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Recent changes in the oxidized to reduced nitrogen ratio in atmospheric precipitation

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HIGHLIGHTS

- The multiyear study of inorganic nitrogen in atmospheric precipitation is presented.
- Urban vs. rural area about 30 km distant from each other are compared.
- The growing share of reduced nitrogen is becoming more common.
- Organic nitrogen accounts for 5–30% of total nitrogen.
- Factors affecting nitrogen species concentration are investigated.

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ABSTRACT

In this study, the characteristics of precipitation in terms of various nitrogen forms (NO_3^-, NO_2^-, NH_4^+, $N_{organic}$, N_{total}) is presented. The samples were collected in the areas of different anthropogenic pressure (urban area vs. ecologically protected woodland area, ~30 km distant from each other; Wielkopolska region, Poland). Based on the N_{ox} and N_{red} emission profiles (N_{ox}/N_{red} ratio), temporal and spatial comparison was carried out. For both sites, during a decade of observation, more than 60% of samples had higher contribution of $N\text{-}NH_4^+$ than $N\text{-}NO_3^-$, the amount of $N\text{-}NO_2^-$ was negligible, and organic nitrogen amounted to 30% of total nitrogen content which varied up to 16 mg/l. The precipitation events w ith high concentration of nitrogen species were investigated in terms of possible local and remote sources of nitrogen (synoptic meteorology), to indicate the areas which can act as potential sources of N-compounds. Based on the chemometric analysis, it was found that N_{red} implies N_{ox} and vice versa, due to interactions between them in the atmosphere. Taking into account the analysis of precipitation occurring simultaneously in both locations (about 50% of all rainfall episodes), it was observed that such factor as anthropogenic pressure differentiates but does not determine the chemical composition of precipitation in the investigated areas (urban vs. woodland area; distance of ~30 km). Thermodynamics of the atmosphere had a significant impact on concentrations of $N\text{-}NO_3^-$ and $N\text{-}NH_4^+$ in precipitation, as well as the circulation of air masses and remote N sources responsible for transboundary inflow of pollutants.

1. Introduction

It is widely recognized that growing anthropogenic activity has enhanced the emission of reactive nitrogen compounds to the atmosphere and their deposition to the world's ecosystems during last few decades (Galloway et al., 2004; Fagerli and Aas, 2008; Hertel et al., 2012; Reis et al., 2012; Jones et al., 2014). Therefore, a number of regulations about limiting the emission of N-compounds have been introduced, e.g. The Nitrates Directive (1991) and Gothenburg Protocol to Abate Acidification, Eutrophication and Ground-level Ozone (1999). As a result, the improvement of some ecosystems, based on the already defined guidelines, has been observed (Van Grinsven et al., 2013; Vet et al., 2014; Lawrence et al., 2016). Simultaneously, another type of environmental problems have occurred. Selective restrictions concerning N-compounds, e.g. NO_x, have led to significant changes in N_{ox}/N_{red} emission profiles (Du et al., 2014; Beyn et al., 2014; Simpson et al., 2014; Van Grinsven et al., 2013, 2015). The growing share of reduced nitrogen in the atmosphere is becoming increasingly more common (EMEP Assessment Report, 2004). The possible

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consequences marked as changes in the redox balance, pH range, bioavailability of different species, etc. can become a serious problem due to the contrast physico-chemical properties of N_{red}- and N_{ox}-compounds, and interactions between these chemicals (Bessagnet et al., 2014; Bloom, 2015; Thomas et al., 2015; Johnson and Goldblatt, 2015; Van den Berg et al., 2016, Li et al., 2016). Hazardous effects of reduced nitrogen on the environment have been widely investigated (Erisman et al., 2007), i.e.: influence of N_{red} deposition on ecosystem condition (Krupa, 2003; Liu et al., 2013), vegetation (Chiwa et al., 2016), biodiversity shifts (Bobbink et al., 2010,Bleeker et al., 2011), soil quality (Fenn et al., 1998; Mulder et al., 2015), eutrophication (Whitall et al., 2003) and impacts related to N_{ox} (Sutton et al., 2011). The increase of N_{red} is a disturbing phenomenon, both to terrestrial and aquatic ecosystems already affected by N overloading, acceleration of N-cycle, eutrophication, and loss of biodiversity (Krupa, 2003; Bobbink et al., 2010; Galloway et al., 2008; Erisman et al., 2007, 2013; Shibata et al., 2015; Thomas et al., 2015; Li et al., 2016).

It should be remembered that the environmental response for changes is always related to the whole ecosystem, so detailed observation and interdisciplinary research programs should be applied for environment investigation and protection (Wright et al., 2005; Battarbee et al., 2014; Bobbink and Hicks, 2014; Verstraeten et al., 2016).

The objective of this study was to present chemical characteristics of precipitation in terms of various forms of nitrogen (NO_3^-, NO_2^-, NH_4^+, $N_{organic}$, N_{total}), over a 11-year period of observations in the areas subjected to different anthropogenic pressure (urban agglomeration vs. protected area of the national park). The hypothesis of changes in the deposition profile of N compounds was examined, as well as factors affecting nitrogen distribution in the atmosphere and their environmental significance.

2. Study area and methodology

The study was carried out in a period from 2004 to 2014, at two sampling sites located in the Wielkopolska region, western Poland: (1) POZ (N 52°25′10″, E 16°52′50″) – in the area of Poznan city (about 600,000 inhabitants), and (2) WNP (N 52°15′56″ E 16°48′6″) – at the Jeziory Ecological Station of the Adam Mickiewicz University in Poznań, within the protected woodland area of the Wielkopolski National Park. These locations are approximately 30 km from each other, in the S-N direction, and differ significantly in the anthropogenic pressure. The urban sampling point is affected by transport, low level emission from domestic heating and industrial pollution emitters distributed both near and far from the sampling point. The sampling point located in the WPN is a forest clearing, which is surrounded by extensive patches of woodland.

The annual sum of precipitation ranged from about 400 to 550 mm in Poznan, and from about 430 to 660 mm in the Wielkopolski National Park, however in the city, annual sum of rainfall was always lower (about 10–30%) than in woodland area.

Bulk precipitation samples were collected on a daily basis. Precipitation amount was measured manually with the use of a Hellman rain gauge. Each sample was filtered (pore diameter of 0.45 μm) and then analyzed for NO_2^-, NO_3^-, NH_4^+ (ion chromatograph Dionex DX120, with conductivity detection) as soon as possible (within a few to dozen of hours after the sampling). Samples were stored in +4 °C, in darkness, until analysis. For the cation analysis, an IonPac CS12A analytical column and 20 mM MSA mobile phase were used, whereas for the anion analysis, an IonPac AS14A and 3.5 mM Na_2CO_3/1 mM $NaHCO_3$ were used, respectively. Concentration of total nitrogen (TN) in aliquots of rainwater samples was determined by high temperature combustion (HTC), using a Shimadzu TOC-L equipped with TNM-L TN unit (Shimadzu, Japan). The solutions for TN determination were prepared from reagent grade potassium nitrate. The content of N organic form was calculated as the difference between N_{total} and the sum of N_{ox} and N_{red} converted to meq N per liter unit. The limit of detection for TN analysis was 0.05 mg/l, and for NO_2^-, NO_3^- and NH_4^+ - 0.02 mg/l, 0.01 mg/l, and 0.02 mg/l, respectively. Quality Control and Quality Assurance procedures were used both during sampling and during chemical analysis. In order to ensure the accuracy of analyses, a certified reference material CRM - RAIN 97 (National Water Research Institute, Canada) and ERM - CA 408 (European Reference Material, Belgium) were used with satisfactory results. For all measured values, the relative standard deviation was below ±10% ($\alpha < 0.05$), and therefore the RSD value was assumed as negligible.

For several precipitation events, the analysis of synoptic meteorology was carried out for the dates of these events and for the preceding days. Synoptic maps as of 00.00 UTC (Daily Meteorological Bulletins, 2007, 2008), data from the National Centers for Environmental Prediction (NCEP) - National Center for Atmospheric Research (NCAR) reanalysis (Kalnay et al., 1996), and the NOAA HYSPLIT model (http://ready.arl.noaa.gov/HYSPLIT.php) were used. The analysis of air mass trajectories at the three altitudes (500, 3000, and 8000 m) provided significant input to the information obtained from synoptic maps and made it possible to identify probable areas of pollution sources.

The chemometrics (Pearson Correlation Analysis, Time Series Analysis - TS, Analysis of Variance - Anova, Principal Component Analysis - PCA) was applied to reveal “hidden” relations between nitrogen species and conditions in the sphere of formation and development of precipitation. These statistical analyses allowed us to assess the quality of atmospheric precipitation in the urban area and ecologically protected area.

3. Results and discussion

3.1. Background – emission of N compounds in Europe

In Europe, after peak emission of N-compounds (N_{ox}, N_{red}) to the atmosphere in the 80s of the last century, a sharp decrease was observed in the 90s, followed by a significant slowdown after the year 2000 (EMEP Report, 2015). In the last decade, the emission of NO_2 showed a slight downward trend or remained at the similar level, depending on a country, whereas the emission of ammonia decreased, but less, remained at a relatively stable level, or increased, depending on a country (Table 1).

If the values of NO_2 and NH_3 emissions were converted into pure component emissions, i.e. N-NO_2 and N-NH_3, it could be observed that the N_{ox}/N_{red} ratio for the total emission from the country area have been decreasing in recent years. For some countries, this ratio is below 1, which means that more nitrogen in the reduced form is released into the atmosphere (Fig. 1).

The type of N-compounds emitted into the environment is strictly related to the type of anthropogenic activity, which has been widely described in many studies (Erisman et al., 2007, Van Grinsven et al., 2015, Johnson and Goldblatt, 2015; Behera et al., 2013; Shibata et al., 2015; INI webpage). Despite dynamic changes that occur in the industrial sectors (transport, energy, etc.) responsible for emissions of oxidized nitrogen forms, the absence of significant changes in the amount of gases being emitted into the atmosphere, including NO_x and particulates, can be observed. The main reason for that is the lack of substantial changes in the structure of energy sources usage (World Data Bank webpage). In many European countries, the primary source of energy is coal, e.g. 40.1% in Poland in 2012 (CIEP Report, 2014). On the other hand, the population growth that drives the demand for food products (meat and grain) increases the development in agro-food and livestock