ACID PRECIPITATION AND ITS IMPACT ON MONUMENTS

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Abstract. *Monitoring the chemical composition of atmospheric precipitation and acid oxides concentrations in the atmosphere in the years 1990-2008 showed the presence of acid rain in Moldova. The value of pH in water samples collected from rainfall varied in limits from 2.65-10.35. During the years 1990-1998 the percentage share of samples showed that acid increased continuously. However, between 1999 and 2001 a change was detected, water samples collected were mostly neutral, but after 2002 to 2008 it was observed an increase in the rate of acid samples. It was found that the Stratus and Stratocumulus clouds, which absorb pollutants from the layer of atmosphere below the clouds, contain less acidic precipitation than Cumulonimbus clouds, which make contact with the upper atmospheric layers and perhaps incorporating pollutants brought by air masses from the front. Analysis of ions content and the pH-value in precipitation was found to be dependent on the direction and structure of the wind at altitude. In the case of descending rainfall the ionic concentration is higher and more acidic. Increasing levels of pollution of the atmosphere with acidic substances increase the aggressiveness to material objects, buildings, monuments of art. Acids and acid gases in the atmosphere cause the chemical and electrochemical corrosion; this sharply reduces the life of inorganic and organic building materials. The effect is stronger in joint action with oxidants, ultraviolet radiation, high temperature and moisture. While studying affected monuments it was established that the corrosion rate of marble in the cities is 3.5 mm in 100 years and in rural areas no larger than 0.5 mm for the same time period. Among the gases responsible for acid rain acidification are sulphur oxides and nitrogen. Sulphur oxides are released in large quantities in the atmosphere together with burning gasses.*

Keywords: *acid rain, atmosphere, transboundary transfer, ecological impact, corrosion.*

Rezumat. Ploile acide şi impactul lor asupra monumentelor. *Monitorizarea compoziţiei chimice a precipitaţiilor atmosferice şi a concentraţiilor oxizilor acizi din atmosferă în anii 1990-2008 au arătat prezenţa ploilor acide în Republica Moldova. Valoarea pH-ului în probele de apă colectate din precipitaţii a variat în limitele de la 2,65-10,35. În perioada anilor 1990-1998 cota mostrelor acide în procente a crescut continuu, însă pentru anii 1999-2001 s-a detectat o schimbare, probele de apă au fost în cea mai mare parte neutre şi după anul 2002 până în anul 2008 se observă o creştere a cotei probelor acide. S-a constatat că precipitaţiile provenite din norii Stratus şi Stratocumulus, care absorb poluanţii acizi din straturile de jos ale atmosferei, sunt mai puţin acide decât mostrele de precipitaţii colectate din norii Cumulonimbus, care contactează cu partea superioară a atmosferei şi care încorporează poluanţi transportaţi de masele frontale de aer. Conţinutul ionilor analizaţi şi valoarea pH-ului în precipitaţii depind şi de direcţia şi structura vântului la înălţime. În cazul vântului descendent concentraţile ionilor analizaţi sunt mai mari şi mostrele de precipitaţii mai acide. Creşterea nivelului de poluare a atmosferei cu substanţe acide duce la creşterea agresivităţii ei faţă de materiale, obiecte, clădiri, monumente de artă. Gazele acide şi acizii din atmosferă provoacă corodarea chimică şi electrochimică. Durata de viaţă a materialelor de construcţie de natură anorganică şi organică brusc se reduce. Efectul este şi mai puternic în cadrul acţiunii comune cu oxidanţi, iradieri ultraviolete, temperaturi înalte şi umezeală. Studiind monumentele afectate s-a stabilit că în oraşe viteza de corodare a marmurei este de 3,5 mm în 100 de ani, iar în mediul rural nu mai mare de 0,5 mm pentru aceiaşi perioadă. Dintre gazele acide responsabile pentru acidularea ploilor cele mai importante sunt oxizii de sulf şi azot. Oxidul de sulf este degajat în atmosferă în cantităţi mari împreună cu gazele de ardere.*

Cuvintele cheie: *precipitaţii acide, atmosfera, transfer transfrontier, impact ecologic, coroziune.*

INTRODUCTION

External baric centres determine climate resources. The atmospheric circulation is predominantly anticyclone, with a relatively reduced activity of the atmospheric processes, expressed by a variety of changes in seasonal movement. Most cyclones cross the territory of Moldova from west and southwest, at an average speed of 20-30 km/hour, the maximum speed reaching 80-90 km/hr. Prevailing winds blow from the West, North, North West, while the South and South-West winds display a lower frequencyn. The average speed reaches 2.5-4.5 m/sec.

Acid rain became a major problem since the introduction of the Arab oil embargo in 1973, because most of the industrialized countries have started using coal as a result (RODHE et al., 1995, ŞERBAN et al., 1993).

The first mentioned acid rain occurred in Uilling (USA) in 1978 and had a pH = 2.0 (BLANCHER et al., 1992). The average annual pH value is 4.5 in Europe and 4.0 in Northern Europe. The theoretical value of the average annual rainfall pH value for Moldova, calculated by EC UN, is 5.0 (BUBURUZ et al., 1993).

Amongst the most important gases responsible for acid rain acidification we mention sulphur and nitrogen oxides. Sulphur oxide is discharged with exhaust gases in the atmosphere.

Increasing levels of pollution of the atmosphere with acid substances lead to an upward aggressiveness toward the material objects, buildings, art monuments. Acids and acid gases in the atmosphere cause the chemical and electrochemical corrosion; this sharply reduces the life of inorganic and organic building materials. The effect is stronger in joint action with oxidants, ultraviolet radiation, high temperature and moisture. While studying affected monuments, it was established that the corrosion rate of marble is 3.5 mm in 100 years in the cities and no greater than 0.5 mm in rural areas for the same period. Limestone or insoluble marble reacts with carbon oxide (IV) and passes in soluble $Ca(HCO_3)_2$ according to the reaction: $CaCO_3 + CO_2 + H_2O = Ca(HCO_3)_2$ (BUBURUZ et al., 1993, 1995, 1997).

In Europe, around 30 million tones of sulphur oxides are released per year, in North-Eastern Canada - 40 million tones per year, in Japan and southeast China - 10 million tones per year. In the Republic of Moldova 230 kt sulphur oxides were discharged in the year 1990 (reference year) and about 10 kt in 2005. The global emission of sulphur oxide (IV) in the atmosphere is valued at around 113 million tones/year, 98 million tons of which reach the atmosphere as SO_2, 3 million tones as SO_3, 9 million tones as aerosols of sulphates, and 3 million tonnes as H_2S (BUBURUZ, 2003, BUBURUZ et al., 1997, RODHE et al., 1995).

NO_x content in the atmosphere varies from tenths of the thousandths mg/m^3. Natural sources of production of nitrogen oxides are electric discharges in the atmosphere, large fires and the elimination from the soil. The intensity of emission from natural sources is 0.27 kg/km^2 in 24 hours. The global anthropogenic quantity of NO_x emissions is estimated at around 40-90 million tonnes/year. Ambiguous sources refer to the transformation of NH_3 to NO_x. Average concentration of ammonia in the atmosphere is estimated at 2.5-3 mkg/m^3 (BUBURUZ et al., 1993, 1997, RODHE et al., 1995).

Under the action of solar radiation, oxidants and free radicals, always present in the atmosphere, sulphur oxides are converted into new compounds - sulphates and sulphites, producing acid substances:

$SO_2 + O_2 \leftrightarrow SO_3 + H_2O \leftrightarrow H_2SO_4 \leftrightarrow 2H^+ + SO_4^= \; SO_2 + H_2O \leftrightarrow H_2SO_3 \leftrightarrow 2H^+ + SO_3^=$

Acid rains are virtually diluted solutions of acids, especially sulphuric and nitric acids. Pollution sources influence the ratio between H_2SO_4 and HNO_3, and it changes within the limits of 1:1 to 4:1. The graphical presentation of the concentration change of sulphur and nitrogen compounds and their transformations depending on time show that the maximum concentration of H_2SO_4 in the atmosphere reaches over 30 hours and that of HNO_3 over 15 hours (BUBURUZ et al., 1993, 1997).

Acids can form not only in the atmosphere, but also in the solution from the sedimentation or absorption surface, lowering the pH and increasing the corrosive aggressiveness degree of the atmosphere.

Aggressive corrosion of the atmosphere is also provoked by the photochemical smog formation. Oxides of CO, NO, NO_2, $(CH_2)_n$ under the solar radiation favour the formation of the ozone.

A typical cycle of reactions for the formation of photochemical smog is rendered below:

Primary reactions: $2NO + O_2 \rightarrow 2NO_2$

$NO_2 \rightarrow hn \rightarrow NO + O^o$

$R\text{-}COH \rightarrow hn \rightarrow R^o + HCO^o$

Undesirable secondary: $O^o + O_2 \rightarrow O_3$

$O_3 + NO \rightarrow NO_2 + O_2$

$NO_2 + O_2 \leftrightarrow hn \leftrightarrow NO + O_3$

$O_3 + olefins \rightarrow R^o, RO^o, RCO^o, ROOH^o, polymers$

$R^o + O_2 \rightarrow ROO^o$

$RCO^o + O_2 \rightarrow RCOOO^o$

These reactions do not consider many chemical processes in the typical organic chemistry. For example, the release of styrene, halogens, chlorine, bromine, under the influence of photochemical reactions, easily pass in an excited state (BUBURUZ et al., 1993, 1997, NICORICI et al., 2003).

Some reactions lead to the formation of free radicals, to the release of hydrogen from the organic substances in the secondary reactions with O^o and O_3. Free radicals are formed in the photochemical decomposition of nitrite and peroxyacetylnitrite in the initial stages.

A source of the formation of free radicals is the aldehydes released with exhaust gas. Radicals form peroxides with the oxygen, which increase the corrosive aggressiveness of the atmosphere (BUBURUZ et al., 1997):

$R^o + O_2 \rightarrow R\text{-}O\text{-}O^o$; $\quad ROO^o + O_2 \rightarrow RO^o + O_3$

$ROO^o + NO \rightarrow ROONO + RO^o + NO_2$

$ROO^o + R_1C\,R_2 = R_3C\,R_4 \rightarrow ROO\text{-}\,R_1CR_2\,\text{-}\,R_3CR_4\text{-} \rightarrow polymers;$

Hydrocarbons under UV irradiation in the atmosphere are oxidized to aldehydes (BUBURUZ et al., 1997). In Fig.1 it is presented the change and transformation of propylene ($CH_2 = CH\text{-}CH_3$) in the presence of NO_x.

Ozone concentration in the air due to photochemical transformations can reach 60.10^{-8} vs. $(3\text{-}4).10^{-8}$ normal concentration. Ozone is a strong oxidant and its presence in the ozone layer is beneficial, but in the troposphere, its increased concentration leads to the disturbance of metabolic processes in plants and animals and increases the corrosive aggression of the atmosphere. Ozone action on plastic and construction materials leads to their rapid degradation.

THE OBJECT OF STUDY AND RESEARCH METHODS

The objective of this research study is the impact exerted by precipitation on the environment and their trends of change during 1993-2008.

Methodology for collecting samples of precipitation (snow, sleet, and rain), their chemical analysis, the monitoring of the acidifier oxides (NO, NO_2, SO_2) and $SO_4^=$ concentration in the air were performed according to the normative document PD 52.04.186-89. Precipitation samples (time of collection 2-60 min) were collected using polyethylene funnels with a total area of 1.28 m^2. From a cycle of rainfall, a series of consecutive samples, which were analyzed separately, were collected in the quantity required for the performance of the analysis. It was measured the pH

value, the concentration of the ions SO_4^{2-}, Cl^-, HCO_3^-, NO_3^-, NH_4^+ and the sum $Ca^{2+} + Mg^{2+}$. At the same time, there was monitored the concentration of the acid oxides (NO, NO_2, SO_2) and $SO_4^=$ in the atmosphere. When samples were collected, there was also made a complex of standard meteorological observations.

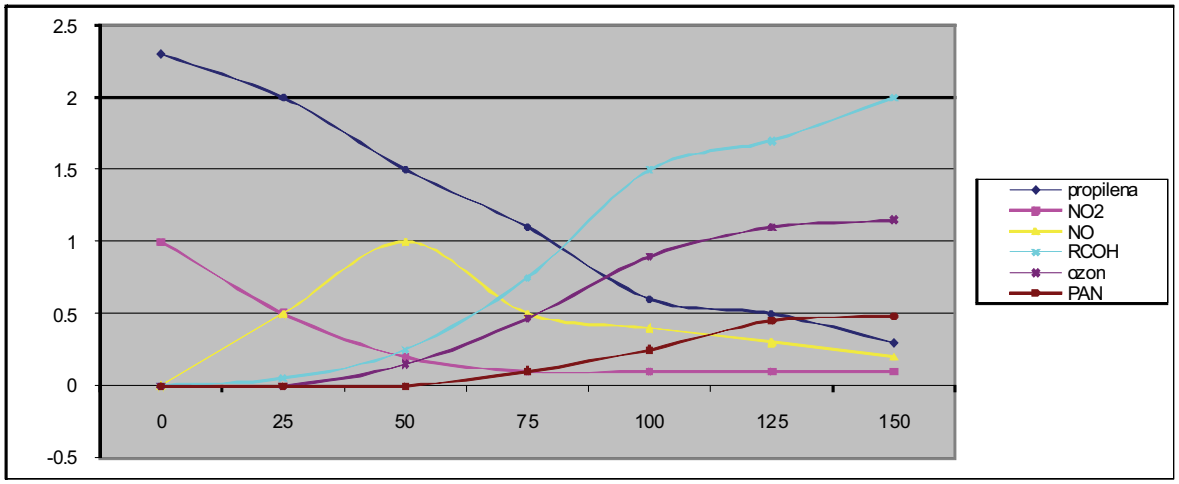

Figure 1. Photochemical smog formation under the irradiation with UV of the polluted air by converting propylene in the aldehyde, ozone and peroxyacetylnitrite in the presence of nitrogen oxides.
Figura 1. Formarea smogului fotochimic în timp la iradierea cu raze UV a aerului poluat prin transformarea propilenei în prezenţa oxizilor de azot în aldehidă, ozon şi peroxiacetilnitrit.

RESEARCH RESULTS

1. Collection and analysis of rainwater samples

The systematic study of acid precipitation was held at the field station Hincesti of the National Institute of Ecology starting with 1993.

During the research period (1993-2008), samples of precipitation were collected, chemical analysis carried out, and the pH of rainfall water determined. At the same time, we determined the concentration of acid oxides (NO, NO_2, SO_2) and sulphates in the atmosphere. A standard complex of meteorological observations was also made. The number of rainfall events, the number of discrete collected samples, the average annual pH and the variation of pH are rendered in Table 1.

Table 1. Number of precipitation and collected samples and their acidity.
Tabel 1. Numărul de precipitaţii şi mostre colectate şi aciditatea lor.

Year	No. of precipitation	No. collected samples	Average annual pH	Interval pH per year
1993 (August-October)	9	43	-	2.65-7.60
1994	49	152	6.71	3.51-9.13
1995	93	272	6.11	3.80-10.35
1996	65	177	5.97	3.75-9.70
1997	43	174	5.70	4.20-7.85
1998	54	125	5.21	2.55-7.30
1999	60	306	5.45	4.10-7.85
2000	58	148	6.60	4.40-8.22
2001	82	253	5.34	3.00-6.80
2002	69	192	4.89	4.00-6.50
2003	64	183	5.97	5.00-6.50
2004	46	59	5.26	3.8-6.00
2006	88	108	6.53	4.00-8.40
2007	82	124	6.02	4.20-7.20
2008	92	116	5.28	3.90-8.40

The average annual pH of the rainfalls (Table 1) oscillates between 5.21 and 6.71, so it is practically neutral. There is a slow increase of acidity of the average annual rainfall from 1994 to 1999, corresponding to: 6.71; 6.11; 5.97; 5.70; 5.21. In 1999, it was observed an increase in the basic features of the mediated samples at pH = 5.45 and in 2000 the average annual pH is 6.60. In 2001, the pH dropped to 5.34, while in 2002 to 4.89. This reduction of the acidity of the rainfalls can be explained by decreasing emissions of alkaline dust in the atmosphere of the Republic of Moldova due to the economic crisis. The presence of alkaline features between 1999 and 2000 is due to the massive transboundary transfer of basic substances from the area of armed conflicts (Balkans, Chechnya) and this is demonstrated by the sudden change in the chemical composition of rainfalls compared to the previous years (BUBURUZ, 2003, BUBURUZ et al., 1993, 1995, 1997, NICORICI et al., 2003).

During the research (1993-2008), the pH of the solutions of discrete collected rainfall ranged from 2.65 to 10.35 (Table 1, 2). According to the World Meteorological Organization methodology, it is considered acid precipitation if the pH value < 6.5 and alkaline for a pH > 7.5. In a pure atmosphere, the pH of rain will be equal to 5.6 due to the dissolution of carbon monoxide (IV) in rain water and carbonic acid production. The first sample of strong acid rainfall was recorded on August 11, 1993 with the pH = 2.65. This discrete sample (one from a number of discrete samples collected consecutively during a rainfall, Table 2) was characterized by an unusually high content of anionic sulphate ($SO_4^{=}$). Hydrocarbons were absent, the other ion concentrations were within normal. Other discrete samples collected during the same rainfall had a pH = 5.95-6.68. The most alkaline sample was collected in 1995 on July 15, with the pH = 10.35 (Table 2).

Table 2. Characteristics of two acid rains (consecutive discrete samples collected at a rainfall) (mg.ecv/m^2.hours).
Tabel 2. Caracteristica a două precipitații (mostre discrete consecutive colectate dintr-o precipitație) (mg.ecv/m^2.oră).

Date	Time for collection (min)	pH	$[SO_4^{2-}]$	$[HCO_3^-]$	$[Cl^-]$	$[Ca^{2+}+ Mg^{2+}]$	$[NH_4^+]$
The 11th of August 1993	2	6.68	0.61	0.44	0.10	0.41	0.09
	2	6.17	0.27	0.30	0.09	0.47	0.11
	4	5.95	0.50	0.40	0.10	0.22	0.08
	2	2.65	16.10	0.00	0.10	0.54	0.12
The 15th of July 1995	5	10.35	3.18	1.68	2.45	4.43	0.0
	5	9.62	0.94	1.18	1.76	2.58	0.0
	10	8.73	0.02	0.37	0.64	1.01	0.0
	7	7.12	0.27	0.63	1.05	2.41	0.0

The analysis of the chemical composition of the rainwater samples from the years 1993-1998 show the dominant role of sulphate and carbohydrate ions, each 40 to 20% on average, corresponding to the amount of ions content. Among cations, the sum Ca^{2+} + Mg^{2+} represents about 37%. The content of carbohydrate ions in discrete samples range from 0.0 to 226.9 mg/l, for the sulphate ion from 0.0 to 178.0 mg/l, while the concentration of chlorine ion ranges from 1.06 to 93.7 mg/l. The chemical composition of rainfall in the years 1999-2002 differs from the composition of rainfalls registered in 1993-1998 and 2003-2008. In 1999, we mention the carbohydrate ion, which represented 52% of the total amount of analysed ions. The maximum value was 44.5 mg. ekv/m^2 hour. Increased cation concentrations are registered by the sum Ca^{2+} + Mg^{2+} (33%), the maximum being of 53.4 mg.ecv/m^2.hours. Higher values compared to the previous years were also registered by the ammonium ion (maximum value - 24.7 mg.ecv/m^2.hours). Transboundary transfer of alkaline substances can explain such a distribution of the chemical composition of atmospheric precipitation in 1999 and 2000 from the areas of armed conflict.

The chemical content of precipitation and the pH changes over time. The concentration and the ratio of various impurities in precipitation depend on their type, intensity and duration. In the first sample, it is observed an increased content of all analyzed ions, when rainfall duration exceeds 60 min, the concentration of ions in rainwater approached the minimum. In some cases, the variation is chaotic indicating dispersion of pollutants in the atmosphere (Table 2).

The analysis of the rainwater samples from 1994, a dry year, showed a higher chemical content and the pH value ranging between 3.50 and 9.10, although the pH value indicated the decreasing acidity in samples during periods with greater rainfalls.

The chemical analysis of the precipitation samples revealed some features in 1994. From April to July, the poorest in rainfall, there was registered a higher content of fix residuum, reaching, for example, $[Ca^{2+} + Mg^{2+}]$ = 19.0 mg.ekv/m^2.hours, $[SO_4^{=}]$ = 10.0-15.0 mg. ekv/m^2.hours, $[Cl^-]$ = 15.0-20.0 mg.ekv/m^2.hours. In August, the intensity of rainfall increased and with it, acidity decreased. Insufficient rainfall should lead to lower rainwater pH value.

Comparing with the data analysis of the rainwater for the first half of 1995, which reveals a large number of heavy rains, we find that the pH ranged between 4.01 and 8.35, with an average of 5.86, which means it was predominantly basic, so we do not take into account the contribution of carbon oxide (IV).

The average annual pH in the studied rainfalls ranges between 5.21 and 6.71, which are neutral, but if we analyze discrete samples, we see that in 1998 the rate of acid precipitation samples increased, while in 1999, the rate of neutral and basic samples increased, followed again by acid rain. Between 2000 and 2001, the value of pH <5.60 oscillated between 35.1% and 60% of the samples; pH values of 5.61-6.50 represented 29.5% and 39.1%, pH> 6.50 had 35.4% and 0.9% corresponding. In 2002, all monitored rainfall are acid (Table 3).

2. The dependence of chemical composition of rainwater on meteorological factors.

It has been studied the relation between the chemical constitution of the rain and the movement of the frontal air masses and the presence of acid oxides in these masses. The influence exerted by the movement direction of air masses on the concentrations of nitrogen oxides in the atmosphere is different during the year. In the cold period, they are smaller and almost and do not depend on the movement direction of air masses. From May to September, the highest concentrations were found in air masses coming from the directions N, NW, NE, S, SW (which coincides with the frequency of occurrence of frontal air masses) and they do not depend on the direction of surface wind at all.

Depending on the direction of frontal air masses, there occurs the change of the chemical characteristics of the water samples, as emphasized by tab.4, which illustrates a variation of the analysed indices (BUBURUZ, 2003, BUBURUZ et al., 1993, 1997, NICORICI et al., 2003).

Table 3. Distribution (%) of the samples of precipitation water according to the value of the pH.
Tabel 3. Repartizarea în (%) a mostrelor de apă din precipitaţiile atmosferice după valoarea pH-ului.

pH/year	1976-95	1994	1995	1996	1997	1998	1999
<5.60	34.0	22,4	24,0	70.0	43.7	68.8	33.0
5.61-6.50	35.0	26,0	43,0	25.0	36.8	27.2	50.0
6.51-7.50	21.0	30,0	19,6	3.0	16.6	4.0	16.0
>7.51	10.0	21,3	13,4	2.0	2.9	0.0	1.0
pH\year	**2000**	**2001**	**2002**	**2004**	**2006**	**2007**	**2008**
‹5.60	35.1	60,0	78,15	83	14,8	29	51
5.61-6.50	29.5	39,1	21,85	17	37	49,2	36,1
6.51-7.50	28.4	0,0	0,0	0	25,9	16,2	9,5
›7.51	7.0	0,9	0,0	0	22,3	5,6	3,4

Together with the analysis of atmospheric precipitation, there were analyzed the acidic oxides from the atmosphere and $SO_4^{=}$ aerosols. The results showed that from April to July, with the increasing circulation of the air in the Republic of Moldova, there also occurs an increase of the atmospheric concentration of oxides. This increase coincides with the N, NE, SW and W direction of the air masses. Depending on the direction of the air masses, the chemical characteristics of the water samples undergo certain changes as well. The results are rendered in Table 4 (BUBURUZ et al., 1997, IANOVCIUC, 1997). Rainfall acidity increases for SE and SW directions and this allows us to see that the most pollutants in the air is brought by frontal air masses.

Table 4. Changes in average indices analyzed in water samples (mg.ecv/m^2.hours) depending on the direction of cyclonic air masses.
Tabel 4. Variaţia indicilor medii analizaţi în mostrele de apă (mg.ecv/m^2.ora) în dependenţă de direcţia maselor de aer ciclonice.

	N	NE	E	SE	S	SW	W	NW
pH	4.80	5.51	5.44	5.43	5.20	5.46	5.53	5.20
$SO_2^{=}$	1.58	0.16	1.06	0.97	0.19	1.07	0.82	0.70
Cl^-	0.37	0.16	0.40	0.56	0.12	0.63	1.11	0.36
HCO_3^-	1.17	0.48	0.90	2.03	0.32	0.98	3.23	1.24
$Ca^{2+}+Mg^{2+}$	0.84	0.51	0.83	1.06	0.29	0.71	2.34	2.07
NH_4^+	0.307	0.042	0.193	0.170	0.0	0.140	0.0	0.279

According to the West Center of Meteorological Synthesizing, referring to the average input/output of polluting substances calculated as transboundary aspect, the Republic of Moldova proved to be a net importer of sulphur, nitrogen oxides, and ammonia. Thus, among the pollutants coming from the neighbouring areas, sulphur and nitrogen register very high levels in Moldova, representing 84% of sulphur emissions, 96% of the nitrogen oxidant deposits and 45% of the reducing nitrogen. This analysis confirms that the transboundary transfer of acid substances plays a decisive role in the pollution of air within the basin of the Republic of Moldova.

It is known that atmospheric precipitation is formed and falls from the bottom layer of the atmosphere (up to 2 km). In this layer, there are the three types of clouds: Stratus - St, Stratocumulus - Sc and Nimbostratus - Ns. There are two types of very important clouds: Cumulus - Cu and Cb – Cumulonimbus, characterized by the occurrence heavy rainfalls. Comparing the results of the analysis of rainwater samples to the type of clouds, we see that the Stratus and Stratocumulus clouds, which absorb pollutants from the layer of atmosphere below the clouds, are less acid precipitation than those generated by Cumulonimbus clouds, which make contact with the upper atmospheric layers and, probably, incorporate pollutants brought by frontal air masses.

3. Harmful effect of acid precipitation

Acid precipitations influence the functionality of the ecosystems by altering life conditions (IANOVCIUC, 1997, KULLBERG, 1992, RODHE et al., 1995).

The harmful effect of acid precipitation, as a rule, refers primarily to the acidification of surface water, which, in its turn, leads to essential changes in the composition of plankton, flora and fauna and also to the trophic chain interruption. The analysis of water samples collected from surface waters on the territory of the Republic have shown that the quality of surface water is not practically influenced by acid rainfall due to the chemical composition of the water bed soil, which has an increased content of carbonates and probably to the average pH of the rainfalls, which is within the limits of 5.21-6.71. When clouds were inseminated with anti-hail agents, surface waters displayed lead and silver ions.

However, the present quantity of pollutants in the acid precipitation is sufficient to influence the vegetation and productivity of crops. Performed experiments allowed us to establish an empirical correlation enabling us to calculate

the productivity of crops depending on the precipitation pH value and to estimate the damage induced by the influence of individual or mixed pollutants (IANOVCIUC, 1997). Fogs and acid rain negatively influenced the productivity of crops and positively the development of pests.

SUMMARY OF RESULTS

The results of our research show that the average annual pH of the collected rainfall samples (at Hincesti) during 1993-2008, oscillates between 5.21 and 6.71, which means slowly acid.

Even more interesting is the information obtained from the analysis of the rainwater samples collected constructively in a cycle of rainfall. If the average annual pH decreases constantly, with the exception of 1999, then the analysis of pH values for discrete samples shows that the pH highly varies during a rainfall. During the research period, with some exceptions, the number of acid samples increases due to the decrease of local emissions of acid substances. More acid rains occur during the warm period of the year, when atmospheric mobility increases and southern air masses became more active, due cyclonic activity.

The analysis of the pH dependence on wind structure shows that acid rain occurs at descending winds. The synthesis of the results shows that the transboundary transfer plays a determining role in the formation of acid precipitation in the Republic of Moldova.

CONCLUSIONS

Moldova is under the influence of acid rain, pH value in the discrete samples of precipitation during 1993-2008 ranging between 2.65 and 10.35.

Ions concentration and pH value in discrete samples collected consecutively during a rainfall varies substantially.

Acid rain is caused by transboundary transfer of acid substances.

The increase of acid precipitation and of their acidity degree leads to the increase of the corrosive aggressiveness of the atmosphere on constructions, monuments etc.

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