The Seawater Pollution Survey in the Northern Black Sea

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Abstract

For the first time the integral scene of the toxicological field in the northern Black Sea as it was in the 1990s, with characteristic seasonal and spatial variations, was obtained by means of the integral indices. Priority pollutants during the investigation time were iron, chrome and copper, the registered concentrations of which exceeded maximum allowable concentrations (MAC). In the surface micro layer of the sea total petroleum hydrocarbons and chlorine organic compounds (PCB, HCCH and DDT and its products) were also found in quantities exceeding MAC.

Most probably, the spring (March, May) peak of pollution observed in the pelagic zone developed as a result of the spring flood. In July, the relative well-being of the sea was owing to that spring-summer phase of plankton succession completed in a mass descent of dead plankton to the sea floor that, together with intensive sedimentation of pollutants by suspended matter, favored natural purification.

Keywords: Index of water pollution, main pelagic layers, priority pollutants, sedimentation, bioaccumulation, spatial and seasonal variability.

Introduction

Ecosystem responses to anthropogenic contamination are among key challenges faced and investigated by marine ecology. A large variety of pollutants have been acknowledged as gravely endangering marine ecosystems. Assessing impacts that toxicants produce on ecosystem as a whole and on its elements, it is expedient to integrally study environmental factors such as water, bottom substrate, suspended matter and hydrobionts which determine the quality of marine environment (Borga et al., 2008; Chainho et al., 2008; Korshenko et al., 2008, 2009; Wilson et al., 2008). This approach proved to be more productive compared to tracing distribution of pollutants one by one, as they largely vary both spatially and temporally. In the Black Sea the quality of marine environment is regularly assessed and reported by researchers of The N.N. Zubov Russian Oceanographic Institute; these studies are an integral part of the National Program of monitoring of marine environment and involve using the integral index of water pollution (IWP) which takes into consideration such factors as dissolved oxygen content (DOC) and concentrations of three key pollutants (Romankevich and Aibulatov, 2004; Korshenko et al., 2008, 2009). The resulting array of evidence refers mainly to coastal zones of cities, the localities receiving river inflow and to some close-to-norm inshore seawater areas and discloses background contamination levels.

Measurements were performed in the upper and near-bottom seawater layers in the relatively shallow sea and in standard hydrological horizons in the pelagic zone (Romankevich and Aibulatov, 2004; BSC, 1998; Korshenko et al., 2008, 2009; Zonn et al., 2008; Burgess et al., 2009). These data do not cover hydrological structure of the studied seawater areas and therefore are of little use to hydrobiologists.

In 1992 – 1993, a series of research cruises was organized by the Ukrainian Research Center of Marine Ecology (UkrRCME, Odessa) of Ministry of Natural Environment Protection within the framework of the project ECOMONOK of the State Program «Global change of natural environment and climate» of the State Committee on Science and Technique of the USSR (Medinets et al., 1994a). Specialists from the Institute of Biology of the Southern Seas (IBSS, Sevastopol) of NAS of Ukraine also participated in the research work. Unique experiment which focused on the annual cycle of main elements composing
pelagic ecosystem has brought comprehensive knowledge about the content of pollutants in pelagial of the Black Sea. Results obtained during these expeditions, in particular about spatial and seasonal variations observed in the distribution of the basic classes of pollutants in the marine environment, have been published (Den’ga et al., 1994; Medinets et al., 1994b; Orlova, 1994). At the same time, integral assessment of pollution in the basic pelagic layers and the seawater quality classification based on relevant estimates have been the subjects in waiting as yet. Our article is intended to fill up the gap by discussing spatial and seasonal aspects of the by-depth contamination in the pelagic zone of the northern Black Sea based on the integral indices.

Material and Methods

Estimates measured during the four seasonal surveys performed in the northern Black Sea were used in computations underpinning this paper. Measurements were made during the 60th and 61st expeditions of the R/V “Georgy Ushakov” (March and May, 1992) and during the 57th and 58th expeditions of the R/V “Ernst Krenkel” (July and September, 1992) launched by UkrRCME; the uniform map of sampling stations did not change. Research interests focused on the seawater area of economic zones of Ukraine, Russia and Georgia. Figure 1 shows how the topography of zero horizon (0 m) changed depending on month in 1992 (see Georgiev et al., 1994 for details). Figure 2 shows position of the stations at which pollutants were measured in standard photic layers to 100 m depth. In these expeditions, researchers from UkrRCME collected seawater samples and then determined the content of eight heavy metals (Hg, Zn, Ni, Cu, Pb, Cr, Cd, and Fe), arsenic, total petroleum hydrocarbons (TPHs), chlorine organic pesticides (DDT, DDE, DDD, hexachlorocyclohexan HCCH) and polychlorinated biphenyls (PCB).

X-ray-fluorescent technique was used for measuring total content of Cr, Cu, Ni, Pb, Zn, and As on Spectroscope Max-G (Spectron, Russia). The content of Fe was measured by extraction-activation analysis. The concentrations of oil hydrocarbons in seawater were determined by infrared spectrometry method with the employment of the infrared spectrophotometer IR-20 (Germany). For extraction, from the uppermost thin surface of the sea (micro layer) 1-1 sample and from other depths 10-1 samples of sea water were collected. Gas-liquid chromatography technique was used in chemical tests conducted for chlorinated hydrocarbons on a Tsvet-100 equipped with chromatographic columns; in the identification procedure we used a blend of standard α, γ-HCCH solutions, solutions of ‘DDT, ‘DDE, ‘DDD and “Clophen A-50” as a PCB standard. Detailed description of the methods is given elsewhere (Den’ga et al., 1994; Medinets et al., 1994; Orlova, 1992, 1994). Weight-average concentrations of the toxicants were computed from the pertinent estimates measured in the surface micro layer (SML, 0-1m), in the upper mixed layer (UML), in the thermocline and in the depth from the lower boundary of thermocline to 100 m depth.

The importance of SML in accumulating the pollutants, primarily petroleum products, has been proved by researches carried out over the World Ocean and in the Black Sea in particular. From the standpoint of hydrobiology, SML is neuston biotope. The underlying UML, homogeneous in every aspect, is biotope of epiplanktonic community. Deeper, the layer of density gradient (thermocline) retains light fractions of a variety of pollutants. The content of pollutants in the depth below thermocline suggests deeper sources of contamination and pollutants’ removal from the active layer with sinking suspended particles. Finally, the depth from below thermocline down to HS zone harbors bathyplanktonic community.

Deriving IWP (or IWP, index of water pollution) index, we used the formula according to Korshenko et al. (2008, 2009):

\[ IWP = \frac{\text{norm } O_{ij}}{C_{ij} \times MAC_{ij}} \]

where \( C_{ij} \) is the content of three priority pollutants and \( C_{ij} \) – dissolved oxygen content evaluated by dividing the norm by the actual content; and \( MAC \) – maximum allowable concentration adopted from ITVA Neue Niederländische Liste, 1993. Seawater quality was assessed in conformity with Table I (Korshenko et al., 2008, 2009).

Table 1. The classification of seawater quality based on the index of water pollution (IWP) by Korshenko et al. (2008, 2009)

<table>
<thead>
<tr>
<th>Grade of seawater quality</th>
<th>Definition</th>
<th>IWP</th>
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<tbody>
<tr>
<td>I</td>
<td>Very pure</td>
<td>IWP &lt; 0.25</td>
</tr>
<tr>
<td>II</td>
<td>Pure</td>
<td>0.26 &lt; IWP ≤ 0.75</td>
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<tr>
<td>III</td>
<td>Moderately polluted</td>
<td>0.76 &lt; IWP ≤ 1.25</td>
</tr>
<tr>
<td>IV</td>
<td>Polluted</td>
<td>1.26 &lt; IWP ≤ 1.75</td>
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<tr>
<td>V</td>
<td>Dirty</td>
<td>1.76 &lt; IWP ≤ 3.00</td>
</tr>
<tr>
<td>VI</td>
<td>Very dirty</td>
<td>3.01 &lt; IWP ≤ 5.00</td>
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</tbody>
</table>
Results

The average and maximum concentrations of pollutants measured in the seawater column in the northern Black Sea during 1992 are given in Table 2 (A, B, C, and D). Table 3 specifies priority pollutants found in the inspected seawater layers during the observation periods. Iron, chrome and copper (Figures 3, 4 and 5, correspondingly) persistently prevailed throughout the pelagic depth including SML in which, additionally, PP (Figure 6) and chlorine organic compounds (COC) such as PHB, HCH and DDT and its metabolites (Figure 7) were also found in concentrations larger than MAC. Such factors as hydrological conditions, sedimentation and the influx of pollutants from economic activity provide explanation to the complicated character of pollutants’ distribution. Noteworthily, in the Sea of Azov iron, chrome and mercury were identified as priority pollutants (Klionkin, 2008).

The special character of spatial, by-depth and temporal distribution of the priority pollutants determines the distribution of indices of seawater pollution (Figure 8). According to IWP, the SML was classified as varying from moderately polluted (III grade) in March to very dirty (VI grade) in September (NW Black Sea), and the UML – from dirty in March (NW Black Sea) to pure in July and in September. Thermocline was ranked as dirty only in May, in the central convergence area of the sea, through concentration and descent of more polluted surface and subsurface seawater mass (Figure 1). Density gradient partly screens this seawater area from pollutants; therefore the layer below thermocline is classified as moderately polluted.

Discussion

Seasonal variations of seawater pollution can be traced through comparing IWP estimates averaged for the season (Table 4). The averages derived from the entire seawater area under the study indicate the best situation in July; in all probability, it was owing to seasonally high temperature and extensive growth of phyto- and bacterioplankton, which adsorbed, transformed and, dying, sank down onto the sea bed thereby removing the pollutants from the active seawater.

The rate at which the toxicants were removed from the photic layer through sedimentation and biosedimentation was computed from the settling rates of total suspended matter (TSM) and suspended organic matter (SOM) measured during the abovementioned research cruises (Samyshev, 2009). Evidently, TPM and SOM sedimentation rates were largest in July, therefore the seasonally safe sea (Figure 9).

Accumulation of chlorine hydrocarbons in suspended matter, mesozooplankton, zoobenthos and bottom sediment was estimated as ratio between the pollutant content in the tested object and in the marine environment. PCB, DDT and its products were found in all samples of suspended matter and HCH – in the majority of the samples. Estimates obtained for chlorine organic compounds were largest in the NW Black Sea. In the tested samples of mesozooplankton Calanus euxinus prevailed. Zooplankton abundantly accumulated PCB; compared to DDT, the corresponding estimates were one to two orders of magnitude greater (Figure 10). The concentrations of chlorine organic compounds measured in the samples of Black Sea mesozooplankton were 2 to 3 times larger than in the samples from the North Atlantic (Orlova, 1992).

Conclusions

For the first time the integral scene of the toxicological field in the northern Black Sea as it was in the 1990s, with characteristic seasonal and spatial variations, was obtained by means of the integral indices (Dzitsky et al., 2011).

Priority pollutants during the investigation time were iron, chrome and copper, the registered concentrations of which exceeded maximum allowable concentrations (MAC). In the surface micro layer (SML) of the sea total petroleum hydrocarbons and chlorine organic compounds (PCB, HCH and DDT and its products) were also found in quantities exceeding MAC.

Most probably, the spring (March, May) peak of pollution observed in the pelagic zone developed as a result of the spring flood. In July, the relative well-being of the sea was owing to that spring-summer phase of plankton succession completed in a mass descent of dead plankton to the sea floor that, together with intensive sedimentation of pollutants by suspended matter, favored natural purification.

The gradation of seawater pollution based on the distribution of pollution indices derived from the basic seawater layers provides a tool that permits to integrally assess contamination in pelagic biotopes. Methodologically, this approach is significantly important in studying various impacts that anthropogenic contamination produces on structure and functioning of components of biota in pelagic ecosystems.

Acknowledgements

Materials underlying this publication were obtained thanks to the Agreement about the scientific cooperation between the IBSS, NAS of Ukraine and the UkrRCME, Ministry of Environmental Protection (1992) in implementing the Program of researches of the annual cycle of basic ecosystem elements of the northern Black Sea during 1992-1993. The research program was developed and performed under the guidance of Dr. V.I. Medinets. The authors are grateful to V.T. Georgiev, S.A. Gerasimov, and Yu.I.
Table 2A. Average and maximum concentrations of pollutants derived for the seawater layers, the northern Black Sea, 1992 (March-April)

<table>
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<tr>
<th>Location</th>
<th>Number of stations</th>
<th>Layer</th>
<th>As μg/L</th>
<th>Hg μg/L</th>
<th>Zn μg/L</th>
<th>Ni μg/L</th>
<th>Cu mg/L</th>
<th>Pb mg/L</th>
<th>Cr mg/L</th>
<th>Cd mg/L</th>
<th>Fe mg/L</th>
<th>TPHs mg/L</th>
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<td>Below thermocline to 100m depth</td>
<td>Av.</td>
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<td>SML</td>
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<td>0.049</td>
<td>7.65</td>
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<td></td>
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<td></td>
<td>Max</td>
<td>1.0</td>
<td>0.057</td>
<td>10.80 2.20</td>
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<tr>
<td></td>
<td></td>
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<td>Av.</td>
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<tr>
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<td></td>
<td>Max</td>
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<td>-</td>
<td>-</td>
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<tr>
<td></td>
<td></td>
<td>Below thermocline to 100m depth</td>
<td>Av.</td>
<td>0.3</td>
<td>0.046</td>
<td>4.58</td>
</tr>
<tr>
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<td>Max</td>
<td>0.5</td>
<td>0.057</td>
<td>6.20</td>
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<tr>
<td>Eastern 2</td>
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<td>SML</td>
<td>Av.</td>
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<td>0.039</td>
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<td>Max</td>
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<td>10.80</td>
</tr>
<tr>
<td></td>
<td></td>
<td>UML</td>
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<td>4.70</td>
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<td>6.95</td>
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<td>Max</td>
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<td>0.045</td>
<td>9.30</td>
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<td>Av.</td>
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<td>0.044</td>
<td>6.15</td>
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<td>Max</td>
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<td>0.048</td>
<td>8.80</td>
</tr>
<tr>
<td>Maximum allowable concentrations</td>
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<td>0.100</td>
<td>50.00</td>
<td>10.00</td>
<td>5.00</td>
<td>10.00</td>
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</table>
Table 3. Priority pollutants in the seawater column, the northern Black Sea, 1992

<table>
<thead>
<tr>
<th>Concentration % of MAC</th>
<th>March-April</th>
<th>May</th>
<th>July</th>
<th>September</th>
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<tbody>
<tr>
<td></td>
<td>Fe</td>
<td>PP</td>
<td>Cr</td>
<td>Cr</td>
</tr>
<tr>
<td>Surface microlayer (SML)</td>
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<tr>
<td>Mean</td>
<td>231.0</td>
<td>205.0</td>
<td>72.5</td>
<td>390.0</td>
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<tr>
<td>Maximum</td>
<td>284.0</td>
<td>400.0</td>
<td>100.0</td>
<td>890.0</td>
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<tr>
<td>Upper mixed layer (UML)</td>
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<td></td>
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<tr>
<td>Mean</td>
<td>241.7</td>
<td>137.0</td>
<td>45.6</td>
<td>109.3</td>
</tr>
<tr>
<td>Maximum</td>
<td>880.0</td>
<td>380.0</td>
<td>90.0</td>
<td>254.0</td>
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<tr>
<td>Layer of thermocline</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>164.0</td>
<td>108.0</td>
<td>164.0</td>
<td>191.3</td>
</tr>
<tr>
<td>Maximum</td>
<td>482.0</td>
<td>547.0</td>
<td>123.0</td>
<td>334.0</td>
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</tbody>
</table>

Figure 1. The dynamic topography of horizon 0 m from the spring to the autumn, 1992 by Georgiev et al. (1994).

Figure 2. The map of sampling stations at which the pollutants were measured in 1992: stations 23, 35, 55, 81, 93, 96 (March-April, May), stations 20b, 23, 25, 35, 40, 55, 76, 81, 93, 96 (July, September). NW, C and E – northwestern, central and eastern parts of the Black Sea, correspondingly.
Figure 3. The content of Fe (as percent of the maximum allowable concentration MAC) measured in the main pelagic layers (SML: surface micro layer, UML: upper mixed layer) of the northern Black Sea during 1992. Shaded areas describe the increase of seawater pollution (estimates greater than MAC). The absolute values are plotted (mg L$^{-1}$).
Figure 4. The content of Cr (as percent of the maximum allowable concentration, MAC) measured in the main pelagic layers of the Black Sea during 1992. The absolute values are plotted (μg L⁻¹).
Figure 5. The content of Cu (as percent of the maximum allowable concentration, MAC) measured in the main pelagic layers of the Black Sea during 1992. The absolute values are plotted (μg L⁻¹).
Figure 6. The content of total petroleum hydrocarbons (TPHs, as percent of the MAC) assessed in the main pelagic layers of the Black Sea during 1992. The absolute values are plotted (mg L⁻¹).
Figure 7. The contents of HCCH, total DDT and PCB (as percent of the MAC) measured in the main pelagic layers of the Black Sea during 1992. The absolute values are plotted (ng L⁻¹.)
Figure 8. The distribution of indices of water pollution (IWP) estimated in the main pelagic layers of the Black Sea during 1992. The absolute values of IWP are plotted.
Table 4. Seasonal variability of the average indices of water pollution (IWP) and the classification of seawater quality in the northern Black Sea, 1992

<table>
<thead>
<tr>
<th>Layer</th>
<th>March-April</th>
<th>May</th>
<th>July</th>
<th>September</th>
<th>Average annual index</th>
</tr>
</thead>
<tbody>
<tr>
<td>SML</td>
<td>1.31 (IV)</td>
<td>2.58  (V)</td>
<td>2.22  (V)</td>
<td>3.05  (VI)</td>
<td>2.29 (V)</td>
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<tr>
<td>UML</td>
<td>0.85 (III)</td>
<td>0.89  (III)</td>
<td>0.83  (III)</td>
<td>0.93  (III)</td>
<td>0.88 (III)</td>
</tr>
<tr>
<td>Thermocline</td>
<td></td>
<td>1.03 (III)</td>
<td>0.93 (III)</td>
<td>1.93 (V)</td>
<td>1.30 (IV)</td>
</tr>
<tr>
<td>Layer from the lower boundary of thermocline to 100 m depth</td>
<td>1.07 (III)</td>
<td>0.88 (III)</td>
<td>1.00 (III)</td>
<td>0.8 (III)</td>
<td>0.94 (III)</td>
</tr>
</tbody>
</table>

Figure 9. The sedimentation rates of total suspended matter (TSM) and suspended organic matter (SOM) in photic layer of the Black Sea (Samyshev, 2009); see Figure 2 for the map of sampling stations.

Figure 10. The coefficients of chlorine organic compounds accumulation in the basic ecosystem elements (SM: suspended matter, ZP: zooplankton (primarily Calanus euxinus), ZB: zoobenthos, BD: bottom deposits) of the Black Sea (1992-1993) by Orlova, 1994. The averages are circled. The rectangle’s color deepens describe the range of the obtained coefficients.
Popov (UkrRCME) who offered hydrological data; to V.I. Medinets, A.A. Kolosov and V.A. Kolosov who measured the content of toxic metals in the sea water; and to Yu.M. Den‘ga, Yu.V. Zarubin, and B.O. Treskunov for measuring total petroleum hydrocarbons.

References


