FLUXES OF INORGANIC NITROGEN IN OPEN FIELD AND UNDER THE CANOPY OF DECIDUOUS FORESTS IN REPUBLIC OF MOLDOVA

BRAŞOVEANU V. [1]

ABSTRACT. Fluxes of inorganic nitrogen in open field and under the canopy of deciduous forests in Republic of Moldova. This study is focused on a comparative analysis of atmospheric $N\text{-}NO_3^-$ and $N\text{-}NH_4^+$ deposition in the open field and under the forest canopy of the Republic of Moldova, which are included in a systematic transnational grid (16x16 km) of forest monitoring throughout Europe. Also, it was appreciated the role of the canopy to reduce the variability of the pH of the precipitation. Monitoring the flux of pollutant ions was performed according to the methodology recommended by International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests (ICP Forests) (ICP Forests, 2010). The $N\text{-}NO_3^-$ and $N\text{-}NH_4^+$ deposition under forest canopy have tended lower in vegetative rest period. The $N\text{-}NH_4^+$ flux is 1.7-3.8 times more than the $N\text{-}NO_3^-$ flux, which clearly demonstrates the dominance of ammonium ion to nitrate ion in atmospheric deposition of Republic of Moldova.

Keywords: atmospheric pollution, deposition monitoring, $N\text{-}NO_3^-$, $N\text{-}NH_4^+$.

1. INTRODUCTION

The problem of forest decline and determine the causes this process underlying specialized studies from the last period. Estimation of nitrogen deposition has become a key task in monitoring programs on to long-term impact of air pollution and other environmental factors on forest ecosystems. Thus, at European level, under the United Nations Economic Commission for Europe (UNECE) Convention on Long-range Transboundary Air Pollution, was released the International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests, which includes measuring the deposition of nitrogen for more than 500 European plots (Lorentz, 2012).

According to the ICP Forests, deposition data are collected on Level II plots in the open field (“bulk deposition”) and under canopy (“throughfall”). Whereas bulk deposition is a basis for estimates of total atmospheric deposition rates in open fields, throughfall deposition typically differs from bulk deposition due to a) wash off of dry deposition from the forest canopy, b) element “leaching” from the tree crowns, and c) absorption of elements by the foliage, so-called “canopy uptake”. The first two effects lead to increased throughfall rates, the latter one, canopy

[1] Institute of Ecology and Geography of the ASM, Chişinău, Moldova
e-mail: brasoveanu1802@mail.ru

uptake of elements by the crown foliage, reduces throughfall deposition compared to bulk deposition (Iacoban, 2009; Fischer, 2010).

Atmospheric deposition of nitrogen compounds can affect the forest ecosystems by several processes, by Aber et al. (1989) the excess of nitrogen maybe leads to nutritional imbalance and in increased sensitivity to the frost insect and fungal attack on trees. The same author submit the acidification hypothesis, arguing that the release of acid anions like NO_3^- and SO_4^{2-}, due to leaching of basic cations, contributes to soil acidification, with negative effects on fine roots and contributes to unbalanced nutrition of forest tree.

2. AREA AND RESEARCH METHODS

The throughfall deposition was measured throughout 2012 in the 10 plots of the Republic of Moldova, included in a systematic transnational grid of 16 x 16 km throughout Europe of forest monitoring (Fig. 1). Also 6 SE (304, 405, 206, 807, 1213 and 1117), it was possible to measure the deposition in free land „bulk precipitation sampler". Experimental surfaces (SE) are placed in altitudes between 127 m (SE 1117) and 266 m (SE 304). Dominant tree species are *Quercus robur*, *Quercus petraea*, *Quercus pubescens*, *Fraxinus excelsior*, *Robinia pseudacacia*, aged between 33 years (ES 304) and 80 years (SE 1117). The consistency of studied forests in most cases was 0.8 to 0.7, and the forest ecosystem (SE 1315) dominated by *Robinia pseudacacia* -0.5.

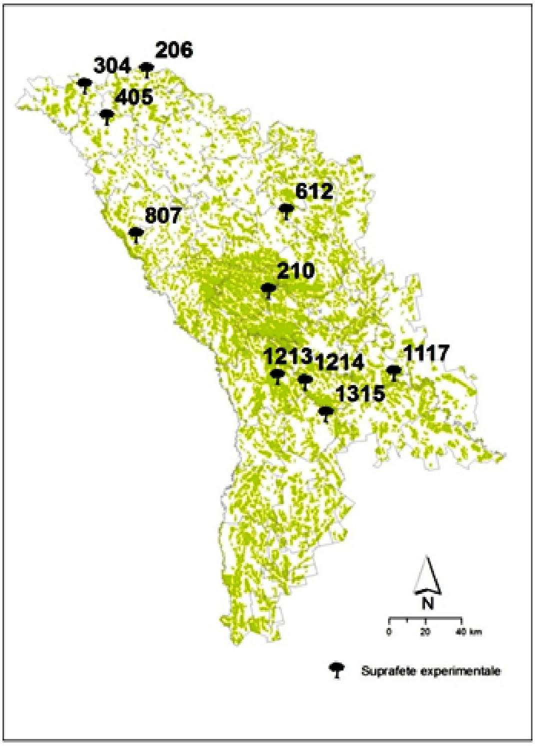

Fig. 1. Location of experimental surfaces from the Republic of Moldova

According to the methodology ICP Forests (2010) in ES was installed the 5-8 by open type collector (collector with polyethylene bag) for precipitation, which were placed under the canopy inside the SE at 7-10 m distance between them in the form of zigzag at the height of 1.2 m above the ground. The collectors were installed in open ground (for vegetation period) at the same altitude and exposure, as in forest land, which were avoided sudden changes in slope and obstacles up to a distance of 30 m from the collector.

Chemical water indices were determined by spectrophotometric method recommended by EMEP (1995), NO_3^- – Griess reagent, NH_4^+ – Nessler reagent and pH - potentiometric method (Sandu, 2010). Nitrogen concentrations of ions analyzed (NO_3^- and NH_4^+) were calculated based on the report of atomic mass of the element to atomic mass of ion. In order to calculate the flow of ions for a certain period of time the fallowing formula was used:

$$F = \sum P_i * C_i/100,$$

where: F – quantitative flow of ion analyzed, in kg/ha/period; P_i – rainfall, in mm, for the period *i*; C_i – concentration of an element or compound, expressed in mg/l for the period *i*.

3. RESULTS AND DISCUSSIONS

According to the State Hydrometeorological Service (SHS) (2013), year 2012 in the Republic of Moldova was mostly warmer than normal and significantly deficient rainfall during in June – September. By applying the norms of characterization at time in relation to amount of precipitation, proposed by Dissescu (1948), the zone SE 304, 405, 612, 1117, 1213, 1214 and 1315 is characterized by annual rainfall regime – *normal* (96-105%), SE 807 and SE 210 with 85-95% rainfall regime is characterized by – *drought* (85-90%) – *less dry* (90-95%). The experimental surfaces 206, where amount of precipitation exceeds 105%, it's not at risk the precipitation insufficiency. Canopy rainfall interception constituted 11-23% and corresponds with the intervals specified in the literature. (10.4-33.8% – at beech and 16-29.4% – at oak) (ONF, 1995; Iacoban, 2009).

For all ES studied (with some exceptions), there is an obvious regularity pH – the dormant period (November – March), in most cases, the pH recorded the lowest values (<6.5). And during the vegetation period (April – October) is recorded trends of increased pH, with maximum values (7.0-7.2) in SE 405 and 1213. The low values of pH in the cold period is due to enhanced concentrations of acidifying ions in this period, from the combustion of fuels, particularly fossil used for heating dwelling sector and the lack of alkaline dust deposits, which would neutralize the pH. During the vegetation period (especially spring – May and autumn – October) trends alkaline pH is due to enhanced deposition of alkaline dust as a result of intensive work the surrounding agricultural land. So, trends are seen for alkaline precipitation months (especially July and October) that follows after a period of low in rainfall, phenomenon that favors the transport of alkaline particle dust from the nearby agricultural fields and deposition them to the forest canopy.

The risk of acidification during the vegetation period is determined by missing foliar cover, after physiological processes would reduce the acidity of precipitation (through buffering or accumulation of pollutants), so reducing the risk of soil acidification in forest ecosystems. On the other hand the trends of atmospheric deposition of acidifying the cold period presents minimal risk (risk indirectly - soil acidification) as deciduous enlightening are the physiological idle. So, for the entire period of observation, only in SE 405, 612 and 1213 were not recorded cases of acid rain (pH <5.6), the rest of the study were recorded 1-3 cases of acid rain.

Fluxes of N-NO_3^-. Annual atmospheric deposition of N-NO_3^- registered under forest canopy studied ranged from 1.53 to 5.2 kgN/ha/year, with the lower trends during the vegetative rest (Fig. 2). An exception is the December, which registered the increased flux of precipitation throughout the observation period, which has resulted respective quantities of atmospheric nitrogen. This diminishing the flow of N-NO_3^- in the cold period can be explained by inactivity or minimal activity of the natural processes of emission of nitrogen compounds (microbiological processes, fires, etc.) and anthropogenic activities.

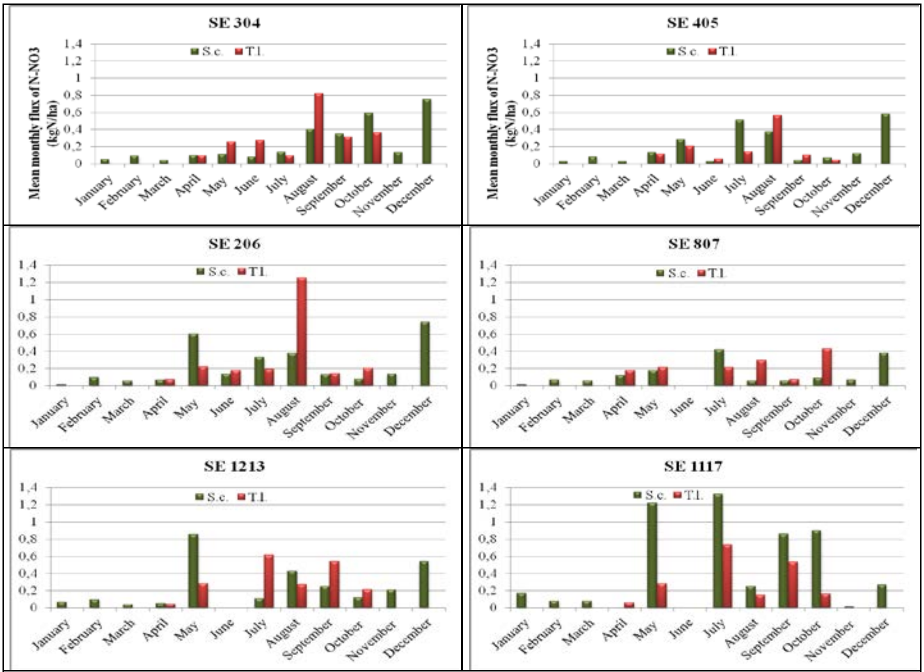

Fig. 2. Monthly flux of N-NO_3^- deposition under the canopy (S.c.) and open field (T.l.), kgN/ha

In the active period of vegetation we see cases where the amount of N-NO_3^- deposition of open field exceeds the values recorded in the canopy (Fig. 2) as a result of absorption of N-NO_3^- ions in the canopy. Average values flow of N-NO_3^- registered under the canopy are significantly higher than the values recorded in the open field only where SE 1117. Probably in this forest ecosystem the nitrate dry deposits are relatively high and even some depositions are taken over irreversible in canopy however the deposits in the canopy exceeds the flow in the open field.

Fluxes of N-NH_4^+. The deposition of ammonium, largely manifested panel of deposition of N-NO_3^-, especially, the ecosystems in the center of the country recorded higher fluxes of N-NH_4^+ to ecosystems located in the north of the country. Comparing the ion fluxes of N-NH_4^+ with N-NO_3^-, determined under the canopy, we find that in studied forest ecosystems the fluxes of N-NH_4^+ are an average of 2.5 times higher than those of N-NO_3^-. The results obtained clearly demonstrate the dominance of N-NH_4^+ ion to N-NO_3^- ion in atmospheric deposition, results observed in research conducted in over 500 intensive monitoring plots for Europe (Lorentz, 2012). Also, as in the case of N-NO_3^-, as mentioned in the literature, the throughfall deposition of N-NH_4^+ (Fig. 3) are controlled the presence and age the leaves. Thus, we observe that in most cases, the fluxes of N-NH_4^+ is the high in May, when the leaves are young and consumption takes place at the high nutrient, then the exchange of substances with the environment and gradually decreases until reaching maturity leaves.

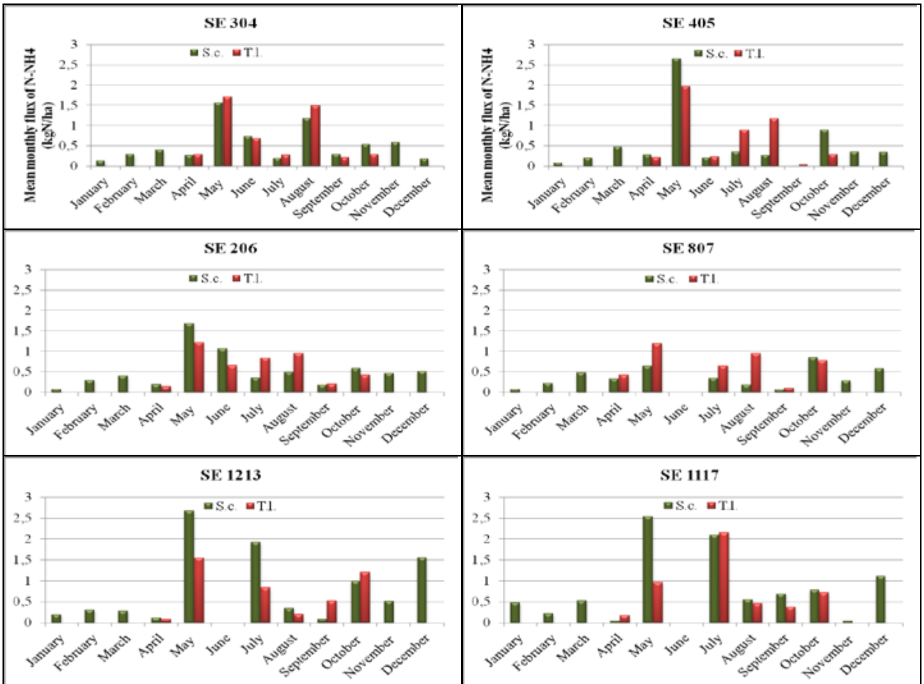

Fig. 3. Monthly flux of N-NH_4^+ deposition under the canopy (S.c.) and open field (T.l.), kgN/ha

The ratio of mineral ion fluxes registered under the canopy of forest and open field is known as loading coefficient (CI). Canopy effect on total deposits of mineral ions in the forest ecosystem, estimated by calculating the loading coefficient which was comprised between 0.59 and 2.39 (Table 1). Both the NO_3^- as well as NH_4^+ records the lowest values of loading coefficient, often the less than one unit. Because nitrogen ions can be ”leaching” or chemical buffered of the exchange with the canopy, they depending on various the biotic and abiotic factors records an greater variability of ecosystems studied.

In forest stands dominated by *Quercus robur* (SE 807 and 304) have recorded the lowest values of CI. These values, under a unit, are an indicator of pollution of low intensity and insufficient reserves of nitrogen in respective ecosystems, also with individual peculiarities of influence of ecological factors. In forest stands dominated by *Quercus petraea* and *Fraxinus excelsior* (SE 1213 and 405) are recorded higher values of CI, indicating a reduced absorption of nitrogen compounds in the canopy, a phenomenon that can lead to acidification and the threat inferior floors forest ecosystems. The highest values of load factors with mineral ions were recorded in SE 1117 and 1213, indicating increased inputs of pollutants from anthropogenic sources. For SE 1117, which is located in the area of enhanced negative impact, exhaust emissions from transboundary and local sources: emissions from road transport - the route Chisinau - Tighina – Tiraspol (distance of the SE 1117 from these anthropogenic sources - 2 km), industrial areas Tighina (8 km), Tiraspol (20 km) and the Thermal Power Plant „Cuciurgan" (50 km).

Table 1. Loading coefficients of the canopy with mineral ions during the vegetation period

SE	Composition	Age (years)	Consistency	$N\text{-}NO_3^-$	$N\text{-}NH_4^+$
SE **304**	7ST2STR1MO	33	0.7	0.81	0.96
SE **405**	10FR	65	0.8	1.19	0.98
SE **206**	7GO1FR1CA1TE	75	0.8	0.77	1.03
SE **807**	10ST+CI	60	0.8	0.67	0.59
SE **1213**	6GO4FR	75	0.8	0.93	1.40
SE **1117**	10STP+SC	80	0.8	2.39	1.39
Average				**1.06**	**1.13**

Note: ST – *Quercus robur*, STR – *Quercus rubra*, STP – *Quercus pubescens*, GO – *Quercus petraea*, FR – *Fraxinus excelsior*, CA – *Carpinus betulus*, MO – *Picea abies*, CI – *Cerasuss avium*, TE – *Tilia tomentosa*, SC – *Robinia pseudoacacia*, ULC – *Ulmus campestris*.

An important factor in the taking the atmospheric inorganic nitrogen (NO_3^- + NH_4^+) by the canopy is the degree of the nitrogen supply of the soil. In the results, on the retention of inorganic nitrogen (NO_3^- + NH_4^+) we observe that the enhanced quantities were retained in ecosystems with soils low in nitrogen (Fig. 4), but this dependence is influenced by other biotic and abiotic factors. The forest ecosystems with a lower degree of soil nitrogen supply (SE 304, 1117, 807 and 1213) recorded a canopy loading enhanced with atmospheric nitrogen.

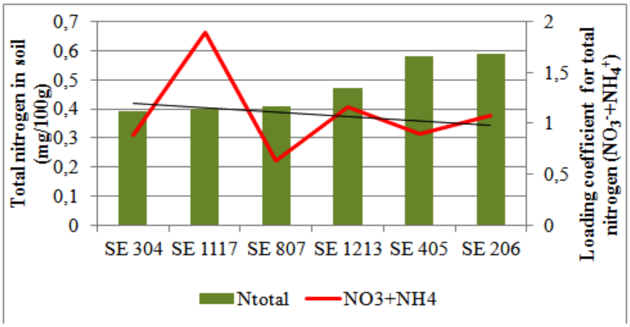

Fig. 4. Relationship between loading coefficients of the canopy with atmospheric nitrogen (NO_3^-+NH_4^+) and N_{total} content of the soil (0-10 cm)

CI of the canopy with atmospheric nitrogen can serve as an indicator of ecosystem nitrogen supply.

Depending on the location of studied forest ecosystems, we can say that in the north of the country (SE 304, 405, 206, 807, 612) have recorded lower depositions compared to ecosystems in the central region (SE 210, 1214, 1213 , 1117, 1315). The latter, recorded a higher pollutants flows are subject to a greater risk of air pollution.

The annual throughfall deposition of $N\text{-}NO_3^-$ and $N\text{-}NH_4^+$ in the Republic of Moldova are comparable to those recorded in the central and eastern – central Europe. Thus according to Fischer (2010) and Lorenz (2012), the throughfall deposition of $N\text{-}NO_3^-$ were within, in most cases, in *low deposition* category, such varying between *very low – high deposition* categories. The throughfall deposition of $N\text{-}NH_4^+$ falls into the category of *high deposition and very high deposition*, except for SE 807 with *medium deposition*. The total inorganic nitrogen deposition (NO_3^- + NH_4^+) falls into the category *low – medium deposition* (Table 2).

Table 2. Flux of atmospheric deposition under the canopy in Republic of Moldova in 2012, kg/ha/year

SE	Composition	**$N\text{-}NO_3^-$**	**$N\text{-}NH_4^+$**	**N_{total}**
SE 304	7ST2STR1MO	**2.83**	**6.36**	**9.19**
SE 405	10FR	**2.27**	**6.15**	**8.42**
SE 206	7GO1FR1CA1TE	**2.79**	**6.31**	**9.10**
SE 807	10ST+CI	**1.53**	**4.04**	**5.57**
SE 612	10ST+FR	**2.81**	**6.35**	**9.16**
SE 210	7FR2ST1ULC	**3.17**	**6.77**	**9.94**
SE 1214	10ST+FR	**4.16**	**9.15**	**13.31**
SE 1213	6GO4FR	**2.77**	**8.99**	**11.76**
SE 1117	10STP+SC	**5.20**	**9.10**	**14.30**
SE 1315	10SC	**3.60**	**6.56**	**10.16**
European scale for evaluation of intensity of atmospheric deposition, Lorentz (2012), Ficher (2010)				
Very low deposition		**0-1.8**	**0-1.6**	**0-5**
Low deposition		**1.8-3.2**	**1.6-3.3**	**5-10**
Medium deposition		**3.2-4.5**	**3.3-5.1**	**10-20**
High deposition		**4.5-6.3**	**5.1-7.5**	**20-25**
Very high deposition		**6.3-23.5**	**7.5-22.4**	**25-70**

After Bolea (2008) for deciduous trees the tolerance threshold to nitrogen is: *Quercus robur* – 30 g/kg; *Quercus petraea* – 30 g/kg, *Fraxinus excelsior* – 22 g/kg; *Carpinus detulus* – 25 g/kg. The studied ecosystems with *low – medium* deposition of total nitrogen (Table 2) will have a minor impact. Even in these conditions we assume a high impact on SE 1117, 1214 and 1213, where deposition of N_{total} are the highest. Thus, the ecosystems in the center of country, dominated by oak species, most representative forest tree species in the Republic of Moldova, in conditions of dendrology competition with tree species more resistant to nitrogen and more aggressive, may change and biodiversity can be replaced/dominated by respective tree species which are often not native.

4. CONCLUSIONS

The N-NO_3^- and N-NH_4^+ deposition under forest canopy have tended lower in vegetative rest period and the N-NH_4^+ flux is 1.7-3.8 times more than the N-NO_3^- flux, which clearly demonstrates the dominance of ammonium ion to nitrate ion in atmospheric deposition of Republic of Moldova. Taking over of atmospheric inorganic nitrogen by the canopy is determined by the presence and leaves age, and degree of soil nitrogen supply.

REFERENCES

1. Aber, J.D. et al. (1989), *Nitrogen saturation in northern forest ecosystems*, Bioscience 39 (6), 378-386.
2. Bolea, V., Chira, D. (2008), *Flora indicatoare a poluării*, Editura Silvică Bucureşti.
3. EMEP (1995), *Manual for sampling and chemical analysis*. EMEP/CCC-Report 1/95, Norwegian In. for Air Res., Kyeller, Norway.Fischer, R. et al. (2010), *Forest Condition in Europe, 2010 Technical Report of ICP Forests*, Work Report of the Institute for World Forestry 2010/1. ICP Forests, Hamburg.
4. ICP Forests (2010), *Manual on methods and criteria for harmonized sampling, assessment, monitoring and analysis of the effects of air pollution on forests,* UNECE ICP Forests Programme Co-ordinating Centre, Hamburg http://www.icp-forests.org/Manual.htm accesed on March, 26, 2013.
5. Lorenz, M. et al. (2012), *Technical Report of ICP Forests,* Work Report of the Thünen Institute for World Forestry 2012/1. Hamburg.
6. Sandu, M. et al, (2010), *Metode şi instrucţiuni privind controlul calităţii apelor*. “Ericon” SRL, Chişinău.
7. Iacoban, C. (2009), *Evaluarea poluării atmosferice în ecosisteme forestiere din România*, Editura Silvică, Bucureşti.
8. Office National des Forests (1995), *Bulletin technique, nr. 30,* Direction Technique et Commerciale, Fontainbleau.
9. http://www.meteo.md/newsait/god2012.htm accesed on September, 23, 2013.