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Conference paper

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Composition of rainfall in the coastal zone of the Kaliningrad region of the Russian Federation (based on data from 2019)

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Abstract: The paper presents the results of a study conducted in 2019 in which 29 rainfall water samples were collected and analyzed. The concentration of insoluble particles in rainwater was determined, and analysis of the material composition was performed by scanning electron microscopy. The content of Al, Mn, Ni, Cu, Zn, Cr, Co, As, Sr, Cd, Mo, Ba, Be, V, and Pb was determined by inductively coupled plasma mass spectrometry on a quadrupole spectrometer Agilent7500a at the P.P. Shirshov Institute of Oceanology of RAS. The highest concentrations of insoluble particles (6.5–12.2 mg/L) with the domination of the anthropogenic components in the rainwater were revealed in the samples of the summer-autumn period, while the lowest ones (1.1–3.9 mg/L), with a predominance of biogenic and mineral components were detected in the spring period. A group of heavy metals (Pb, Cd, Zn, Cu, and Ni) of anthropogenic origin was identified by calculating the enrichment factor (EF).

Keywords: Aerosols; atmospheric precipitation; chemistry and climate; heavy metals; material composition; rainfall; snow cover.

Introduction

The elemental composition of rainfall is formed during the formation of clouds, at a considerable height and distance from the study area. When dropped, the atmospheric water purifies the air. For example, it was discovered [1] that when it falls from a height of 1 km, every liter washes 326 m^3 of air and the water is enriched with the matter of natural and anthropogenic origin, occurring in the atmosphere in solid (insoluble) and gaseous forms.

Investigation of the composition of the insoluble matter in rainfall and the relationships between the concentrations of elements, makes it possible to identify the entry pathways of pollutants, including heavy metals, onto the underlying surface. This becomes particularly relevant for the coast of the Kaliningrad region (the south-eastern part of the Baltic Sea), where on average there are 205 days with precipitation a year, and the average annual rainfall is 818 mm [2].

Due to its geographical location on the way of transboundary atmospheric transport of air masses from west to east, the territory of the Kaliningrad region of the Russian Federation in addition to various aeolian natural sedimentary substances receives a significant amount of accompanying anthropogenic pollutants having a negative impact on the environment [3, 4]. The study and assessment of airborne anthropogenic pollutants, as well as the identification of their transfer pathways are important for the coastal zone of the

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Kaliningrad region being a tourist and recreational area. The region has shallow coastal lagoons and unique Vistula and Curonian sand spits, separating them from the Baltic Sea. The Curonian Spit is protected by the UNESCO Convention on the Protection of the World Cultural and Natural Heritage.

Data and methods

The study of insoluble particles in rainfall in the coastal zone of the Kaliningrad region was carried out in 2019. For the entire period of the study, 29 samples of rainwater were collected and analyzed. Samples were collected at stations located in the coastal zone of the Sambian Peninsula and on the Vistula Spit (Fig. 1).

Rain water harvesting was carried out using special devices for collecting atmospheric precipitation. The device consists of plastic vessels in the form of a funnel, a platform on which they are installed, and a storage plastic container connected to the funnels with drain pipes [5]. Depending on the intensity and duration of precipitation, the sampling exposure ranged from 1 h to 24 h.

The insoluble components of rainfall were collected on pre-weighed particle track membranes (D = 47 mm and D_{Pore} = 0.45 μm) by the method of vacuum ultrafiltration [6]. The total concentration of insoluble particles (mg/L) was calculated from the ratio of the obtained mass of the substance on the membrane to the amount of filtered water.

The material composition of insoluble particles collected on the membrane and the elemental composition of individual particles were studied using a Vega 3 SEM scanning electron microscope (TESCAN, Czech Republic) with an INCA Energy X-ray microanalyzer (microprobe) (Oxford Instruments Analytical, United Kingdom).

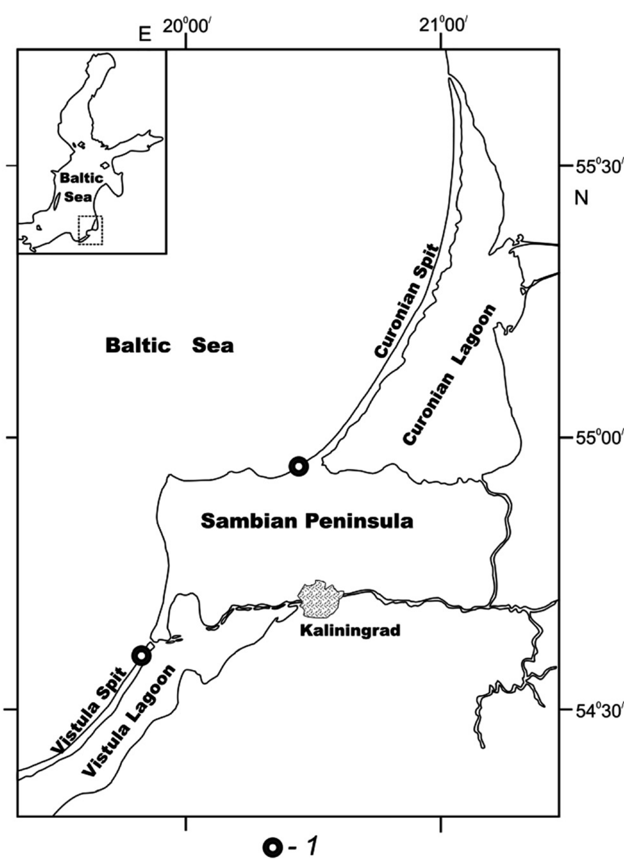

Fig. 1: Studied area: 1—positions of the sampling sites.

The content of chemical elements Al, Mn, Ni, Cu, Zn, Cr, Co, As, Sr, Cd, Mo, Ba, Be, V, and Pb was determined by inductively coupled plasma mass spectrometry on an Agilent7500a quadrupole spectrometer at the P.P. Shirshov Institute of Oceanology of RAS. An internal standard (indium) was used to improve the accuracy of the analysis. An equal aliquot of indium was added to each sample immediately prior to measurement. To assess the quality of the analysis, the results obtained were compared with the certified values of the GSD-2 standard concentrations. The standard errors of estimate did not exceed 15 %.

Results and discussion

The content of insoluble atmospheric particles in rainfall varied from 1.03 to 12.2 mg/L and averaged 5.3 mg/L for the entire study period (from April to November 2019) The results of field studies revealed significant seasonal fluctuations in their concentrations. The main components of the insoluble matter in rain water in the spring-summer period are particles of biogenic origin, and in the autumn period – of anthropogenic origin. This is due to the active development and flowering of vegetation in the spring-summer period, and the entry into the troposphere of a large number of pollen, spores, plant detritus, and fibers. Large particles (up to 50 μm) include plant detritus and fibers, as well as pollen and spores. The lithogenic component is present in samples from all seasons and mainly consists of particles of quartz and aluminosilicate (Fig. 2a). Quartz is the most widespread mineral on the coast of the Kaliningrad region; and therefore, its massive presence in the samples indicates its predominantly local transfer.

The anthropogenic component of insoluble particles dominates the rainfall collected in late summer and throughout the autumn of 2019. The anthropogenic component is represented by coal ash of a thermal power

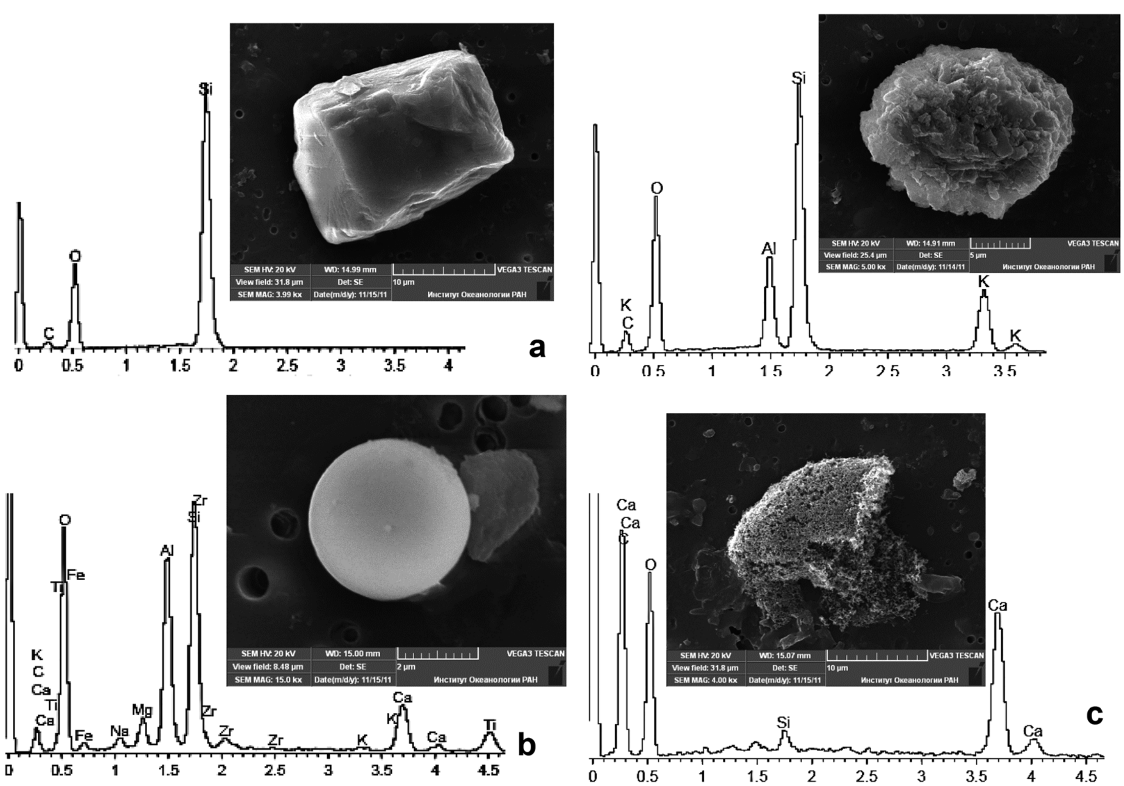

Fig. 2: Typical insoluble particles of rainfall in different seasons of 2019 and their elemental composition: a – mineral particles of quartz and aluminosilicate, b – coal ash of a thermal power plant with a smooth spherical surface, c – black carbon particle aggregate.

plant with a smooth spherical surface (2–8 μm in size) of various elemental composition (Fig. 2b), black carbon particle aggregate (Fig. 2c), and ash particles. The formation and emission of ash with a smooth spherical surface into the atmosphere [7] occurs during the operation of thermal power plants, metallurgical plants, and other industrial complexes. The submicron size of ash with a smooth spherical surface allows them to be transported in the atmosphere by air currents over considerable distances. Since the studied region is located on the path of the western transboundary atmospheric transport of air masses, a significant number of submicron anthropogenic particles in the composition of rainfall may be associated with the activity of industrial complexes in Western Europe. The soot emissions may come both from local sources (chimneys of the residential sector in the region), and remote ones [8, 9].

Analysis of the content of chemical elements in the samples by inductively coupled plasma mass spectrometry showed that the average concentrations of Al, Cr, Pb, Ba, Mn, Cu, Ni, Zn, As, Sr, Mo on the Vistula Spit are higher than their concentrations in the sedimentary matter of the rainfall on the Sambian Peninsula. The exception is the average content of Cd, Co, Be, and V, the values of which are higher on the Sambian Peninsula (Fig. 3).

To assess the role of various sources of heavy metals in the formation of the elemental composition of insoluble particles in rainwater, the enrichment factors (EFs) were calculated relative to the average composition of the earth's crust using the formula:

$$EF = (El./Al)\ sample/(El./Al)\ crust, \tag{1}$$

where El. and Al is the content of the element and aluminum, which we consider as an indicator of lithogenic material in the sample and in the upper part of the continental earth crust [10].

It was revealed that the EF for insoluble matter in rainfall with regard to such chemical elements as Cr, Mn, Co, As, Sr, Mo, V, Be, and Ba, both on the Sambian Peninsula and on the Vistula Spit does not exceed the Clarke values of these elements in the upper part of the continental crust, which indicates their lithogenic origin. At the same time, the EF for the insoluble matter in rainfall with regard to Ni, Cu, Zn, Cd, and Pb significantly exceeds their Clarke values, which indicates the enrichment of sedimentary material with these heavy metals mainly of anthropogenic origin (Fig. 4), due to air pollution by emissions from traffic and industrial enterprises, including long-range transported pollutants.

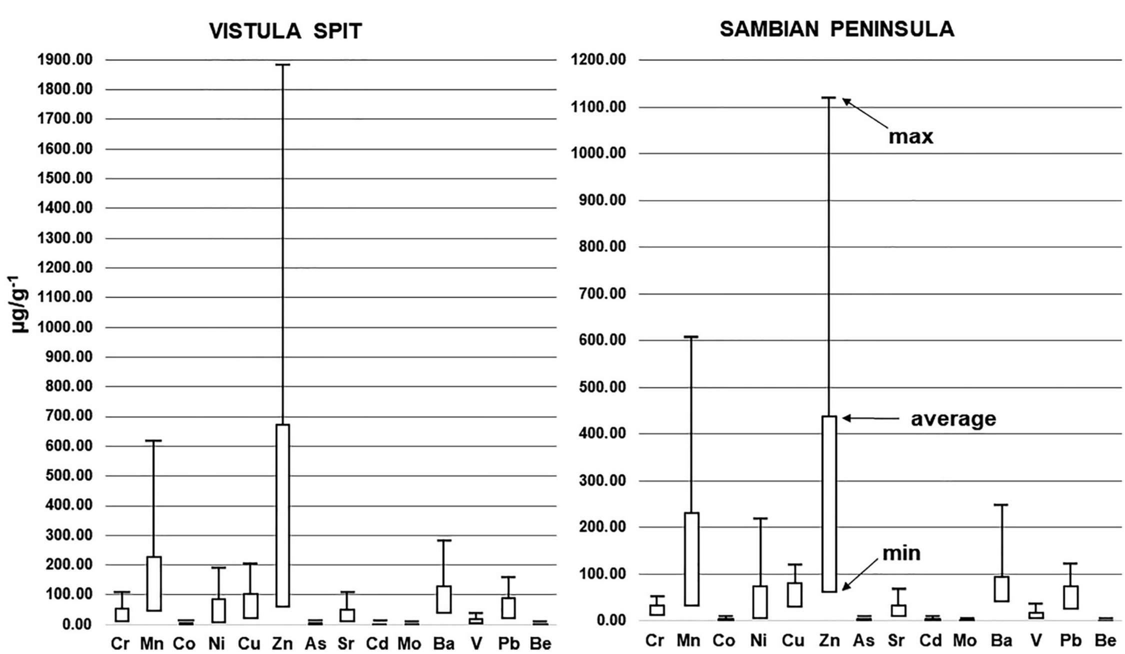

Fig. 3: Content of elements in samples from the Vistula Spit and the Sambian Peninsula.

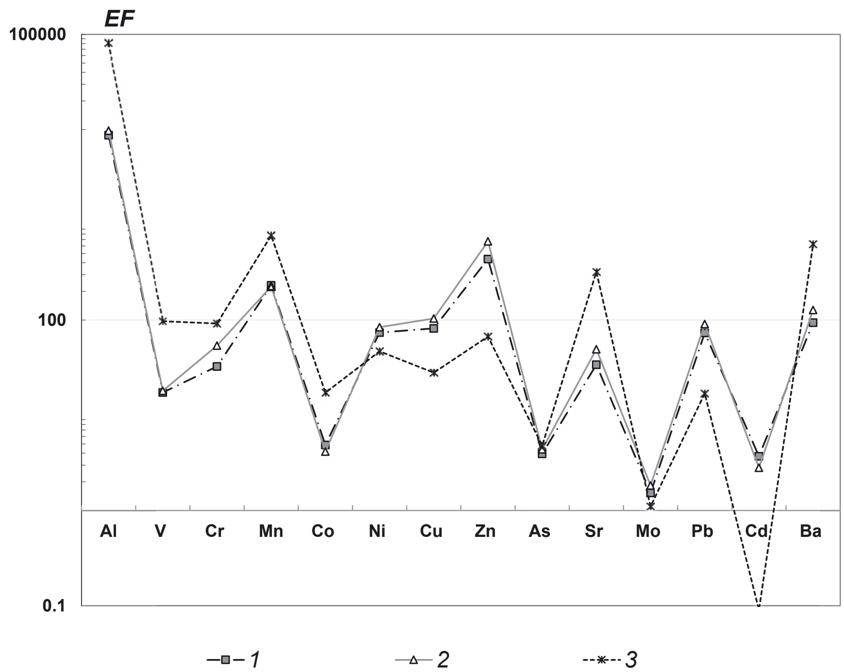

Fig. 4: Enrichment factor (EF) for heavy metals in sedimentary matter of rainfall in the Kaliningrad region of the Russian Federation, relative to the average composition of the upper layer of the continental earth crust. 1 – Sambian Peninsula, 2 – Vistula Spit, 3 – Clarke values of these elements in the upper part of the continental crust [10].

Conclusions

The average content of insoluble atmospheric particles in rainfall in 2019 is 5.3 mg/L. The main components of the insoluble matter in rainfall in the spring-summer period are particles of biogenic origin, and in the autumn period – of anthropogenic origin. The heavy metals of anthropogenic origin (Ni, Zn, Cu, Cd, and Pb) revealed as a result of the analysis are toxic metals. All those elements have a negative impact on the environment, with lead and cadmium belonging to the first hazard class, and thus being the most toxic metals.

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