within 0.04 - 0.08 and 0.14 - 0.35umol/l in surface and near bottom waters (100 m), respectively. Surface waters of PGB had no

nitrate as a rule. However at depths 40 m concentrations of nitrate ions may exceed 10 µmol/l. Nitrite concentrations revealed high variability. Maximal concentrations of nitrite (within 0.03 -0.17 µmol/l) in PGB corresponded near bottom waters in October 1934. For surface waters concentrations of silicates reached up to 29 µmol/l in the northern part of Amursky Bay that was explained by influence of Razdolnaya River. In the western part of the PGB maximal silicate concentrations revealed in near bottom waters (36 µmol/l) (Voronkov, 1941a). Also it was found that studied hydrochemical parameters demonstrated strong daily variability in the PGB, that is explained by wind-induced current system (Voronkov, 1941b). Very extensive seasonal observations on meteorological, hydrological and hydrochemical parameters in Amursky Bay and Ussuriisky Bay were implemented by FERHRI during 1959-1961 years. Hydrological observations contain temperature, salinity, depth, transparency, water color, waves, tidal currents, currents and ice distribution. Following hydrochemical parameters were measured: dissolved oxygen, pH, total alkalinity, nitrite, phosphates, and silicates. Detail description of this study was given by Lastovetsky and Veshcheva (1964). It is should be noted that minimum concentration of dissolved oxygen was observed in bottom waters of Amursky Bay at August 1961 and was 2.04 ml/l or 40% from saturation by air. This minimum of oxygen content corresponds maximum in phosphates and silicates concentrations, 1.26 and 125 umol/l, respectively.

### II.1.2. Monitoring of contaminations of PGB

One of the main goals of the FSBIPAHEM and FERHRI activity is monitoring of quality water of PGB. List observing parameters is following: dissolved oxygen, pH, nitrite, nitrate, ammonium, total nitrogen, phosphates, total phosphorous, silicates, oil hydrocarbons, trace metals (Pb, Cu, Zn, Ni, Cd), pesticides, phenols and detergents (Lishavskaya et al., 2010). It should be to say that above noted contaminants have different sources and differently impact on marine ecosystem. In this paragraph we shortly review publications which focused on such contaminants as trace metals, pesticides, phenols and detergents and oil hydrocarbons. This is important for understanding general ecological situation with PGB. Most extensive observations of contamination of PGB were carried out during 80<sup>th</sup> -90<sup>th</sup> years of last century by Tkalin with colleagues from FERHRI (Tkalin et al., 1990; Tkalin et al., 1993; Tkalin, 1995; Tkalin, 1996; Tkalin et al., 1997; Tkalin, 1998; Tkalin et al., 1998; Tkalin, et al., 2000). These investigations with others (Anikiev, 1987; Polyakov and Botsul, 2004; Shulkin, 2004; Naumov, 2006; Kovekovdova et al., 2012) demonstrated that waters and sediments of Zolotoj Rog Bay and Nakhodka Bay were chronically contaminated by trace metals, persistent organic pollutants and oil hydrocarbons. The main source of this pollution was activity of ports in Zolotoj Rog Bay and Nakhodka Bay and industrial waste waters. Amursky Bay and Ussurijsky Bay are characterized as moderate and weak contaminated areas respectively. These conclusions were supported by recent investigation (Lishavskaya et al., 2010). Impacts of trace metals contaminations and persistent organic pollutants on biota of PGB were extensively discussed elsewhere (Khristoforova et al, 1993; Shulkin and Kavun, 1995; Vaschenko, 2000; Shulkin et al., 2003; Zhadan, 2005; Lutaenko, Vaschenko, 2008; Lukyanova et al., 2009). Many authors noted that waste waters generated by industry in Primorye region was reduced since 1990 till present time (Fig. 2) (Shulkin and Semykina 2012; Lukyanova et al., 2012). Nevertheless some regions of PGB are still contaminated.

We suggest that there are three directions in studying of eutrophication of PGB in the past which can be used in Screening Procedure. These are: 1) an unacceptable deviation in trophic structure of PGB; 2) land based sources of nutrients; 3) seasonal hypoxia of bottom waters and related nutrients concentrations. These investigations can be used for detection of eutrophication symptoms.



**Fig. 2.** The water usage and waste water discharge  $(10^6 \text{ t/y})$  within Peter the Great Bay watershed and all Primorye region  $(10^6 \text{ t/y})$  during 1991-2007 years. Reprinted with permission from Shulkin and Semykina (2012).

## **III. Screening Procedure**

There are three directions in study of PGB which carried out in the past and can be use for detection of eutrophication symptoms.

III.1. Trophic structure of PGB and its variability

The investigations of benthic communities in Peter the Great Bay were conducted from 1925 to the early 2000s. During long time distribution and variability of benthic community in Peter the Great Bay were analyzed in TINRO-center (Nadtochy at al., 2005a, 2005b; Nadtochy, Galysheva, 2012). In general, the total biomass varied from 4 to 7260 g/m<sup>2</sup> (mean 360  $\pm$ 38 g/m<sup>2</sup>). The maximum value of the total biomass of 7260 g/m<sup>2</sup> is fixed in the inner part of the Ussuriisky Bay. In all these areas bivalves dominated. The major taxonomic groups of macrobenthos in Peter the Great Bay, playing a major role in the formation of its total biomass (86 %), are bivalve molluscs, polychaetes and holothurians, to a lesser extent – barnacles, and higher plants, sea stars, sea urchins and phoronid. Comparing to 30 years old data, the biomass of macrobenthos in the Amursky Bay (sub-area A) became almost in 4 times higher (in average 430  $g/m^2$  in 2003 and 118  $g/m^2$  in 1970s) due to greater abundance of bivalves and cirripedias. It became almost twice higher in the central and eastern parts of Ussuriisky Bay (sub-area B) caused by abundance of holothurians and foraminifers (not noted here earlier) in the central part, and by bivalves and sponges – in its eastern parts. Joint investigations of FERHRI and IMB FEB RAS (Belan, 2003; Belan et al., 2003; Belan, Moshchenko, 2005; Belan, Belan, 2006; Moschchenko, Belan, 2008; Boyarova, Lukyanova, 2012) in northern part of Amursky Bay (sub-area A) allowed to get data on species composition, structure and quantitative distribution of macrozoobenthos in 2000s years. Trophic structure of macrozoobenthos changed: in the 1930s, swallowing detritophages prevailed in the community, whereas in the 1970s, collecting detritophages began to dominate (Klimova, 1971, 1976). However, judging by cited publications, up to the middle of the 1970s, a cardinal transformation of bottom fauna structure was not registered. Maximal changes in composition and structure of the Amursky Bay bottom fauna occurred within the period from the 1970s to the 1980s (Tkalin et al., 1993; Belan, 2003). Amursky Bay is characterized by a high content of organic matter in the environment and with the clear transformation of benthic biocenoses occupying vast areas in the bay (Belan, 2003; Belan and Belan, 2006).

In this period, and eutrophication-tolerant animals which early observed occasionally, became common species such as Polychaeta, Bivalvia and Amphipoda had maximal abundance

(Moschenko and Belan, 2008). The peak of technogenic impact on PGB falls at the 1960s-1980s (Petrenko, 2003). Therefore change in species structure of benthos in the bay could be in many respects connected with processes of chronic pollution and eutrophication (Tkalin et al., 1993; Belan, 2003; Moschenko and Belan, 2008). Moschenko and Belan assume that eutrophication and variation of granulometric composition of sediments are the most possible important reasons for macrozoobenthos changes in the Amursky Bay (2008). Galysheva noted (2009) that in Peter the Great Bay the processes of community transformation that lead to the simplification of species structure and the predominance of species tolerant to organic pollution were recorded in the areas subjected to the most intensive inflow and increase of organic matter content. Thus, the predominance of the polychaetes *Tharyx pacifica* and *Dipolydora cardalia*, which are tolerant to organic contamination, was observed in benthic biocenoses in the area of the Tumen River estuary and in the basin near Furungelma Island.

Long-term observations of the community of Japanese Scallop and its epibionts in the Amursky Bay documented that during 1982-1993s the mean age of scallops in the settlement increased and the rate of linear growth of the mollusks dropped (Silina, Ovsyannikova, 1995). The most noticeable changes occurred in the species composition and quantitative distribution of cirriped barnacles. Less tolerant epibionts were gradually replaced by species highly resistant to silting and organic pollution. The Polychaetes appeared the most tolerant to pollution (Silina, Ovsyannikova, 1995). Dramatically changes of bentic flora in Amursky Bay were found (Levenets, Skriptsova, 2008). The total species number of macrophytes in 2005 decreased 1.5 times as compared to record of 1970 – 1980s. The most pronounced qualitative and quantitative changes of the flora were observed in the zones subjected to an anthropogenic press and the direct impact of the Razdolnaya River drain. It was found that the algal thickets with domination of kelps and sargassum have reduced, and extensive thickets of sea grasses have disappeared from these sites. The reduction of the species number, biomass decrease, change of dominants in plant communities along with an increased importance of green algae testify to a human-induced transformation of vegetation towards its degradation (Levenets, Skriptsova, 2008). Biological investigations (Silina, Ovsyannikova, 1995; Levenets, Skriptsova, 2008; Moshchenko, Belan, 2008) strongly suggest that trend of increasing eutrophication is occurred in sub-area A. We did not find any data which may clearly suggest about any trend of eutrophication in Sub-areas B and C.

The first data on the phytoplankton of the PGB and adjacent areas were reported in the 1920s-1930s. Reviews of these investigations were published somewhere (Konovalova et al., 1989; Stonik and Orlova, 1998; Stonik and Orlova, 2002). Konovalova (1972) was the first who carried out yearround study of the species composition and dynamic of the phytoplankton in Amursky Bay. Microalgal community of PGB is dominated by one species, S. constatum, which accounted for about 70-90 % of the total density of phytoplankton as a rule (Konovalova, 1972; Konovalova et al., 1989; Stonik and Selina, 1995; Stonik and Orlova, 1998; Stonik and Orlova, 2002; Shevchenko et al., 2004; Morozova and Orlova, 2005; Orlova et al., 2009). Microalgal bloom is characterized three peaks spring, summer and autumn (Stonik and Selina, 1995; Shevchenko et al., 2004). The maximal peak of phytoplankton density reveals at August-beginning September in Amursky Bay (Stonik and Orlova, 1998). The overall cell numbers of phytoplankton were 0.01 to 31.1 million cells/liter and biomass 0.3 to 29 g/m<sup>3</sup> (Stonik and Orlova, 1998). Distributions of phytoplankton in PGB permits to make conclusion that this area is high productive and waters characterized as eutrophic and extremely eutrophic (Stonik and Selina, 1995; Stonik and Orlova, 1998, 2002). In comparison with the late 1960s and early 1970s, the species richness of phytoplankton increased markedly and greater number of bloom-forming species was recorded. It is mean that eutrophication of PGB becomes stronger with time (Orlova et al., 2009). New toxic microalgal species were appeared with time in PGB (Orlova et al., 1996; Orlova, 2012). Zooplankton aboundance had two seasonal peaks in Amursky Bay: the first driven by mass development of cold-water copepods occurred usually in June, and the second caused by warm-water copepods was observed in the southern part of the bay in September but in the northern part in October. Total zooplankton biomass had lesser seasonal variability in the range 500-1600  $\text{mg/m}^3$  (Nadtochy, 2012).

## III.2. Land based sources of nutrients

There are two main inputs of nutrients into PGB. These are waste waters from Vladivostok + other small towns and villages and riverine fluxes. Loads of nutrients and organic matter into Amursky Bay by waste waters and Razdolnaya River were intensively studied (Gavrilevsky et al., 1998; Ogorodnikova, 2001; Nigmatulina, 2005; POMRAC, 2006; POMRAC, 2009; CEARAC, 2011; Mikhailik et al., 2011; Zvalinsky et al., 2012). Gavrilevsky et al. (1998), Ogorodnikova (2001) and Nigmatulina (2005) made estimations of nutrient loads into Amursky Bay using Municipal Data on total annual volume of waste water inflowing into Amursky Bay and concentrations of pollutants. For estimations nutrients loads by Razdolnaya they used annual discharge of the River and concentrations pollutants measured by Prymorsky Center on Hydrometeorology and Environmental Monitoring. Mikhailik et al. (2011) estimated daily fluxes of pollutants supplied into Amursky Bay by Razdolnaya River. Some results were summarized in Table 1 (CEARAC, 2011).

**Table 1.** Annual loads (T/year) of nutrients, COD, SS into Amursky Bay by river runoff and waste waters of Vladivostok

Nutrients, COD, SS	DIN	N-tot	DIP	P-tot	COD	DISi	SS	BOD <sub>5</sub>
River runoff	1800	4200	120	450	36560	17040	117840	$37800^{***)}$
Waste-water	700	$1150^{**)}$	100	140**)	$8000^{****)}$	nd*)	$2156^{***)}$	$1733^{***)}$

<sup>\*)</sup>nd means no data; <sup>\*\*)</sup> N-tot and P-tot values were calculated assuming that organic forms of nitrogen and phosphorus are 40 and 30 % from total its contents, respectively (Henze, 2006); <sup>\*\*\*)</sup> (Gavrilevsky et al., 1998); <sup>\*\*\*\*)</sup> POMRAC, 2006.

More than 70% supplied by nutrients causes by loading of Razdolnaya River. There are available data of water quality trends of Razdolnaya River (POMRAC, 2009). Review of data by POMRAC clearly demonstrates trends in increasing concentrations of phosphates and ammonium with time in Razdolnaya River. Enrichment of Amursky Bay by nutrients, suspended substances and organic matter causes eutrophication of the bay as it is considered by many scientists. These works were recently reviewed (Lutaenko, Vaschenko, 2008). Killed fishes event and recently discovered hypoxia of bottom waters (Tishchenko et al., 2008; Tishchenko et al., 2011a, 2011b) are consequences of eutrophication of Amursky Bay. Estimations of nutrient loads into Ussuriisky Bay (sub-area **B**) and open part of PGB (sub-area **C**) are given in Tables 2 and 3, respectively. Due to monsoon climate the heavy rains, water discharge may increase some of the warm period, and a large amount of nutrients and suspended matter are supplied into surface layer of Amursky Bay by Razdolnaya River during high water periods. In 2008, such eutrophication pulses occurred on June 2 and July 19 (Fig. 3; Mikhailik et al., 2011)

**Table 2.** Annual loads (T/year) of nutrients, COD, SS into Sub-area **B** (Ussuriisky Bay) from river runoff and waste waters of Vladivostok

Nutrients, COD, SS	DIN	N-tot	DIP	P-tot	COD	DISi	SS
River runoff	178	400	24.3	90	$7550^{***)}$	4400	$7300^{***)}$
Waste-water	950	1600**)	130	185 <sup>**)</sup>	10000	nd*)	nd*)

<sup>&</sup>lt;sup>\*)</sup>nd means no data; <sup>\*\*)</sup> N-tot and P-tot values were calculated assuming that organic forms of nitrogen and phosphorus are 40 and 30 % from total its contents, respectively (Henze, 2006); <sup>\*\*\*)</sup> (POMRAC, 2006).

Table 3. Annual loads (T/year) of nutrients,  $COD_{Cr}$ , SS into Sub-area C from river runoff and waste waters

Nutrients, COD, SS	DIN	N-tot	DIP	P-tot
River runoff	250**)	500	11**)	40
Waste-water	450	750 <sup>*)</sup>	100	160 <sup>*)</sup>

<sup>\*)</sup> N-tot and P-tot values were calculated assuming that organic forms of nitrogen and phosphorus are 40 and 30 % from total its contents, respectively (Ecological... 2000); <sup>\*\*)</sup> POMRAC (2009).



**Fig. 3.** Fluxes of nutrients (a - DIN; b - DIP; c - DISi) loaded into Amursky Bay by Razdolnaya River as function of Julian Days (Mikhailik et al., 2011).

III.3. Seasonal hypoxia of bottom waters and related nutrients concentrations

According to Anderson's definition of eutrophication (Anderson et al., 2006) the nutrients concentrations are immediately following as variable indicators for assessment of trophic status of PGB regarding to some reference state. However, excepting few recent publications (Tishchenko et al., 2008; Tishchenko et al., 2011a, 2011b; Semkin et al., 2012; Zvalinsky et al., 2012), the distributions of nutrients in PGB were rather studied as geographical or/and oceanographic descriptions than ecological problems of PGB (Voronkov, 1941a, 1941b; Lastovetsky and Veshcheva, 1964; Podorvanova et al., 1989; Rachkov, 2002; Luchin et al., 2005, 2007; Rachkov, 2006; Zuenko, 2008). It is necessary to note that nutrients from land-sources load by means of fresh-waters inflow into photic layer of PGB. However, excepting winter time (Tishchenko et al., 2011a), there were no observations of high nutrients concentrations in surface layer. Vice versa, higher concentrations of nutrients were observed in bottom waters of PGB (Voronkov, 1941a; Lastovetsky and Veshcheva, 1964; Podorvanova et al., 1989; Rachkov, 2002; Rachkov, 2006; Tishchenko et al., 2011a, 2011b; Semkin et al., 2012). This feature can be explained by existence of biological pump which convert inorganic nutrients into organic matter (phytoplankton) then after settling of phytoplankton on the bottom, the organic matter releases nutrients into seawater by mineralization process (microbial destruction). Many scientists observed low dissolved oxygen concentrations near bottom in summer time (Voronkov, 1941a; Lastovetsky and Veshcheva, 1964; Redkovskaya, 1980; Rodionov, 1984; Podorvanova et al., 1989; Rachkov, 2002; Rachkov, 2006; Tishchenko et al., 2011a, b; Semkin et al., 2012; Fig.4).



**Fig. 4.** Distribution of oxygen concentration (µmol/kg) in Amursky Bay. August, 2007 (upper panel). August, 2008 (bottom panel).



**Fig.5.** Distribution of ammonium, Phosphates, Silicates (umol/kg) and CO2 partial (uatm) in the bottom water of the Amursky Bay. August, 2008.

However most of researchers did not link together causes of observed low oxygen concentrations with causes of observed high nutrients concentrations (phosphates, silicates, ammonium). In recent publications (Tishchenko et al., 2008; Tishchenko et al., 2011a, b; Semkin et al., 2012) hypoxia of bottom waters and high nutrients concentrations of phosphates, silicates and ammonium in Amursky and Ussuriisky Bays were considered as consequence of eutrophication and working of biological pump which supplies nutrients from photic layer into bottom waters and consumes oxygen from near bottom layer. Figures 4 and 5 demonstrate that there are similar shapes of spatial distributions in chemical anomalies (ammonium, phosphates, silicates and  $CO_2$  partial pressure) and oxygen concentrations in the bottom waters of the Amursky Bay during August 2008. Similar shapes prove that these are the result of one process that governs hydrochemical features observed in the bottom waters of the bay during August. This process is a microbiological degradation of the "excess" phytoplankton, the main part of which is diatoms. Phylogenic studies show that the microalgae population in the area of the Razdolnaya River mouth and the adjacent

waters of Amursky bay is dominated in population density by diatoms and cryptophytes (64% and 27%, respectively) and in biomass by diatoms (94%) (Stonik et al., 2009). Rate of oxygen consumption was directly measured by Water Quality Monitor (Fig. 6).



**Fig. 6.** Temporal variability of hydrological parameters near bottom layer of the Amursky Bay (43°10.881' N; 131°49.893' E) was logged by Water Quality Monitor (Wet Lab firm) during warm period in 2011. Red line corresponds to hypoxia condition. (Tishchenko P.P. et al., 2013 in press).

Our data of oxygen concentration in hypoxia area suggest that detected hypoxia in the Amursky Bay has seasonal character (Fig. 7).



**Fig.7.** Seasonal variability of Apparent Oxygen Utilization (a) and Oxygen Concentration (b) in near-bottom waters in the hypoxic area of the Amursky Bay. Using Data: 1 – March 04, 2008; 2 – May 23, 2008; 3 - July 08, 2008; 4 – August 20, 2007; 5 – August 25, 2008; 6 – October 15, 2006; 7 – November 01, 2006.

In contrast to Amursky Bay, the Ussuriisky Bay is much less studied. Recently we carried out comprehensive hydrochemical study of this bay. Seasonal distributions of dissolved oxygen concentrations in the bottom waters are given on Fig. 8. Lowest concentration of dissolved oxygen was 68 uM, that is close to hypoxic conditions. It was detected in the bottom waters at August, 2011. Nevertheless dissolved oxygen concentrations in the bottom waters of the Ussuriisky Bay are generally higher than those in the Amursky Bay. Vice versa is in distributions of the nutrient concentrations. We did not find some symptoms of significant eutrophication of the Ussuriisky Bay.



**Fig. 8.** Seasonal distributions of dissolved oxygen concentration (µmol/kg) in the bottom waters of the Ussuriisky Bay. a – February, 2010; b – May, 2011; c – August, 2011; d – October, 2011.

#### **IV. Comprehensive Procedure**

The objective of this comprehensive procedure is assessment of eutrophic status of Peter the Great Bay with aiming to improve management and healthy of coastal environment of area where symptoms of eutrophication were detected.

IV.1. Peculiarities of Peter the Great Bay

Peter the Great Bay (PGB) is situated in a northwestern part of NOWPAP region (Fig. 9). From open sea, border of the bay is line connecting two points. One is mouth of Tumannaya River (western side), another one is Povorotniy Cape (eastern side). Distance between these points is about 200 km. Distance of the coastal line around bay is about 1500 km. Total area of PGB is about

9500  $\text{KM}^2$ . The bay contains about 500  $\text{KM}^3$  of water. Muravjev-Amursky peninsula and group of islands (Russky Island, Popov Island, Rejnike Island and smaller others) divide PGB on two subareas – Amursky Bay (western part) and Ussuriisky Bay (eastern part). Besides, there are more four small bays within PGB. They are Posjet Bay, Strelok Bay, Vostok Bay and Nakhodka Bay (Fig. 9). Northern part of the bay is shallow. The depths of the bay smoothly increase in southward and reach maximum (120 – 150 m). There is steep continental slope off PGB, where depths sharply change from 200 to 2000 m within width 6 – 15 km. PGB is partly covered by ice in winter season. Ice formation usually starts at the end November. The northern part of Amursky Bay is covered by consolidated sea-ice during late December – beginning March. There is non-consolidated ice in southern part of Amursky Bay and a most part of Ussuriisky Bay during winter season. Due to seaice formation and brine rejection dense waters are forming on the shelf of PGB. Deep convection and renewal of bottom waters through brine rejection had occurred sometimes in NOWPAP region (Talley et al., 2003). Due to upwelling the Intermediate Waters of the NOWPAP Sea comes up on the shelf of PGB at autumn season (Zhabin et al., 1993).



**Figure 9.** Peter the Great Bay and its sub-areas: **A** - Amursky Bay; **B** - Ussuriysky Bay ; **C** - South part of The Peter the Great Bay. 1 – Muravejev-Amursky Peninsula; 2 – Russky Island; 3 – Popov Island; 4 – Rejnike Island; 5 – Mouse Tumannaya River; 6 – Povorotnij Cape. Star notes site of reference station.

Some rivers inflow into PGB. Largest one is Razdolnaya River which inflows into northern part of Amursky Bay. Average annual runoff of Razdolnaya River is about 2.46 m<sup>3</sup>. Smaller rivers – Artemovka, Shkotovka, Sukhodol inflow into Ussuriisky Bay. Annual runoffs of Artemovka River, Shkotovka River, Sukhodol River and Petrovka River are 0.29, 0.22, 0.14 and 0.1 km<sup>3</sup>, respectively. Partizanskaya River inflows into Nakhodka Bay, its annual runoff is 1.32 km<sup>3</sup>. Total annual river runoff into PGB varies within 2.1 - 8.2 km<sup>3</sup>, and its average value is about 4.72 km<sup>3</sup>.

Due to monsoon climate, the main part of river runoff (70-90%) is occurred in during April – September.

Vladivostok is largest city in Primorye and it situated on a coast of Amursky Bay and Ussuriisky Bay. Its population is about 630,000 peoples. Smaller cities – Nakodka and Slavyanka are situated in Nakhodka Bay and Slavyansky Bay, respectively. Main anthropogenic pressure on PGB is caused by inputs of Razdolnaya River and waste waters of Vladivostok city. Summation of peculiarities of PGB is given by sketch (Lobanov et al., 2009; Fig. 10).



**Figure 10.** Sketch of main peculiarities of Peter the Great Bay: a) Inputs waters enrichment by nutrients via Razolnaya River inflow and waste waters of Vladivostok-city (yellow ring); b) sea-ice formation and winter convection mostly occur in yellow ring; c) There is water exchange between shelf and NOWPAP area through steep continental slope.

## IV.2. Collection of relevant information

From our historical review is following that there are only two organizations which carry out environmental monitoring on Peter the Great Bay (PGB) and keep information about this. These are Federal State Budgetary Institution Primorskoe Administration for Hydrometeorology and Environmental Monitoring (FSBIPAHEM) and Far Eastern Regional Hydrometeorological Research Institute (FERHRI). However row data of annual reports and reviews produced by these organizations were unavailable in the open access publications at the Soviet time (up to 1991). From 1991 to present time annual reports and reviews of FSBIPAHEM are available after payment only. On these reason for getting relevant information we used open accessed publications such as monographs:

Anikiev V.V. (1987) Short-scale of geochemical processes and pollution of ocean. Moscow. Nauka. 192 p. (POI, Rus.).

Condition of Marine Ecosystems Influenced by the River Flow. Ed. L.M. Gramm-Osipov. Vladivostok, Dalnauka, 2005, 260 p. (POI, collective monograph, Rus.).

Current Ecological State of Peter the Great Bay, Sea of Japan. Ed. N.K. Khristoforova. Vladivostok, Far Eastern Federal University Press, 2012, 438 p. (FEFU, collective monograph, Rus.).

Current state and tendencies of changes of environment of Peter the Great Bay of Japan Sea. Eds. V.B. Lobanov, A.C. Astakhov. Moscow. GEOS, 2008, 460 p. (POI, collective monograph, Rus.).

Ecological Studies and the state of the Ecosystem of Amursky Bay and the Estuarine Zone of the Razdolnaya River (Sea of Japan). Eds. K.A. Lutaenko and M.A. Vaschenko. Vladivostok, Dalnauka, 2008, V. 1, 301 p. (IMB, collective monograph, Rus.).

Ecological Studies and the state of the Ecosystem of Amursky Bay and the Estuarine Zone of the Razdolnaya River (Sea of Japan). Eds. K.A. Lutaenko and M.A. Vaschenko. Vladivostok, Dalnauka, 2009, V. 2, 331 p. (IMB, collective monograph, Rus.).

Konovalova G.V., Orlova T.Yu., Pautova L.A. Atlas of phytoplankton of the Japan Sea // L.: Nauka, 1989. 160 p. (IMB, Rus.).

Naumov. Y.A. Anthropogenez and ecological condition of geosystem marine-coastal zone of Peter the Great Bay the Sea of Japan. Vladivostok. Dalnauka, 2006. 300 p. (FEFU, Rus.).

Ogorodnikova A.A. Ecological and economical estimations of impacts of land-sources pollutants on the environment and bioresources of Peter the Great Bay. TINRO-Center, 2001. 193 p. (TINRO-Center, Rus.)

Podorvanova, N.F., T.S. Ivashinnikova, V.C. Petrenko, L.S. Khomichuk. 1989: Main features of hydrochemistry of Peter the Great Bay (Japan Sea). Vladivostok: DVO AN SSSR DVGU, 114 p. (FEFU, Rus.).

Response of Marine Biota to Environmental and Climatic Changes. Ed. A.V. Adrianov. Vladivostok, Dalnauka, 2007, V. 2, 331 p. (IMB, collective monograph, Rus.).

Shulkin V.M. Trace metals in ecosystems on the marine shelf. Vladivostok. Dalnauka, 2004, 279 p. (PGI, Rus.).

Tkalin A.V., Klimova V.L., Shapovalov E.N. et al., Some of regional consequences of anthropogenic impacts on marine environment. Ed. A.V. Tkalin. Leningrad. Hydrometeoizdat, 1990, 107 p. (FERHRI, collective monograph, Rus.).

Zuenko Yu.I. Fisheries Oceanography of the Japan Sea. Vladivostok. TINRO-Center, 2008, 228 p. (TINRO-Center, Rus.).

These above cited monographs provide us information relevant to the eutrophication assessment of the PGB such as: a) marine flora/fauna; b) pollutant sources (e.g. municipal, industrial, agricultural wastewater, marine aquaculture); c) supplementary information (e.g. oceanography, meteorology, catchment area population, wastewater management, coastal recreation).

For the eutrophication assessment of the PGB we used data-set collected by Pacific Oceanological Institute during 1999 to 2011, which include hydrochemical observations. Aim of the hydrological surveys carried out by POI was rather establish of hydrochemical status of the PGB then control of water quality. Usually measurements were carried out for surface and bottom horizons on following parameters: CTD – conductivity (salinity), temperature, depth using probe; salinity (salinometer), dissolved oxygen, nutrients (as rule as ammonium. nitrite, nitrate, phosphate, silicate), pH, Total Alkalinity, Humic Substances, Chlorophyll *a*, disk Secchi depth. At all, during 1999 to 2010 more than 2660 samples were analyzed (Fig.11). However obtained data are quite non-uniform with time and space (Fig. 11, 12).



**Figure 11.** A level of study of Peter the Great Bay. Number of samples used for assessment parameters of eutrophication status of PGB.



**Figure 12.** Distribution of hydrochemical stations which were implemented during 1999 – 2011 in Peter the Great Bay. a – Winter; b – Spring; c –Summer; d – Autumn. Points are locations of stations.

IV.3. Categorization and selection of assessment parameters

Selection of assessment parameters should be immediately follows from definition of eutrophication. According to Nixon's definition of eutrophication (Nixon, 2009) we have to measure allokhtonous and autokhtonous fluxes of organic matter in ecosystem. Using only these basic data we can conclusion about rate of supply of organic matter to an ecosystem. Another words rate of supplying of organic matter is balance of different fluxes of organic matter inside and crossborders of ecosystem. There are available data about allokhtonic fluxes caused by river runoff as rule. However there are no information about the export organic matter which caused by existence of current system or living organisms as rule. There are scarce data about the primary production for two reasons. One is that measurement of the primary production is not still ordinary observation. Another reason is that the primary production reveals considerable fluctuations from day to day at one station and site to site for different stations. Such strong spatial and temporal variability is caused by occasional observation of stage of the succession of primary production at given time in given place. In practical sense, Nixon's definition gives clear distinguishes between phenomena (eutrophication), causes (depth penetration of PAR, nutrient enrichment, grazing pressure, residence time of water) and consequences (hypoxia, fish kills, turbidity) (Nixon, 2009). Nevertheless, we prefer Anderson's definition of eutrophication (Andersen et al., 2006) in choice of assessment parameters in estimation of eutrophication status of the PGB. This definition is: "the enrichment of water by nutrients, especially nitrogen and/or phosphorus and organic matter, causing an increased growth of algae and higher forms of plant life to produce an unacceptable deviation in structure, function and stability of organisms present in the water and to the quality of water concerned, compared to reference conditions" (Andersen et al., 2006). According to this definition and recommendation of NOWPAP we accept assessment parameters, which are presented in Table 4. There are three categories of the parameters. First category (I) is concentrations of nutrients which presumably directly demonstrate enrichment of ecosystem by nutrients. Category II is chlorophyll concentration which is indirect parameter of primary production. Third category is oxygen concentration which may shows hypoxia or anoxia as consequence of eutrophication.

Assessment parameters	Methods					
Category I parameters used in this case study						
Nutrients	Methods of Sea Water Analysis // Eds. K.Grasshoff, K. Kremling,					
DIN, DIP, DISi, TN, TP	M. Ehrhardt. Viley-VCH: Weinheim, New York, 1999.					
Category II parameters used in this case study						
Chlorophyll	Standart oceanological methods (UNESCO, 1966; Koblenz-					
	Mishke, 1983)					
Category III parameters used in this case study						
Dissolved oxygen at bottom	Winkler method (Carpenter, 1965)					
layer, Transparency						

**Table 4.** Assessment and categorization parameters and methods of their measurements

IV.4. Preparation of assessment data sets

Values of each assessment parameters have been measured using commonly accepted methods (Methods..., 1999; UNESCO, 1966; Koblenz-Mishke, 1983; Carpenter, 1965). Data set includes values of NH<sub>4</sub>, NO<sub>2</sub>, NO<sub>3</sub>, PO<sub>4</sub>, H<sub>2</sub>SiO<sub>3</sub>, Chlorophyll *a*, oxygen concentrations and transparency (depth of disk Secci) along following information: date, time, location (Latitude, Longitude), depth (pressure), in situ temperature, salinity, pH, Total Alkalinity. All measurements were carried out by same scientific group and were crossed checked. Therefore assessment parameters have reliable values. Data of assessment parameters were collected into Excel-file for each survey. Obtained dataset was sorting for each Sub-area of Peter the Great Bay.

IV.5. Division of assessment area into sub-area

PGB reveals strong spatial and seasonal variability of all parameters of ecosystem that causes uncertainty of natural character in eutrophication assessment. These peculiarities provide necessity to divide this area on several sub-areas. Due to natural peculiarities and real distribution of anthropogenic pressure on PGB, its area can be divided on three sub-areas. These are Amursky Bay (A), Ussuriisky Bay (B) and South part of PGB (C) (Fig. 9).

Sub-area **A**. Amursky Bay is semiclosed basin (Fig. 13). It is located in the northwestern part of PGB. Its average width is about 15 km, and its length is about 70 km. Depth of Amursky Bay varies from 0 up to 53 m (average depth is about 15 m). Square of the bay is about 1000 km<sup>2</sup>, volume – 15 km<sup>3</sup> [http://pacificinfo.ru/data/cdrom/3/]. Razdolnaya River inflows into northern part of Amursky Bay. Average discharge is about 76 m<sup>3</sup>/c. Smaller rivers – Shmidtovka, Amba, Barabashevka and Narva play insignificant role in ecosystem of the bay. Total annual river-runoff into Sub-area **A** is about 3.26 km<sup>3</sup>. We consider Amursky Bay as estuarine basin, because river water propagates up to Yankovsky Peninsula, when Razdolnaya River has high water. At normal condition, when discharge of Razdolnaya River is about 76 m<sup>3</sup>/c, area of mixing river and sea waters is situated between mouse Razdolnaya River and Peschanij Peninsula and depends from direction and strength of wind. About half of bay is covered by consolidated ice in winter season (from middle December to middle March). Other outer half has non-consolidated ice in winter. It is partly caused by work of icebreaker. Largest city of Primorye district is Vladivostok which is located on eastern coast of Amursky Bay. There are small towns on coast of the bay. They are Trudovoe, Uglovoe, Tavrichanka, Volno-Nadezhdenskoe, and Slavyanka.



**Figure 13.** Amursky Bay – Sub-area **A**. It is semi-closed estuarine basin. 1 – Peschanij Peninsula; 2 – Yankovsky Peninsula; 3 – Shmidtovka River; 4 – Amba – River; 5 – Barabashevka River; 6 – Narva River.

There are two main inputs of nutrients into Amursky Bay: a) It is part of waste waters from Vladivostok city (about 55%) + other small towns. These waste waters are from about 300,000 peoples and they almost untreated input into Amursky Bay (Fig. 4); b) It load from Razdolnaya River. This load include waste waters from, Sujfunkhe City (China), Ussuriisk City and small villages which total population is about 150,000 and diffusive sources from agriculture fields which are in valley of the River (Fig. 14). According to Municipal Data, the total annual volume of waste waters are given in Table 5.

Table 5. Annual waste waters load into Amursky Bay  $(m^3/year)$  and concentrations of nutrients, BOD<sub>5</sub>, SS in waste waters.

Nutrients, BOD, SS	$V \ 10^{6}$	BOD <sub>5</sub>	DIN	N-tot	DIP	P-tot	DIS	SS
References	m³/y	mg/l	Mg/l		mg/l		i	
Qualifying, 1988	54	$100-650^{*}$	18-45	nd*)	5-8	nd*)	nd*)	100-350
Ecological, 2000	47	nd*)	16.6	$27.7^{**)}$	2.1	3**)	nd*)	nd*)
Gavrilevsky et al., 1998	55	32.6	4.2	7 <sup>**)</sup>	1.9	$2.7^{**)}$	nd*)	39.2

\*)nd means no data; <sup>\*\*)</sup> N-tot and P-tot values were calculated assuming that organic forms of nitrogen and phosphorus are 40 and 30 % from total its contents, respectively (Henze et al, 1992).

Annual loads of nutrients, suspended solids and  $COD_{Cr}$  into Amursky Bay supplied by Razdolnaya River were published somewhere (Mikhailik et al., 2011). Annual loads (T/year) of nutrients,  $COD_{Cr}$ , SS into Amursky Bay from river runoff and waste waters of Vladivostok are given in Table 1.

More than 70% supplied by nutrients causes by loading of Razdolnaya River. Enrichment of Amursky Bay by nutrients, suspended substances and organic matter causes eutrophication of the bay as it is considered many scientists. These works were recently reviewed (Lutaenko, Vaschenko, 2008). Killed fishes event and recently discovered OMZ (Fig. 4, Tishchenko et al., 2008) are consequences of eutrophication of Amursky Bay.

Sub-area **B**. <u>Ussuriysky Bay</u> is open basin (Fig. 14). It is located in the northeastern part of PGB. Square of the bay is about 2100 km<sup>2</sup>. Depth varies from 0 up to 75 m (average depth is about 35 m) [http://pacificinfo.ru/data/cdrom/3/]. We also include Golden Horn Bay into Sub-area **B**. There are small rivers which inflow into Ussuriisky Bay. These are Artemovka, Shkotovka, Sukhodol, and Petrovka. Total annual river-runoff to the bay is about 1.3 km<sup>3</sup>. Hydrochemical characteristics of waters of these rivers are presented in Table 6.

Nutrients, COD, SS	Runoff	DIN	N-	DIP	P-tot	$\mathrm{COD}_{\mathrm{Cr}}$	DISi	SS
	km³/y		tot					
Artemovka River	0.29	100	380	20	59	4350	1600	2700
Shkotovka (0,65)	0.22	35	134	2	15	1500	1400	2200
Sukhodol	0.14	25	91	1.3	10.3	1000	900	1400
Petrovka	0.10	18	64	1.0	7	700	500	1000
Total	0.75	178	669	24.3	91	7550	4400	7300

Table 6. Annual loads (T/year) of nutrients, COD<sub>Cr</sub>, SS into Ussuriisky Bay from river runoff.

During winter season ice formation is occurred in Sub-area **B**. However, it does not form consolidated ice because basin is open and strong winds, intensive water exchange between the bay and the Sea are unfavorable conditions for forming of consolidated ice. Around Ussuriisky Bay 400,000 peoples live. Vladivostok is situated on western coast of Usseriisky Bay. There are small towns on the coast of the bay. They are Artem, Shkotovo, Petrovka, Bolshoy Kamen. There are two main inputs of nutrients into Ussuriisky Bay: a) It is part of waste waters from Vladivostok city

(about 45%) + other small towns; b) It is load from river runoff. These waste waters are from about 400,000 peoples and they almost untreated input into Ussuriisky Bay. Using Municipal Data about concentrations of nutrients and annual volume of waste waters we estimated annual loads of nutrients into Ussuriisky Bay and presented in Table 2. These estimations assume that waters of Golden Horn Bay inflow into Ussuriisky Bay. Knowledge about nutrient concentrations and water discharges of main rivers inflowing into the bay permits to estimate annual loads of nutrients by river runoff which presented in table 2.



**Figure 14.** Ussurijsky Bay – Sub-area **B**. It is open basin. 1 – Russky Island; 2 – Popov Island; 3 – Rejnike Island; 4 – Putyatina Island; 5 – Artemovka River; 6 – Shkotovka River; 7 – Sukhodol River; 8 – Petrovka River.

We have to emphasize that the Golden Horn Bay is actually inner harbor of Vladivostok. This bay is suffering under high anthropogenic pressure, due to inputs of untreated waste waters high concentrations of nitrate, phosphate and low oxygen were observed in the past (Tkalin et al., 1993). Nevertheless we included Golden Horn Bay into Sub-area **B** which is presumably expected less anthropogenic impact. The main reason of this including is existence of current system at present time. Industrial waters which are originally seawaters from Ussuriisky Bay strongly flush Golden Horn Bay at present. Power Station of the Vladivostok (TEC-2) takes seawater from Ussuriisky Bay for cooling and then, after Power Station warm seawaters are disposed into Golden Horn Bay. Surface waters from the Harbor mostly flow into Ussurijsky Bay. Probably, clean of Harbor by means of dredging of bottom and flushing of water masses by means of existent current system result in elevating of oxygen concentration with time (Luchin et al., 2007). Main feature of Ussuriisky Bay is high dynamic circulations and water exchange between Ussuriisky Bay and open part of Peter the Great Bay. Winds play is a governing role in appearance of high dynamic waters of Ussuriisky Bay (Zuenko, 2008).

Sub-area C. It is south part of PGB. Its square is about 6400 km<sup>2</sup>. Depth varies from 0 up to 150 m (average depth is about 70 m). There are four bays. One of them is Posyet Bay which is situated in southwestern part of PGB. Another bays are Vostok Bay, Strelok Bay and Nakhodka Bay. They are in eastern part of PGB (Fig. 9). In this sub-area, biggest town is Nakhodka with population about 180,000. Total population around this sub-area is about 200,000. There are small rivers which inflow in this sub-area. Biggest one is Partizanskaya which average discharge is 37 m<sup>3</sup>/c. Total annual river runoff is about 1.2 km<sup>3</sup>. We do not include Tumannaya River in our consideration because we do not know how much water of this river comes into PGB. Our estimations of nutrient loads into Sub-area C are presented in Table 3.

Most distinct feature of this sub-area is intensive exchange between shelf waters of the bay and deep waters of the Sea by downwelling and upwelling processes along steep slope. These processes are poor understood at present time. However they have a significant effect on assimilation capacity of the PGB.

Summation of loads of the nutrients into the PGB and each of its Sub-area as well are listed in Table 7. Thus, according to Table 7 we can conclude that anthropogenic pressure is highest for Sub-area **A** (Amursky Bay) and lowest for sub-area **C**.

Nutrients	DIN	TN	DIP	ТР	
		Sub-area A A	mursky Bay (S=10	00 km <sup>2</sup> )	
River runoff, t/y	1800	4200	120	450	
Vladivostok, t/y	700	1150	100	140	
Total, t/y	2500	5350	220	590	
Load per square, t/km <sup>2</sup> /y	2.5	5.35	0.22	0.59	
		Sub-area B U	ssuriisky Bay (S=21	$100 \text{ km}^2$	
River runoff, t/y	180	400	25	90	
Waste waters, t/y	950	1600	130	185	
Total, t/y	1130	2000	155	275	
Load per square, t/km <sup>2</sup> /y	0.54	0.95	0.07	0.13	
Sub-a	rea C south	part of Peter the (	Great Bay (S=6400 k	$(m^2)$	
River runoff, t/y	250	500	11	40	
Waste waters, t/y	450	750	100	160	
Total, t/y	700	1250	111	200	
Load per square, t/km <sup>2</sup> /y	0.11	0.2	0.017	0.031	
	Peter tl	he Great Bay (S=95	500 км <sup>2</sup> )		
River runoff, t/y	2230	5100	156	581	
Waste waters, t/y	2100	3500	330	485	
Total, t/y	4330	8600	486	1066	
Load per square, t/km <sup>2</sup> /y	0.46	0.9	0.05	0.11	

**Table 7.** Annual loads of nutrients and specific loads (per square) into PGB and each its subarea from river runoff and waste waters.

IV.6. Setting of assessment criteria

There are numerous methods developed for the quantitative assessment of eutrophication. Recent review of these methods was given by M. Karydis (2009). The classification of ecosystem regarding to trophic levels provides a useful tool for assessing environmental quality and help coastal managers in the making of decision. From Andersen's definition of eutrophication nutrients and chlorophyll concentrations are immediately following as variable indicators for assessment of trophic status of PGB regarding to some reference state. If we formally set "maximum permissible concentration" which accepted in Russia (DIN 680 µM; DIP 1.61 µM; DO 94 µM (POMRAC, 2006) as threshold values and apply these values for assessment eutrophic status for three regions: NW-Pacific; Sea of Okhotsk and NOWPAP Sea, we will get no sense result (Fig. 15). According to Fig. 15a, waters of NW-Pacific, Sea of Okhotsk and NOWPAP area have a bad quality below 50, 100 and 400 m respectively for these areas. However ecosystems of these regions are mostly undergoing by natural processes. So far, in setting of assessment criteria two fundamental problems rise: What is the reference values used for comparison? What are the threshold values characterizing a water body that gets into eutrophic phases? There is approach when unimpacted ecosystems can be used as reference sites for compare variable values related to eutrophication (Karydis, 2009). This approach was criticized by Duarte et al. (2009). They argue that concurrent changes, human-induced and otherwise, lead to shifting baselines imposing dynamic trajectories for reference ecosystem status. Expectation that ecosystems can be returned to an idealized past reference status by virtue of reducing direct human pressures is as likely as the existence of Neverland (Duarte et al., 2009).



Figure 15. Vertical variations of assessment parameters (DIP -a, DO -b, DIN-c, DINSi-d) in NW-Pacific -1  $\varphi$ =44.49°N,  $\lambda$ = 153.20°E; Sea of Okhotsk -2  $\varphi$ =47.49°N,  $\lambda$ =147.91°E, NOWPAP Sea -3  $\varphi$ =43.54°N,  $\lambda$ =139.20° E. Purple vertical lines correspond "maximum permissible concentration" accepted in Russia.

We use actual properties of body water as "reference" site of which is noted by star (Fig. 9). Vertical profiles of some properties are shown on Fig. 16. It is should be noted that depth of

euphotic layer is about 50 m. And DIN and DIP concentrations in this layer are almost zero, and then concentrations of nutrients sharply increase for depths deeper euphotic layer. This increasing of nutrient concentrations with depth has natural character. We set reference conditions as follow: – there are almost zero nutrient concentrations in layer with thick 50 m.



**Figure 16.** Vertical distribution of **1** - temperature (°C), **2** - PO<sub>4</sub> ( $\mu$ M), **3** - NO<sub>3</sub> ( $\mu$ M), and **4** - H<sub>2</sub>SiO<sub>3</sub> ( $\mu$ M) on the station which is accepted as "standard" (42.417° N; 131.588° E, it is noted by star on Fig.1). Data obtained at August 1999 on R/V "Professor Khromov "-36.

The second problem is to set threshed values for nutrients (DIN, DIP, DISi) and Chlorophyll concentrations. We do not know why Russian Government accepted "maximum permissible concentration" for DIN DIP and DO tabled by POMRAC (2006). Hypoxia is one of the common effects of eutrophication in coastal marine ecosystems. Under low-oxygen conditions, the physiological processes and life cycles of biota can be disrupted. Among fishes and invertebrates, different taxonomic groups, body sizes and skeletal types have different oxygen tolerances and thresholds (Levin, 2009). Hypoxia is often defined as a content of DO concentration below 2 mg liter<sup>-1</sup> (63  $\mu$ M) O<sub>2</sub> (Diaz, 2001) or 2 ml liter<sup>-1</sup> (89  $\mu$ M) (Breitburg et al., 2009). The average value (76  $\mu$ M) of these noted DO concentrations corresponds with the median lethal oxygen concentration for half of the tested species by Vaquer-Sunyer, Duarte (2008). This oxygen concentration was used as a threshold value for the assessment of the eutrophication status of Peter the Great Bay (NOWPAP CEARAC, 2011) and will be accepted as a definition of hypoxia here. Using supposition that in water initially equilibrated with atmosphere, mineralization of organic matter consumes DO, then we able to calculate thresholds values of nutrients by following equations:

$$DIN_{th}(\mu M) = \frac{(DO_{sat} - DO_{th}) \cdot 16}{138} = \frac{(DO_{sat} - 76) \cdot 16}{138}$$
(1)

$$DIP_{th}(\mu M) = \frac{(DO_{sat} - DO_{th})}{138} = \frac{(DO_{sat} - 76)}{138}$$
(2)

DISi<sub>th</sub> (
$$\mu M$$
) =  $\frac{(DO_{sat} - DO_{th}) \cdot 17}{138} = \frac{(DO_{sat} - 76) \cdot 17}{138}$  (3)

Here  $\text{DIN}_{th}$ ,  $\text{DIP}_{th}$ ,  $\text{DISi}_{th}$  are threshold values of DIN, DIP and DISi, respectively;  $\text{DO}_{th}$ ,  $\text{DO}_{sat}$  are threshold value and value at saturation conditions of oxygen concentration, respectively. It is assumed that Redfield stoichiometrical relations between oxygen, nitrogen and phosphorus are proved (Redfield, et al., 1963). Atomic ratio between Si:N in diatoms was accepted 1.05 (Brzezinski, 1985) which results "17" in equation (3). Thresholds values of nutrients were calculated by equations (1)-(3) and presented in Table 8. Meaning of these nutrient threshold values is that such content of nutrients in the photic layer is in principle enough for forming of hypoxia in bottom layer for same thickness. We accepted 5  $\mu$ g/L as threshold value of chlorophyll concentration.

**Table 8.** Threshold values of nutrient concentrations calculated at summer temperature and salinity correspond those in near bottom waters of Amursky Bay. These values can be use for assessment of eutrophic status of PGB.

t,	S,	DIN <sub>th</sub> ,	DIP <sub>th</sub> ,	DIS <sub>th</sub> ,
٥C	‰	$\mu M$	$\mu M$	$\mu M$
20	33	18.3	1.1	19.4

## IV.7. Identifying the trend

Coastal waters reveal high biogeochemical dynamic, since they are influenced by both of natural and anthropogenic factors. The monsoon climate of the Primorye Region is the main influencing factor on the seasonal character of all hydrochemical, hydrological and atmospheric coastal environment. For example, a major part of atmospheric precipitations occurs during the summer. Heavy rains may cause occasional flooding and make impulses in supplying of nutrients by river (Fig. 3). Increase of atmospheric temperatures and increased fresh water discharge from rivers result in a strong vertical stratification of the water column during the summer season. The topography of Amursky Bay reveals a depression in its central portion (Fig. 13) which limits horizontal advection and water exchange in the bottom layer. These natural features of the bay cause weak dynamics in the bottom waters during the summer season. Monsoon winds change their phase from southern to western and northwestern, usually during September-October. These winds induce the development of upwelling along Primorye coast and advection of the Sea water onto the shelf of Peter the Great Bay (Zhabin et al., 1993; Zuenko, 2008). Thus, an upwelling and advection of cold open sea water in the bottom layer of the bay occurred at the autumn. All these physical mechanisms influence on rate of nutrient transformations and primary production. Due to highly dynamic variations of nutrients, chlorophyll and oxygen concentrations in space and time on seasonal scale and short-term scale as well, it is seemed very difficult to establish any trends of these parameters on long-term scale. Nevertheless, we try to recognize the trend of assessment parameters for Sub – area A in summer season, because this Sub-area is most investigated in the summer time. In this Sub-area we choose local area in the central part of Amursky Bay. It is situated on contrary of Peschanij Peninsula (Fig. 13). We have data of assessment parameters for surface and bottom horizons. It was found that values of parameters for bottom horizons are strongly dependent from depths of basin (Fig.17). For excluding this dependence we calculate values of assessment parameters for certain depth, namely, for 15 m using linear regression as it is shown on Fig.17. Number of stations used in such linear regressions vary within 7 (2001 year) -22(2008 year). Values of assessment parameters for surface horizons were simply averaged using data of same stations as for bottom horizons. Obtained such way values of assessment parameters were

presented on Fig.18. Graphs on Fig.18 reveal trends in increasing of DIN, DIP, DISi, and decreasing in oxygen concentrations for bottom horizons. However, vice versa is for surface horizons excepting DIN case. This figure demonstrates trend in increasing concentration of Chlorophyll.

Available historical published data demonstrates that the lowest values of DO concentrations obtained in the summer season at the bottom waters of Amursky Bay have been systematically decreasing with time over the last eighty years (Fig. 19).

There are available data of water quality trends of Razdolnaya River (Fig. 20; POMRAC, 2009). Fig. 20 clearly demonstrates trends in increasing concentrations of phosphates and ammonium with time in Razdolnaya River.

Long-term observations of the community of Japanese Scallop and its epibionts in the Amursky Bay documented that from 1982 through 1993 the mean age of scallops in the settlement increased and the rate of linear growth of the mollusks dropped (Silina, Ovsyannoikova, 1995). The most noticeable changes occurred in the species composition and quantitative distribution of cirriped barnacles. Less tolerant epibionts were gradually replaced by species highly resistant to silting and organic pollution. The Polychaetes appeared the most tolerant to pollution (Silina, Ovsyannoikova, 1995). Dramatically changes of bentic flora in Amursky Bay were found (Levenets, Skriptsova, 2008). The total spaces number of macrophytes in 2005 decreased 1.5 times as compared to record of 1970 - 1980s. The most pronounced qualitative and quantitative changes of the flora were observed in the zones subjected to an anthropogenic press and the direct impact of the Razdolnaya River drain. It was found that the algal thickets with domination of kelps and sargases have reduced, and extensive thickets of sea grasses have disappeared from these sites. The reduction of the spaces number, biomass decrease, change of dominants in plant communities along with an increased importance of green algae testify to a human-induced transformation of vegetation towards its degradation (Levenets, Skriptsova, 2008). The investigations of long-term changes of macrozoobenthos in Amursky Bay suggest negative tendency in ecosystem of the bay (Moshchenko, Belan, 2008). Eutrophication and silting of the bay are supposed to be most probable reasons of macrozoobenthos change in the northern part of Amursky Bay in end of the XXbeginning of the XXI centuries, and to be an obstacle for restoration of the bay fauna (Moshchenko, Belan, 2008). Hydrochemical data (Figs. 4, 5), and biological investigations (Silina, Ovsyannoikova, 1995; Levenets, Skriptsova, 2008; Moshchenko, Belan, 2008) strongly suggest that trend of increasing eutrophication is occurred in sub-area  $\mathbf{A}$ . We did not find any data which may clearly suggest about any trend of eutrophication in Sub-areas **B** and **C**.



**Figure 17.** DIP concentrations in bottom layers as function of depth in chosen local area of central part of Amursky Bay which is situated on contrary of Peschanij Peninsula. Data obtained at August, 2008.



**Figure 18.** Trends of assessment parameters in the Peter the Great Bay (Sub-area A). Solid lines and fill circles correspond to bottom horizon -15 m. Dash lines and open circles correspond to surface horizon.



Figure 19. Minimal values of dissolved oxygen concentrations (saturation degree) observed in bottom waters of Amursky Bay in summer season by different investigators (1 – Voronkov, 1941; 2 – Lastovetsky and Veshcheva, 1964; 3 – , 5 – Redkovskaya, 1980; 4 – Rodionov, 1984; 6 – Podorvanova et al., 1989; 7 – 12 – Hydrochemistry Laboratory of POI).



Figure 20. Trends of the water quality chemical parameters for some Russian rivers within NOWPAP area.

IV.8. Determine the eutrophication status of assessment category (I-IV) by setting assessment category classification criteria

Sub-area A (Amursky Bay) was most extensively studied in comparison with sub-areas B and C. Distributions of DIN, DIP, DISi, DO, Chlorophyll concentrations in surface and near bottom layers are given by Figs. 21 and 22. Red color means that nutrients concentrations exceed threshold values and dissolved oxygen concentrations less threshold value. We have to emphasize that waters which supply nutrients (river waters and waste waters) have lower density than surround seawater and should be revealed in distributions in the surface water. However it is actually observed for Razdolnaya River inputs only. Low concentrations of DIN (about 2 µM), DIP (about 0.1 µM) are observed in surface for most part of Sub-area A. Explanation of this feature is in there is biological pump which transforms nutrient concentration into biomass of diatoms. Part of diatoms is grazed by zooplankton. However "excessive" biomass of phytoplankton settles on the bottom. We suggested (Tishchenko et al., 2011) that phytoplankton bloom might be caused by enhanced supply of nutrients into the upper layer by increased discharge of the river on the short-time scale (Fig. 3). At high water phase of Razdolnaya River, its discharge approaches up to 1000 m<sup>3</sup>/s at the summer time due to monsoon climate. Under these conditions river waters enriched by suspended matter and nutrients cover major part of the bay area (Fig. 23). Just after settling of suspended matter perfect conditions for phytoplankton bloom are occerred because of a strong stratification of water column, a nutrients enriched surface layer and almost absence of zooplanktons due to fast dynamics of processes. Therefore blooming phytoplankton dies and then sinks on the bottom in a large amount.



**Figure 21.** Distribution of **a** - DIN ( $\mu$ M), **b** – DIP ( $\mu$ M), **c** – DISi ( $\mu$ M), **d** – DO ( $\mu$ mol/kg), and **e** – chlorophyll a ( $\mu$ g/L) in surface layer of Amursky Bay. f – Depth of disk Secci (m). Data obtained at August 2007 on R/V "Malakhit". Red color means that nutrients concentrations exceed threshold values.



**Figure 22.** Distribution of **a** - DIN ( $\mu$ M), **b** - DIP ( $\mu$ M), **c** - DISi ( $\mu$ M), **d** - DO ( $\mu$ mol/kg), **e** - chlorophyll a ( $\mu$ g/L), f - atomic ratios of DIN/DIP in near bottom layer of Amursky Bay. Data obtained at August 2007 on R/V "Malakhit". Red color means that nutrients concentrations exceed threshold values and oxygen concentrations less threshold value.



**Figure 23.** Ocean color satellite images from MODIS showing high content of suspended material from Razdolnaya River (a) and then high Chl-a concentration (b) in the Amursky Bay in Summer period.

Microbiological decay of died diatoms under conditions of light deficiency (at depth more than 15 m) intensively consumes dissolved oxygen and produces phosphates, ammonium, and silicates which we observed on Fig. 22. Direct observations on concentration cells of phytoplankton support that maximum number of bloom events corresponds to July and August months (Fig. 24). Seasonal distributions of DIN, DIP, DISi, DO, Chlorophyll are demonstrated by Figs. 19 – 23. Our data suggest that hypoxia has seasonal character with a peak in the end of summer. Upwelling in the beginning of fall season and its advection across the shelf is the main process which destroys the hypoxia. Ecosystem of Amursky Bay was completely recovered in winter because of intensive ventilation.



**Figure 24.** Number of bloom events by month in Amurskyi Bay (1991–2007). Source: Center of Monitoring of HABs & Biotoxins of the Institute of Marine Biology FEB RAS <u>http://www.imb.dvo.ru/misc/toxicalgae/index.htm</u> (Tatiana ORLOVA, IMB, FEB RUS).



**Figure 25.** Seasonal distribution of DIN concentration ( $\mu$ M) in bottom waters of Amursky Bay. **a** – Winter, **b** – Spring, **c** – Summer, **d** – Autumn 2008. Red color means concentrations of DIN higher than threshold value.



**Figure 26.** Seasonal distribution of DIP concentration ( $\mu$ M) in bottom waters of Amursky Bay. **a** – Winter, **b** – Spring, **c** – Summer, **d** – Autumn 2008. Red color means concentrations of DIP higher than threshold value.



**Figure 27.** Seasonal distribution of DISi concentration ( $\mu$ M) in bottom waters of Amursky Bay. **a** – Winter, **b** – Spring, **c** – Summer, **d** – Autumn, 2008. Red color means concentrations of DISi higher than threshold value.



**Figure 28.** Seasonal distribution of Chlorophyll *a* concentration  $(mg/m^3)$  in bottom waters of Amursky Bay. **a** – Winter, **b** – Spring, **c** – Summer, **d** – Autumn, 2008. Red color means concentrations of DISi higher than threshold value.



**Figure 29.** Seasonal distribution of dissolved oxygen concentration ( $\mu$ M) in bottom waters of Amursky Bay. **a** – Winter, **b** – Spring, **c** – Summer, **d** – Autumn, 2008. Red color means concentrations of DO less than threshold value.

Sub-area **B** (Ussuriisky Bay) was recently extensively studied (Semkin et al., 2011). Seasonal distributions nutrients, chlorophyll and dissolved oxygen concentration are presented for surface and bottom waters on Figs. 30-34. During winter season ice formation is occurred in Sub-area **B**. However, it does not form consolidated ice because basin is open and strong winds, intensive water exchange between the bay and the Sea are unfavorable conditions for forming of consolidated ice. Our data suggest that Ussuriisky Bay reveals highest productivity in winter season. Because highest chlorophyll concentration was 11 mg/m<sup>3</sup> which detected in winter (Fig. 33). Simultaneously Sub-area **A** and **B** are extensively studied at end February and September in 2010. In winter time ecological situation was very nice in both sub-areas. There are very low concentrations of DIN, DIP, DISi, and very high concentrations of DO (it was supersaturated regarding to atmosphere) for surface and bottom layers in winter season (Figs. 30-32, 34).

However, situation is quite different for both sub-areas at warm seasons. In contrast with Subarea A, practically there is not any hypoxic region in Ussuriisky Bay, and region where concentrations of DIN exceed threshold values. There are large areas where concentrations DIP and DISi of bottom waters exceed threshold values for summer and autumn seasons (Figs. 31-g,h 32g,h). Shapes of distributions of DIP and DISi in bottom layer are not coincided to those of oxygen concentrations. Probably high concentrations of nutrients in bottom layer are partly caused by upwelling of the intermediate waters of the Sea which contains high nutrient concentrations. However historical data documents that for summer time there are local sites with low oxygen concentration near bottom which is less than threshold value (Podorvanova et al., 1989). We carried out observations of hydrochemical parameters at August 31 in 2008, 2009. These results are presented on Fig. 35. This figure shows that DIP, and DISi exceed threshold values in bottom layer at 2008, 2009 years. However low DO concentrations in bottom layer are observed in 2008 only. Moreover, in 2009 DO concentrations in bottom layer were higher than ones in surface layer. We explain this finding that in 2009 survey was carried out just after upwelling. We suggest that water from Sub-area C, from deep about 100 m comes to Ussuriisky Bay. This water was enriched by oxygen and DIN. This result is very important because demonstrates another source of nutrients in enrichment of Sub-area B. This source is natural. It is deep water of Sub-area C and even deep water of Sea. Upwelling is mechanism which supplies nutrients on the shelf of Sub-area B and Subarea A as well at autumn season. Main feature of Ussuriisky Bay is high dynamic circulations and water exchange between Ussuriisky Bay and open part of Peter the Great Bay. Winds play is a governing role in appearance of high dynamic waters of Ussuriisky Bay (Zuenko, 2008).

Sub-area C is open part of PGB. This Sub-area is less studied. Nevertheless, Tables 3 and 7 suggest that this Sub-area has minimal anthropogenic pressure in comparison with sub-areas A and B.

Table 8 summarizes spans of variations of assessment parameters for different Category. This Table shows variations of nutrients and DO concentrations are minimal for Sub-area C. This sub-area reveals maximal Secci disk depth. At present time, ecosystem behavior of most part of Sub-area C is close to natural character.



Fig. 30. Seasonal distributions of DIN concentration ( $\mu$ M) in the surface waters (upper penal) and bottom waters (bottom penal) of the Ussuriisky Bay. a, e – February, 2010; b, f – May, 2011; c, g – August, 2011; d, h – October, 2011.



**Fig. 31.** Seasonal distributions of DIP concentration ( $\mu$ M) in the surface waters (upper penal) and bottom waters (bottom penal) of the Ussuriisky Bay. a, e – February, 2010; b, f – May, 2011; c, g – August, 2011; d, h – October, 2011.



**Fig. 32.** Seasonal distributions of DISi concentration ( $\mu$ M) in the surface waters (upper penal) and bottom waters (bottom penal) of the Ussuriisky Bay. a, e – February, 2010; b, f – May, 2011; c, g – August, 2011; d, h – October, 2011.



**Fig. 33.** Seasonal distributions of chlorophyll *a* concentration  $(mg/m^3)$  in the surface waters (upper penal) and bottom waters (bottom penal) of the Ussuriisky Bay. a, e – February, 2010; b, f – May, 2011; c, g – August, 2011; d, h – October, 2011.



Fig. 34. Seasonal distributions of dissolved oxygen concentration ( $\mu$ M) in the surface waters (upper penal) and bottom waters (bottom penal) of the Ussuriisky Bay. a, e – February, 2010; b, f – May, 2011; c, g – August, 2011; d, h – October, 2011.



**Figure 35.** Distributions of a – DIN, b – DIP, c – DISi, d – Chlorophyll a content, e – DO, f – N:P ratios along longitudinal section. **1**, **3** – surface horizon, **2**, **4** – bottom horizon. Ussuriisky Bay. Red liens correspond threshold values of assessment parameters. 1, 2 – 31 August 2008; 3, 4 – 31 August 2009.

	Sub-area A Amursky Bay											
Category	Assesment parameter	Units	Sub-area A		o-area <b>A</b> Sub-area <b>B</b>		Sub-area C					
			TN	TP	TN	TP	TN	TP				
Ι	Total load,	t/y	5350	590	2000	275	1250	200				
	Winter, DIN,	uM	4.9	0.4	0.45	0.25	7	0.25				
	DIP											
	Winter ratio DIN/DIP	inter ratio atomic IN/DIP		12.5		1.8		14				
II	Chlorophyll	Mg/m <sup>3</sup>	min	max	min	max	min	max				
		_	.02	26	0.2	11	0.05	11				
	Red-tide	event	n/d		n/d		n/d					
III	DO bottom	uM	min	max	min	max	min	max				
			4.7	600	55	450	240	450				
	Fish kill	event	two	two		•	n/d	•				
	Transparancy	m	min	max	min	max	min	max				
			0.5	8	5	20	10	20				

#### IV.9. Results and discussion

IV.9.1 Eutrophication status of PGB. There are three types of nutrient sources for Peter the Great Bay: a) Local sources are wastewaters of Vladivostok, Ussuriisk, Nakhodka, Suyfunkhe. Obviously they are caused by urbanization of studied region. These sources have almost constant fluxes during year. b) Diffusive sources are agriculture fields, atmospheric precipitations. Nutrients from these sources are loaded into PGB by rivers, coastal runoff and atmospheric precipitation. Fluxes of these sources have distinct seasonal variability due to seasonal atmospheric precipitation. c) Deep or/and intermediate waters of the Sea which contain high concentration of nutrients is natural source of nutrients. Fluxes from this source are determined by frequency and intensity of cross-shelf water exchange between deep/intermediate water of the Sea and waters of the PGB. We quantify only two types of nutrient sources (a, b), which enhance eutrophication of PGB. These types of nutrient sources (wastewaters, river runoff) are associated with fresh water. Therefore we expect high nutrient concentrations in surface layer of PGB. However, high nutrient concentrations are observed in bottom layer (Figs. 5, 22, 25, 26, 27). Explanation of this feature is existence of biological pump which transforms inorganic nutrients into biomass of phytoplankton. Then, "excess" of phytoplankton dies, settles on the bottom and decays releasing inorganic nutrients and consuming dissolved oxygen (Tishchenko et al., 2011a). Therefore high concentrations of nutrients exceeded threshold values are observed in near bottom layer where deficit of light is occurred. Also it is should be noted that maximal square with nutrients concentrations exceeded threshold values correspond DISi. There are two reasons which explain this feature. One is denitrification on interface seawater/sediments:

$$(CH_{2}O)_{106}(NH_{3})_{16}H_{3}PO_{4} + \frac{7314}{63} \cdot O_{2} + \frac{97}{63} \cdot H^{+} \rightarrow$$

$$106 \cdot CO_{2} + \frac{160}{63} \cdot NH_{4}^{+} + \frac{424}{63} \cdot N_{2} + \frac{7950}{63} \cdot H_{2}O + H_{2}PO_{4}^{-}$$
(4)

Reaction (4) is result of two consequence microbiological processes:  

$$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 138 \cdot O_2 \rightarrow .$$

$$106 \cdot CO_2 + 122 \cdot H_2O + 16 \cdot HNO_3 + H_3PO_4$$
(5)

and

$$\frac{(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 84.8NO_3^2 + 99.8H^+ \rightarrow}{106CO_2 + 148.4H_2O + 16NH_4^+ + 42.4N_2 + H_2PO_4^-}.$$
(6)

In Eqs. (4) – (6) Redfield stoichiometric ratios were used in "formula" of organic matter. Evidences that mass-balance of mineralization of organic matter corresponding scheme (4) are given in (Tishchenko et al., 2011b). Additional argue is Fig. 22f which demonstrates low DIN:DIP ratios. Actually they are ranged between 6 – 10 for most part of Sub-area A. Second reason is that DIP is involved into recycling.

According to Table 7 Sub-area A is subjected maximal annual loads of nutrients. Especially, significance difference between Sub-areas reveals via comparison of nutrients loads per square. Annual loads per square into Amursky Bay are higher in 3 – 5 times than ones into Ussuriisky Bay and more than ten times higher in comparison with Sub-area - C. Thus, high nutrient enrichment of Amursky Bay results in seasonal hypoxia which recently discovered (Tishchenko et al., 2008; Tishchenko et al., 2011a). Using hydrochemical data (nutrient concentrations, chlorophyll and DO contents) we can to conclude that Sub-area A (Amursky Bay) has high eutrophication status. Similar conclusion was made before using phytoplankton data as indicator of assessment of the trophic state of Amursky Bay (Stonik, Selna, 1995).

As mention above, nutrients loads per square into Sub-area **B** are significantly less. We believe that main source of nutrients for sub-area **B** is deep/intermediate waters of the Sea which comes on the shelf during upwelling (type **c** of source). There are different mechanisms of upwelling which are poorly understood and they are extensively discussed somewhere (Zuenko, 2008). At present time we have no approach to quantify type **c** of nutrient source. Nevertheless, using assessment criteria and parameters of category 1 (nutrient concentrations) and 2, 3 (chlorophyll and DO) we obtained results (Table 7 and Figs. 30 - 35) which **permits to make conclusion that eutrophication status of sub-area B can be considered as "Low".** 

Sub-area C is highly dynamic area. Again, main nutrient source for this sub-area is deep water of the Sea which quantification is beyond of the report. Our scarce data about Sub-area C which summarized in Tables 7 and 8 say that **Sub-area C has low eutrophication status** as well.

Hydrochemical data (Figs. 4, 5), and biological investigations (Silina, Ovsyannoikova, 1995; Levenets, Skriptsova, 2008; Moshchenko, Belan, 2008) strongly suggest that trend of increasing eutrophication is occurred in sub-area **A**. We did not find any data which may clearly suggest about any trend of eutrophication in Sub-areas **B** and **C**.

<u>IV.9.2 Final eutrophication status of PGB</u>. Final identification of eutrophication status in PGB is summarized in Table 9. Another words: a) Sub-area A has High eutrophic status and positive trend toward eutrophication; b) Sub-area B has a Low eutrophication status due to specific natural conditions (natural eutrophication caused upwelling) with non-detectable trend; c) Sub-area C has low eutrophication status with non-detectable trend.

Cate	Assessment	Assessme	Identific	ation tool	s		Parameter	Remark
-	parameter	nt value	Value	Comp	Occur-	Trend	Identificati	S
gory			*)S/B	a-rison	rence		on	
	Riverine	Annual	1800	Н	-	Ι	HI	
	input DIN, t/y	mean						
Ι	Riverine	Annual	120	Н	-	Ι	HI	
	input DIP, t/y	mean						
	DIN, μM	Annual	<u>5.9</u>	Н	-	Ι	HI	
		mean	12.6					
	DIP, µM	Annual	<u>0.3</u>	Н	-	Ι	HI	
		mean	0.96					
	DISi, µM	Annual	<u>16</u>	Н	-	Ι	HI	
		mean	36					
	N/P	Annual	<u>7.4</u>					
		mean	7.2					
II	Chlorophyll	Annual	1.9	L	-	Ι	LI	
	a, μg/l	mean						
		Annual	30	Н	-	Ν	HN	
		max						
III	DO	Annual	<u>310</u>	Н	-	D	HD	
	concentration,	mean	250					
	μM	Annual	5	Н	-	Ν	HN	
		min						
IV	Zoo-							
	Phytobentos							
	Kill fishes				L	N	LN	

Table 9A. Identification of eutrophication status in Peter the Great Bay for Sub-area A.

\*)S/B means corresponding concentrations of substance in Surface and Bottom horizons less than 50 m.

Cate	Assessment	Assessme	Identific	ation tool	s		Parameter	Remark
-	parameter	nt value	Value	Comp	Occur-	Trend	identificatio	S
gory			*S/B	a-rison	rence		n	
	Riverine	Annual	180	L	-	Ν	LN	
	input DIN, t/y	mean						
Ι	Riverine	Annual	25	L	-	Ν	LN	
	input DIP, t/y	mean						
	DIN, µM	Annual	<u>2.2</u>	L	-	Ν	LN	
		mean	10					
	DIP, µM	Annual	<u>0.2</u>	L	-	Ν	LN	
		mean	0.86					
	DISi, µM	Annual	<u>6.3</u>	L	-	Ν	LN	
		mean	25					
	N/P	Annual	<u>1-15</u>					
		mean	1-12					
II	Chlorophyll	Annual	1.9	L	-	Ν	LN	
	a,	mean						
	µg/l	Annual	6	L		Ν	LN	
		max						
III	DO	Annual	<u>310</u>	L	-	Ν	LN	
	concentration,	mean	270					
	μM	Annual	70	Н	-	Ν	HN	
		min						
IV	Zoo-							
	Phytobentos							
	Kill fishes				**N/D			

Table 9B. Identification of eutrophication status in Peter the Great Bay for Sub-area B.

<sup>\*)</sup>S/B means corresponding concentrations of substance in Surface and Bottom horizons less than 50 m.

\*\*)N/D means No Data

Cate	Assessment	Assessme	Identification tools				Parameter	Remark
-	parameter	nt value	Value	Comp	Occur-	Trend	identificatio	S
gory			*S/B	a-rison	rence		n	
	Riverine	Annual	250	L		Ν	LN	
	input DIN, t/y	mean						
Ι	Riverine	Annual	11	L		Ν	LN	
	input DIP, t/y	mean						
	DIN, μM	Annual	<u>1.7</u>	L		Ν	LN	
		mean	8					
	DIP, µM	Annual	<u>0.3</u>	L		Ν	LN	
		mean	0.8					
	DISi concen-	Annual	<u>7</u>	L		Ν	LN	
	tration, µM	mean	21					
	N/P	Annual						
		mean						
II	Chlorophyll	Annual	0.86	L		Ν	LN	
	a.	mean						
		Annual	11	Н		Ν	HN	
		max						
III	DO	Annual	<u>312</u>	L	-	Ν	LN	
	concentration,	mean	293					
	μM	Annual	185	L		Ν	LN	
		min						
IV	Zoo-							
	Phytobentos							
	Kill fishes				**N/D			

Table 9C. Identification of eutrophication status in Peter the Great Bay for Sub-area C.

<sup>\*)</sup>S/B means corresponding concentrations of substance in Surface and Bottom horizons less than 50 m.

<sup>\*\*)</sup>N/D means No Data

## V. Macroscopic view on eutrophication status of PGB

We include this short chapter because fully agree with S.W. Nixon which states "Seeing eutrophication in the macroscopic view is important for understanding and managing the phenomenon." (Nixon, 2006). Obviously, eutrophic status of ecosystems of Sub-areas **B**, and **C** directly depends from eutrophic status of the open sea area. This area is intensively studied during many decades by many scientists. It was clearly established that this Sea reveals temporal variations in oxygen content in deep waters. T. Gamo with colleagues was first, who found temporal variability (decline oxygen concentration of deep water) (Gamo et al., 1986). Trend of oxygen decreasing of deep water is still continue and some authors supposed that this Sea will become anoxic in 2200 (Chen et al., 1996). Many researches explained the decreasing of oxygen concentration of deep waters (no ventilations and renewal) (Gamo et al., 1986; Chen et al, 1996; Kim and Kim, 1996). However stagnation process should be result in vertical redistribution of hydrochemical parameters. Actually, below 100 m oxygen content reduces, nutrients (phosphates, nitrate) and NDIC contents increase with time (Fig, 36, Tishchenko et al.,

2002). Tishchenko and coauthors (2002) explained theses temporal variability of observed hydrochemical parameters by eutrophication of this Sea. Main considered causes are eutrophication of East China Sea (Chen, 2000) and existent of system of surface currents.

The driving forces on the global scale include human population growth (mostly around the East China Sea), increased anthropogenic emission of reactive nitrogen species to the atmosphere (mostly through agriculture, the increase in automobile use, oil exploration, and deforestation), increased atmospheric CO<sub>2</sub> (global acidification), and climate change (Duarte, 2009). It is well documented that the exponential increasing of fossil fuel combustion, production of N-fixing crops, and the industrial production of fertilizers corresponds to periods of exponential spreading of coastal eutrophication (Boesch, 2002; Rabalais et al., 2010; Zhang et al., 2010; Kim et al., 2011). There is a period between 1960s–1980s , in which Amursky Bay became hypoxic during the summer, most likely originating in the 1970s (Fig. 19). This could be the result of global processes. Obviously, the natural drivers have been active in the area over many years. However, analysis of available published data and our observations suggests that a negative tendency in DO content of the bottom water of Amursky Bay has started only in the second half of the last century. This could be explained by an increasing role of non-local sources of nutrients over time. This is in agreement with the conclusion of Rabalais et al. (2009), that eutrophication of coastal waters by non-local sources of nutrients is a part of global change. Lack of efficient management of non-local nutrient loading is a global social problem at the present time.



**Figure 36.** Temporal variability of nutrients (phosphates, nitrate), DO, and normalized dissolved inorganic carbon (NDIC) in NOWPAP Sea from data of station 177 ( $\varphi$ =40.16°N,  $\lambda$ =134.00 °E, 1999) and HS-11j ( $\varphi$ =40.12°N,  $\lambda$ =133.98 °E, 1992) [46].

## VI Conclusion and recommendation

Within "narrow view", on the basis of distributions of assessment parameters and literature data about biological changes, we make conclusions as follows:

a. Northwestern part of Peter the Great Bay (Sub-area A, Amursky Bay) has current eutrophication status as "**High**" and "**Increase**";

b. Most part of Sub-area B can has eutrophication status as a "Low" with non-detectable trend;

c. At present time, most part of sub-area  ${f C}$  has a "Low" eutrophication status with non-detectable trend.

2. Within "macroscope view" PGB is undergoing by eutrophication as part NOWPAP Region.

Recommendations

1. To provide monitoring assessment parameters in sites where hypoxia was observed.

2. To provide monitoring assessment parameters estuarine parts of sub-areas **B** and **C** because they are still terra incognito at present time.

3. To build treatment facilities for sewage of the city which are important part of nutrients loads into Sub-area A.

4. To form artificial downwelling/upwelling system [48] in hypoxia sites which will increase carrying capacity of ecosystem of Sub-area A (Pshenichny, Shevchenko, 1989).

## VII. List of Acronyms

Biological oxygen demand					
Coastal Environment Assessment Regional Activity Center					
Chemical oxygen demand					
Dissolved inorganic nitrogen (active forms: $NH_4^+ + NO_2^- + NO_3^-$ )					
Dissolved inorganic phosphates					
Dissolved inorganic silicates					
Dissolved oxygen					
Land Ocean Interaction Coastal Zone					
Normalized Dissolved Inorganic Carbon					
Action Plan for the Protection, Management and Development of the Marine and					
Coastal Environment of the Northwest Pacific Region					
Peter the Great Bay					
Pacific Geographical Institute, Russian Federation					
Pacific Oceanographic Institute, Russian Federation					
Pollution Monitoring Regional Activity Center					
Suspended Solids					
Total Nitrogen					
Total Phosphorou					

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