



## **Atmospheric nitrogen depositions in a highly human impacted area.**

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Human perturbation of the nitrogen cycle represents one of the major actions that allowed the human population to expand and grow in the twentieth century. Nowadays, the environmental consequences of excessive reactive nitrogen include atmospheric pollution, nutrition unbalance in aquatic and terrestrial ecosystems, surface and groundwater quality degradation.

Nitrogen can enter the water cycle through atmospheric depositions on ground and water surfaces, leakages from point and diffuse sources (i.e., sewage treatment plants or sewage systems, fertilizer and manure applications), and erosion processes affecting nitrogen rich soils. However, integrating all nitrogen forms, processes and scales is still a major challenge for the understanding and the management of the nitrogen cycle.

This study aims to evaluate the impacts of atmospheric pollution on terrestrial and groundwater ecosystems, focusing on nitrogen compounds. A monitoring experiment was set up to collect wet atmospheric depositions in a human impacted area with multiple land uses, representing different emission sources (i.e., extended urban areas with residential buildings and industrial activities, high traffic roads and agricultural activities).

Wet deposition is measured at 17 sites, homogeneously distributed in the western sector of Lombardy Region (northern Italy), in the surroundings of Milan. Rainfall collection started in February 2017. By the end of 2018, 15 precipitation events were monitored and 144 rainwater samples were collected, involving an average of 10 sites per event. After collection, samples were analysed for pH, electric conductivity, ammonium, nitrate, nitrite, major cations (calcium, magnesium, sodium, potassium), and major anions (sulphate, chloride, fluoride). Rainfall chemistry was compared to atmospheric pollution, derived from air quality data from ground-based stations and pollutant emissions data provided by the Regional Environmental Agency (ARPA Lombardia).

Results show a direct relationship between high levels of air pollutants (e.g.,  $\text{NO}_2$ ,  $\text{SO}_2$ ,  $\text{NH}_3$ ) and relatively high contaminant concentrations (e.g.,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ ) in rainwater samples. Consequently, rainfalls sampled in autumn-winter or during the fertilisation period (April-May) show higher contaminant concentrations respect to those sampled in spring-summer or before the fertilisation period. In addition, the chemical composition of rainfall samples reflects local meteorological conditions and local emission sources. In fact, samples collected in urban or agricultural areas show higher concentrations of specific chemical species (e.g.,  $\text{Ca}^{2+}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ) in comparison to those collected in rural areas or close to natural environments (i.e., Alps and Como Lake). Such results allowed estimating wet nitrogen depositions, as nitrate and ammonia, in the study area. The average concentrations of nitrate and ammonia in precipitation during the monitoring period were  $5 \text{ mg L}^{-1}$  and  $2.5 \text{ mg L}^{-1}$ , respectively. Consequently, given an average annual precipitation of about 800 mm for the period 2016-2018, a wet deposition of inorganic nitrogen equal to  $9 \text{ kg } (\text{NO}_3^- \text{-N}) \text{ ha}^{-1} \text{ yr}^{-1}$  and  $12.4 \text{ kg } (\text{NH}_4^+ \text{-N}) \text{ ha}^{-1} \text{ yr}^{-1}$  was estimated. As leaching of nitrogen compounds from soils generally increases at nitrogen deposition rates higher than  $10 \text{ kg ha}^{-1} \text{ yr}^{-1}$ , this study suggests that the nitrogen atmospheric input to soils should not be neglected when evaluating the impacts of nitrogen sources to terrestrial and aquatic ecosystems.