

HEAVY METALS IN MARINE AEROSOLS OF THE AZOV SEA

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ABSTRACT. The content of heavy metals and Al in the aerosol matter over the Sea of Azov has been studied. According to the special test the vast majority of samples were attributed to the type of marine aerosol. The ranges of contents were determined as following: Fe (200 – 2000 ng / m³), Al (20 – 200 ng / m³), Zn (10 – 280 ng / m³), Cu (2 – 23 ng / m³), Ni (1 – 16 ng / m³), Pb (3 – 30 ng / m³), Cd (0.4 – 2.8 ng / m³); Mn (3 – 23 ng / m³), Cr (1 – 15 ng / m³). The spatial distribution of HMs in the marine aerosol of the Sea of Azov depends on the influence of the river-sea geochemical barrier zone in the Taganrog Bay and the anthropogenic impact of the coastal industrial cities. HM concentrations decrease from the northern coast of the bay and the mouth of the Don River towards the open sea. The maximum HM content in marine aerosol observed in the mouth area of the Don River. It may be associated with the HM accumulation at the river-sea geochemical barrier, and also with the anthropogenic impact of the cities of Rostov-on-Don, Azov and Taganrog. Anthropogenic impact of the city of Mariupol cause the maximum values of Fe, Cr, and Cd in marine aerosol matter of the western part of the Taganrog Bay.

KEY WORDS: heavy metals, spatial distribution, aerosol, micro particles, sea surface microlayer, pollution, Don River, Taganrog Bay

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INTRODUCTION

The aerosol of the surface layer of the atmosphere, including over water areas, is a mixture of particles of various genesis – from the local sources to the long-range atmospheric transport. Calculations show that over the territory of Europe, marine aerosol accounts for about 25-36% of the total aerosol matter (Georgoulas et al. 2016). Aerosol transport from the continent to water bodies is currently well reported (Marín-Beltrán et al. 2019; Akinori et al. 2019; Mahowald, 2018; Von Glasow 2013; Jordi et al. 2012; Paytan et al. 2009). The phenomena of transcontinental transport of aerosols and abundant atmospheric deposition to the surface of the ocean in the Arctic zone, over the waters of the North Atlantic are known (Vinogradova et al. 2019; Maslennikova et al. 2018; Sullivan et al. 2017; Lukashin et al. 2018; Vinogradova et al. 2017). It is shown that among the sources of marine aerosol generation (marine, dust, urban, black carbon, volcanic), the ocean surface is the most powerful, delivering up to 10¹⁶ kg per year (Kondratiev et al. 1999). The reverse process of transporting aerosol matter of marine origin towards coastal territories is also being investigated.

The concentrations of chemical elements in the Sea Surface Microlayer (SSM), their interaction and removal with marine aerosol have been reported in a number of papers (Li et al. 2019; Li et al. 2018, Rastelli et al. 2017). It has been shown that marine aerosol is formed mainly from SSM during the destruction of air bubbles that occur in the thickness of the sea water during gas evolution in the dispersed phase. In addition, it is formed by a direct wind breakdown of water droplets from the sea surface when waves collapse. Aerosol particles formed under these conditions are referred by dimension to the PM 10 group. The mechanisms of marine aerosol formation suggest a significant similarity between

the chemical composition of aerosol particles and the surface microlayer (Lapshin et al. 2002; O'Dowd et al. 2007; O'Dowd et al. 2002).

The climatic role of marine aerosols is significant (Van Dolah et al. 2000; Li et al. 2019). Cloudiness is strongly modulated by the emission of aerosols from the sea surface, affecting its formation and microphysical properties. The mechanism of the effect of aerosol on cloudiness in general can be described as follows. An increase in the concentration of aerosol in the atmosphere changes the water content of clouds and the size of cloud droplets, prolonging the lifetime of the cloud and thus reducing the amount of precipitation (Brooks et al. 2017; Chandrakar et al. 2016; Buseck et al. 1999; Takata et al. 2009).

Many studies are currently devoted to studying the concentration of heavy metals (HM) in aerosol particles. Scientific research is carried out within the framework of the UN programs: GESAMP, National Institute of Health, USA – Marine biotoxins. The mechanisms of toxicant concentrating in SSM and their further aerosol transportation in coastal areas are studied (Li et al. 2018). The accumulation and transfer of toxic substances at the ocean-atmosphere boundary can lead to significant pollution of the near-water layer of the atmosphere (Song et al. 2019; Qureshi et al., 2009; Kolesnikov et al. 2005). The studies are carried out by groups of scientists in various areas of the world (Furness et al. 2017), the North Sea (Salomons et al. 1988), the Arctic Seas (Shevchenko et al. 2003; Golubeva et al. 2011), the Atlantic and Indian Oceans (Witt et al. 2006; Rädlein et al. 1992), Antarctic seas (Tuohy et al. 2015). HMs were found in aerosol matter above the Ross Sea off the Antarctic coast.

HMs as part of aerosol particles are involved in global atmospheric circulation processes, and therefore HM monitoring in marine aerosol considered urgent. The European

Monitoring and Evaluation Program (EMEP; <http://www.emep.int>) and the Acid Deposition Monitoring Network in East Asia (EANET; <http://www.eanet.cc>) internationally cover the origin, spatial distribution aerosols, monitor their chemical composition, use methods of computer simulation of migration flows (Sajeev et al. 2014). The EMEP and EANET monitoring programs rely on satellite-based atmospheric sounding data, as well as data on the chemical composition of aerosols (including HM concentrations) from a network of reference stations in Eurasia, where aerosol sampling is carried out. Computer simulation is corrected by observations on the ground. Thus, remote monitoring methods rely on routine monitoring of aerosol composition.

Toxic substances entering the atmosphere with marine aerosol microparticles, along with urban aerosol sources, pose a serious potential threat to public health in the coastal zone of the seas and oceans (Mahowald et al. 2018; Aryasree et al. 2015; Van Dolah et al. 2000; Syroeshkin 2002; Lapshin 2002). HM entering the body through the respiratory system, penetrating the skin, inhalation and swallowing pathways (Wang et al. 2018) can increase morbidity and mortality from cardiovascular, respiratory diseases, cirrhosis, anemia, neuropathy (Liu et al. 2018), and also affect the kidneys, liver and gastrointestinal tract, causing cancer (Csavina et al. 2013; Izhar et al. 2016; Sánchez-Rodas 2017). There is an increased risk of pulmonary (asthma) and allergic diseases (Walsh et al. 2017; Kirkpatrick et al. 2011; Fleming et al. 2009). The role of marine aerosol as a carrier of palitoxins and endotoxins to the coastal zone has been shown (Patocka et al. 2018; Lang-Yana et al. 2014).

The ecological state of the Sea of Azov, despite the long decline in production activity that began in the 1990s, remains tense. The sea has a relatively small area and depth, there are large industrial centers along its shores, and thereby it is one of the most polluted seas in Russia (Klenkin et al. 2009). The mouth area of the Don River presents hydrodynamic and geochemical barrier. That's why the Sea of Azov considered an interesting and extraordinary subject for studying aerosol matter in the lowest atmosphere. The purpose of this work was to establish the levels of content and spatial distribution of HMs in the marine aerosol microparticles of the Sea of Azov.

MATERIALS AND METHODS

The paper presents data on the concentration of heavy metals in aerosol microparticles of the Sea of Azov obtained by the Azov-2006 complex ship expedition from the Taganrog Bay to the port of Temryuk. The studies were carried out in 2 stages: July 16 – 25 and September 25 – October 1, 2006. Each aerosol sampling period lasted 3-5 hours. Points of change of aerosol filters are marked at the map (Fig. 1). Simultaneously, the content of HM in the sea surface microlayers of 0.2 and 1 mm thick was studied. It has been previously shown that the main source of pollution of the atmospheric near-water layer is aerosol emission from the sea surface, which enables enrichment of the SSM due to the heterogeneous convection (Lapshin et al. 2005; Kolesnikov et al. 2005). A total of 54 aerosol filters and 168 samples of the bulk water and sea surface micro layer were collected.

Aerosol sampling was carried out on AFA-RMP-3 analytical filters using a Karcher NT 351 ECO vacuum cleaner with a maximum air flow rate of 78 dm³/s. The basis of the AFA filter is Petryanov's filter cloth made of perchlorovinyl fiber, in accordance with state specifications TU 951892-89. This is a fibrous material using mechanical methods of particle capture, as well as the electrostatic attraction of aerosol particles to charged filter fibers. Due to this, the material is characterized by high capture efficiency. The canvas is characterized by an irregular arrangement of polymer fibers of the different thickness, so the filter has a different pore diameter. Using the sampling technique methodology, these filters provide collecting 99.9% of aerosol particles with a linear size more than 0.3 microns. 3 filters were exposed simultaneously, the exposure time was 3-5 hours. The volume of pumped air was 16.0±0.1 m³/h, the height of the filter holder was not more than 10 m above the water edge in the headwind. Aerosols were not collected in the rain, and the sampler was not visibly sprayed. During the selection, the following meteorological parameters were controlled: wind direction and speed, air temperature, humidity, pressure, cloud cover (Syroeshkin et al. 2005).

For the elemental analysis, filters were packaged in a special snap-on polypropylene bags. After being delivered to the laboratory, the filters were incubated in Teflon bombs in 10 ml of aqua regia for 1 day. The samples were mineral-

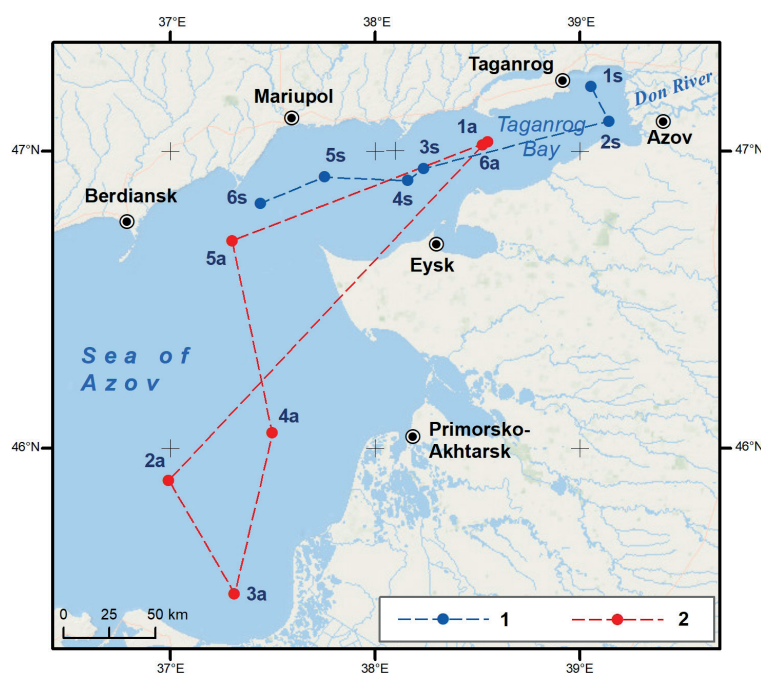


Fig. 1. Aerosol filter change points in the expedition Azov-2006: 1 – July, 2 – September – October

ized under pressure in an MDS2000 microwave oven in the following mode: 2 min. 20 sec – at 80% power, 5 min. – at 100% power. In all experiments, processing and subsequent analysis of the control filter were carried out.

The concentrations of HM in aerosol samples were determined using a SpectrAA-800 atomic absorption spectrometer with electrothermal atomization and the Zeeman effect according to the Varian protocol with modifications according to the results of international intercalibration with the IAEA MEL laboratory (Coquery et al. 2001; Kolesnikov 2005). In parallel, an analysis of 3-5 samples was carried out. The content of elements in the reference sample, see Appendix (Table 2). In all series of measurements, the background content of elements in the AFA control filters was taken into account. The volume of air pumped through the filters allowed the elements to accumulate in an amount significantly exceeding the background content. The average relative error in determining parallel samples did not exceed 20% with a confidence level of 0.95 (Syroeshkin et al. 2005).

The size spectrum of aerosol particles was not studied. However, according to the published data, it is possible to assume the size of aerosol matter generated by the sea surface. The amount of aerosol particles in the drive layer of air sharply increases at winds of about 7-10 m/s. This is due to the emergence of a direct wind failure of water droplets from the ridges of sea waves. This mechanism was noted as one of the first. O'Dowd in the article "Marine aerosol production: A review of the current knowledge" gives a graph of the dependence of the generation of the aerosol substance on the wind speeds for the particles of Aitken and for particles from 10 to 100 nm (O'Dowd et al. 2007). Process of destruction of the air bubbles on the surface of the sea is the most important for the generation of marine aerosol on a global scale producing two types of droplets of film (0.9 microns) and reactive (2 – 2.5 microns) (Syroeshkin et al. 2005; Syroeshkin et al. 2006; Syroeshkin et al. 2014).

RESULTS AND DISCUSSION

To determine the genesis of aerosol particles, a method was used based on their dispersed composition and element content normalized to Al content. The test showed mainly marine origin of the aerosol collected during the studies (Kole-

nikov et al. 2005; Syroeshkin et al. 2006; Syroeshkin 2005).

It is known that heavy metals can be found in natural waters in dissolved and suspended forms and have both natural and anthropogenic origin. A significant part of the suspended forms of HM entering the seas with river runoff is deposited on the river-sea geochemical barrier. The suspended matter remaining in the water column tends to be distributed at the water-bottom (sedimentation process) and water-air (particle flotation) interfaces. Marine aerosol formed from the surface microlayer of the sea inherits its chemical composition. It can include both sea salts and solid microparticles of various origin.

In most cases, the concentration of elements in sea waters is significantly lower than in river waters, where up to 75% of Fe, Mn, Ni, Cu are transported in conjunction with organic substances. Fe, Al, Mn, Ni, and Cu migrate in river waters in forms of colloids, simple and complex ions with a positive and negative charge. The river-sea barrier zone acts as a trap for the most substances (Gordeev 1983).

The main source of pollutants for the Sea of Azov is the runoff of large and small rivers: Don, Kuban, Mius, Eya, Beisug, Kagalnik, etc. (Mikhailenko et al. 2018). The catchment area of the Sea of Azov is about 570 000 km², with the Don and Kuban River catchments account for about 85% of the total (Matishov et al. 2002). The ratio of dissolved and suspended forms of HM at the marine edge of the Don River delta is different. For Fe, Mn, Cr, Pb, the predominance of suspended forms is noted. For Zn, Ni, Cu, and Cd, dissolved forms are prevailing. The flows of metals in the lower reaches of the Don River are largely determined by the influence of the city of Rostov-on-Don. Flows of dissolved and suspended forms of Ni, Cu, Zn, Cd and other HMs significantly increase downstream the city (Tkachenko et al. 2017). As shown below, this also affects the chemical composition of aerosols, especially in the mouth area of the Don River.

Spatial distribution of Heavy Metals and Al in marine aerosols

Iron. The Fe distribution is characterized by the presence of two regions with elevated elemental abundances (Fig. 2). Concentration increases from the open central part of the sea towards the northern and northeastern parts, especially sharply in the Taganrog Bay. On average, the concentration of

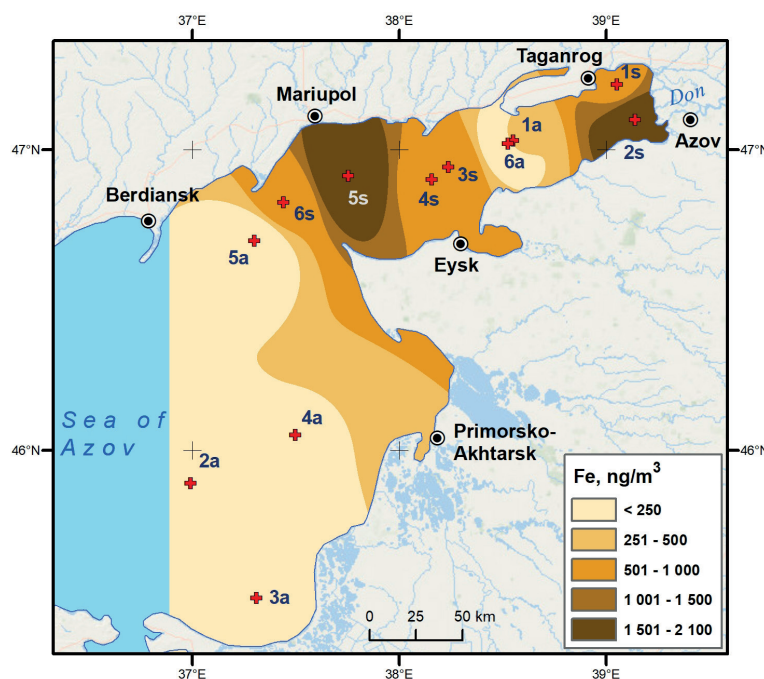


Fig. 2. Distribution of Fe in marine aerosols

Fe in the open sea is 200-1000 ng/m³. The gulf zone is marked by Fe values of about 1800-2000 ng/m³, which is an order of magnitude higher than the average concentration over the entire water area.

Perhaps this fact is explained by the presence of a dynamic geochemical barrier in the mixing zone of fresh and salt waters, the stirring up of bottom sediments and the lifting of suspended particles to the sea surface, where they can be captured in marine aerosol during wind-wave disruption and other processes of formation of marine aerosol. The zone of the northern coast also stands out, in the area of Mariupol, Fe is about 1800 ng / m³, which can be associated with the technogenic influence of the city. Pollutants can also come from the precipitation, as well as from the coastal abrasion, which provides the terrigenous material (Mikhailenko 2018).

Aluminum. The average concentration of Al in marine aerosols in most of the water area is 20–50 ng / m³ (Fig. 3). It rises up to 90-100 ng / m³ at the northern coast in the region of Mariupol, and even higher up to 200 ng / m³ in the Don River mouth area and the Taganrog Bay. This is an order of magnitude higher than the average concentration over the sea. Probably, the maximum in the Taganrog Bay can be explained by the secondary mobilization of aluminosilicate particles and their lift to the surface due to the turbulent mixing and flotation processes. Aerosol particles are enriched with Al, since their main source is the sea surface.

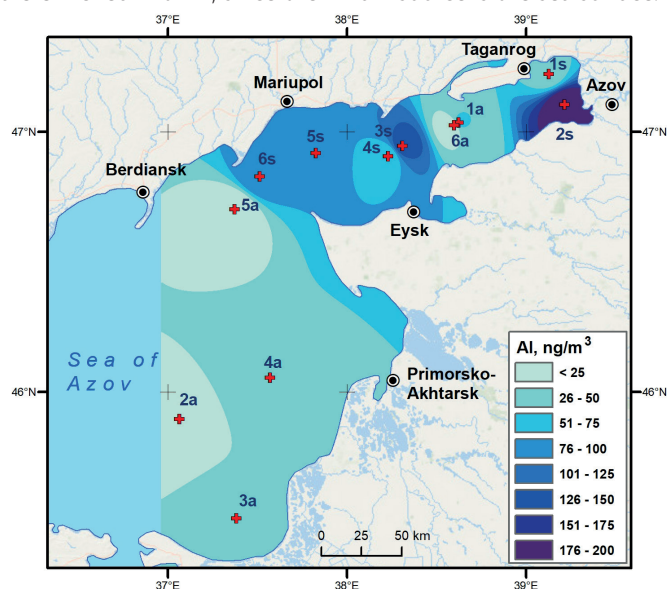


Fig. 3. Distribution of Al in marine aerosols

The maximum of Al in the area of Mariupol is less pronounced than for the most part of chemical elements, which indicates a low Al content in wastewaters.

Lead. The distribution of Pb in the marine aerosol is characterized by a maximum content at the mouth of the Don River, where it reaches 30 ng / m³. Moving towards the sea, the Pb content at first sharply (5 times), and then gradually decreases (Fig. 4). The high content of Pb in the aerosol of the Taganrog Bay may be due to the anthropogenic impact of Taganrog, which is an industrial city, port and center of ferrous metallurgy.

Cadmium. The average Cd value in marine aerosols over the Sea of Azov is about 0.4 – 0.6 ng / m³. Its content increases up to 2.2 ng / m³ in the mouth of the Don River and Taganrog Bay. The concentration of Cd reaches maximum values up to 2.8 ng / m³ in the north-western part of the sea nearby Ukrainian town of Mariupol (Fig. 5). Since the greatest values are comparable and located close to the industrial centers of the northern coast of the sea, it can be assumed that the supplier of Cd is mainly atmospheric emissions and wastewater from industrial cities.

Zinc. In the open part of the Sea of Azov, the Zn content in aerosol particles is from 10 to 60 ng / m³ (Fig. 6). For the Zn distribution, as for Cd, 2 peaks were noted – in the area of Mariupol (100-110 ng / m³) and in the mouth of the Don River. The second maximum is more contrasting, the values here are 200-280 ng / m³. It is caused by water pollution in the lower reaches of the

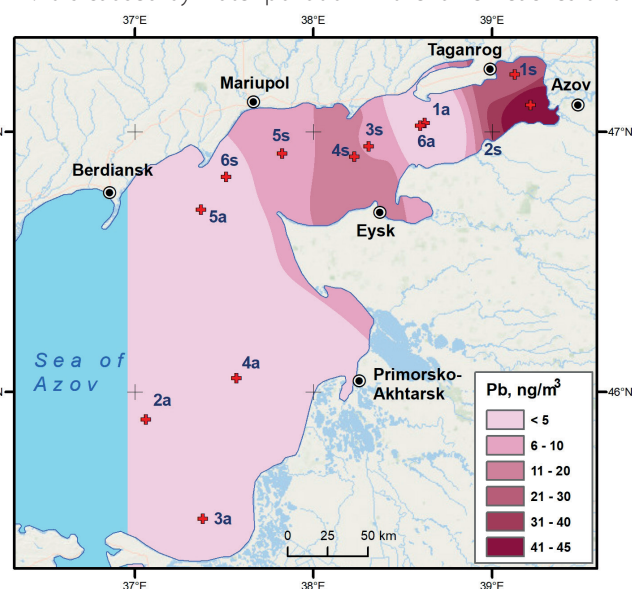


Fig. 4. Distribution of Pb in marine aerosols

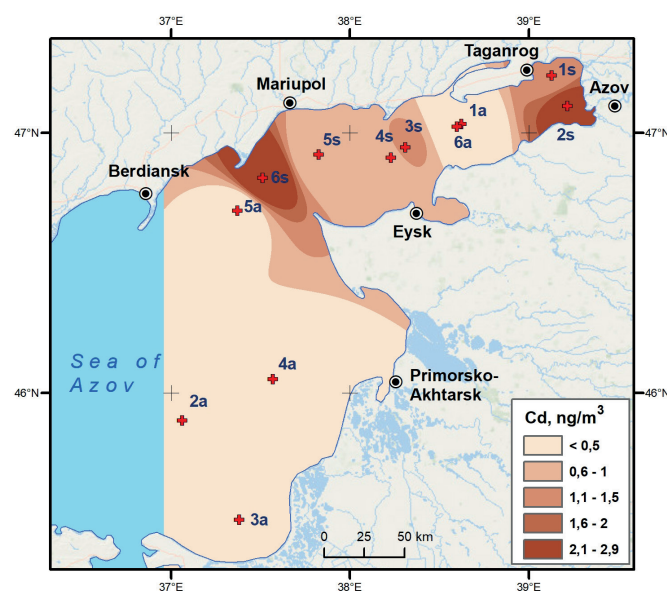


Fig. 5. Distribution of Cd in marine aerosols

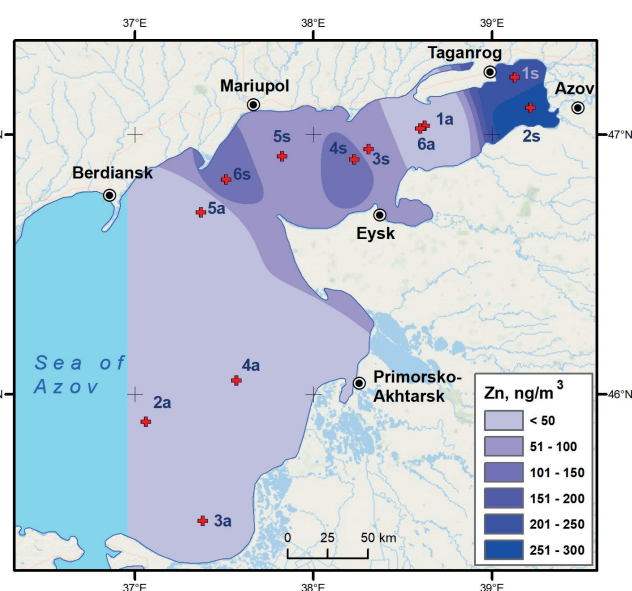


Fig. 6. Distribution of Zn in marine aerosols

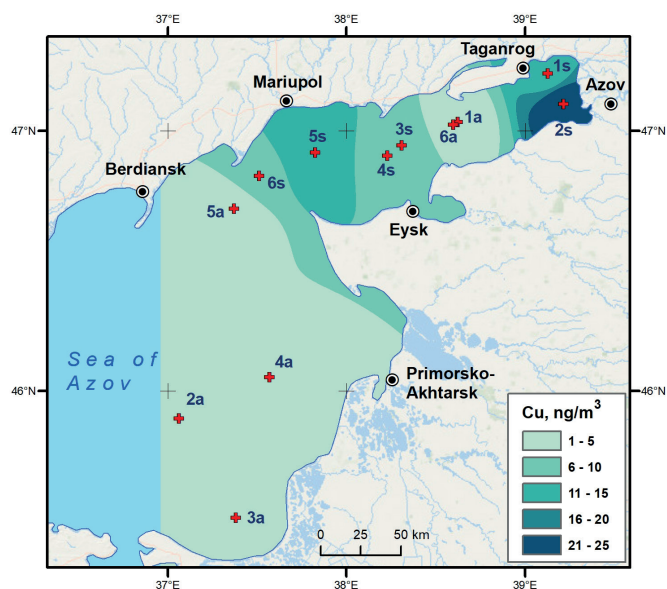


Fig. 7. Distribution of Cd in marine aerosols

river by wastewaters of Rostov-on-Don and Azov town, which is noted by many authors (Tkachenko et al. 2017; Bufetova et al. 2019; and others).

Copper. The average Cu content in the open part of the Sea of Azov is 2–8 ng / m³. The Cu concentration increases as it approaches the coast of Ukraine, reaching 12–16 ng / m³ in the area of Mariupol (Fig. 7). Taganrog Bay is a zone of high Cu content in marine aerosol. Here, the concentration increases to 20–23 ng / m³, which can be attributed to the influence of the city of Taganrog, as well as the barrier zone of mixing of salt waters of the Sea of Azov and fresh water of the Don River, which acts as the main source of Cu for the adjusting water area (Bufetova et al. 2019).

Chromium. The Cr distribution in the marine aerosol (Fig. 8) is characterized by a slow increase from the southern part of the open sea, where it is 1–5 ng / m³ to the northern (15 ng / m³ in the region of Mariupol) and the northeastern part up to the entrance to the Taganrog Bay, where it reaches 18 ng / m³. This is consistent with trends in concentrations of the most HMs. High contents are confined to industrial centers on the north and north-east coast of the Sea of Azov (Mariupol, Taganrog), as well as to the water area of the Taganrog Bay.

Thus, for most of the heavy metals, the concentrations increase as they move from the open part of the sea towards the northern coast and the mouth of the Don River, where under the influence of industrial centers and the geochemical river-sea barrier, local maximums of values are associated with increase in anthropogenic load. Maximum contents of Fe, Cr, and Cd are confined to the mouth part of the Don River, and the city of Mariupol. For Pb, Zn and Cu, the main maximum content in the aerosol is observed in the eastern part of Taganrog Bay and the mouth of the Don River.

A large role in the pollution of the Sea of Azov belongs to the cities located on the coast and in the Don River Delta: Azov, Taganrog, Yeysk, Primorsko-Akhtarsk, Temryuk – due to the discharge of insufficiently purified “conditionally clean” water from enterprises directly into water bodies and streams (Khovansky et al. 1990). It is also worth noting the contribution of ports, shipping, landfills and dumping.

Taganrog is one of the leading industrial centers on the coast of the Sea of Azov, in which industrial enterprises are located: car assembly enterprises (TagAZ), steel manufacturing, pipe production (TagMet), energy and heating boilers, repair and reconstruction of ships, aircraft, etc. There are 51 organizations that have emissions of harmful substances into the atmosphere. The general indicators of pollutant emissions into the atmosphere of Taganrog range from 3.6% to 5.1% of the pollutant emissions of the entire region (Nechipurenko et al. 2019).

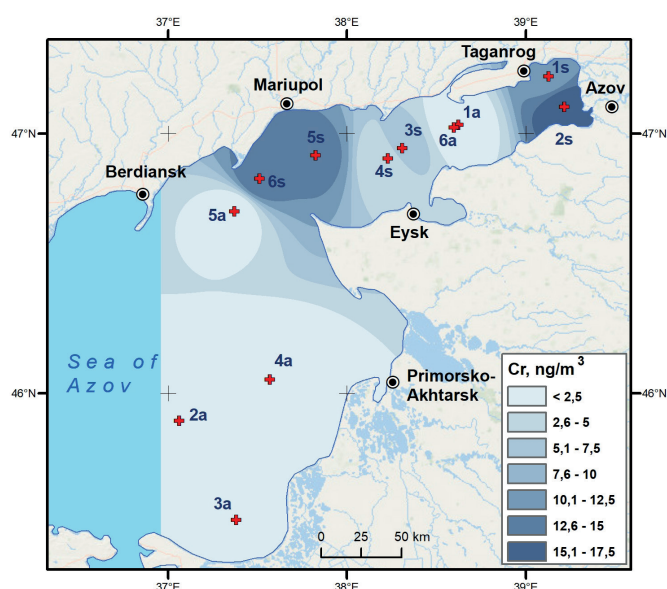


Fig. 8. Distribution of Cr in marine aerosols

Mariupol is one of the most disadvantaged cities in Ukraine in terms of air pollution in Pb, Zn, Cu, Ni, Mn, Cr and Cd compounds. Two large metallurgical enterprises are located on the territory of the city, which are powerful sources of atmospheric emissions (Grishchenko et al. 2018; Voityuk et al. 2018). Industrial dust includes toxic oxides of Fe, Si, Al, Mg, Mn, Cr, etc. (Monin et al. 2012).

The behavior and distribution of trace elements is influenced by the mixing of fresh and salt waters of the rivers and the Sea of Azov, where the great majority (70–95%) of river suspended matter precipitates at the river-sea geochemical barrier, capturing pollutants brought by the river, including heavy metals (Mikhailenko et al. 2018). Shallow-water Taganrog Bay also belongs to the such zones. Here HM content in the marine aerosol rises sharply due to the enrichment SSM with pollutants. Concentrations of HM in the water of the Sea of Azov in places exceed MPC, especially in the Taganrog Bay. The sum of multiples of the MPC TM for the Taganrog Bay in 2005 amounted to 4.7 MPC, while for the open sea it is less (3.7 MPC), which is consistent with the data obtained during the study of the composition of the sea aerosol of the Sea of Azov (Klenkin et al. 2009).

Based on the comparison with the data from other regions, the Sea of Azov can be attributed to the group of seas with the medium or high HM content in marine aerosol. The research of aerosol particles was carried out: 2002–2007 in Black Sea (Yablokov et al. 2002; Lapshin et al. 2003; Syroeshkin et al. 2004; Syroeshkin et al. 2014; Syroeshkin et al. 2006), 2005–2008 in the Kara, Barents and White Seas (Syroeshkin et al. 2010), 2001–2004 in the Baltic Sea (Syroeshkin et al. 2004), 2006–2008 in the Atlantic Ocean (Syroeshkin et al. 2012), 2007–2009 in the Arctic Ocean (Lapshin et al. 2010). The concentration levels of Ni and Cr are shown in Fig. 9 A. It is clearly seen that aerosols of the Sea of Azov contain these metals in low concentrations 10–100 ng / m³ comparable with the Arctic seas. The concentration range of Cd and Mn (Fig. 9 B) is 2 orders of magnitude with the lowest levels in the Arctic Ocean, and the highest values in the Baltic, Azov and Mediterranean Seas. The content of Pb in the marine aerosols (Fig. 9 C) varies from 0.1 – 10 ng / m³ in the group of subjects with a relatively low anthropogenic impact (White, Barents, and Kara seas, Arctic and Atlantic oceans), to 10–100 ng / m³ in the group of southern seas (Black, Azov, Mediterranean, and Baltic seas), subjected to the strong anthropogenic pressure.

In general, the HM content in aerosol microparticles is determined by a number of factors. The first group includes the natural factors, primarily climate related and associated with the geographical position of seas, such as precipitation, evaporation, water salinity, etc. The second group is associated with the hu-

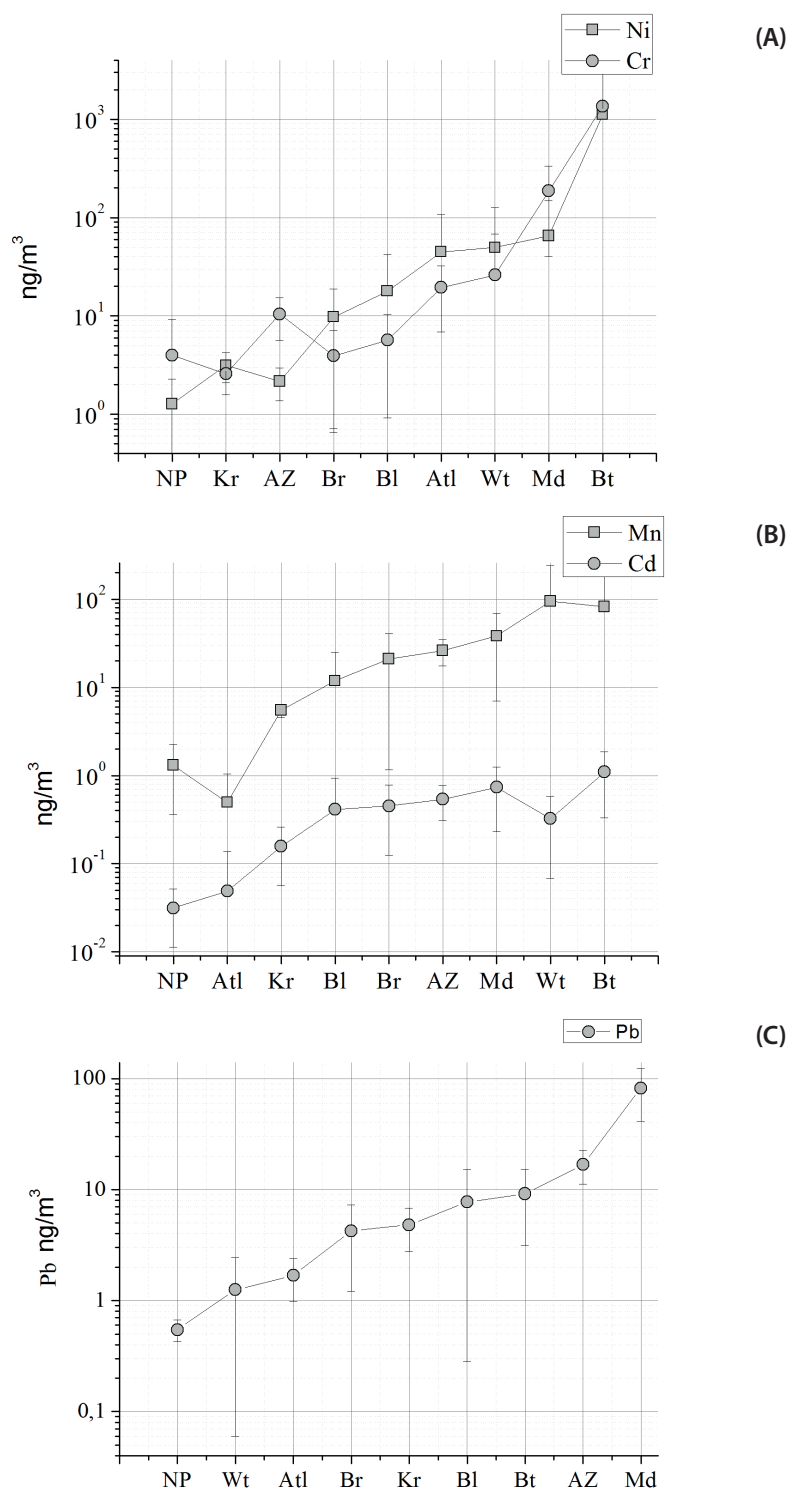


Fig. 9. Concentration of Ni and Cr (A), Mn and Cd (B), Pb (C) in marine aerosols of different areas: NP- North Pole; Wt- White Sea; Atl- South Atlantic; Br – the Barents Sea; Kr – Kara Sea; Bl – Black Sea; Bt – the Baltic Sea; Az.- Sea of Azov; Md – the Mediterranean Sea

man economic activity. The Mediterranean Sea, the Black Sea, and in particular the shallow enclosed Sea of Azov are subjected to the high anthropogenic pressure, which affect the content of various elements in the sea water, and therefore in the sea surface microlayers and marine aerosols. The natural distribution of elements plays a subordinate role here. It is worth considering that it is almost impossible to determine the specific pollution sources while studying aerosol particles in the vast water areas.

CONCLUSIONS

1. The spatial distribution of heavy metals in the marine aerosol of the Sea of Azov is determined by the influence of the river-sea geochemical barrier zone in the Taganrog Bay and

the anthropogenic impact of the coastal industrial cities. HM concentrations increase from the open part of the sea towards the northern coast and the mouth of the Don River.

2. The maximum content of HM in marine aerosol was observed in the mouth area of the Don River in the eastern part of the Taganrog Bay, which can be associated with the anthropogenic impact of the cities of Rostov-on-Don, Azov and Taganrog. High contents of Fe, Cr, and Cd were also found in the western part of the Taganrog Bay, due to the technogenic impact of the city of Mariupol.

3. The Sea of Azov can be attributed to the group of seas with the moderate or high HM content in marine aerosol in comparison with the data from other regions. ■

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