

Water pollution of the Black Sea

Alexander Korshenko (Russia)

1. Petroleum Hydrocarbons in the Water

1.1. IAEA Cruise 1998

Total petroleum hydrocarbons (TPHs) pollution of the Black Sea waters and their suspended matter (SM) contents were studied during 11-20 September 1998 cruise of the research vessel "Professor Vodyanitskiy". The research was carried out in the framework of the IAEA project RER/2/003 "Marine Environmental Assessment of the Black Sea Region"[1]. Over 27 water samples have been collected and analyzed from different depths of 16 stations placed at the central western basin, in the Danube offshore area and Romanian shelf.

Dissolved and total TPHs were extracted with CCl_4 , from filtered and unfiltered water samples, and determined in the extracts by infra-red spectrophotometry [2]. The accuracy of the method was about 15% and the detection limit for a 2000 ml sample approximately 0.05 mg/l. This value is accepted in Russian Federation as Maximum Allowed Concentration for marine waters. The concentrations of the TPH particulate fraction were calculated by subtracting the dissolved TPH concentration from the total one.

The average concentration for all sampled area is 0.084 mg/l (fig.2.1). The maximum reached level of 0.23 mg/l and was marked in the shallow waters off Romania coast south of Constanta close to the border with Bulgaria. The salinity in this waters was rather high (17.73 ‰) and they were not influenced by the Danube discharge but probable the result of the southward drifting polluted waters from Constanta area, where ship traffic, harbor and oil refinery activities are important features. The low salinity waters with 7.81 ‰ close to the Danube delta were not strongly polluted by petroleum hydrocarbons. Their concentration here was 0.05 mg/l only.

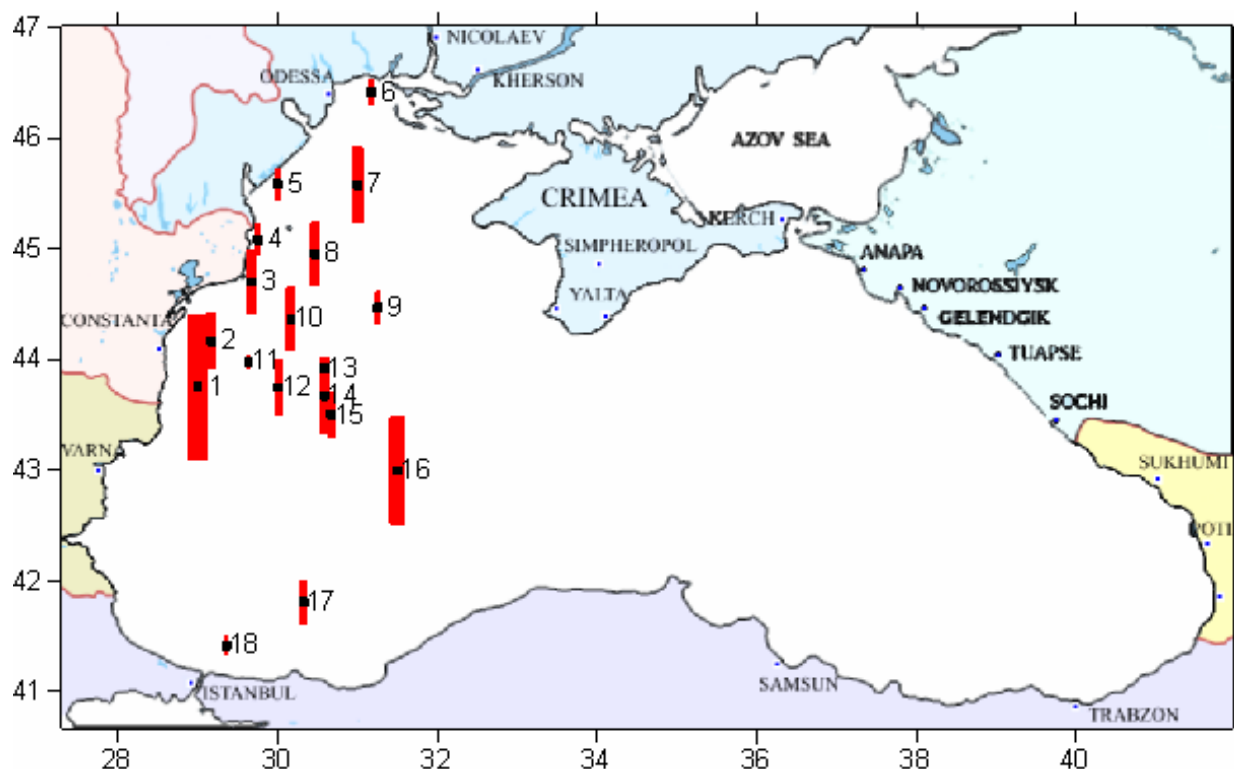


Fig. 2.1. Average Total Petroleum Hydrocarbons distribution (mg/l) at 11-20 September 1998.

The lowest concentrations in the Western part of the Sea were about 0.03 mg/l. The minimums were recorded in front of the Bosphorus strait entrance and in the northern part near Odessa. In general the spatial distribution of petroleum hydrocarbons in September 1998 was rather low and uniform. The area extends southward of Western part of the Sea cannot be estimated for the spatial distribution of dissolved and emulsified petroleum hydrocarbons, because samples were not collected here.

The vertical distribution of TPHs at the deepest station in the center of the western wire has maximums close to surface, in intermediate layer and in near bottom layer but the changes depended from the depth were rather weak. At the surface the total concentration of petroleum hydrocarbons was 0.15 mg/l; at 23.5 m and 29 m depth fell down to 0.06 and 0.02 mg/l consequently, at 51 m depth had 0.11 mg/l; at 102 m reached maximum level 0.17 mg/l; at 508 m – 0.08 mg/l; at 1009 m, almost 1 km above bottom, it was 0.13 mg/l. At another two shallow stations placed at less than 50 m depth PTHs vertical concentration were almost uniform.

The ratio of dissolved and emulsified petroleum hydrocarbons during this expedition varied in a very wide range from zero to 100 %. The mean value for all western part of

the Black Sea in September 1998 was 55% versus 45% correspondingly. The amount of suspended matter in the water varied significantly from 0.21 to 1.83 mg/l with one exception in surface layer at station near the Danube delta where 9.50 mg/l were registered. As mentioned above, the TPHs in this place was rather low despite of high SM concentration.

1.2. IAEA Cruise 2000

In the Eastern and Central Basin of the Black sea 46 water samples were taken at 32 stations during the IAEA scientific cruise from 22 September to 9 October 2000 (Fig. 2.2) [1]. At the beginning of the study one station was sampled in the central part of the Western Basin. Others were placed in the deep central part of the sea and at the rather shallow waters of Kerch transect, Coruh (Georgian waters) and Sinop (Turkish waters) polygons.

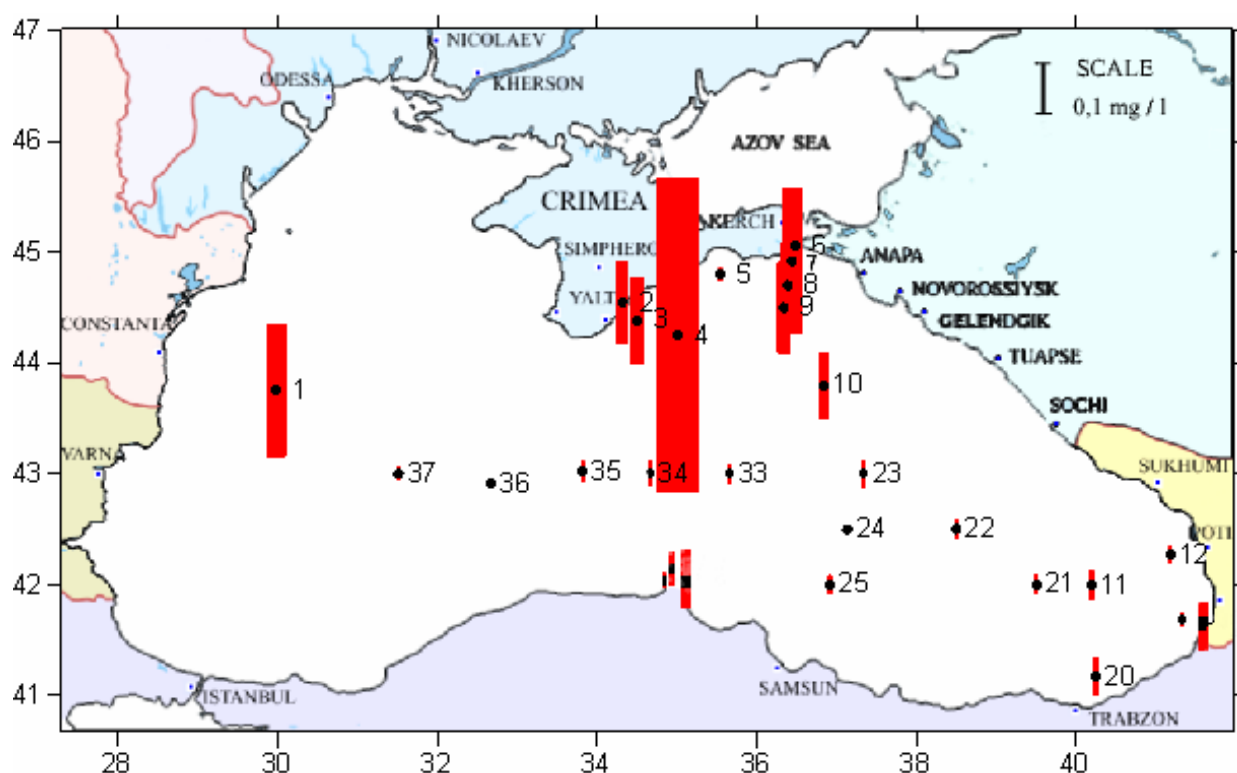


Fig. 2.2. Average Total Petroleum Hydrocarbons distribution (mg/l) at 11-20 September 1998. The anomalous high concentration 3,27 mg/l near Feodosiya isn't shown on the map.

The concentration of Total Petroleum Hydrocarbons in the water varied in the range of absence to 0.73 mg/l and average concentration for all the analyzed samples is 0.097 mg/l. The anomalous high concentration reached level 3.27 mg/l and find in the surface

layer at shallow stations with 62 m depth close to Feodosiya. This level exceeded the Russian standard Maximum Allowed Concentration (0.05 mg/l) for marine waters more than 65 times. With this outstanding number the average reached 0.166 mg/l. The second high value (0.73 mg/l) measured close to this place in front of Yalta. Two other stations near Yalta also have quite high TPHs concentrations varied in different horizons from 0.13 to 0.19 mg/l. Such local patch of oil pollution in the Southern Coast of Crimea was the biggest at that time in the Black Sea waters and could be the result either of local spill or municipal discharge of large tourist centers in the end of the season (Tab. 2.1).

Table 2.1.

The average concentration of total petroleum hydrocarbons (mg/l) in different part of the Black Sea, 22.09-09.10.2000.

Region	Central West	Crimea Cost	Kerch Strait	Georgians waters	Sinop polygon	Central East	Central open
Concentration	0.3	0.78	0.20	0.05	0.05	0.03	0.03

The waters at the Kerch transect was rather high polluted by TPHs especially at the closest to the entrance of the Kerch Strait. One could suggest the discharge of oil pollution from the Azov Sea together with brackish waters taking wastes of Kerch harbor and intensive ship traffic.

In contrary with the northern coasts the level of pollution in Georgian and Turkish waters was relatively low despite of a well-known center of oil processing in the Batumi area. In that time the concentration of TPHs in surface and subsurface layers at Coruh polygon not exceed 0.08-0.09 mg/l and sometimes were under the detection limit of analytical procedure. At Sinop polygon the concentration varied from 0.02 to 0.12 mg/l.

The Central part of the sea and the Eastern Basin showed pollution by petroleum hydrocarbons only a little. Often data was lower of detection limit and never exceed 0.05 mg/l.

If the pollution could occur in the open sea it have to be suggested the accidental spill from the ship with contrary to the idea of the chronic pollution characterizing the whole

Eastern Basin of the Black Sea. The only coastal waters showed sometimes the high level of oil pollution problem.

The vertical distribution of TPHs at one station in the centre of Eastern Basin (for 0 m depth – 0.05 mg/l, 14 m – 0.03 mg/l, 18 m – 0 mg/l, 44 m – 0.03 mg/l, 202 m – 0.01 mg/l, 506 m – 0 mg/l, 1011 m – 0 mg/l) clearly indicated the absence of strong correlation between concentration and depth. It could be possible mention only that in the upper layers of the sea the petroleum hydrocarbons content somehow higher. It could be taken into account also all this data at the border of the detection limit of the analytical method.

In the study in autumn 2000 the distribution of TPHs between the dissolved and particulate phases is practically unpredictable and highly variable: the relative ratio between two forms was ranging from 0 to 100%. The reason of distribution hydrocarbons between different forms isn't clear. For instance, among three stations in the Georgian waters at one the concentration of total petroleum hydrocarbons in the surface layer was 0.05 mg/l and dissolved form took 60%, suspended matter – 0.43 mg/l. At the next stations TPHs had 0.02 mg/l and all 100% these hydrocarbons were dissolved in the water, while SM was 0.61 mg/l. At third station here TPHs had 0.02 mg/l and all 100% hydrocarbons were connected with suspended matter (2.57 mg/l), no hydrocarbons in the water at all. The other Georgian stations showed that water enrichment with particles doesn't lead to increasing of particulate phase of TPHs. At two stations at Coruh polygon the solids in the water increased up to 109 and 80 mg/l but all TPHs (0.09 and 0.07 consequently) was dissolved in the water. One could suggest that distribution hydrocarbons between different phases rather complicated and depend upon many factors. Probably analytical methods used in the study isn't good enough to trace such dependence especially for TPHs values close to the detection limit.

LITERATURE

1. IAEA Regional Technical Co-operation Project RER/2/003 "Marine Environmental Assessment of the Black Sea Region", Working paper: Project Report, 2004, 356 p.
2. Oradovsky S. G., Guidance on the methods of chemical analysis of seawater, Ed., St.Petersburg, Hydrometeoizdat, 1993, 220 p.

Bottom Sediment Pollution of the Black Sea

Alexander Korshenko, B.Gvakharia, N.Machitadze

1. Petroleum Hydrocarbons in the Bottom Sediment

1.2. Russian part

In June-July 2002 south of Taman the sediments were tested on the content of aliphatic and aromatic hydrocarbons in the rather shallow 20-40 m and deep part with 70-100 m. It was marked huge difference between both depths. In deep part the aliphatics reached level 45-84 mkg/g and aromatics – 35-62 mkg/g, while in shallow stations they had only 5-9 mkg/g and 2 mkg/g correspondingly. The difference in scale 10-20 times could be the result of size spectrum of bottom sediments particles, which have to be much smaller in the deep zone with active sedimentation.

2.2. Georgian part

According to preliminary forecasts in 2010-2015 the volume of oil and oil product transportation through Georgian ports is estimated to be about 50-60 mln/t per year. Intense development of marine infrastructure will aggravate current complex ecological state of the marine ecosystem of the sea for which pollution with oil and oil products is the most dangerous.

In the frame of International project on the Study of the background ecological status of the Eastern part of the Black Sea along the coast of Georgia (2000, RV “Piri Reis” of Izmir University) the concentration of petroleum hydrocarbons (PHs) in the bottom sediments was determined using gas-liquid chromatography. Samples of bottom sediments were taken from 75 stations on the Georgian shelf in the depth range from 10 to 1500 m. Preparation of samples, extraction, concentration and tests were done in compliance with the standard [5]. For complete separation of hydrocarbon fractions step-wise programmed optimum temperature regime was applied [6].

In the coastal part of the underwater slope down to the depth of 200 m gradual decrease of petroleum hydrocarbon concentration was observed. The average concentration for the sites with the depth less 50 m depth was 26,9 mkg/g, from 50 to 100 m – 19,5 mkg/g, and from 100 to 200 m - 11,4 mkg/g. High content of petroleum hydrocarbons was detected in the bottom sediments of the Poti harbour area, 35,3 mkg/g on the average. In the bottom sediments north of the Batumi harbour the concentration of petroleum hydrocarbons also was increased up to 17,7 - 21,7 mkg/g, in average 10,5 mkg/g. Apparently, flows of sediments contaminated with petroleum products moved from the Batumi area northwards.

In the gorge of Natanebi river petroleum deposits and oil manifestations both on dry land and in the section of underwater slope have long ago been investigated. Technological boreholes are in operation over the years. The high content of petroleum hydrocarbons in the bottom sediments of the estuary of Natanebi river (152,7 mkg/g) was explained by existence of the local source of oil and originates from the boreholes located not far from the coast, in the river gorge area.

Method used for identification of petroleum hydrocarbons was enable to identify not only the groups of petroleum products, but also to determine approximate time of an oil spill [6,7]. The PHs in the bottom sediment was of different origin and differs in terms of light and heavy

fractions content. Latest spills were mostly found in the regions of Batumi and Poty harbours as well as between estuaries of Khobi and Tsivi rivers. Basically, at the small depths, pollution of bottom sediments with oil and petroleum product was of man-caused nature and is due to the impact of ports and terminals.

In the deep stations starting from the depth of 200 m, concentration of PHs increased. Reason for that could be the re-deposition of petroleum products absorbed on the clay particles transported from the coastal water to the deep water area. At the same time, anoxic conditions prevent biogenic degradation of the hydrocarbons. It could be suggested, the high content of petroleum hydrocarbons in the bottom sediments of the deep part of the Black sea was of both man-caused and natural origin. In the first case it comes from precipitation of heavy fractions of oil from the sea surface, in the second – from oil manifestations on the sea bottom.

2. Heavy Metals in the Bottom Sediments

2.1. Russian part

South of Taman in summer 2002 the metal concentration in bottom sediments varied in the very wide range in fact independent from the depth. The local condition at the depth 40 m could be the reason of minimum concentration here of many metals, namely aluminum, vanadium, chromium, manganese, nickel, copper and arsenic (Table 2.7.2.1). The opposite case was at the station with 70 m where those elements had maximum, except manganese. Lead reached level 7,6 mkg/g of bottom sediments near the shore, and cadmium was lower of detection limit in all places.

Table 2.1.1. The metal concentration (mkg/g) in the bottom sediments June-July 2002 south of Taman.

Depth, m	Al	V	Cr	Mn	Ni	Cu	Zn	As	Cd	Pb
20	2184	128,4	47	661	28,6	53	31,06	7,25	0	7,6
40	876	54	27	163,5	5,5	38	30,08	2,02	0	4,3
70	3206	293	64	377,5	44	92	56,28	4,47	0	0,6
100	1488	115,2	42	255	32,2	79	25,61	5,35	0	5,0

2.2. Georgian part

In 1993-1995 the bottom sediments samples were taken at shallow areas of Georgian shelf in the depth range from 3 to 15 m at stations placed on transects perpendicular to the coastal line. In 186 samples the concentration of Fe, Mn, Cu, Zn, Cr, V, Ni, Pb, Mo were measured (Table 2.7.3.1).

Table 2.2.1. The metals concentration (mkg/g) in the bottom sediments of Georgian shelf in 1993-1995 and 2000.

	Cr	Mn	Cu	Zn	As	Pb
1993-1995						
min/max	10/1300	700/9300	40/900	60/300	-	7,0-48
average	215	1937	50	136	-	17,7
2000						
min/max	40/700	-	20/325	60/260	5,0/95	7-50
average	81	-	81	102	15	20

In 2000 the study of pollution level of bottom sediments by heavy metals was performed in the framework of International project on the Study of the background ecological status of the Eastern part of the Black Sea along the coast of Georgia. The expedition was carrying out onboard scientific research vessel "Piri Reis" of Izmir University (Turkey). About 170 samples of bottom sediments from 75 stations throughout entire shelf of the Georgian sector of the sea, in the depth range from 10 to 1500 m, were collected and concentration of metals Fe, Al, Cu, Zn, Cr, As, Ba and Pb were analysed. Preparation of samples and determination of metals by atomic-absorption method was carried out in compliance with procedure described in the manual [1].

Copper and Zinc. High concentration of copper and zinc has been found in the sea bottom sediments collected from the small depths within southern part of the Georgian sector of underwater slope in the estuary of Chorokhi river: Cu - to 325 mkg/g, Zn - to 260 mkg/g. Their concentration somewhat decreases to the north. Copper and zinc accumulated in the sea bottom sediments is of man-caused origin, since they get into Chorokhi river from the ore regions, located in the river drainage basin. Along with the natural weathering of the oxidizing horizons of ores, the mouth of Chorokhi river is getting polluted with waste discharged from mining enterprises in Turkey, in particular in Murgul and Artvin regions, in immediate proximity of the boundary with Georgia, and within the Georgian sector - from Meria (Adjara).

In the sediments of the underwater slope of Kolheti lowland, Cu and Zn are distributed evenly and their content is of the background level: Cu - from 20 to 45 (in average 30 mkg/g) and Zn - from 62 to 170 (in average 110 mkg/g).

Arsenic. The distribution of arsenic in the sea sediments collected from the small depths within Adjara section of underwater slope, is analogous with distribution of Cu and Zn. This is explained by introduction of arsenic as a part of the sulphide minerals within the heavy fraction of sediments, flowing in together with other chalcophilic elements from the mining regions of Georgia and Turkey.

Chromium. This metal is distributed unevenly in the bottom sediments of the Georgian sector of the Black sea. It mainly accumulates in the sediments of Chakvistskali-Supsa inter-mouth region; at the small depths its concentration reaches 700 mkg/g. The main carriers of chromium are dark minerals (magnetite, biotite, pyroxene), the rock-forming minerals of the volcanic ores of basic composition (basalts, andesites, porphyrites, tuffs, tuff breccias, etc.) [2]. The products of their weathering are carried into the sea by the small rivers of the region (Korolistskali, Chakvistskali, Choloki, Natanebi, Supsa). In contrast to the copper and zinc, accumulation of chromium is natural, since it is not connected with any anthropogenic action.

Lead. Lead was distributed practically evenly throughout entire part of the shelf. The maximum concentration does not exceed 50 mkg/g, minimum was 7 mkg/g, and average for all Georgian shelf - 18 mkg/g, which is obviously the local background level. Situation has not changed since mid 1990-ies.

Barium. High content of barium in the bottom sediments was mainly linked to the coastal part of the shelf. The maximum concentration (in the limits of 0,1 - 0,2%) was found in the area from Chorokhi river mouth to Batumi city. The distribution of it connected with the products of weathering of the barites- polymetallic layers of the South Caucasus, transported to the sea by Chorokhi river. Also accumulations of barium was observed in the estuary sediments of Kintrishi river (0,05-0,1%). In the coastal area of the West Georgia metamorphic geological formations containing clay minerals (in particular zeolites), rich in barium, are found. Possibly, that terrigenous material on the underwater slope is enriched by above mentioned minerals, which explains comparatively high content of barium along the coast.

Aluminium. Being one of the basic rock-forming elements, aluminium was contained in the bottom sediments of the Georgian shelf in the limits from 2 to 7.5 %. The highest level up to 6.0-7.5% was observed in the area of Kolkheti lowland. Obviously, the most fine-grained fractions with high Al_2O_3 content, intensively carried out from the swampy regions of Kolkheti and redeposit by gravity separation. On the average, in the northern part of the Georgian shelf, content of aluminium is 3-4% higher than in south, since in the sea bottom sediments the content of clay fractions increases in the northwards direction.

Iron. Coastal region of the shelf, located in the inter-mouth part of Korolistskali, Chakvistskali, Kintrishi, Natanebi and Supsa rivers, was characterized by high content of iron (>11%). These rivers drain the western extremity of Adjara-Trialeti folded system and carry the products of red soil crust weathering into the sea. High content of iron is related with the dark minerals (magnetite, black mica, etc.) [3,4]. In this section the high content of iron coincides with the high content of chromium, which points to the common source of their entry into the sea sediments. Within the limits of Kolkheti lowland iron content in the sediments of the underwater slope was from 3 to 5%.

LITERATURE

1. Manual for the Geochemical analyses of Marine Sediments and Suspended Particle Mater. Reference Methods for Marine Pollution Studies. No. 63. UNEP 1995.
2. Machitadze N., V. Gvakharia, A. Tvalchrelidze (2001). Vanadium and chromium content in present sediments of Georgian sector of the Black sea. - Bull. of Georg. acad.of Sci., 164, No 3, p. 501-503.
3. Machitadze N., M. Tvalchrelidze, V. Gvakharia (2001). Particularities of geochemical zones formation in the sediments of south-eastern sector of the Black sea Georgia. - Bull. of Georg. acad.of Sci., 163, No 2, p. 297-300.
4. Gvakharia V.G., N.O.Machitadze, A.G. Tvalchrelidze (2002). Distribution Cu, Zn, Mo and Fe in contemporary marine sediments of the Georgian sector of Black sea. - A. Janelidze Geological Institute, Proceeding, New Series, Vol. 117, p. 424-429.
5. USEPA Method 418.1, TNRCC Method 1006.
6. Gvakharia V.G., Gelashvili N.E., Gvakharia T.A., Adamia T.M., Janashvili N.D., Maisuradze G.B. (2004). Method for determination of petroleum hydrocarbons and the study of pollution level of bottom sediments within the Georgian section of the Black Sea water area. - Georgian Engineering News, №2, p. 108-110.
7. Gvakharia V., Tsitsishvili V., Maisuradze G., Gelashvili N., Loria Kh., Girgvliani D. (2002). Use of Chromatography in Ecological Audit of Water Areas and Neighboring Territories of Bleak Sea coast of Georgia. - Second West Ukrainian Symposium on Adsorption & Chromatography, p. 151-155.

Heavy Metals in Marine Aerosols of the Russian Part of the Black Sea

Anton V. Syroeshkin, Irina S. Matveeva, Sergey

S. Pletenev, Alexandr V. Grigor'ev & Vladimir B.

Lapshin

Heavy metals may be supplied to the atmosphere as a component of aerosols owing to different processes and from different sources.

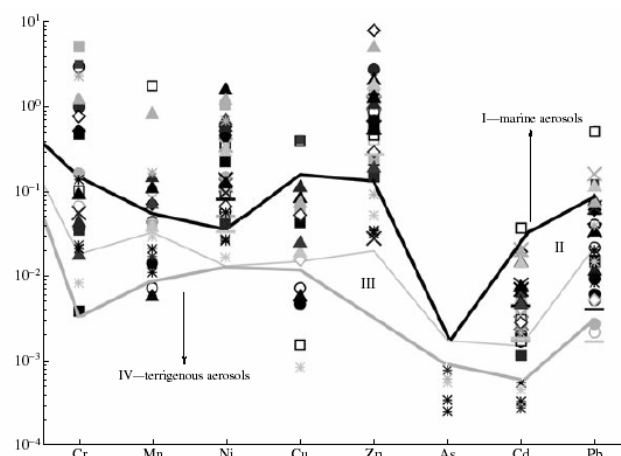
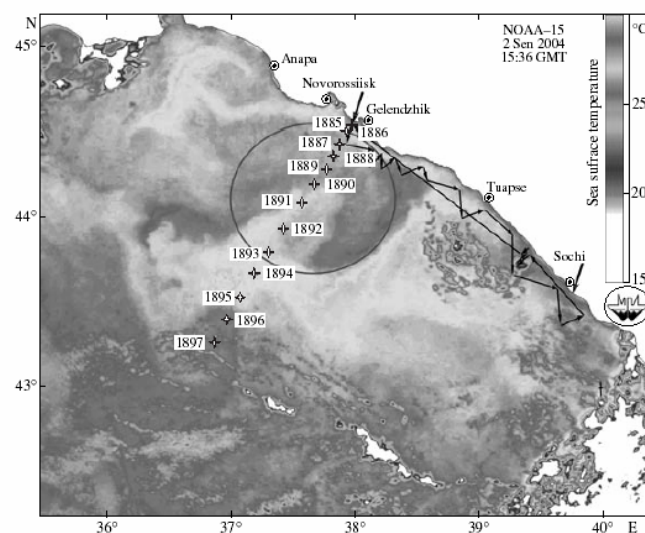


Fig. 1. Examples of relative elemental profiles of aerosols (concentrations of elements normalized with respect to that of aluminum) sampled in June–September 2004 in the Black Sea and previously characterized as marine substances by the data of the size spectra (different symbols refer to different samples of aerosols). Zones II and III correspond to mixed aerosols with prevailing marine and terrigenous components, respectively.

Among them, volcanic activity, dust formation under soil surface weathering, operation of industries and transport producing technogenous aerosols, generation of salt particles under wave and wind interaction in the ocean, and many other sources are distinguished [4, 23]. Thus, an atmospheric aerosol is always a mixture of particles of a great variety of origins. The problem of the long-range transboundary transfer of pollutants is the subject of the EMEP program (Co-operative Program for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe, <http://www.emep.int>) joining many dozens of European (including Russian) monitoring stations, centers of sampling, and analytical centers. One must emphasize a very important fact that the intensity of the marine source of saline aerosol generation, taken to be 5900 Mt/year, is almost six times as high as the power of the dust generation source of 1–10 μ m aerosols, ~24 times as high as that of submicron soil dust aerosol, almost 40 times as high as that of sulfate aerosol, and ~70 times as high as that of carbonic (including carbon black) aerosol [3]. Thus, potentially, 80% of the aerosol mass may be composed of marine matter. The mechanisms of the marine aerosol generation from the surface microlayer by the burst of bubbles [17] formed within the seawater mass during the gassing on a dispersed phase, or during wave breaking, or during direct wind-induced stripping of water drops from the rising sea surface [4, 5, 7, 20, 23] imply a considerable similarity in the composition of the chemical substances between the surface microlayer and marine aerosols [1, 4, 8, 27]. The enrichment of the surface microlayer (SML) by pollutants is well known [4, 12, 25]. This was noted as the cause of the abnormally high content of heavy metals over the aquatic area of the Baltic Sea [21]. We suggested an inverse SML–air path (with respect to atmospheric precipitation) of heavy metal transport within the composition of aerosols as the main reason for the significant excess of the heavy metal contents in marine aerosols, compared to the Moscow urban aerosols and terrigenous ones [1, 5, 6, 8, 12, 19, 25, 26]. Probably, the same path causes the abnormally high contents of nutrients in the dry atmospheric precipitations from the northwestern part of the Black Sea collected in a passive mode [10]; thus, the calculated flux of nutrients from the atmosphere may equal up to 20% of that supplied with the Danube River runoff. The studies of aerosols received a lot of attention within the EMEP and Aerosols of Siberia programs, as well as in the work of many research groups [3, 4, 11, 14, 15, 24, 28, 29]. However, the aerosols generated by the surface of the Black Sea, until now, have not been a subject of systematic studies involving a large number of coastal sampling stations and vessel surveys. Initiated by the State Oceanographic Institute (SOI), the aerosol monitoring and scientific programs required, in particular, for the health planning of recreational policy [16], within the framework of the International Commission for the Black Sea pollution protection (BSERP protection) and of the International Black Sea Organization for Economic Cooperation (BSEC), are in their developmental stage. Since 2002, to partially make up for the existing deficiency, we have performed annual studies of the spatiotemporal variations in the contents of heavy metals, aluminum, and arsenic in marine aerosols of the Russian part of the Black Sea.

Comparison of the Heavy Metal Contents in Marine Aerosols of the Black, Mediterranean, White, and Baltic Seas

The well-known mass transfer of the principal salts of alkaline and alkaline-earth metals with marine aerosols implies the



3 and 2004 on the basis of the satellite image on September 2, 2004. The Golubaya Bay and in Sochi. The series of arrows shows the route of station numbers of the cruise of R/V Akvanavi on September 1–3, 2004 by.

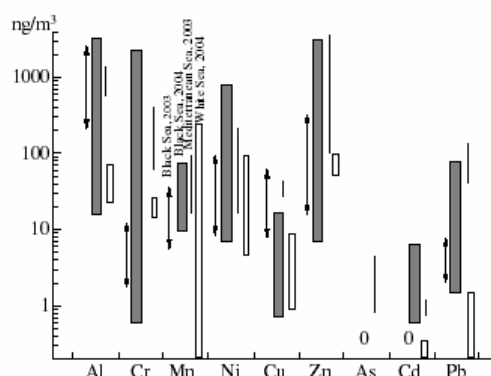


Fig. 3. Absolute contents of selected heavy metals, aluminum, and arsenic in marine aerosols of the Black Sea in 2003 (12 samples) and 2004 (89 samples), the Mediterranean Sea (2003, 5 samples), and the White Sea (2004, 9 samples). For the data on 2004 in the Black Sea, the content ranges from the minimum to the maximum are given for values with a recurrence frequency of 6% or more.

transfer of microelement compounds as well. The contents of microelements in marine

aerosols exceed their clarkes in seawater owing to the enrichment of the surface microlayer by their complexes with organic substances and to the supply of suspended matter particles into the aerosol phase [11, 12, 19, 21, 24]. Because of this, the enrichment of marine aerosols in microelements must not depend on the salinity, especially in the coastal zones. This statement is illustrated by Fig. 3 when comparing the content ranges of heavy metals, aluminum, and arsenic in marine aerosols of the Russian part of the Black Sea, the western Mediterranean, and the northwestern part of the White Sea. The enrichment mechanism for marine aerosols generated by the sea surface must be the same for different seas. Actually, the concentration ranges of heavy metals, aluminum, and arsenic for different seas overlap (Fig. 3; the concentrations are given here and in the following figures in nanograms per cubic meter of air). It is seen that heavy metals with the highest concentrations are chromium, zinc, and nickel. One should note that chromium and nickel are the only pair of heavy metals showing a pairwise correlation of their contents in aerosols. Without considering the deviations for selected elements (Cd and Mn), the epicontinental seas form the following series with respect to a decrease in contamination:

Mediterranean Sea > Black Sea > White Sea.

The content variations of heavy metals, Al, and As in marine aerosols may be caused by temporal variations (due to changes in weather conditions) and altitude and geographic zoning.

Altitude Zoning in the Contents of Aluminum and Heavy Metals in Marine Aerosols

The determination of altitude zoning was also required from the methodological point of view, namely, to substantiate the sampling height above sea level. Several ways to vary the sampling height within 0–10 m above sea level were applied. In the first way, with stationary coastal basing, the filter holders were installed in different areas at the pier of Golubaya Bay. The second way was to install the filter holders at three heights onboard the *Ashamba* launch at the bow. The aerosol was collected while the vessel was moving against southerly winds at distances up to 4 miles from the coast. The extraordinary nonuniformity of the nearwater air layer is well known and confirmed by the authors with the vertical temperature profiles obtained in the course of the field studies. To obtain results less dependent on the local atmospheric fluctuations, the data were averaged over long periods (during June or June–September) at different locations of the samplers (0–4 miles from the coast) to eliminate the height dependence within 1–10 m for most of the elements (Fig. 4).

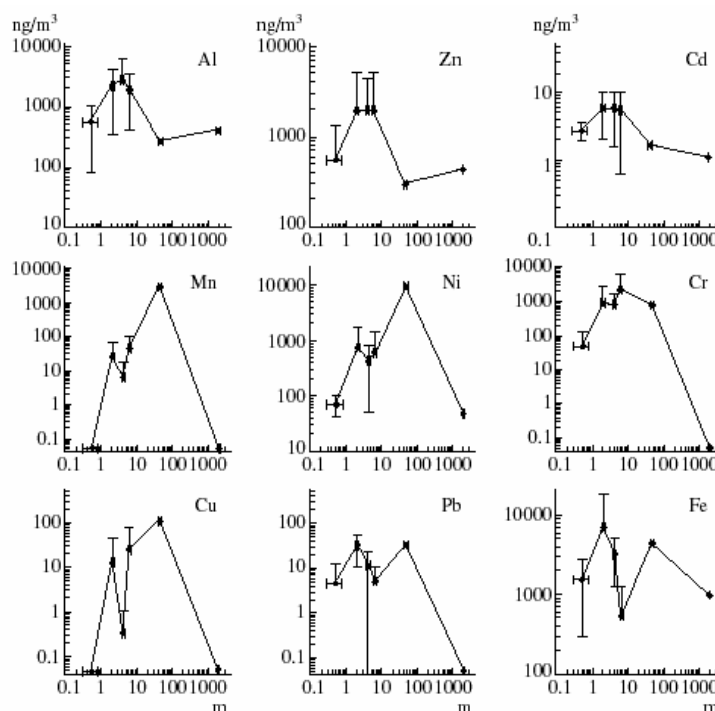


Fig. 4. Height dependence of the contents of aluminum and heavy metals in marine aerosols averaged over the observation period in June 2004. The numbers of independent cycles of aerosol sampling at heights below 1, 1–10, 40–60, and 2100 m are 7, 15, 3, and 3, respectively. When calculating the standard deviations for series of samples, the average values obtained from the chemical analyses were used.

The decrease in the heavy metal contents at heights below 1 m points to a pronounced velocity (over 1 m/s) of the aerosol emission from the sea surface [17]. The difference in the degree of content changes between different groups of elements is the following (with the maximum about 1–10 m for all but Mn and Ni). The most pronounced height dependences are shown by Mn, Ni, Cr, and Cu, while the weakest height dependences are characteristic of Al, Zn, and Cd. Pb and Fe have intermediate positions. The differences in the character of the height dependences (including the standard deviations) between different elements point to their emission within the composition of particles of different origins. The latter, in turn, implies both different geochemical behavior of elements and various mechanisms of marine aerosol formation; i.e., the burst of bubbles and direct wind blowaway are not unique ways of marine aerosol formation. One must note that the samples of aerosols collected on the Azish-Tau Ridge (2100 m) far away from cities and industrial zones are the reference ones representing the total content of heavy metals and aluminum in the aerosols of the long-range transboundary atmospheric transfer, the aerosols of weathering, the biogenic ones, etc. One must emphasize that the concentrations of all elements at a height of 2100 m were lower than those at 1–10 m above the sea (excluding aluminum), and the concentrations of Cr, Mn, Cu, and Pb were in this case below the detection limit. Thus, an additional source of aerosol enrichment in heavy metals exists in the coastal zone, as was noted earlier [5, 25, 26]. This is also confirmed by the comparison of our expedition results to the data of the EMEP [18, 27]. In 2002 and 2004, the averaged concentrations of cadmium and lead (table) were considerably higher than the calculated EMEP data (with a computational grid scale of 50 km) and the averaged data on the concentration of these heavy metals in the aerosols of Europe. It should be mentioned that, according to the EMEP estimations, first, ~70% of cadmium and lead in aerosols are of a technogenous origin and, second, the trends for the last decade show a decrease in the concentrations of these elements by several times.

Comparison of the lead and cadmium contents in aerosols according to the results of the field studies in the Black Sea (present study) and the EMEP data [18, 27]

Element	Average concentration in aerosols, ng/m ³				
	expeditionary studies in the Russian part of the Black Sea			EMEP, modeling calculation for the Russian part of the Black Sea for 2002	experimental data of the EMEP stations, total continental aerosols of Europe, 2002
	June 2004*	June* and November** 2003	June 2002**		
Pb	30	4.5	23	5–7	4.5
Cd	6	0.1	0.5	0.1–0.15	0.11

*Golubaya Bay and the neighboring parts of the aquatic area within 4 miles (Fig. 3, height 1–10 m).

**Weather station at the mouth of the Malyi Brook, Sochi.

Spatial (over the Geoid Surface) and Temporal Deviations in the Marine Aerosol Contamination with Heavy Metals, Aluminum, and Arsenic

As has already been mentioned [1], the area of calculations of the marine aerosol generation for point sampling equaled about 10 km². Including the wind direction variability, during the coastal collection of aerosols, a sector of this area is covered. The data obtained on the pollutant contents in marine aerosols conforms to the average

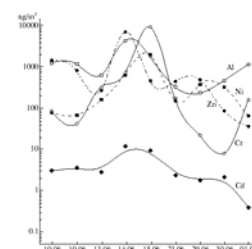


Fig. 5. Example of temporal variation of the concentration of selected heavy metals and aluminum in marine aerosols sampled at a fixed site (the part of Golubaya Bay) and height (7 m).

value for the time of sampling (1–5 h). One would expect that changes in the weather conditions should cause changes in the heavy metal contents in marine aerosols with weekly kinetics (within the synoptical cycle). Actually, these one- or two-weekly variations were found in the course of the coastal sampling of marine aerosols in Golubaya Bay (Fig. 5). The time dependence is pronouncedly degenerated with the increase in area of marine aerosol generation, which was realized over the cross sections made by the R/V

Akvanavt. For example, when collecting aerosols on board a marine vessel (at a velocity of 10 mile/h) for 3 h, an integrated sample of aerosols generated from a water surface area at least 20 times as large as that for point coastal sampling is obtained. Actually, the changes in the element contents shown in Fig. 6 are reversible, which confirms their geographically zonal character. The spatiotemporal “hysteresis loop” is not closed only for Zn (aerosols were sampled in series during the same cruise). As seen from Fig. 6, the

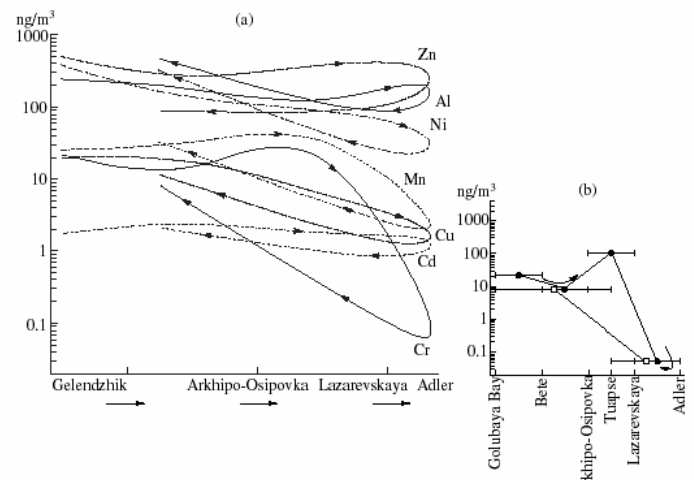


Fig. 6. (a) Reversibility of the zonal dependence of the contents of heavy metals and aluminum in marine aerosols during movement of the R/V *Akvanavt* along the depth break from Gelendzhik to Adler and back. Each interval of the abscissa axis corresponds to one cycle of aerosol sampling. (b) Example of the filter replacement aboard settlements during the vessel movement along the depth break from Gelendzhik to Adler and back in the process of determining the chromium contents. Aerosols were collected onto the first filter during the movement from Golubaya Bight to Bete, onto the second filter from Bete to Arkhipo-Osipovka, etc. The arrows mark the direction of the vessel movement.

concentrations of Al and heavy metals in marine aerosols decreased along the Gelendzhik–Adler line, excluding cadmium, which displayed no significant changes. Figure 6a shows the lines of variability for all the elements when moving from Gelendzhik to Adler and back. The example for chromium showing the zones of

aerosol sampling (replacement of filters) is given in Fig. 6b. When making the 100-mile secular cross section, the elements appeared to be subdivided into two groups. In the first group

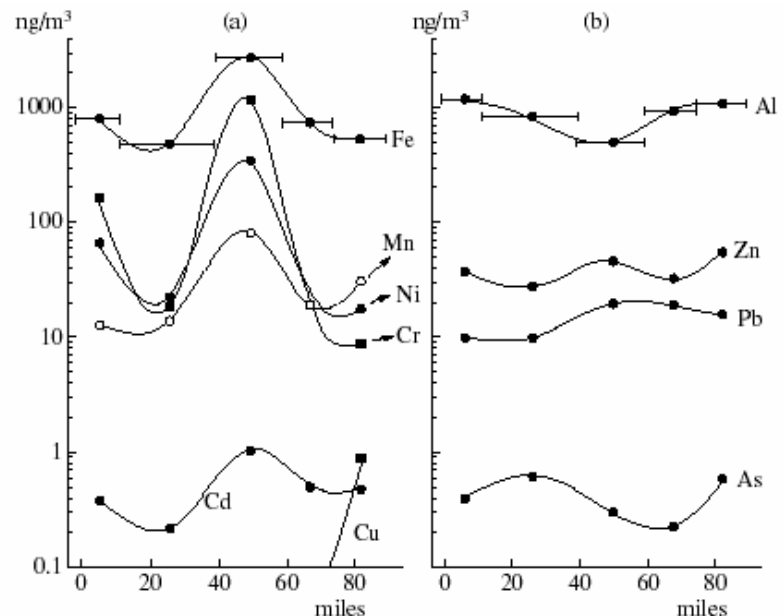


Fig. 7. Variations in the contents of heavy metals, aluminum, and arsenic in marine aerosols of the zones at different distances from Gelendzhik along the secular 100-mile section. The boundaries of the zones (filter replacements) are shown on the curves for chromium and aluminum.

(Ni, Cr, Mn, Fe, Cu, and Cd), a sharp concentration increase was observed within the zone 40–60 miles from the coast, which was most pronounced for chromium and nickel (up to two orders of magnitude,

Fig. 7a). In the second group (Al, Zn, and Pb), the concentrations changed with distance from the coast as little as within a twofold range (Fig. 7b). The variation of the arsenic content has a special character with a minimum about 65 miles from the coast. One should note the depletion of copper in marine aerosols in the open part of the Black Sea. The increase in the element concentrations within the 40- to 60-mile zone may be caused by the occurrence of a well-pronounced region of an anticyclonic eddy in the area treated. A satellite photograph corresponding in time to the survey (September 2, 2004) was kindly provided by S.V. Stanichnyi (Marine Hydrophysical Institute, National Academy of Sciences of Ukraine). This area is marked by the circle in Fig. 2 and possesses a characteristic spatial size of ~90 km, which is typical of the anticyclonic eddies localized within the region of the Black Sea continental slope [2, 31]. The above-mentioned maximum of the heavy metal concentrations in aerosols is evidently caused by the corresponding maximum of their concentrations at the water surface. Microelements may be concentrated in global hydrodynamical structures exclusively in the case of their occurrence within the composition of the particles of the dispersed phase. The concentration of the suspended matter in anticyclones is caused by the corresponding vertical water movements (downward in this case; see, e.g., [13]). The presence of nickel and chromium in the composition of the dispersed phase particles captured into aerosol is indicated by the data on the pronounced increase in their concentrations in marine aerosols near the coast off Sochi. After a storm of force 4, the concentrations of Cr and Ni exceeded their maximum allowable values for working zone air by two orders of magnitude. The contents of As and Cd, which were below the detection limits in marine aerosols in 2003, increased significantly as well. This effect was probably caused by the roiling of bottom sediments (Fig. 8) polluted precisely with these elements, because the contents of other elements did not exceed their maximum values for this area in 2003.

CONCLUSIONS

The Black Sea surface may represent an additional source of atmosphere pollution with heavy metals and arsenic, up to the following concentrations: Cr, 200 000 ng/m³; Ni, 100000 ng/m³; Mn, 4000 ng/m³; Fe, 20000 ng/m³; Zn, 5000 ng/m³; As, 1 ng/m³; Cd, 10 ng/m³; and Pb, 50 ng/m³ (Figs. 4–7). The range of temporal variations of the heavy metal concentrations obtained for point coastal sampling may be as wide as several orders of magnitude. By the degree of spatial variability of the concentrations, the elements form the following series:

$$\text{Cr, Mn, Ni} > \text{Fe, Cu, Pb} > \text{Al, Zn, As, Cd}$$

(Figs. 3, 4, 6, 7).

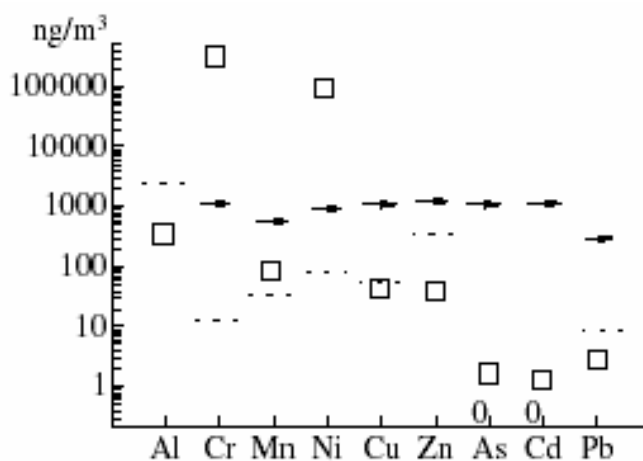


Fig. 8. Concentrations of elements (squares) in marine aerosols of the coastal zone after a force-four storm (Sochi, November 2003). The arrows show the maximum allowable contents of the elements in the air of industrial plant working zones. The dotted line marks the maximum element contents in marine aerosols of the Russian part of the Black Sea in 2003, which were below 0.1 ng/m³ for arsenic and cadmium (zero marks on the graph).

The contents of heavy metals and aluminum in the aerosols of the region of the Black Sea are heightdependent within the range from 0.2 to 2100 m, with various positions of the maxima from 7 to 50 m (Fig. 4). The concentrations of Al and heavy metals in marine aerosols along the Gelendzhik–Adler line decrease, excluding cadmium and zinc, whose contents showed no significant variations (Fig. 6). Along the 100-mile secular cross section, the elements are subdivided into two groups with respect to the character of the concentration variability in marine aerosols (Fig. 7). For the first group (Ni, Cr, Mn, Fe, Cu, and Cd), a sharp decrease in the concentrations, which is most pronounced for chromium and nickel (up to two orders of magnitude), was observed within the 40- to 60-mile zone. For the second group (Al, Zn, and Pb), the concentrations changed with distance from the coast only within a twofold range. The arsenic content variations had a special character (with a minimum about 65 miles from the coast). The spatiotemporal averaged contents of heavy metals in marine aerosols of the Black Sea are higher as compared to those in continental aerosol according to the results obtained on the Azish-Tau Ridge, the averaged data of the EMEP stations for atmospheric aerosol contamination monitoring, and the EMEP calculated values (Fig. 4, table).

REFERENCES

1. A.S. Bugaev, V.V. Zhmur, V. B. Lapshin, *et al.*, RF Patent No. 2248595, Byull. Izobret., No. 8, 21–26 (2005).
2. A. V. Grigor'ev, V. A. Ivanov, A. I. Kubryakov, and N. B. Shapiro, "Anticyclonic Eddy of a Ring Type at the Shelf Edge in the Northwestern Black Sea," in *Ecological Security of the Coastal and Shelf Zones and Complex Use of the Shelf Resources* (Geoek, Sevastopol, 2001), No. 3, pp. 7–12 [in Russian].
3. K. Ya. Kondrat'ev, "Aerosol and Climate: Selected Results and Perspectives of Remote Sensing. 1. Multifactor Character of the Climate Changes and Diversity of the Aerosol Properties," *Ekologicheskaya Khimiya* **7** (2), 73–85 (1998).
4. V. D. Korzh, "Study of the Microelement Contents in Marine Aerosols and Surface Microlayer of Seawater," *Dokl. Akad. Nauk SSSR* **286** (6), 12–15 (1986).
5. V. B. Lapshin, I. S. Matveeva, M. Yu. Yablokov, *et al.*, "Toxic Properties of Marine Aerosols As a New Geoecological and Medical–Geographical Problem," *Trudy GOIN* **209**, 153–169 (2003).
6. M.V. Kolesnikov, I.S. Matveeva, V.B. Lapshin, S.S. Pletenev, A.V. Grigoryev, A.N. Smirnov, A.V. Balyshev, P.I. Popov, A.V. Ignatchenko, A.V. Syroeshkin. Heavy metals in marine aerosols of the Russian part of the Black sea// *Oceanology*. –2005. V. 45. – Suppl. 1. P. S102-S111
7. V. B. Lapshin and A. V. Sidorenko, "Interaction between The Gravity–Capillary Structures in the Surface Layer of the Ocean," *Elektronnyi Zhurnal "Issledovano v Rossii"* **135**, 1561–1570 (2001) [<http://zhurnal.are.relarn.ru/articles/2001/135.pdf>].
8. V. B. Lapshin, M. Yu. Yablokov, I. S. Matveeva, *et al.*, "Are Marine Aerosols Toxic?," *Elektronnyi Zhurnal "Issledovano v Rossii"* **118**, 1302–1316 (2002). [<http://zhurnal.are.relarn.ru/articles/2002/118.pdf>].
9. I. S. Matveeva, T. V. Pleteneva, T. L. Berezinskaya, *et al.*, "Elemental Profiles of Metals As a Vector Characteristic of a Species and Its Physiological Condition," *Mikroelementy v Meditsine*, No. 4, 15–21 (2003).
10. V. I. Medinets and V. A. Ivanitsa, "Problem of Anthropogenic Contamination of the Near-Shore Waters in the Northwestern Black Sea," in *Management and Protection of the Coasts of the Northwestern Black Sea Region* (Astroprint, Odessa, 1996), p. 41 [in Russian].
11. V. S. Savenko, "Geochemistry of Oceanic Aerosol," *Vestn. Mosk. Un-ta. Ser. 5. Geografiya*, No. 1, 28–32 (1998).
12. A. V. Syroeshkin, O. I. Shokina, V. A. Isakov, *et al.*, "Chemical Contamination in the Eastern Part of the Gulf of Finland and the Problem of Toxicity of Marine Aerosols," *Trudy GOIN* **208**, 260–276 (2002).
13. B. V. Titov, "On the Role of Eddies in the Formation of the Current Regime on the Black Sea Shelf and in the Coastal Zone Ecology," *Okeanologiya* **32** (1), 39–48 (1992).
14. A. P. Shetilin, V. F. Lubyshkin, N. M. Kulik, *et al.*, "Distribution of Marine Aerosols in the Coastal Zone of the Eastern Crimea and Degree of Their Deposit in Human Lungs," *Vopr. Kurort. Fizioterap. i Lech. Fizkul't.*, No. 3, 6–8 (1986).
15. K. V. Desboeufs, A. Sofikitis, R. Losno, *et al.*, "Dissolution and Solubility of Trace Metals from Natural and Anthropogenic Aerosol Particulate Matter," *Chemosphere* **58** (2), 195–203 (2005).
16. G. D'Amato, G. Liccardi, M. D'Amato, *et al.*, "Outdoor Air Pollution, Climatic Changes, and Allergic Bronchial Asthma," *Eur. Respir. J.* **20**, 763–776 (2002).

17. G. B. Deane and M. D. Stokes, "Scale Dependence of Bubble Creation Mechanisms in Breaking Waves," *Nature* **418**, 839–844 (2002).
18. I. Ilyin, O. Travnikov, W. Aas, *et al.*, *Heavy Metals: Transboundary Pollution of the Environment* (EMEP Status Report 2, M., MSC-E & CCC, 2004).
19. M. Kuznetsova, C. Lee, J. Aller, *et al.*, "Biogeochemical Nature of Proteinaceous Matter in Marine Aerosols," in *Solas Open Science Conference* (Solas Science, Halifax, 2004), p. 104 [http://www.uea.Antarctic.uk/environment/solas/ss04/SOLAS_Halifax_Abstracts.pdf].
20. R. Marks, K. Jankowska, M. Michalska, *et al.*, "The Sea to Air Bacteria Transfer from the Coastal Waters," *Bull. Inst. Marit. Trop. Med.* **47**, 93–103 (1996).
21. J. Matschullat, "Trace Element Fluxes to the Baltic Sea: Problems of Input Budgets," *AMBIO* **26** (6), 363–368 (1997).
22. J. B. Milford and C. I. Davidson, "The Sizes of Particulate Trace Elements in the Atmosphere," *JAPCA* **35** (12), 1249–1260 (1985).
23. J. O. Nriagu, "A Global Assessment of Natural Sources of Atmospheric Trace Metals," *Nature* **338**, 47–49 (1989).
24. C. D. O'Dowd, M. C. Facchini, F. Cavalli, *et al.*, "Biogenically Driven Organic Contribution to Marine Aerosol," *Nature* **431**, 676–680 (2004).
25. S. S. Pletenev, V. B. Lapshin, V. V. Goncharuk, *et al.*, "The Global Novel Transboundary Source of Coastal Ecosystems' Pollution and Methods of Monitoring and Minimization of Damage to Human Health of the Sea Megapolices," in *Proc. Clean Black Sea Working Group* (BAS, Varna, 2005), pp. 45–46.
26. S. S. Pletenev, V. B. Lapshin, and A. V. Syroeshkin, "Are the Marine Aerosols Toxic?," in *International Conference "The Impact of Global Environmental Problems on Continental and Coastal Marine Waters"* (NEAR, Geneva, 2003), p. 42.
27. A. Ryaboshapko, I. Ilyin, A. Gusev, *et al.*, *Monitoring and Modeling of Lead, Cadmium, and Mercury Transboundary Transport in the Atmosphere of Europe* (EMEP/MS-C-E Report 3, M., MSC-E & CCC, 1999).
28. V. Shevchenko, A. Lisitzin, A. Vinogradova, *et al.*, "Heavy Metals in Aerosols Over the Seas of the Russian Arctic," *Sci. Total. Environ.* **306**, 11–25 (2003).
29. B. Wolterbeek, "Biomonitoring of Trace Element Air Pollution: Principles, Possibilities, and Perspectives," *Environ. Pollut.* **120**, 11–21 (2002).
30. E. J. Wyse, S. Azemard, and S. J. de Mora, *World-Wide Intercomparison Exercise for the Determination of Trace Elements and Methylmercury in Marine Sediment*, IAEA-433 Report no. IAEA/AL/147, IAEA/MEL/75 (MEL/IAEA, Monaco, 2004).
31. A. G. Zatsepin, A. I. Ginzburg, A. G. Kostianoy, *et al.*, "Observations of Black Sea Mesoscale Eddies and Associated Horizontal Mixing," *J. Geoph. Res.* **108** (C8), 3246–3273 (2003).