Analysis of Level of Technogenic Impact on Water Area of Uglovoy Bay

V I Petukhov\textsuperscript{1}, E A Petrova\textsuperscript{2}, O V Losev\textsuperscript{1}

\textsuperscript{1}Department of Life Safety in Emergencies and Environment Protection, Far Eastern Federal University, 8, Sukhanova St., Vladivostok 690090, Russia
\textsuperscript{2}Laboratory of Hydrological Processes and Climate, V.I. Il’ichev Pacific Oceanological Institute, FEB RAS, 43 Baltiyskaya St., Vladivostok 690041, Russia

E-mail: losev_ov@dvfu.ru

Abstract. Industrial effluent discharge and man-induced soil fills play a decisive role in increased pollutant concentrations. Several areas which are unfavorable in terms of the heavy metal and oil product content have been identified by the environmental monitoring results in the Uglovoy Bay in February 2015. Maximum permissible concentrations (MPC) of heavy metals and oil products were exceeded in the northeastern part of the Uglovoy Bay in locations where the Peschanka River and the Aerodromnaya River drain into the sea. Integral heavy-metal index calculations showed that this area is the most polluted in the Uglovoy Bay. Other significantly polluted areas were identified off the Zima Yuzhnaya settlement in the mouth of the bay and in vicinity of the low-level bridge.

1. Introduction
The Uglovoy Bay is located in the northeastern part of the Amur Bay (Sea of Japan). It intrudes into the mainland between Cape Tikhiy and Cape Klykov. There are two parts in the Uglovoy Bay: the bay itself and its mouth (strait) connecting it with Brazhnikov Inlet and Amur Bay. There is “Sadgorod” resort area on the eastern coast of the bay. There is Vesennyyaya railway station in the north of “Sadgorod”, and a residential area with private houses lying beyond it extends toward an industrial zone. Trudovoye settlement (Ugolnaya railway station) lies farther northwards. On the northern coast of the bay, there is Uglovoye, formerly a separate settlement and now a precinct of Artem city, Prokhladnoye village and Zima Yuzhnaya settlement. In the west, Uglovoy Bay waters wash De-Friz Peninsula with De-Friz settlement on it. The M-60 Highway, crossing the bay over a low-level bridge constructed on the eve of the 2012 APEC Summit meeting, passes here.

The Uglovoy Bay is a locality being used for health-related purposes due to the medicinal mud and has resort zones and water protection zones; however, its waters are exposed to significant anthropogenic pollution. Pollution sources in the water basin are being considered waters of the Amur Bay and numerous local rivers and streams flowing into the Uglovoy Bay. Peschanka River drains into the northeastern part of the bay. It flows across Trudovoye settlement with an industrial zone comprising food processing factories, warehouses and many other facilities. Both surface runoff from populated areas and sewage waters treated at Vladivostok water treatment facilities get into this river. Sewage treatment plant (Sewage Treatment Plant of Fruit & Berry Breeding Farm) with a capacity of...
200 m³/day is located in vicinity of a fruit & berry breeding farm upstream on Peschanka River to which waste water is discharged after bio-treatment [1].

Aerodromnaya River is one of the most polluted streams. It receives waste water discharged from Nadezhdinskaya poultry farm and waters of Ugolnaya River and Saperka River which, in turn, receive industrial and domestic waste water from Artem City and other communities. The most polluted area of the Uglovoy Bay is its northern part covered with weed beds. The function of sea grasses as kind of a protective screen is to hinder movement of pollution from near-shore areas farther to the central part and mouth of the bay. Sanitary conditions are most unfavorable in July-August and January-February. Oil product and phenol concentrations grow and dissolved oxygen declines to 0.2-2.0 mg/l in water due to exposure of effluents discharge [2].

Lowered water exchange with the Amur Bay leads to accumulation of harmful substances are discharged by production facilities of the industrial zone in the basin of Uglovoy Bay. This situation was aggravated during construction of the low-level bridge between peninsular De-Friz and coastline of Sedanka when causeways were filled into the sea from both shores.

V. I. Zvalinsky et al. [3] point out at emerging zones with anomalous organic matter contents around outlets of effluents from Vladivostok city in the winter season. Measured chlorophyll “a” concentrations near the Peschanka river mouth was critical that is evidence of water blooming resulting in reduced concentrations of dissolved oxygen in the sea water [3].

Studies of heavy metal content in seagrasses of the Uglovoy Bay were performed by N. V. Savinok et al. [4] in 2006-2007. Zostera marina L. is a kind of marine eelgrass with accumulation properties, it was used as a biological indicator. According to data presented in that paper, Uglovoy Bay eelgrasses contain much manganese which may be a result of the high content of this metal in the sea water [4].

Heavy metal concentrations in the Uglovoy Bay significantly vary depending on location. Quantitative chemical analysis of the near-shore sea water of the Uglovoy Bay was performed by N. M. Voronkova et al. [5] in 2010 showed that lead and cadmium accumulation occurs primarily in leaves of plants growing here. The degree of sea water pollution in this area is high. According to International Environment Protection Committee, lead and cadmium are among elements which are the most toxic for biota. The source of pollution is industrial waste water and overland runoff from nearby motor roads [5].

The negative impact of the road runoff is mainly associated with pollution of marine environment with Zn, Pb, Cu, Cd, Ni and PHCs. Vehicular component wear is a source of Cr, Zn, Fe and Al deposition on the road surface. Wear of car brakes deposits Cu, Pb, Cr, Mn and Zn. Engine wear and fluid leakage is also a source of Al, Cu, Ni and Cr deposition on roads [6].

2. Methods

Sea water samples in the Uglovoy Bay were taken by specialists and students of the Engineering School (ES) of the Far Eastern Federal University (FEFU) on February 03-04, 2015. Sampling locations are shown in Figure 1.

Water samples were collected from under ice using a portable navigation system (GPS Garmin Trex), Niskin Water sampler and storage containers (plastic and glass) for samples. A total of 38 sea water samples were collected of which 26 samples were taken from the surface and 6 samples were taken from the near-bottom layer. Water samples were taken for analysis for heavy metals (iron, manganese, copper, nickel, cadmium, lead and zinc) and oil products.

Sea water samples were analyzed in an eco-analytical laboratory – the Interagency Center for Analytical Control of the Environment (Common Use Center “The Interagency Center for Analytical Control of the Environment” of ES of FEFU). All laboratory chemical and analytical tests were performed in compliance with regulatory documents. Sea water samples were tested for heavy metal content in accordance with [7,8] and for petroleum hydrocarbons (PHC) in accordance with [9]. The following specialist equipment was used for sample investigation: ICPE-9000 inductively coupled plasma emission spectrometer (Shimadzu, Japan); AA-6300 double beam atomic absorption
spectrophotometer (Shimadzu, Japan) with HVG-1 hydride vapor generation assembly; FTIR-8400S Fourier infrared spectrometer (Shimadzu, Japan).

Figure 1. Sampling locations in Uglovoy Bay.

An integral heavy-metal index (Z) was calculated for cumulative assessment of sea water pollution in the Uglovoy Bay. Z calculations were performed in accordance with the method stated in [10] for a combinatorial index of water pollution (for 4 priority parameters exceeding MPC by more than 1). Calculation procedures are presented in equations (1), (2) below.

\[
K = \frac{C_i}{MPC}
\]

\[
Z = \sum_{i=1}^{n} \frac{K_i}{n}
\]

where \(C_i\) – heavy metal concentration, mg/L; \(MPC\) – maximum permissible concentration, mg/L; \(K_i\) – coefficient showing how much MPC is exceeded and \(n\) – amount of pollutants used in the calculation.

3. Results and discussion

According to results of the environmental monitoring performed in February 2015, it was found that maximum permissible concentrations of PHCs on the surface of the Uglovoy Bay were exceeded at nine sampling stations (Figure 2).

In terms of spatial distribution of PHCs on the surface, increased concentrations were also registered in the eastern part of the study area and in the mouth of the bay. Exceptions were Station 10 located off the western coast of the Uglovoy Bay near Zima Yuzhnaya settlement and Stations 11 and 12 in the central part of the study area. A maximum PHC concentration (0.293 mg/L) was registered at Station 8 near the Peschanka River mouth (Fig. 2).

Sea water samples from the near-bottom layer were collected at Stations 1-6 in the mouth of the Uglovoy Bay and in vicinity of the low-level bridge. PHC concentrations at Stations 1–5 were within MPC and varied in the range from 0.041 to 0.049 mg/L. An exception was Station 6 (0.054 mg/L) located at the eastern end of the low-level bridge.
**Figure 2.** Spatial distribution of petroleum hydrocarbons (mg/L) on the surface of Uglovoy Bay.

**Table 1. Content of pollutants on the surface of Uglovoy Bay (times exceeding MPC).**

| Station No | Fe   | Mn   | Cu   | Ni   | Cd   | Pb   | Zn   | PHCs |
|------------|------|------|------|------|------|------|------|------|
| 1          | 0.27 | 0.34 | 1.00 | 0.05 | 0.15 | 0.44 | 0.04 | 2.52 |
| 2          | 0.33 | 0.11 | 0.56 | 0.03 | 0.03 | 0.10 | 0.06 | 2.92 |
| 3          | 0.48 | 0.30 | 3.10 | 0.12 | 0.28 | 0.78 | 0.05 | 1.30 |
| 4          | 0.22 | 0.16 | 2.88 | 0.10 | 0.78 | 0.34 | 0.11 | 0.98 |
| 5          | 0.26 | 0.11 | 0.60 | 0.03 | 0.21 | 0.71 | 0.04 | 1.24 |
| 6          | 0.53 | 0.13 | 1.08 | 0.05 | 0.15 | 0.44 | 0.11 | 1.16 |
| 7          | 1.21 | 0.71 | 4.28 | 0.13 | 1.03 | 2.70 | 0.07 | 1.48 |
| 8          | 2.14 | 12.10 | 1.22 | 0.12 | 0.01 | 0.03 | 0.15 | 5.86 |
| 9          | 0.26 | 0.47 | 0.80 | 0.12 | 0.48 | 1.28 | 0.06 | 5.14 |
| 10         | 0.53 | 0.46 | 3.66 | 0.10 | 0.72 | 1.84 | 0.05 | 0.92 |
| 11         | 0.33 | 0.17 | 0.78 | 0.05 | 0.09 | 0.27 | 0.11 | 1.48 |
| 12         | 0.46 | 0.23 | 0.70 | 0.07 | 0.25 | 0.69 | 0.15 | 0.58 |
| 13         | 0.20 | 0.27 | 2.06 | 0.10 | 0.25 | 0.67 | 0.08 | 0.50 |
| MPC, mg/L  | 0.05 | 0.05 | 0.005| 0.01 | 0.01 | 0.01 | 0.05 | 0.05 |

Data on the content of heavy metals and PHCs in sea water samples from the Uglovoy Bay taken on the surface in the near-bottom layer are presented in Tables 1 and 2 below. The following conclusions can be made upon analysis of these data:

1. The most polluted area of the Uglovoy Bay in terms of heavy metals and oil products on the surface is its northern part (Stations 7 and 8 in the place where Aerodromnaya River and Peschanka River drain into the bay; Station 9 and 10 near Prokhladnoye village and Zima Yuzhnaya settlement).
MPCs are exceeded here as follows: iron – 1.21 to 2.14 times, manganese – 12.10 times, cadmium – 1.03 times, lead – 1.28 to 2.70 times (Table 1).

2. Surface water pollution with copper (1.08-4.28 MPC) and PHCs (1.14-5.86 MPC) was observed virtually at all sampling stations except the central part of the bay (Table 1).

3. Nickel and zinc concentrations in the waters of the Uglovoy Bay, both on the surface and in the near-bottom layer, were within MPCs (Tables 1 and 2).

4. Analyzing of water samples taken from the near-bottom layer showed (Table 2) that the content of heavy metals and PHCs was within MPC virtually in the entire basin being considered. Exceptions were PHCs at Station 6 (1.08 MPC) and copper at Stations 3, 4, 6 (1.32-1.80 MPC).

Table 2. Content of pollutants in the near-bottom layer of Uglovoy Bay (times exceeding MPC).

| Station № | Fe   | Mn   | Cu   | Ni   | Cd   | Pb   | Zn   | PHCs |
|-----------|------|------|------|------|------|------|------|------|
| 1         | 0.14 | 0.21 | 1.00 | 0.09 | 0.21 | 0.58 | 0.05 | 0.98 |
| 2         | 0.40 | 0.16 | 0.58 | 0.03 | 0.11 | 0.36 | 0.06 | 0.88 |
| 3         | 0.52 | 0.18 | 1.32 | 0.08 | 0.20 | 0.58 | 0.34 | 0.82 |
| 4         | 0.03 | 0.18 | 1.80 | 0.10 | 0.04 | 0.12 | 0.03 | 0.90 |
| 5         | 0.21 | 0.14 | 0.94 | 0.05 | 0.08 | 0.26 | 0.04 | 0.94 |
| 6         | 0.31 | 0.10 | 1.50 | 0.06 | 0.06 | 0.19 | 0.03 | 1.08 |

In accordance with the classification of the water of water bodies based on MPC exceedance [7], the waters on the surface of the Uglovoy Bay were characterized by degree of their pollution. Station 7 is characterized as having a “low” pollution level by iron, cadmium and PHCs and a “medium” level by copper and lead content. Station 8 is characterized as a “medium” level by iron and PHC content and as a “high” pollution level by manganese. Station 10 is characterized as a “medium” pollution level by copper content and as a “low” level by lead content.

An integral heavy-metal index (Z) was calculated for assessment of sea water pollution in the Uglovoy Bay by four priority parameters (iron, manganese, copper and lead). Fig. 3 shows spatial distribution of the integral index (Z) on the surface of the bay.

Figure 3. Spatial distribution of integral index (Z) on the surface of Uglovoy Bay.
According to calculated values of Z, the most polluted areas in the main part of the Uglovoy Bay are Stations 7 and 8 near mouths of Aerodromnaya River and Peschanka River (Z = 2.23 and 3.87 respectively) and Station 10 off the western coast of the basin being considered near Zima Yuzhnaya settlement (Z = 1.62). Also, significant pollution was observed at Station 3 in the mouth of the Uglovoy Bay (Z = 1.17) and Station 4 near the low-level bridge on the side of De-Friz Peninsula (Z = 0.90).

The integral index value in the near-bottom layer was much smaller than on the surface and varied in the range from 0.38 to 0.65. Its maximum values were also observed at Station 3 in the mouth of the Uglovoy Bay (Z = 0.65) and Station 4 near the low-level bridge (Z = 0.53).

The pollutants concentrations found at stations 4-6 can be related to the influence of exploitation of low-level bridge and the consequences of construction activity (2009-2012). However, ice cover in the Bay limits the input of contaminants from a road runoff in marine environment before the ice clearance (end March – early April) [2]. In this case, it should be made mention the material of causeways filled into the sea in terms of an additional source of pollution. As the argument in favour of this judgement can consider the samples of the dam material of the low-level bridge collected in 2014 where the pollutants contents were: Ni 292.1 mg/kg, 1043.3 mg/kg Cr, 2578.6 mg/kg Mn, 224.6 mg/kg Pb, 1031.3 mg/kg Cu, 311.2 mg/kg Zn.

4. Conclusions
In summary, several areas unfavorable in terms of the content of heavy metals and oil products have been identified by results of the environmental monitoring of the waters in the Uglovoy Bay performed in February 2015: northeastern part of the Uglovoy Bay near mouths of Peschanka River and Aerodromnaya River, western coast of the basin being considered near Zima Yuzhnaya settlement, mouth of the bay and area in vicinity of the low-level bridge.

References
[1] Loseva Y, Mishchenko Y and Grivanova S 2013 Fundamental Studies (Penza: Academy of Natural History) pp 1383–88
[2] Rakov V 2010 Current Environmental Condition and Tendencies its Change in the Peter the Great Bay, the Sea of Japan Astakhov A and Lobanov V (Moscow: GEOS) pp 278–91
[3] Zvalinsky V, Tishchenko P P, Mikhailitik T and Tishchenko P Y 2012 Current environmental condition of the Peter the Great Bay of the Sea of Japan: monograph (Vladivostok: FEFU Publishing House) pp 76–113
[4] Savinok N, Shishlova M 2008 Progress in Modern Natural Sciences (Penza: Academy of Natural History) p 163
[5] Voronkova N, Burkovskaya E and Timofeeva Y 2012 Proceedings of the Irkutsk State University. Series: Biology. Ecology vol 5 (Irkutsk: Irkutsk State University) pp 73–8
[6] Stengel D, Reilly S and Halloran J 2006 The Ecology of Transportation: Managing Mobility for the Environment Davenport J and Davenport J (Dordrecht: Springer) p 392
[7] 1993 RD 52.10.243-92 Guide on Chemical Analysis of Sea Water (St.-Petersburg: HydroMeteolzdat Publishing House) p 264
[8] 2008 RD 52.24.377-2008 Mass concentration of aluminium, beryllium, vanadium, iron, cadmium, cobalt, manganese, copper, molybdenum, nickel, lead, silver, chromium and zinc in waters. A methodology of measurement using direct electrothermal atomic absorption method (Rostov-on-Don: RosHydroMet Publishing House) p 22
[9] 2014 RD 52.10.779-2013 Mass concentration of petroleum hydrocarbons in sea water samples. A methodology of measurement using infrared spectrometry (Moscow: RosHydroMet) p 19
[10] 2003 RD 52.24.643-2002 Methodological guidelines. A method for integrated assessment of the degree of surface water pollution by hydrochemical parameters (St.-Petersburg: HydroMeteolzdat Publishing House) p 89