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Short communication

Mercury and iron in atmospheric precipitation of the Azov Sea basin

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ABSTRACT. In different seasons of the year, the iron and mercury concentration levels in liquid and solid phase were studied in the troposphere above the Azov Sea waters, its coasts, and some cities of the Rostov Region. These levels in hydrometeors depend on seasons, sampling places, wind activity, rain and snow precipitation.

Keywords: Azov Sea, cities, precipitation, iron, mercury, migration forms, distribution

Iron and mercury are the priority heavy metals, the content of which often exceeds the MPC in the surface waters of the Azov Sea. Precipitation is an important source of iron and mercury in the surface waters of the Azov Sea basin (Fedorov et al., 2002; Klenkin et al., 2007). 38% of iron and 28% of mercury (from their total input into this basin) are transported to the Azov Sea via precipitation. Mercury can enter the structure of sulfide minerals isomorphically – e.g., Fe_2S (Thomas, 1972; Gilles and Bancroft, 1986) and $FeS * nH_2O$ (Fedorov et al., 2019), or it can be adsorbed on their surface. Iron hydroxides are also sorbents for mercury. The above-said is the reason for considering precipitated mercury and iron together.

The data on iron and mercury concentrations obtained in the course of the expeditions in 2001-2002 and later in February 2020 have been analyzed (Fedorov et al., 2002). Rain and snow samples were carried out in the cities Rostov-on-Don (Ostrovsky Park), Taganrog, Azov, Shakhty, and Novocherkassk, and in the village of Margaritovo. The highest mercury concentrations were registered in precipitation in the cities Shakhty and Novocherkassk (from 0.43 to 0.82 μg/dm³). In Rostov-on-Don, the precipitated mercury content varies during the year from 0.06 to 0.62 μg/dm³. The maximum concentrations of this metal were registered in the precipitation samples taken in autumn and winter. In the coastal cities Azov, Taganrog, and the Margaritovo village, the precipitated mercury content in autumn was 0.20, 0.26, and 0.15 μg/dm³, respectively. According to Klenkin et al. (2007), the mercury content in the hydrometeors above the sea varied widely, i.e. from 0.06 to 0.60 μg/dm³ (0.24 μg/dm³ on average), and that of iron varied from 0.01 to 0.39 mg/dm³ (0.1 mg/dm³ on average). The maximum

concentration changes for both mercury and iron were established in autumn. According to our calculations, the correlation between the mercury and iron content is weakly reverse. In winter 2020, the total content of iron varied from 0.11 to 1.0 mg/dm³ (0.29 mg/dm³ on average) in fresh and recrystallized snow, the total content of dissolved total iron (Fe_{total}) varied from 0.015 to 0.088 mg/dm³ (0.048 mg/dm³ on average), the content of suspended Fe varied from 0.052 to 0.095 mg/dm³ (0.24 mg/dm³ on average). The calculations also show that from 6.5 to 63% (on average 31%) of iron occurs in snow in dissolved form. The maximum total contents of dissolved and suspended iron (4.1, 0.1, and 4.0 mg/dm³, respectively) were found in a sample of roadside dark-grey ice with frozen organomineral particles. This sample was essentially a conglomerate of roadside dust and ice, where Fe_{total} content was only 0.25% of the total content. The snow and ice pH values varied from 5.0 to 7.0 (6.1 on average). A reverse ratio is established between the pH values and Fe_{total} content.

In conclusion, it should be noted that there is an increasing tendency in the mercury concentrations in rain and snow sampled in the cities of the Rostov Region, compared to precipitation over the sea and its coast.The maximum mercury concentrations in the hydrometeors were found in the cities in autumn and winter. It is due to its penetration into the troposphere as a result of the rapidly increasing dust amounts and gas emissions sourced by combustion of coal, fuel oil, and gas during the hot season. According to Fedorov et al. (2002), the mercury concentrations are higher in stale snow, than in just-fallen snow. It is suggested that stale snow is a depositing material absorbing mercury from the troposphere, where it accumulates due to activity of various enterprises with pollutant emissions.

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This statement is confirmed indirectly by the fact that the Donbass coals are characterized by high mercury concentrations (Rylov et al., 2012; 2016). Another mechanism could be mercury re-distribution during the compaction of snow cover and its interaction with soil. In the course of the winter expeditions, a clear snow stratification was registered: just-fallen powder and stale crystallized grey snow with a large amount of mineral and organic material. The dissolved and suspended forms of iron migration prevail in stale snow. The suspended iron content tends to exceed Fe_{total} from stale snow to just-fallen snow. According to our calculations using the data by Klenkin et al. (2007), there was no correlation between the mercury and iron content in rain precipitation above the sea area and on seasonality. Bursts of the maximum mercury and iron concentrations were typical for autumn. Wind activity and atmospheric precipitation affect the iron and mercury content in the hydrometeors. When wind activity increases, the atmosphere surface layers in the cities are enriched by technological substances, and the input of soil particles increases during dust storms. According to our observations, there is intensive mercury leaching from the atmosphere during torrential rains. It leads to a sharp decrease in its atmospheric concentrations. However, there is increase in the mercury content in the rainfall after a dry period under calm weather conditions.

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