DEPOSITION OF SULPHUR AND NITROGEN VIA RAINWATER (CASE STUDY - the administrative territory of the Hincesti district)

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ABSTRACT - Deposition of Sulphur and Nitrogen from rainwater (case study – the administrative territory of the Hincesti district)*. The quantitative estimation of rainfall and determination of their chemical composition (samples collected in open area and under the canopy) lead to periodic assessment of the annual flow of ions and mineral deposits of sulfur and nitrogen oxide in the atmosphere. In accordance with agreed European Scale for assessing levels of atmospheric deposition it can be appreciated that the study area (Hincesti, central part of Moldova) in 2006-2010 corresponds to the class of large sulfur deposits, varying from 14.9 kg/ha/year (2009) to 24.8 kg/ha/year (2010). Quantities referring to study area recorded intermediate values – 16.8 kg/ha/year and 22.4 kg/ha/year respectively for the years 2007 and 2008.

A comparison between annual average values of sulfur deposition recorded in open area at European level in the period 2006-2010 lies in the study area comparable to the central-eastern Europe region, exceeding 60% of the average. In relation to this scale deposition of total nitrogen (from nitrate ion and ammonium ion) are small-sized deposits in the area, with averages ranging from 2.2 to 4.3 kg/ha/year N-NO_3^- and 7.2-9.3 kg/ha/year for N-NH_4^+. There are slight oscillations of annual averages from year to year that do not exceed 0.6 kg/ha/year.

Keywords: air pollution**,** rainfall, sulfur and nitrogen deposition, heavy metals, mineral ion flows and hydrogen ion.

1. INTRODUCTION

During the 2006-2010 study period 522 samples of wet deposition were collected and analyzed, including 429 in the form of rain, 55 - sleet and snow for determination of 14 indicators (pH, alkalinity, acidity, PO_4^{3-}, NO_2^-, NO_3^-, NH_4^+, Cl^-, HCO_3^-, SO_4^{2-}, fixed residue, Ca^{2+}, Mg^{2+}), including organic component and load with pollutants (Lasse (1989); Patroiescu (1980); Stum and Morgan (1981)). Checkpoints throughout the years were as follows: –Ecological Stationary - Hîncesti (permanent); Leova Environmental Inspection (temporary); Ecological Stationary – Recea (in the northen part of the republic) and Chisinau Weather Station (temporary).

2. EVALUATION METHODS, WORK METHODOLOGY

Analysis methods of physical-chemical parameters of water from rainfall, and research methodology, as well as models of calculation are recommended by

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the European Environment Agency (EAA) and the Convention on Long Range Tran boundary Pollution (CLRTP).

Ionic balance method, calculated by comparing the measured conductivity, analysis of at least two synthetic samples in each series of 30 samples to verify the accuracy of measurement were used to check validity of the obtained results.

Samples of dust, wet deposition (rain, snow and sleet) were collected according to the methods described in EMEP EEA Guidebook 2009 revision.

3. RESULTS AND DISCUSSION

Comparing the evolution of quantitative rainfall in the study area a rather large fluctuation has been noticed, from 4 mm (minimum quantity, April 2009) to 193 mm (maximum, June 2009, 2010). 70-85% of rainfall fell during warm period (April-November) remaining quantity is refer to cold period (December-March). The average annual rainfall ranged from 353 mm (2007) to 747 mm (2010). The average annual rainfall between 400-700 mm (24-41%) is the most common amount (Fig. 1,2).

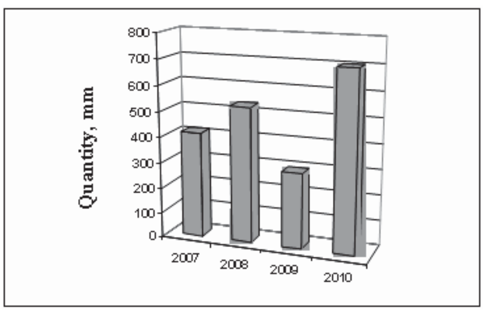

Fig.1. ***Quantitative characteristics of rainfall during 2007 - 2010, (Hîncesti)***

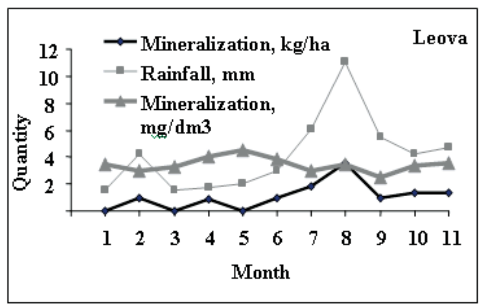

Fig. 2. ***Evolution of the monthly amount of rainfall and mineralization of rainwater, (Leova, 2007)***

The dynamics of air masses determines the maximum annual variation of rainfall in the warm season (193 mm in June) and a minimum in the cold season (20 mm in January). Annual maximum occurred almost always in hot months (Fig. 3).

The concentration of hydrogen ions (pH) has values ranging from 4.3 to 8.0. pH values indicate how much substances that cause acidity or alkalinity of water from rainfall are contained and can characterize the aggressive properties of water and the impact on the environment factors (natural waters, soil, vegetation) (Fig. 4).

The annual flux of hydrogen ions in this period was between 45-52g H^+/ha/year (Fig.5). Maximum monthly amount of hydrogen ions reached 54 g H^+/ha, and the minimum 3g H^+/ha under the canopy, while in open area this quantity was 17.0 and 1.3 g H^+/ha. Hydrogen ion flux ranging from 0.07 to 1.17 g/ha under the canopy and 0.03 to 0.37 g/ha in open area, which leads to intensification of soil acidification, increasing of ion exchange capacity and as a result to soil degradation. Evaluation of annual and periodic flux of mineral ions in the atmosphere is based on quantitative rainfall estimation and determination of its chemical composition. Obtained comparative results are given in fig.6

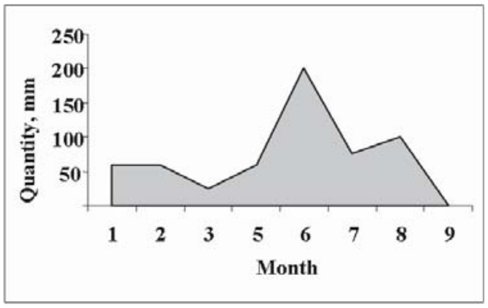

Fig.3. ***Evolution of the monthly amount of rainfall, (Hîncesti, 2010)***

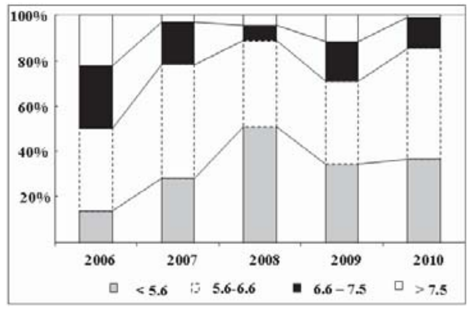

Fig.4. ***Distribution (%) of water samples according pH index***

Total annual flux of mineral ions with rainfall in open area ranged from 132 kg/ha/year (2008) to 212 kg/ha/year (2010), being a function of the quantity of rainfall and concentration of mineral ions, which in turn depends on the accumulation of solid deposits, the origin and chemical parameters of deposition (Cojocaru (1995); Gavrilescu (2004); Logan (1999).

Following from obtained results an experimental model for interpreting flow of ions in forest ecosystem, capturing rainfall under canopy was proposed.

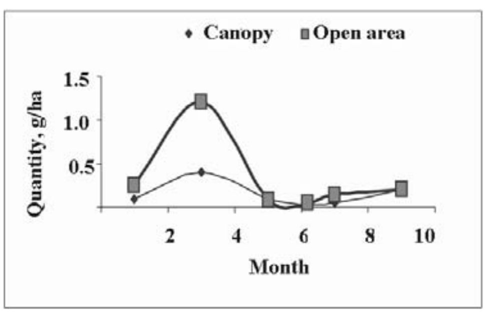

Fig. 5. ***Hydrogen ions flux with rainfall***
**** - were selected 2-3 days with rainfall in these months***

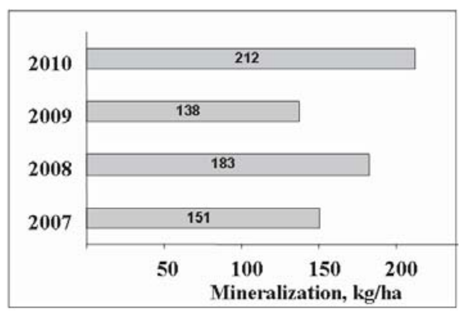

Fig. 6. ***Mineral ion flux from rainfall (open area)***

Obtained results show the following:

- Loading in mineral ions (expressed in mineralization) of the rainwater collected under canopy is much higher than that of rainwater in the open area, which indicates the high degree of accumulation of dry deposition of the canopy in the interval between two drops of rain;

- Retention degree of rainfall by the canopy has values between 2-33%, being a function of the rainfall character (heavy, quiet). In periods of low rainfall, maximum retention by the canopy has exceeded 30%;

- Nitrogen compounds (ammonium ion, nitrate, nitrite) are found in rainwater in amounts that vary widely: for ammonium ions ($N\text{-}NH_4^+$) - from 1.35 to 4.30 mg/dm^3 (open area) and 2.1 – 7.8 mg/dm^3 (canopy); for nitrogen ($N\text{-}NO_3^-$) - from 1.35 to 6.7 mg/dm^3 (open area) and 2.9 to 13.6 mg/dm^3 (canopy); for nitrogen ($N\text{-}NO_2^-$) – 0.02 – 0.25 mg/dm^3 (open area) and canopy 0.043 to 0.38 mg/dm^3.

Under the canopy all these parameters recorded higher values, which is explained by the active pursuit of the processes of decomposition of organic substances (ammonium appearance) and its microbial oxidation (occurrence of nitrates) in the natural nitrogen cycle: organic matter (protein complex) - amino acid - ammonia - nitrogen. Active response from rainwater reaches pH values ranging from 4.5 to 8.2.

Analyzing data on sulfur and nitrogen deposition compared with the scale for different regions of Europe it can be noticed that the study area (Hincesti) in 2006-2010 corresponds to the class of large sulfur deposits, varying from 14.9 kg/ha/year (2009) to 24.8 kg/ha/year (2010). For the years 2007-2008 sulfur and nitrogen deposition recorded intermediate values – 16.8 kg/ha/year and 22.4 kg/ha/year respectively (Fig.7).

A comparison between annual average values of sulfur deposition recorded in open area at European level in the period 2006-2010 lies in the study area comparable to the central-eastern Europe region, exceeding 60% of the average. In relation to this scale deposition of total nitrogen (from nitrate ion and ammonium ion) are small-sized deposits in the area, with average values ranging from 2.2 to 4.3 kg/ha/year $N\text{-}NO_3^-$ and 7.2 to 9.3 kg/ha/year for $N\text{-}NH_4^+$. There are slight oscillations of annual averages from year to year that do not exceed 0.6 kg/ha/year.

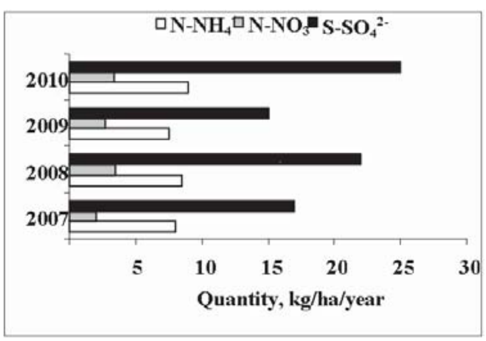

Fig.7. ***Sulfur and mineral nitrogen flux (Hîncesti)***

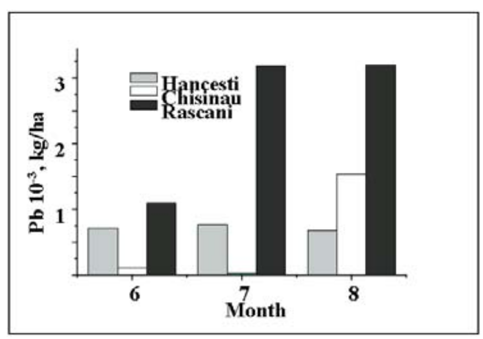

Fig. 8. ***The contribution of lead in soil from rainfall***

Besides the main constituents (Ca^{2+}, Mg^{2+}, Na^+, HCO_3^-, SO_4^{2-}, Cl^-) some more constituents of the secondary and minor were determined (Cr, Cd, Zn, Pb, Cu, Fe, Al), which indicated small amounts (0.0001 to 0.1 mg/dm^3), but may have a point of considerable importance of atmospheric pollution (Schmidt and Andern (1980); Kondratiev (2004). The results of the heavy metal content (minor constituents) have values that fall within acceptable limits, except Pb, which exceeds the contents of the health index (30 mg/kg) (Fig.8).

The main source of air pollution is the combustion processes in order to obtain electricity, heating or different industrial processes.

Acidifying greenhouse gases in the atmosphere result from different activities and may persist for several hours to several days in the atmosphere, and can be transported hundreds of miles away from the place of production. To determine the air emissions, four basic methods are used, each with advantages, disadvantages and limitations of use.

These are: measurement of emissions, emissions balances determination by determining correlations and emission factors based on emission characteristics. During the field research we used a single method - systematic measurement of emissions is measured using a chain of appropriate measurements of the concentration of various substances in harmful emissions. The most widespread application of this method is monitoring of gas emitting sources from a fixed point (ecological stationary Hincesti)

In particular, concentrations of sulfur dioxide (SO_2) and nitrogen (NO_2) are continuously measured. Measurements of the sulfur dioxide concentration and nitrogen emissions have been made continuously and give the possibility to estimate annual average values of these gases in the emissions (Fig. 9, 10).

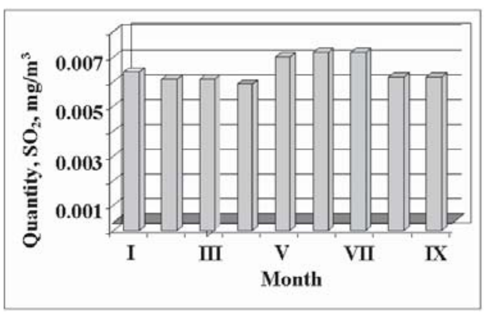

Fig.9. ***Evolution of monthly average concentrations of sulfur dioxide, (Hincesti, 2010)***

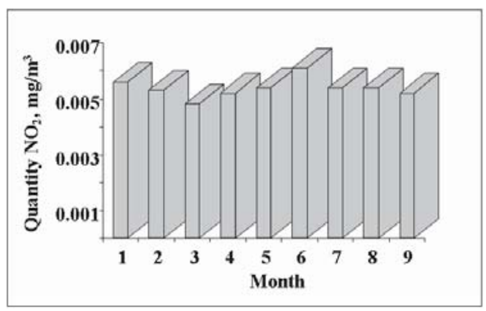

Fig.10. ***Evolution of monthly average concentrations of nitrogen dioxide, (Hincesti, 2010)***

It can be seen that values for gaseous pollutants track were well below the limits set by current standards. There were no exceedances of the limit value (60 µg/m³ for SO_2 and 40 µg/m³ for NO_2) in comparison with the limit value for SO_2 and NO_2 in the years 2007 - 2010. Annual averages are ranging from 2 µg/m³ and 7 µg/m³ for SO_2 and between 3 µg/m³ and 9 µg/m³ for NO_2.

Air pollution study involves description and explanation of the origin of pollutants and predicts the behavior of substances emitted into the atmosphere. These substances are transported by wind and mixed into the atmosphere by the phenomena of turbulence and sometimes land area involved and deposited by rainfall. Turbulence is actually responsible for the dispersion of pollutants in the area. The diffusion of atmospheric meteorological factors that have a direct influence is wind, vertical structure of temperature and humidity and rainfall.

Processes to reduce the pollutant content are: 1. washing by rain - wet deposition; 2. uptake by soil particles - solid deposits; 3. chemical transformations of pollutants (Atkinson (1980); Logan (1999).

It was established that dispersion of pollutants emitted into the atmosphere is weak due to: low wind speed (2.2 m/s) and high frequency of calm (51%).

Wind direction in the study area is influenced by the general appearance of the landscape. Prevailing winds show western component SW, W, NW, 25%, 13% and 27%. General circulation of the atmosphere requires a moderate frequency of winds from the N (13%), NE (9%) and E (4%). The lowest annual frequencies were S and SE winds (2.2 to 6.7%). Comparative analysis between different years shows permanent dominance of the western component, which reached 61-65% (Fig. 11, 12).

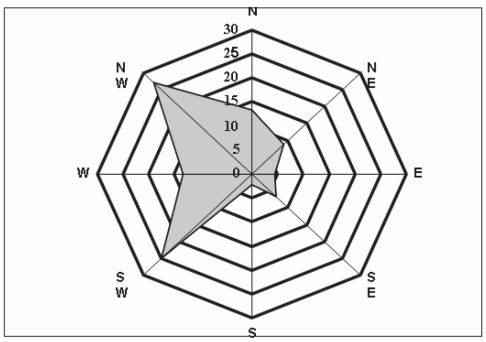

Fig.11. ***Distribution (%) on the direction of frontal air masses (2006)***

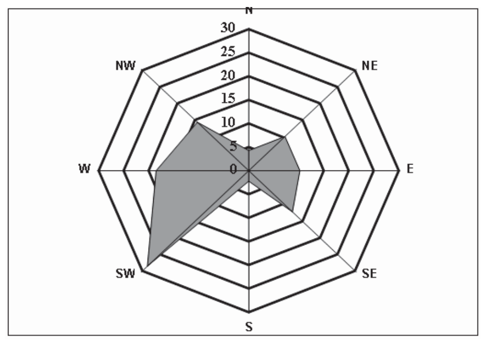

Fig.12. ***Distribution (%) on the direction of frontal air masses (2010).***

4. CONCLUSIONS

1. Ion charge in rainfall is very different, being based on various factors, such as: the origin of air masses, the degree of purity and the crossed area in which rainfall occurs. Total annual flux of mineral ions with rainfall in open area ranged from 132 kg/ha/year (2008) to 212 kg/ha/year (2010), being a function of the rainfall quantity and concentration of mineral ions, which in turn depends on the accumulation of solid deposits, the origin and chemical parameters of deposition;

2. The degree of retention of rainfall in the canopy has values ranging between 2-33%, depending on the rainfalls character (heavy, quiet). In periods of low rainfall, maximum retention in the canopy has exceeded 30%;

3. Sulfur and nitrogen deposition compared with the scale for different regions of Europe in 2006-2010 corresponds to the class of large sulfur deposits, varying from 14.9 kg/ha/year (2009) to 24.8 kg/ha/year (2010). Quantities referring to study area recorded intermediate values – 16.8 kg/ha/year and 22.4 kg/ha/year respectively for the years 2007 and 2008. Total nitrogen deposition ($N\text{-}NO_3^-$ and $N\text{-}NH_4^+$) is in the reduced-sized deposits with average values ranging from 2.2 to 4.3 kg/ha/year $N\text{-}NO_3^-$ and 7.2 to 9.3 kg/ha/year for $N\text{-}NH_4^+$;

4. Dispersion of pollutants emitted into the atmosphere is poor, due to low wind speeds and high frequency of calm. Comparative analysis between different years shows that western dominance is frequently, reaching 61-65%;

5. Correlation between the direction of air masses and the evolution of the ions content in rain waters has been emphasized. It was established, where the predominance of western component of rainfall, pH is between 5.6 to 6.7, to the south - between 6.65 to 6.85, to the north-north-east – 5.8 to 5.9. Mineral ion content is also higher when air masses "comes" from western and eastern directions. These results indicate on transboundary pollution, which plays a significant role in the pollution of the atmospheric air both in studied area and the republic as a whole;

6. The content of heavy metals (minor constituents) has values that fall within acceptable limits except Pb, which exceeds the contents of the health index (30 mg/kg).

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