Fenomene şi procese hidrice de risc

ACID PRECIPITATION INFLUENCE ON THE QUALITY OF SURFACE WATER

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ABSTRACT. – Acid precipitation influence on the quality of surface water. Research chemical composition of precipitation and air monitoring concentrations of oxides and sulphates acidification in the years 1990-2008 showed the presence of acid rain and the Republic of Moldova. pH value of samples of water collected from rainfall varied in limits from 2.65 to 10.35. During the years 1990-1998 the percentage of water samples acid increased continuously. In the years 1999-2002 the water samples were mostly neutral and a further increase in acid samples was detected during 2002-2008. It was found that the Stratus and Stratocumulus clouds, which absorb pollutants from the layer of atmosphere below the clouds, are 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. Content analysis of ions and pH investigated, depending on the wind we see that the rainfall fell in descending air masses are more acidic compared with the masses of air upward. Analysis of water samples collected from surface waters in the territory of the Republic have shown that the quality of surface water is not practical influenced of acid rainfall due to the chemical composition of soil water bed, which has an increased content of carbonates. Moldova is affected by the phenomenon of acid rain and the determining factor is the transfer of transboundary acid substances.

Key words: acid rain, atmosphere, transboundary transfer, ecological impact.

1. Introduction

Moldova's climate is temperate continental. On average per year are 2060 hours in the sun in northern and 2350 hours in the southern regions of the republic. The average annual temperature of air in Moldova is positive and is 10^{o}C. The annual quantity of atmospheric precipitation is 380 mm in the south and 560 mm in the north of Moldova.

The climate is determined by external baric centers. The atmospheric circulation is predominantly anticyclone with relatively low atmospheric processes, expressed by a variety of changes in seasonal movement. Most cyclones crossing the territory of Moldova from the Western Balkans with an average speed of 20-30 km/hour, range 80-90 km/hr. Prevailing winds directed from the West, North, North West and a low frequency in South and South-West. Average speed of 2,5-4,5 m/sec.

Most acid rain have been imposed as a major problem with the introduction in 1973 the Arab oil embargo and the industrial countries have started using coal.

The documentary mentioned acid rain occurred in the town Uilling (USA) in 1978 and had the pH = 2.0. Average annual precipitation for pH is 4.5 in Europe, to Northern Europe - 4.0. Theoretical value of average annual rainfall pH value Moldova calculated EC UN is 5.0 [1].

According to research carried out in Moldova in the years 1986-1988 the average annual pH was 5.7, the minimum was 3.5. During 1992 the pH of rainwater samples ranged from 5.7 to 6.9 [1.2].

Among the gases responsible for acid rain acidification are the most important oxides of sulfur and nitrogen. Sulfur oxide into the atmosphere is informal with the combustion gases.

In Europe the release of sulfur oxides by about 30 million tones/year, the overall emission of sulfur oxide(IV) in the atmosphere is valued at around 113 million tones/year [3-4]. A quantity global anthropogenic emission of NO_x is estimated at 40-90 million tons/year. In the Republic of Moldova were free in 1990 (reference year) 230 thousand tons/year of sulfur oxides and about 10 thousand tons/year in 2005.

Acid rains are virtually diluted solutions of acids, especially sulfuric and nitric acids. Sources influence the ratio of H_2SO_4 and HNO_3, and it changes within the limits of 1:1 to 4:1. Graphical presentation of change of concentrations of sulfur compounds and nitrogen transformations and their dependence on time shows that the maximum concentration of H_2SO_4 in the atmosphere reaches over 30 hours of HNO_3 over - 15 hours [3.4] (table 1).

2. The object of study and research methods

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

Methodology for collecting samples of precipitation (snow, sleet, and rain), their chemical analysis, monitoring the concentration in air acidifier oxides (NO, NO_2, SO_2) and sulphate was performed according to normative document PD 52.04.186-89. Precipitation samples (time of collection 2-60 min) are collected using polyethylene funnel with total area of 1.28 m^2. From a cycle the fall of rainwater collect a series of consecutive samples in the quantity required for the performance analysis, which is analyzed separately. It measure the pH value, concentration ions SO_4^{2-} ,CI^-, HCO_3^-, NO_3^-, NH_4^+ and Ca^{2+} sum + Mg^{2+} . Parallel monitors concentration in the atmosphere in acid oxides (NO, NO_2, SO_2) and sulphates. When collecting samples of water parallel to make a complex standard meteorological observations.

3. Research results

3.1. Collection and analysis of rainwater samples

Systematic study of acid precipitation was held at the field station Hincesti of the National Institute of Ecology since 1993. In the research period (1993-2008) were collected samples of precipitation, chemical analysis carried out, determining value water pH of rainfall. Parallel to the concentration in the atmosphere of acid oxides (NO, NO_2, SO_2) and sulphates. When collecting samples to make a full standard meteorological observations. Number of rainfall, number of discrete samples collected, average annual pH and the variation of pH are presented in table 1.

Table 1. The number of precipitation samples collected and their acidity

Year	No. of precipitate.	No. samples collected	pH medium annual	Interval pH per year
1993(VIII-X)	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

Average annual pH of rainfall in the research (see table. 1) fall within the limits of 5,21-6,71, so practically neutral. 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 observed an increase mediated basic samples at pH = 5.45, in 2000 the average annual pH of 6.60 is already. Since 2001 the pH drops to 5.34 in 2002 to 4.89. Acidification slow rainfall is explained by decreasing emissions of alkaline dust in the atmosphere RM thanks economic crisis, while alcanizate in 1999-2000 is due to massive transboundary transfer of basic substances in the area of armed conflicts (Balkans, Chechnya) and that is demonstrated by changing sudden chemical composition of rainfall compared with other year's precede.

During the research (1993-2008) the pH of the solutions of discrete rainfall collected ranged from 2.65 to 10.35 (table. 1.2). According to World

Meteorological Organization methodology is considered acid precipitation with pH value <6.5 and the alkaline pH> 7.5. In a pure atmosphere, the pH of rain will be equal to 5.6 due to dissolution in rain water for carbon monoxide (IV) and carbonic acid production [4-6]. The first sample of strong acid rainfall was recorded on 11 August 1993 with the pH = 2.65. This discrete sample (one from a number of discrete samples collected consecutively during a rainfall, see Table. 2) was characterized by an unusually high content of anionic sulphate. Hydrocarbons missing, the other ion concentrations were within normal. Other discrete samples collected from rainfall had the same value in the pH = 5.95 - 6.68. The alkaline sample was collected in 1995 from July 15, with the pH = 10.35 (table 2).

Table 2. Characteristics of acid rain (consecutive discrete samples) (mg. ecv/m^2. hours)

Date	time for collection	pH	$[SO_4^{2-}]$	$[HCO_3^-]$	$[Cl^-]$	$[Ca^{2+} + Mg^{2+}]$	$[NH_4^+]$
11.08.93	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
15.07.95	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

Analysis of chemical composition of rainwater samples from the years 1993-1998 show the dominant role of sulfate ions and carbohydrate, each 40 to 20% on average, corresponding to the amount of ions content . Cation between the amount of Ca^{2+} + Mg^{2+} is about 37%. Carbohydrate content of ions in discrete samples range from 0,0-226,9 mg/l for sulfate ionic from 0,0-178,0 mg/l concentration of chlorine ion ranges from 1.06 to 93 , 7 mg/l [6]. Chemical composition of rainfall in the years 1999-2002 differ from the composition of rainfall in the 1993-1998 and 2003-2008. In 1999 in the foreground is carbohydrate and ion constituted 52% of the total amount of ions analyzed. The maximum recorded was 44.5 mg. ekv/m^2 hour. Of cation concentrations in increased the amount of registered ions Ca^{2+}+ Mg^{2+} (33%) and the maximum 53.4 mg ekv/m^2 hours. Values increased in comparation with previous years were recorded and the content of ammonium ion (maximum value - 24.7 mg ekv/m^2 hours). A distribution of such chemical composition of atmospheric precipitation in 1999 and 2000 can be explained by transboundary transfer of alkaline substances in areas of armed conflict.

Chemical content of precipitation and the pH changes over time. And the concentration of various impurities in precipitation depends on the type, intensity

and duration. In the first probe is observed an increased content of all analyzed ions, where rainfall duration exceeds 60 min, the concentration of ions in rain water is approaching the minimum. In some cases the variation is chaotic scratchy indicating dispersion of pollutants in the atmosphere (table 2).

Analysis of rainwater samples from 1994, dry year, showed a vary bigger sufficient chemical content and pH value in the range 3. 50-9. 10, although in periods with more rainfall pH value indicates the decreasing acidity of samples.

Chemical analysis of samples of precipitation since 1994 has revealed some features. In the months April to July, the poorest in rainfall, the corresponding content is increased to fix residuum, reaching, for example, [Ca^{2+} + Mg^{2+}] = 19. 0 mg. ekv/m^2. hours, [SO_4^{2-}] = 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 has increased and with it, and acidity decreased. Insufficient rainfall you should not only lead to lower water pH value of rainwater.

Comparing with the data analysis of rain water for the first half of 1995, which reveals a large number of heavy rains we find that the pH of rain water ranged between 4. 01 - 8.35 being the average of 5. 86 predominantly basic so if we do not take into account the contribution of carbon oxide (IV).

Table 3. Distribution in (%) of samples of water from atmospheric precipitation pH value after

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

Average annual pH in the research fall within 5.21 - 6.71, so basically neutral, but if we analyze discrete samples acidity see that by the year 1998% increase acid precipitation samples, in 1999 sharply increased% neutral and basic samples, followed by acid rain reinstalled dominance. Between 2000 and 2001 the value of pH <5.60 were 35.1% and 60% of samples; pH 5,61-6,50 were 29.5% and 39.1%, pH> 6.50 had 35.4% and 0.9 % corresponding. In 2002 virtually all monitored rainfall are acidic (table 3).

3.2.The dependence of chemical composition rainwater by 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 masse. Influence the direction of movement of air masses of the concentrations of nitrogen oxides in the atmosphere is different at different times of the year. During the cold of the year they are smaller and almost not depend on the direction of movement of air masses. During May to September the highest values of concentrations were found in air masses coming from the directions N, NW, NE, S, SW (which coincides with the frequency of occurrence of air masses front) of the land the wind strength practically do not depend. In dependence by direction of travel of the front air mass change and chemical characteristics of water samples in tab. 3 shows the variation indices are analyzed in the direction-dependent displacement of air masses [6.7].

Parallel with the analysis of atmospheric precipitation was analyzed acidic oxides in the atmosphere and SO_4^{2-} aerozols. The results showed that in the months April to July, with mobility increasing atmospheric concentration of oxides increases analyze air basin in the Republic of Moldova. This increase coincides with the direction of the front air masses N, NE, SW and W. Depending on the direction of travel of the front air mass change and chemical characteristics of water samples. In tab. 4 presents the variation indices analyzed depending on the direction of movement of air masses [6.7].

Table 4. Changes in average indices analyzed in water samples (mg. ecv/m^2 hour) depending on the direction of air masses during cyclone IV-X. 1998

Direction / Indices	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

Least rainfall acidity increases for directions SE, SW that allows us to see that the most pollutants in the air is brought in front of air masses.

After frontal structure of air masses are distinguished as the air mass upward and downward. If air masses upward, when the transfer is performed in the lower levels, air pollution is caused by local sources. Masses of air descending pollute the atmosphere with impurities, to the frontal air masses through

transboundary. Research has shown that rainfall fell in the descending air masses have a higher content of pollutants such as acid, from transboundary transfer of substances acidifier. (table 7).

Table 5. Changes in annual average concentration of ions investigated (mg. ekv/m2oră) in precipitation and pH values depending on the wind

The wind	pH	$[SO_4^{=}]$	$[HCO_3^{=}]$	$[Cl^-]$	$[Ca^{2+}+Mg^{2+}]$	$[NH_4^+]$
Ascendant	6.43	1.24	0.80	0.59	1.43	0.20
Descending	5.70	3.65	1.53	1.35	2.06	0.36

According to the Center of Western Meteorological synthesize, on average import/export of polluting substances calculated as cross-border aspect, RM proved to be a net importer of sulfur, nitrogen oxide and ammonia. Thus, from an import quota transfer of pollutants such as sulfur and nitrogen is very high in Moldova, accounting for 84% of sulfur emissions, 96% for the deposition of nitrogen oxidant and 45% for reducing nitrogen. This analysis confirms that the transboundary transfer of acidic substances play a decisive role in the pollution of air basin of the Republic of Moldova.

It is known that atmospheric precipitation is formed and fall of the bottom layer of the atmosphere (up to 2 km). In this layer are the 3 types of clouds: Stratus - St, Stratocumulus - Sc and Nimbostratus - Ns. There are two types of clouds very important: Cumulus - Cu and Cb-Cumulonimbus where strong rain fall. 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 acidic precipitation than Cumulonimbus clouds, which make contact with the upper atmospheric layers and, probably, incorporating pollutants brought by air masses from the front.

3.3. Harmful effect of acid precipitation

Acid Precipitation breaks ecosystem function by altering the conditions of existence [1]. Harmful effect of acid precipitation, as a rule, turn primarily on surface water acidification consists of water acidification leading to essential changes in the composition of plankton, flora and fauna and the food chain interruption. Analysis of water samples collected from surface waters in the territory of the Republic have shown that the quality of surface water is not practical influenced of acid rainfall due to the chemical composition of soil water bed, which has an increased content of carbonates and probably the average pH rainfall, which is within the limits of 5,21-6,71. When the clouds were processed with anti-established agent's aggregation in surface waters of the ions of lead and silver.

Present quantities of pollutants in the acid precipitation is sufficient to influence the vegetation and productivity of crops. Experiments performed revealed that the empirical correlations that allow the calculation of productivity of crops, depending on the pH of precipitation and evaluation of losses in crop productivity on the influence of individual pollutants in the mixture [4]. Fogs and acid rain negative influenced productive of crops and positive development of pests.

In the years 1970-1980 began drying oak and the Republic of Moldova. Injury indirectly oak is not resistant to the fungus Mikorriza soil acidification, which vegetate on oak roots in symbiosis, increasing the absorption capacity of soil water. Injury indirectly oak is not resistant to the fungus Mikorriza soil acidification, which vegetate on oak roots in symbiosis, increasing the absorption capacity of soil water. Acid deposition affects the growth of forests through disturbance of calcium balance soil which hamper the evacuation of aluminum root system, which prevents absorption of nutrients by plants. Acid deposition affects the growth of forests through disturbance of calcium balance soil which hamper the evacuation of aluminum root system, which prevents absorption of nutrients by plants.

Acids are formed not only the atmosphere but also in the solution on the surface of sedimentary or absorption, lowering the pH, the increasing degree of aggressiveness of acid pollutants in the atmosphere. Acids are formed not only the atmosphere but also in the solution on the surface of sedimentary or absorption, lowering the pH, the increasing degree of aggressiveness of acid pollutants in the atmosphere.

4. Summary of results

The results of research show that the average annual pH of rainfall collected at the branch Hincesti during 1993-2008 is situated within 5,21-6,71, ie weak acid.

Even more interesting is the information obtained from analysis of rainwater samples collected constructive in a cycle of falling rain. If the average annual decrease of pH constant, with the exception of 1999, and then analyze pH values for discrete samples shows that the pH in the range of rain and fairly strong in research with some exceptions acid increases the number of samples based on the decrease emissions of local acidic substances.

More acid rain is found during the year when warmer atmosphere increases mobility and exchange activity Southern air masses due activity cyclone.

Analysis of the pH dependence of the wind, in May shows that acid rain is produced when wind descending. Synthesis results show that the transboundary transfer plays a determining role in the formation of acid precipitation in the air basin of the Republic of Moldova.

5. Conclusions

Moldova is under influence of acid rain, pH value in the discrete samples of precipitation during 1993-2008 ranged between 2,65-10,35.

Ions concentration and pH value in discrete samples collected consecutively in the fall of precipitation varies substantially.

Acid rain are caused by virtually transboundary transfer of acidic substances.

Surface water to agricultural crops by differ and vegetative practically not influence the content of acid rain due to increased basic substances in water, mud and soil.

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