

ENVIRONMENTAL IMPACT STUDIES RELATED TO ICE-FORMING AEROSOL USAGE IN CLOUD SEEDING ACTIVITIES IN MOLDOVA

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Abstract

The results of studies of the lead and silver content in water bodies and air and the ice nuclei concentrations in the regions subjected to hail protection in the Republic of Moldova in 1977–1991 are summarized. Until 1983, hail-hazardous clouds were seeded mostly with crystallizing pyrotechnic compositions based on lead iodide; subsequently, silver iodide was used. The problems of environmental pollution in the regions involved in the activities using various crystallizing reagents based on heavy metals are discussed. Accumulation of these metals depending on the type and lifetime of the reagents used is estimated.

1. Introduction

Weather manipulation to mitigate the adverse effects of climate change and the damage caused by natural disasters, such as drought, devastating downpours, and hail, is one of the most important problems of modern science and practical life. In this context, it is particularly important to develop and improve the methods and techniques of active impacts (AIs) aimed at artificial precipitation control, hail prevention, and dissipation of fogs and clouds.

A significant effect on the climate—both globally and regionally—is exerted by aerosols. Aerosols have an impact on both the development of ecosystems and human health.

Aerosol particles in the atmosphere affect the climate directly (absorbing and scattering radiation) and indirectly (impacting and changing the cloud properties). The latter effect, which is referred to as "indirect aerosol effect," occurs because aerosols act as cloud condensation nuclei (CCN) and ice nuclei and thus influence the cloud albedo, lifetime, and other cloud properties. The indirect aerosol effect represents the most uncertain components in future climate scenarios. A challenge in quantifying the aerosol indirect effect is the assessment of both the spatial and temporal variation of CCN. The answer to the question whether an aerosol acts as a CCN to form cloud droplets is determined by both the size and chemical composition of the aerosol [1]. In this case, only an insignificant portion of particles—on the order of particle per million—is the active ice nucleation sites [2].

A particular case of aerosols is artificial ice-forming aerosols used for AIs on atmospheric processes. These impacts are conducted for the protection of agricultural crops and industrial facilities from hail and for the simulation of artificial precipitation. In this case, an important issue is the study of their effect on the environment.

In Moldova, the formation and development of activities on AIs on clouds dates back to the 1960s–1970s. The use of ice-forming compositions (reagents) based on lead iodide (PbI₂) or silver iodide (AgI) for this purpose has necessitated the study of potential accumulation of components of these substances (Pb, Ag) in natural objects, particularly taking into account the fact that, in common with all heavy metals, excessive amounts of lead and silver in the body are toxic. This is particularly true for regions subjected to a long-term and intensive application of these reagents. In the world, the potential environmental impacts of cloud seeding using silver iodide have been studied since the 1960s [3].

Based on the data of studies in different regions of the USSR, it has been found that, during the dissipation of clouds, the reagent is largely entrained with precipitation onto the earth's surface; the rest of its mass penetrates the free atmosphere and then can be transported by air flows to a distance of up to 150 km. It has been shown that, during hail-protection activities, high concentrations of lead and silver are observed in the air in the AI regions; these concentrations depend on the amount of artificial ice-forming compositions introduced into the atmosphere. In seeding convective clouds, the residence time of AgI in the cloud medium is about 20 min [4–13].

To study the effect of systematic AIs using ice-forming reagents on the accumulation of Pb and Ag metals in natural objects, research in the regions subjected to antihail protection in the Moldavian SSR was conducted from 1977 to 1991. The objects of observation were surface and landlocked water bodies---mostly artificial---and ground air. Since 1967, in Moldova, AIs on hail processes have been conducted using ice-forming compositions made of pyrotechnic mixtures containing 60% of lead iodide. Since 1979, formulations containing 2% AgI have been introduced into practice. At present, silver iodide is the most common cloud-seeding material in weather modification projects.

A systematic monitoring of lead and silver content in water bodies and air covers the period from 1977 to 1991 and from 1983 to 1991, respectively. By 1983, the total number of water bodies under observation was 103; 64 of them were located in the protected areas (PAs); the rest, in the control areas (CAs).

Aerosol measurements were conducted at the center of the PA. To determine the Pb and Ag concentrations in the air, every day, from 9 a.m. to 9 p.m., aerosol samples were taken at a height of 12 m above the ground according to a special procedure. The samples were collected on AFA-KhA-20 analytical filters. The filters and water samples were analyzed by atomic absorption spectrophotometry. The sensitivity of the method was 10⁻⁸–10⁻⁹ g, the error was ±15% [14]. The experimental design and routine, the accuracy of measurements of analyzed samples, and the confidence level of the results were confirmed by international expert estimates on the basis of comparative measurements with the participation of specialized research institutes of Russia, Ukraine, and the Republic of Moldova in the 1990s.

Average consumption of PbI₂ and AgI (g/ha) in hail-protection seasons in Moldova in 1978–1991

Agent	Year														Average
	1978	1979	1980	1981	1982	1983	1984	1985	1986	1987	1988	1989	1990	1991	
PbI	11.5	17.1	13.3	10.2	8.5	10.5	7.2	7.2	–	–	–	–	–	–	10.7
AgI	–	–	–	–	–	0.35	0.24	0.24	0.43	0.28	0.28	0.22	0.12	0.16	0.26

In a hail-protection season, depending on its intensity and duration, the consumption of PbI_2 and AgI in ice-forming pyrotechnic compositions was 7.2–17.6 and 0.12–0.43 g/ha of protected area, respectively (table). These data suggest that, every year, significant amounts of lead penetrated the atmosphere in limited areas subjected to AIs.

Figure 1 shows the scheme of location of water bodies in the PAs and CAs and the location of the aerosol measurement site. The CAs were selected so as to minimize the risk of impact on them from AIs in PAs. A necessary requirement for the selection of CAs was their proximity to PAs with respect to physicogeographical and geological features. These conditions were most completely met by water bodies in the CAs in Ukraine and the south of Moldova.

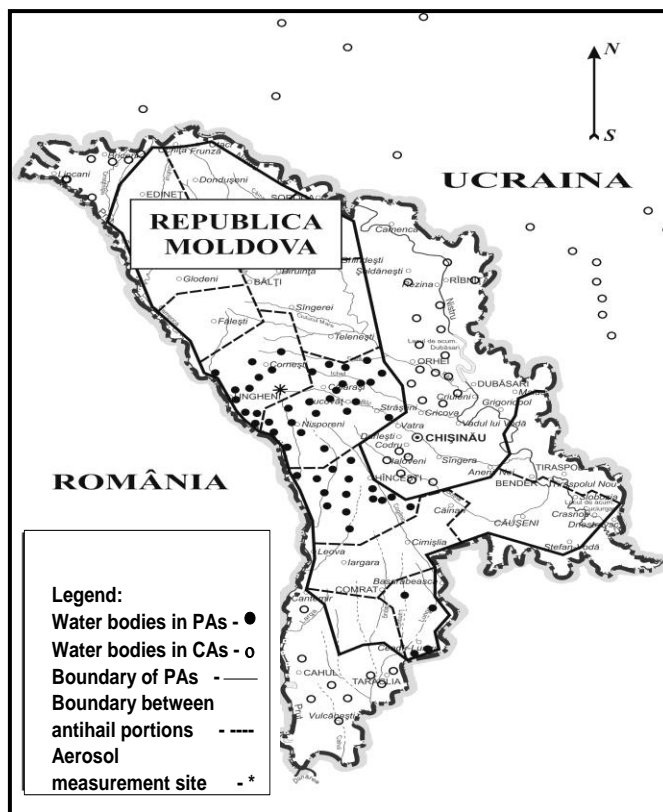


Fig. 1. Scheme of location of the aerosol measurement site and water bodies in the PAs and CAs in the Republic of Moldova in the period of 1983–1991.

A systematic sampling of water from water bodies was conducted twice a year—before (April) and after (October) hail protection season—from 1983 to 1991, except for 1990. The maximum permissible concentration (MPC) of silver was 50 $\mu\text{g/L}$ in drinking water, 0.5 $\mu\text{g/m}^3$ in air, and 2.82 mg/kg in soil. The MPC of Pb is 30 $\mu\text{g/L}$ in water and 3 $\mu\text{g/m}^3$ in air. It should be noted that lead is one of the most toxic metals; some international organizations and similar government agencies in different countries have included it into the list of priority pollutants. This fact was one of the reasons for switching to pyrotechnic compositions containing silver iodide for using in AIs on atmospheric processes.

2. Results of measurements of lead and silver concentrations in water bodies

Under conditions of Moldova with the priority development of the agricultural sector, there were no metallurgical, merchant-coke, and oil-refining complexes, which are sources of atmospheric pollution with metals. The used organic and mineral fertilizers and pesticides contained extremely small amounts of lead and silver. Therefore, these factors were not taken into account.

A powerful source of lead emission in the atmosphere was automotive transport. The concentrations of lead [Pb] in soil in regions with heavy traffic were ten times higher than their baseline values [15]. Therefore, water bodies located at a distance of no less than 200–300 m from automobile roads with heavy traffic were selected for observations.

In rivers and lakes of Europe, the [Pb] content was 0.4–7.3 $\mu\text{g/L}$ [16]. There are some evidences of a tendency of metal accumulation in natural environment objects [17]. In the late 1970s and the early 1980s, in the central part of Moldova, the lead content in surface waters did not exceed 10 $\mu\text{g/L}$ [15]. This value coincides with the results obtained by us for this region in the period of activities [16].

Figure 2 shows the average [Pb] values in the autumn samples of water from water bodies in the PAs and CAs in Moldova and the CAs in Ukraine. The highest [Pb] values for the entire period of studies were recorded in the PA at the center of Moldova. In 1977, there, the average [Pb] value was 9.5 $\mu\text{g/L}$ against a value of 4.5 $\mu\text{g/L}$ in the water bodies of the CAs. In 1983, the average Pb concentration in the PAs was 22.9 $\mu\text{g/L}$ against 10.7 $\mu\text{g/L}$ in the CAs (Ukraine). In 1988, [Pb] was 26 $\mu\text{g/L}$ in the PAs and 13 $\mu\text{g/L}$ in the CAs (Ukraine). The [Pb] increment was 2.213 $\mu\text{g/L}$ per year in the PAs and 1.0 $\mu\text{g/L}$ in the CAs.

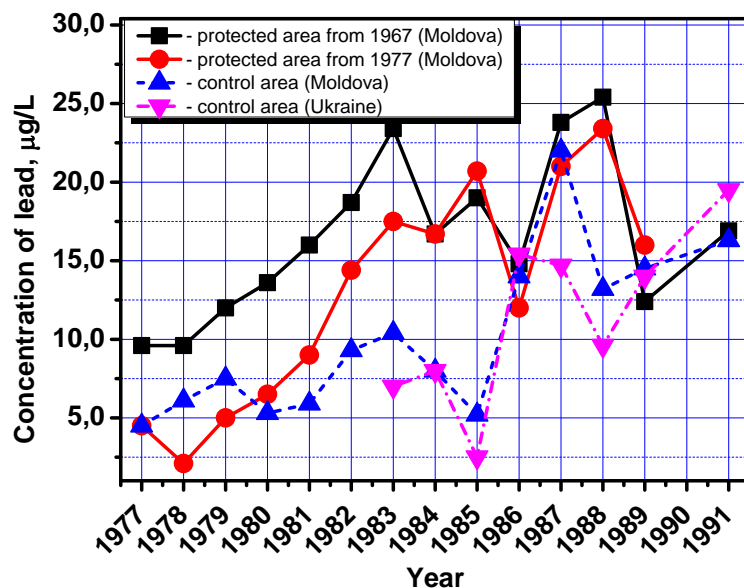


Fig. 2. Average lead concentration in autumn water samples from the water bodies in the PAs and CAs in the period of 1977–1991.

High lead concentrations in the water bodies in the PAs compared to the values in the CAs were observed almost in the entire period of observations. An exception was provided by the last two years, when the metal concentrations were almost equal in all the studied water bodies. It should be noted that, since 1986, only AgI-based reagents were used in AIs.

To estimate the impact of AIs as a source of the studied metals (Me), the metal concentrations in water bodies in the autumn and spring water samples were compared: $\Delta[\text{Me}] = [\text{Me}]_{\text{autumn}} - [\text{Me}]_{\text{spring}}$.

Figure 3 shows the $\Delta[\text{Pb}]$ values according to the results of measurements in water bodies in the PAs in Moldova and the CAs in Ukraine. By 1986, for water bodies in the PAs and CAs, the $\Delta[\text{Pb}]$ values began to decrease. A short series of $\Delta[\text{Pb}]$ values for water bodies in the PAs with the intensive use of PbI_2 (1981–1982) cannot be a basis for making an unambiguous conclusion about the role of AIs as a lead source affecting the increment of this metal in summer. However, in these two years, in the PAs, $\Delta[\text{Pb}] \approx 2 \mu\text{g/L}$; this value coincides with the concentration increment in the AI seasons. Noteworthy is the fact that, in the summer periods of 1986 and 1987, $[\text{Pb}]$ abruptly increased in water bodies both in the PAs and in Ukraine and that, in subsequent years, the self-purification processes were dominant in the compared territories, i.e., $\Delta[\text{Pb}] < 0$.

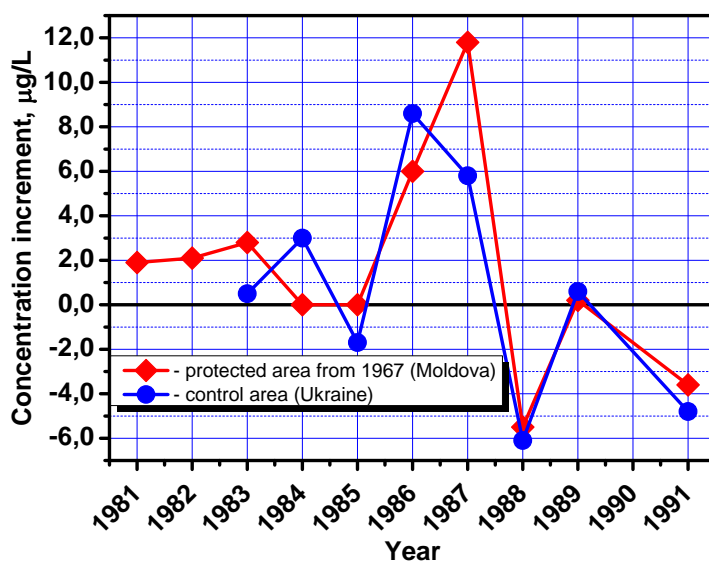


Fig. 3. $\Delta[\text{Pb}]$ values for water samples from the water bodies in the PAs (the central regions of Moldova) and CAs (Ukraine).

According to various estimates (the 1980s), in the world, anthropogenic sources of silver, particularly weather modification, amounted to about 1200 tons per year, while the natural sources yielded 150 tons per year [19]. These data suggest that the silver concentration ($[\text{Ag}]$) in natural media should be negligible. A low global background level of Ag in water is evidenced, for example, by analysis of water from the lakes in the Tien Shan Mountains, which gives a value of $0.6 \mu\text{g/L}$ [14].

Figure 4 shows the time variation of the silver content in the water bodies in the PAs and CAs (Ukraine). Throughout the entire period of observations, after AI seasons, the $[\text{Ag}]$ value was in a range of $1.7\text{--}7.4 \mu\text{g/L}$ in the water bodies in the PAs and $0.9\text{--}4.1 \mu\text{g/L}$ in the water bodies of the CAs.

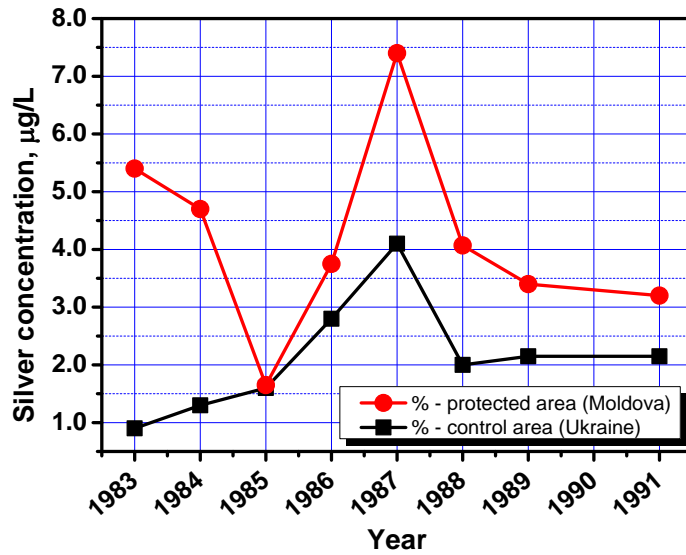


Fig. 4. Silver concentration in the autumn water samples from the water bodies in the PAs in Moldova and the CAs in Ukraine.

Correlation analysis has revealed no relationship between the silver content and the amount of AgI reagents consumed during hail suppression activities. However, the variation of the $\Delta[\text{Ag}]$ values in the PAs (Fig. 5) shows that the highest values are registered in years with the maximum consumption of AgI during AIs (1983, 1986). Since 1988, $\Delta[\text{Ag}] < 0$ for all water bodies in the PAs and CAs.

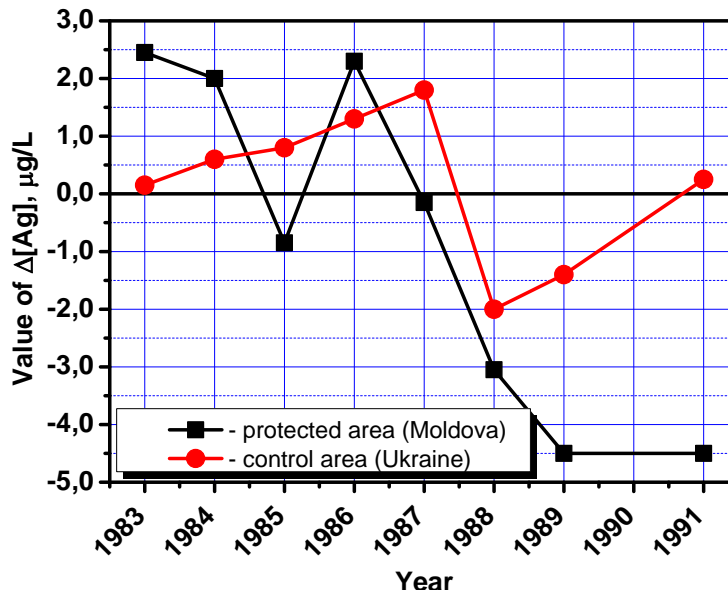


Fig. 5. Silver concentration increment in the water bodies in the PAs and CAs in the summer periods of 1983–1991.

The highest $\Delta[\text{Ag}]$ values are registered for the central regions of Moldova; in some years, these values are 3–4 $\mu\text{g/L}$ higher than $\Delta[\text{Ag}]$ in the water bodies in the PAs with a lower level of hail

precipitation. It should be emphasized that $\Delta[\text{Ag}]$ in the PAs in the south regions of Moldova is almost the same as the $\Delta[\text{Ag}]$ value for the water bodies located in the territory of Ukraine. The studies have shown that differences in $[\text{Ag}]$ values in water bodies of different PAs can be attributed to their natural variability. This assumption is confirmed both by the absence of a correlation between the silver content and the amount of AgI-containing compositions introduced into clouds annually and by the fact that $[\text{Ag}]$ in water bodies in PAs is inversely related to the total amount of precipitation (Q_{mm}) occurring there in summer periods. For the central regions of Moldova, which is a territory with the longest use of AgI, correlation coefficient $r(Q, [\text{Ag}]) = -0.69$. For other regions of the PAs, this relationship is even weaker; however, all of them are characterized by an inverse correlation. This result suggests that the silver content in the studied water bodies in the PAs is determined by factors that are not directly related to hail suppression activities.

In discussing the nature of the time series of $[\text{Ag}]$, it is essential to determine the trends. In this case, the trend is understood as a tendency of variation in the metal concentration in the studied water bodies for the entire period of observations. Taking into account the specific features of the studied experimental units (research subjects) and the nature of the possible effect on them exerted by a silver source (AIs), it is possible to use the following linear equation:

$$y_t = \alpha_0 + \alpha_1 t,$$

where y_t is the value of the studied quantity; α_0, α_1 are coefficients (α_1 -trend), and t is the number of years (seasons) of measurements ($t = 1, \dots, n$).

For all the studied territories, $\alpha_1 > 0$; that is, a positive tendency of increase in $[\text{Ag}]$ in the water bodies was observed regardless of their location. The average value was $\alpha_1 = 0.52$ and $0.35 \mu\text{g/L}$ per year for the PAs and CAs, respectively. However, the confidence levels (statistical reliability) of these trends are not high. Therefore, the hypothesis that stable increments in the silver content in water bodies in Moldova are attributed to hail-suppression activities with the use of AgI could not be confirmed with a high degree of probability.

3. Results of measurement of the lead and silver content in the ground air in PAs

In the 1960s, the average lead concentration in the air was $0.03 \mu\text{g/m}^3$ in the industrial cities of the USSR and $0.02 \mu\text{g/m}^3$ for rural areas. In the 1970s, in the United States, these concentrations were 1.6 and $0.3 \mu\text{g/m}^3$, respectively [20]. In the European countries, the metal content in the air was in a range of 0.03 – $0.05 \mu\text{g/m}^3$ [21].

According to [22], in autumn and summer, in the cities of the USSR, the average silver concentration in the air was 0.03 – $0.06 \mu\text{g/m}^3$. From 1974 to 1979, in regions of hail-suppression activities in the Krasnodar Territory and North Caucasus, the average multiyear value was $[\text{Ag}] = 0.087$ and 0.045 ng/m^3 , respectively [13].

Figure 6 shows the average concentration of Ag and Pb in the air in hail-protection seasons. The high lead content was registered in the periods of AIs using mostly PbI_2 -based compositions, i.e., until 1983. In subsequent years, the seasonal values of $[\text{Pb}]$ did not exceed $0.17 \mu\text{g/m}^3$. In this period, the decrease was about tenfold compared with the level in 1977–1980.

In hail-protection seasons, the Ag concentrations were in a range of 0.001 – $0.043 \mu\text{g/m}^3$; this level characterized the studied region as environmentally friendly. In the annual variation of $[\text{Ag}]$, the highest values were registered in the period of June–August, the lowest concentrations occurred in autumn and winter (Fig. 7).

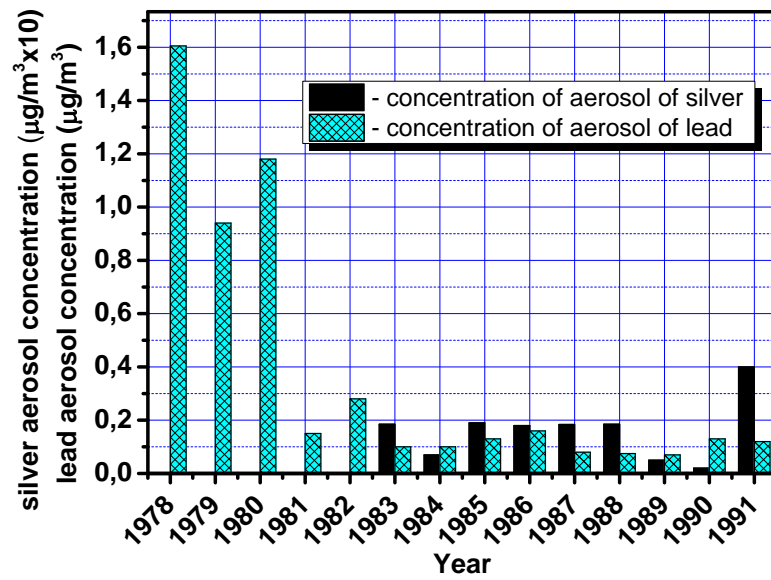


Fig. 6. Average concentration of silver ($\mu\text{g}/\text{m}^3 \times 10$) and lead ($\mu\text{g}/\text{m}^3$) in the ground air in hail-protection periods in the Republic of Moldova in 1978–1991.

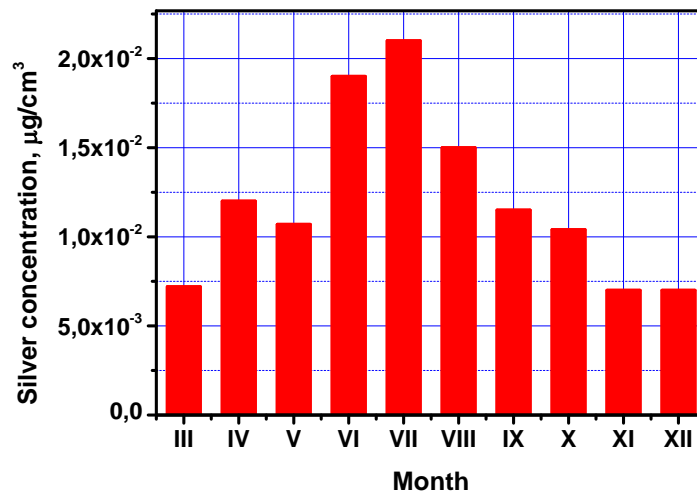


Fig. 7. Annual variation of $[\text{Ag}]$ in the ground air (1983–1991).

The absence of silver accumulation in the air is also evidenced by the values of Ag concentration trends: $\alpha_1 < 0$ for both the annual average and the summer seasons (AI seasons) at $\sigma = 0.037$ and $0.007 \mu\text{g}/\text{m}^3$, respectively.

4. Conclusions

Our studies of the effect of long-term cloud seeding with crystallizing reagents based on lead iodide and silver iodide on the environmental conditions in the regions involved in hail-suppression activities in the Republic of Moldova have revealed the following.

- (1) There is a tendency of lead accumulation in surface waters from one hail-protection season to another with a value of about 2 μg per liter of water in the periods of use of lead iodide as a reagent.
- (2) In some PAs, the lead content in water was close to maximum permissible values (MPC = 50 $\mu\text{g/L}$).
- (3) There is a positive correlation between an increase in the lead concentration in water bodies and the amount of precipitation in the AI seasons in the studied territory.
- (4) In the hail-protection seasons in 1978–1981, in some months, the average lead aerosol content in the ground air exceeded 1.0 $\mu\text{g/m}^3$.
- (5) The monthly average lead aerosol concentrations in the ground air positively correlated with the amount of the reagent consumed in these periods.
- (6) Upon switching to the use of ice-forming compositions based on 2% AgI for AIs, the water bodies and the ground air underwent self-purification of lead.
- (7) In the cases of using ice-forming compositions with 2% AgI in hail-suppression activities, no statistically significant events of silver accumulation in water samples from water bodies in the PAs were registered.
- (8) In the period of studies, the average silver concentration in water bodies in the PAs did not exceed 6.2 $\mu\text{g/L}$.
- (9) Long-term observations of the use of AgI-based ice-forming compositions have not revealed either a tendency of silver aerosol accumulation in the ground air or its correlation with the amount of the consumed reagent.
- (10) The results clearly show that there are no environmentally harmful effects arising from cloud seeding programs involving silver iodide aerosols in Moldova.

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