Atmospheric deposition of mineral nitrogen and soil properties of forests in European Russia (Kostroma and Vologda regions)

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Abstract
In coniferous and mixed forests of Kostroma and Vologda regions of European Russia the sites (totally 39) were selected. In each site snow cores (March) and soil (August, soddy podzolic or Umbric Albeluvisols, 0-20 cm layer, litter excluded) samples were taken from a 10 m^2 plot by augering (corners and center). Bulk sample of snow and soil for each site was prepared. Ammonium (NH_4^+) and nitrate (NO_3^-) content in snow (melt water, atmospheric deposition) and soil was measured, mineral nitrogen (N_{min}) calculated as NH_4^++NO_3^-. In the soil sample contents of total organic carbon (C_{tot}), total nitrogen (N_{tot}), P, Al, Ca; pH, texture and microbiological properties: microbial biomass carbon (C_{mic}) and microbial respiration (MR) were determined. The ratios of MR / C_{mic} = $q$$CO_2$ and C_{mic} / C_{tot} were calculated. Atmospheric deposition of N_{min} was reached on average 0.9 kg N ha^{-1} yr^{-1} and 4.5 kg N ha^{-1} yr^{-1} for Kostroma and Vologda regions, respectively. For studied regions a significant ($p<0.05$) positive correlation (r) between N_{min} and Al, Ca, MR, C_{mic}, C_{mic} / C_{tot} was found. Soil values (C_{mic}, MR, C_{mic} / C_{tot}, Al, Ca) in Vologda region were significantly ($p<0.05$) higher those in Kostroma region.

Keywords: atmospheric deposition, mineral nitrogen, soil, forest, microbial biomass, microbial respiration

Introduction

During the last two centuries, agriculture and fossil fuels burning (anthropogenic activity) are resulted to the emission and atmospheric deposition of nitrogen compounds [nitric oxide (NO_x), nitrates (NO_3^-), ammonia (NH_3), ammonium (NH_4^+)]. Over the last 150 yrs. this deposition increased globally by 200% (Intergovernmental Panel…, 2001). Nitrogen compounds from atmosphere put into terrestrial ecosystems with wet (snow, rain) and dry (dust, mist, and etc.) depositions and estimated at present from 1 to 100 kg N ha^{-1} yr^{-1} (Galloway et al., 2008; Sutton et al., 2011; Jiang et al., 2012). Areas with high nitrogen deposition (≥20 kg N ha^{-1} yr^{-1}) are subject to more attention of researchers in Western Europe, USA, Canada and China (Aherne, Posch, 2013; Sutton et al., 2014) and, in particular, within the Project "The Convention on Transboundary Air Pollution long distances".

It was shown atmospheric nitrogen on average 2-3 times intensively compared to herbs and shrubs (Koptsik et al., 2008). Therefore, for forest ecosystems atmospheric nitrogen deposition might be a source of some environmental risk, which associated firstly with additional income of nitrogen to soil (MacDonald et al 2002; Manzoni et al, 2008). The consequence of such soil property changes could be an increase of primary plant production (de Vries et al., 2010; Bobbink et al., 2010) and respiration (mineralization) activity of soil microorganisms (Compton et al., 2004; Allison et al., 2008).

Nowadays atmospheric nitrogen deposition on European Russia is roughly, so we selected two areas with different deposition level. The aim of our study was focused on assessment of atmospheric nitrogen deposition and its influence on chemical and microbiological soil properties in forests of Kostroma and Vologda regions.

Materials and methods

Localization and sampling. The regions of Kostroma: 57°21'-59°36' N / 40°31'-47°05' E (few sources of atmospheric nitrogen: power stations, motor roads) and Vologda: 59°07'-61°02' N / 36°18'-39°57' E (plenty sources: production of ammonium fertilizer, timber, mechanical engineering, metallurgy, power stations, motor roads) were studied. Atmospheric deposition of nitrogen and some properties of sodddy podzolic soil (Umbric Albeluvisols, WRB) were studied in deciduous, coniferous and mixed forests (40-60 yrs. age) of these two regions. Dominants of woody trees in Kostroma region were represented by *Picea obovata Ledeb., Abies sibirica Ledeb., Betula pubescens Ehrh.*, in Vologda were *Calamagrostis arundinaceae, Trientalis europaea, Maianthemum bifolium, Pyrola rotundifolia, Dryopteris carthusiana.* The average annual air temperature is +3.0 and + 3.2°C, annual precipitation is 570 and 600 mm for Kostroma and Vologda regions, respectively.

The plots (10 m^2, 19 and 20 for Kostroma and Vologda regions, respectively) were selected at different distance from the main sources of atmospheric pollution (cities, factories, roads). In each plot the snow cores (center and corners) were collected by plastic sampler (diameter 5 cm, depth 50 cm) in March (the greatest snow accumulation). Bulk snow sample for each site was prepared, melted at 22°C and filtered through ash-free paper filter and fixed volume. It allow us to take into account "wet" and "dry" atmospheric nitrogen deposition and thereby to estimate the accumulation of these pollutants for a long time.

Soil samples (upper mineral layer, 0-20 cm) were taken (center and corners) in August, bulk sample for each site was prepared (totally 39), delivered in the lab, air-dried (22ºC), sieved (mesh 1 mm) and used further for chemical and microbiological analysis.

Methods. $N_{мин}$ content in melted water (December-January-February) was calculated using formula: $N'_{min} = N_{min} \times V$, where N'_{min} – nitrogen content in snow, kg N ha^{-1}; N_{min} – nitrogen in melted water, mg N L^{-1}, *V* – melted water per one site (100 cm^2), L. In order to calculate atmospheric nitrogen deposition for whole year (snow, rain) the N'_{min} value should be multiplied by 4. Additionally in soil samples the contents of total carbon (C_{tot}), total nitrogen (N_{tot}) (analyzer Elementar Vario EL III) and elements of Al, Ca, P (x-ray fluorescence analysis, Spectroscan Max GV) were measured. Soil texture (pyrophosphate method) and soil pH (soil : water=1 : 2.5) were determined.

Soil microbial biomass carbon (C_{mic}) was measured by substrate-induced respiration (SIR) method, based on the maximal initial response (CO_2 production) on adding easily oxidized and available substrate (glucose, 10 mg g^{-1}, 0.1 mL g^{-1} soil) (Anderson and Domsch, 1978; Ananyeva, 2011). The C_{mic} (μg C g^{-1}) was calculated using the following formula: C_{mic} = SIR (μL CO_2 g^{-1} h^{-1}) × 40.04 + 0.37 (Anderson and Domsch, 1978). Microbial respiration (MR) was measured in native soil samples (2 g, 24 h, 22°C, instead glucose the water added, 0.1 mL g^{-1} soil). The MR is expressed in μg CO_2-C g^{-1} soil h^{-1}. The ratio of MR to C_{mic} (microbial metabolic quotient, qCO_2, μg CO_2-C mg^{-1} C_{mic} h^{-1}) and C_{mic} / C_{total} ratio (in %) were calculated. Preparation of soil samples prior microbiological analysis included moistening up to 55% of water holding capacity and pre-incubation (soil ≥150 g, 22°C, 7 d, air exchange).

Soil chemical and microbiological properties were performed in three replicates. The results were calculated for dry soil (105°C, 8 h) and expressed as the mean ± standard deviation. Significance of difference ($p<0.05$) of chemical and microbiological properties between two regions was tested by t-test. Relationship between atmospheric nitrogen deposition and soil properties was analyzed through Pearson's correlation coefficient. All experimental data were statistically processed and visualized (dot chart, box-plot, scatter plot) using R 3.2.4 software (http://www.r-project.org/)

Results and discussion

Atmospheric NH_4^+ *deposition* was ranged from 0.1 to 0.9 kg N ha^{-1} yr^{-1} in Kostroma region, it was higher (from 0.6 to 7.9 kg N ha^{-1} yr^{-1}) in Vologda region (Fig. 1). However, atmospheric NO_3^- deposition$^-$ in Kostroma and Vologda regions was not significantly ($p<0.05$) differed (on average 0.6 and 0.7 kg N ha^{-1} yr^{-1}, respectively). Besides, in Kostroma region atmospheric NO_3^- deposition was on average 2 times higher than that NH_4^+, and opposite in Vologda region it was on average 5 times low. Atmospheric N_{min} deposition in Kostroma region was significantly ($p<0.05$) low (on average 0.9 kg N ha^{-1} yr^{-1}) compared to Vologda (on average 4.5 kg N ha^{-1} yr^{-1}).

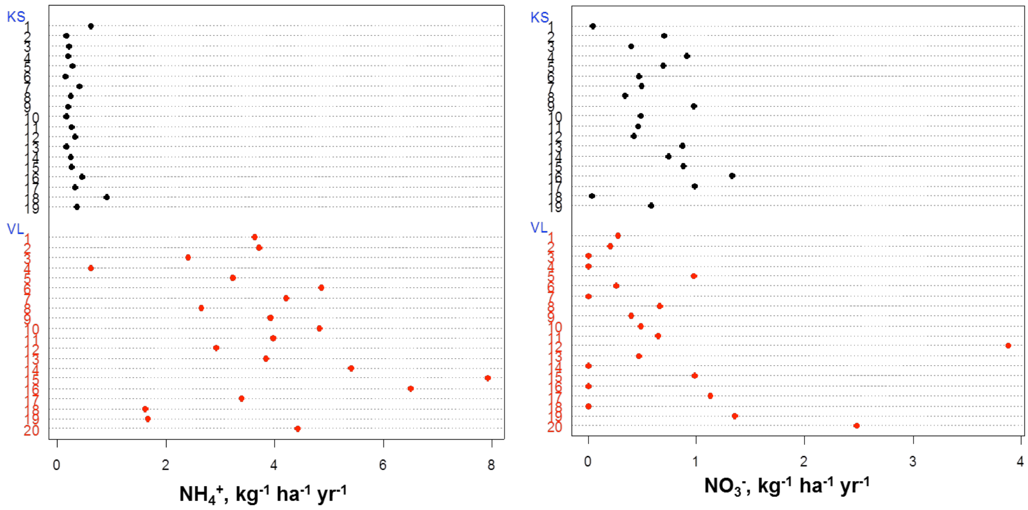

Figure 1. Dot chart of atmospheric ammonium (NH_4^+) and nitrate (NO_3^-) deposition for forest ecosystems of Kostroma (KS, 1-19 sites) and Vologda (VL, 1-20 sites) regions

Our previous research shown that atmospheric N_{min} deposition in forest ecosystems of Moscow region was varied from 4 to 11 kg N ha^{-1} yr^{-1}, on average 4.5 kg N ha^{-1} yr^{-1} (Averkieva, Ivashchenko, 2015). Atmospheric N_{min} deposition was ranged 5-10 and 10-18 kg N ha^{-1} yr^{-1} for forests and industrial centers, respectively, of Croatia (1996-2008) (Alebic-Juretic, 2014), it was reached on average 0.6 and 9 kg N ha^{-1} yr^{-1}, respectively, in England and China (Cape et al., 2012; Jiang, 2013). Atmospheric N_{min} deposition for 200 observation areas (23 countries of Western Europe) was reached on average 14 kg N ha^{-1} yr^{-1} (1.4-42 kg N ha^{-1} yr^{-1}), at that the authors consider the dependence of the fallout from urbanization (De Vries et al., 2010).

Soil properties (0-20 cm layer). Soil of studied regions was characterized by various texture (from light sandy loam to clay) and pH value, 3.3-6.5 units (Table 1). Content of soil C_{tot}, N_{tot}, NH_4^+, NO_3^-, P and C / N, Al / Ca ratios in Kostroma region were not significantly (p >0.05) differed compared to Vologda, however the contents of Al and Ca in Kostroma region were significantly (p <0.05) less than those in Vologda (on average 1.2 and 1.4 times, respectively).

Table 1. Soil chemical properties (0-20 cm layer, range / mean) of Kostroma and Vologda regions (number of sites). Values with different letters significantly (p<0.05) differ between regions (t-test)

Parameter	Kostroma (19)	Vologda (20)
N_{total}, %	0.04-0.43 / 0.20 **a**	0.05-0.56 / 0.24 **a**
C_{total}, %	0.60-6.30 / 2.98 **a**	0.93-10.47 / 3.73 **a**
C / N	13-19 / 15 **a**	12-26 / 16 **a**
$pH_{вод}$	3.3-6.5 / 5.1 **a**	3.5-5.6 / 5.2 **a**
Al, %	1.75-3.28 / 2.72 **b**	1.52-5.11 / 3.34 **a**
Ca, %	2.49-6.06 / 4.56 **b**	1.53-9.49 / 6.24 **a**
Al / Ca	5-10 / 6 **a**	3-12 / 6 **a**

mg kg^{-1}		
N-NH_4	0.60-18.20 / 6.50 **a**	0.46-29.44 / 6.72 **a**
N-NO_3	0-20.91 / 7.34 **a**	0.25-31.14 / 10.09 **a**
$N_{мин}$	2.10-31.88 / 13.84 **a**	4.21-37.87 / 16.81 **a**
P	95-522 / 302 **a**	35-532 / 326 **a**

Soil C_{mic} and MR values of studied regions were varied from 51 to 1032 μg C g^{-1} and from 0.2 to 4.3 μg CO_2-C g^{-1} h^{-1}, respectively (Fig. 2). In soil of Kostroma region these values were on average 240 μg C g^{-1} and 0.98 μg CO_2-C g^{-1} h^{-1}, respectively, it was 2.4 and 2.0 times significantly ($p < 0.05$) less compared to Vologda region. The soil qCO_2 was on average 4.44 and 3.74 μg CO_2-C mg^{-1} C_{mic} h^{-1} for Kostroma and Vologda regions, respectively. The C_{mic} / C_{total} ratio varied from 0.4 to 1.6% and from 0.9 to 2.5% in Kostroma and Vologda regions, respectively, it was on average (0.86 and 1.6%, respectively) significantly ($p < 0.05$) differed for Kostroma and Vologda regions.

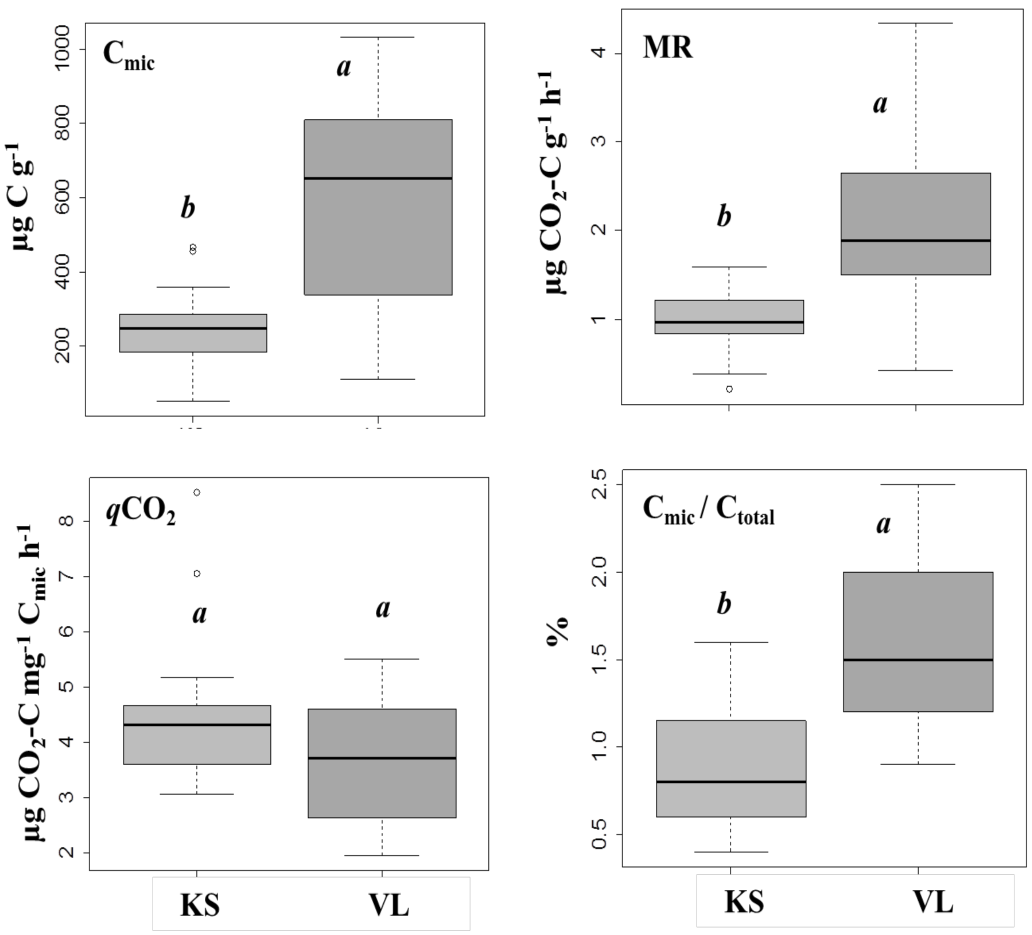

Figure 2. Soil microbial biomass carbon (C_{mic}), microbial respiration rate (MR), microbial metabolic quotient (qCO_2) and C_{mic} / C_{total} ratio in soils (0-20 cm) of Kostroma (KS) and Vologda (VL) regions. Values with different letters significantly ($p < 0.05$) differ between regions (t-test)

Box-plot: median; interquartile range, IQR (difference between the third, Q_3, and the first, Q_1, quartiles); lower whisker is 1.5 IQR-Q_1, upper whisker is 1.5 IQR+Q_3; outliers (circle) are values more and less upper and lower whiskers, respectively

Atmospheric N_{min} deposition for two regions was significantly ($p < 0.05$), but not strongly, correlated with soil Al, Ca, C_{mic}, C_{mic} / C_{tot} (Figs. 3, 4). Found that soil pH decreasing resulted atmospheric N_{min} deposition might be caused the release and subsequent leaching Al and Ca from silicate minerals (Dise, 1995; MacDonald et al., 2002). Moreover, atmospheric N_{min} deposition (≤10 kg N ha^{-1} yr^{-1}) was not be able to leach nitrates from soil, even in sandy soil (Neuvonen, 1990), and when it was ≥20 kg N ha^{-1} yr^{-1} this process was accelerated (Gundersen et al., 2006).

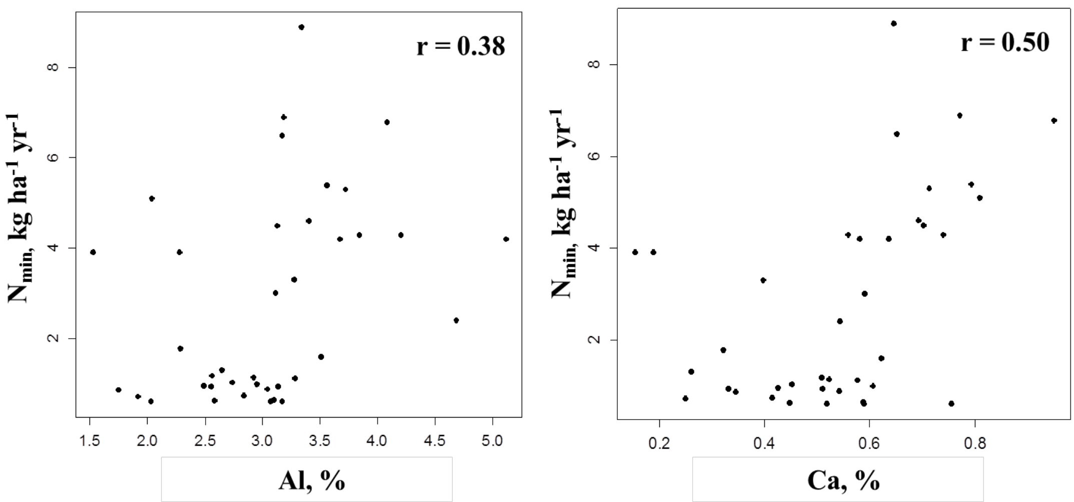

Figure 3. Relationship between atmospheric mineral nitrogen deposition (N_{min}) and soil (0-20 cm) chemical properties (Al, Ca) of Kostroma and Vologda regions, 39 sites (r is Pearson correlation coefficient, $p<0.05$)

An impact of atmospheric nitrogen deposition on soil microbial community functioning remains unclear, although additional nitrogen income in soil might be affected “directly” or “indirectly”. “Directly” impact of nitrogen might be considered as nutrition element for soil microbial biomass. “Indirectly” impact may be related to increasing forest primary production (Vitousek, Howarth, 1991; Magill et al., 2004) and changes of soil chemical properties: pH decreasing, C availability, Mg- or Ca-limitation and Al-toxicity (Compton et al., 2004; Treseder, 2008; Hu et al., 2010). Some authors shown that addition of N_{min} to forest soils might be led to decrease soil microbial biomass and its respiration (Lee, Jose, 2003; Bowden et al., 2004; Compton et al., 2004; Frey et al., 2014), on the contrary, others authors found some increase of these parameters (Gallardo and Schlesinger, 1994). Moreover, there is an information that atmospheric N_{min} deposition was not effected on soil microbiological properties (biomass, microbial respiration) of forest ecosystems (Nohrstedt, Börjesson, 1998; Brenner et al., 2005). We found the significant ($p < 0.05$) positive correlation ($r=0.61$) between atmospheric N_{min} deposition and soil C_{mic} / C_{tot} ratio. It was found that increase of C_{mic} / C_{org} or C_{mic} / C_{tot} ratios (so-called index of C-availability) might be resulted to availability of soil C to microorganisms (Anderson, Domsch, 1986; Sparling, 1992). In our study the high atmospheric nitrogen deposition in forest ecosystems was increased soil C availability for soil microorganisms (increasing C_{mic} / C_{tot} ratio).

Conclusion

Atmospheric N_{min} deposition in Kostroma region was on average 0.9 kg N ha^{-1} yr^{-1}, it was 5 times less in Vologda region (on average 4.5 kg N ha^{-1} yr^{-1}). Umbric Albeluvisols C_{tot}, N_{tot}, N-NH_4^+, N-NO_3^-, N_{min}, P contents were not significantly differed between two studied regions. Soil microbiological (C_{mic}, MR, C_{mic} / C_{tot}) and chemical (Al, Ca) properties of Umbric Albeluvisols in Kostroma region were significantly less compared to Vologda region. It might indicated, on the one hand, a more "favorable" functioning of soil microbial community and, on the other hand, some silicate minerals destruction of soil in Vologda region.

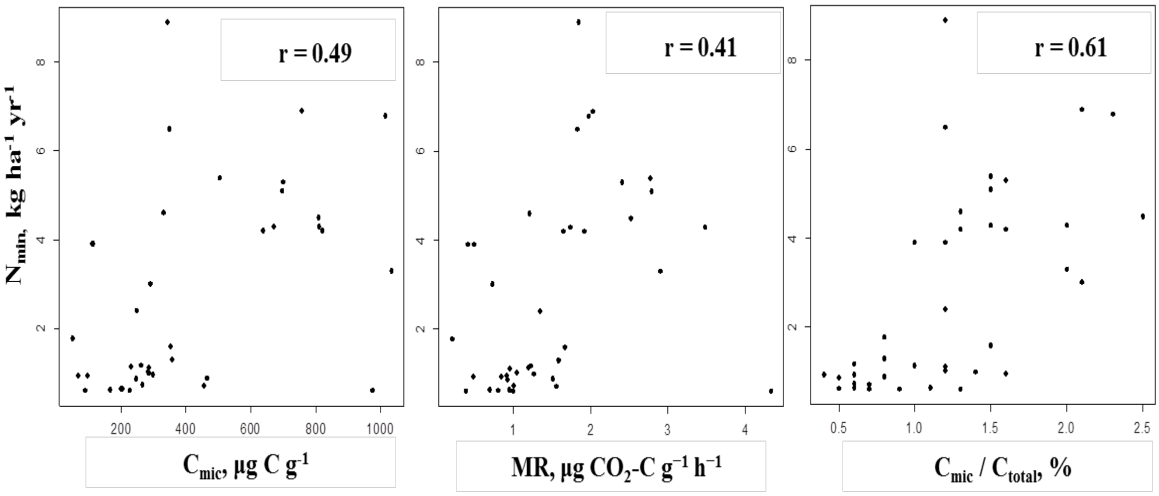

Figure 4. Relationship between atmospheric mineral nitrogen deposition (N_{min}) and soil (0-20 cm) microbial biomass carbon (C_{mic}), microbial respiration (MR), C_{mic} / C_{total} ratio of Kostroma and Vologda regions, 39 sites (r is Pearson correlation coefficient, $p<0.05$)

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