Rates of atmospheric nitrogen deposition to agricultural and natural lands within the Lower Dniester catchment

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SUMMARY

Purpose of the work was to quantify and compare the rates of atmospheric bulk nitrogen (N) deposition to the natural wetland and two managed areas within the Lower Dniester catchment in 2011-2019. Methodology. To collect atmospheric bulk (dry and wet) deposition we used custom-made accumulative samplers. We determined dissolved inorganic N (DIN) compounds in samples with ion chromatography and water soluble and total N (TN) with routine wet chemistry. Results and Conclusions. Croplands in the Lower Dniester basin have been recognized as a highly N polluted areas being both local sink and potential source of TN acting as a local threat for nearby natural and semi-natural ecosystems. Mean annual TN depositions have been quantified to be 20.1±0.3, 14.1±0.1 and 10.0±0.3 kgN/ha for cropland, garden and natural wetland sites respectively. We have found significant increase of NH_4^+ and decreased of NO_3^- in DIN deposition with overall decrease and stabilization of DIN in 2018-2019. Substantial contribution of 'previously unaccounted' TON (66-72%) to TN was assumed to be region-specific. Besides, ca. 52-68% of water soluble TN had an organic origin and could be considered as additional easy available N source for both terrestrial and aquatic ecosystems within the study region.

Introduction

Increased reactive N (N) emissions from the intensified anthropogenic activities (e.g. fossil fuel combustion, fertilizer application, livestock husbandry) having a strong impact on climate (Fowler et al., 2013) lead to excessive N deposition affecting air quality, biogeochemical N cycling, ecosystem function and services, *inter alia* harming human health, impacting soil and water quality, reducing biodiversity and influencing the greenhouse gas balance (Sutton et al., 2011; Stevens et al., 2015). It is also known that N deposition can be considered as an important nutrient source for natural ecosystems, particularly in N-load regions (Sparks, 2009; Medinets et al., 2016b, 2019). Moreover, recently the significance of 'often unaccounted' organic N deposition and its large contribution to the total N deposition has been revealed (Cornell et al., 2003, 2011; Medinets and Medinets, 2012; Medinets et al., 2014). Western Europe with mean annual deposition rate of *ca.* 24.1 kg N ha^{-1} yr^{-1} is still considered as one of the global hotspots (Vet et al., 2014), despite of a pronounced decrease and stabilization of atmospheric deposition across Europe compared to the 1980s owing to the EU legislation implementation aimed at a substantial reduction of reactive N emissions (Billen et al., 2013). Stevens et al. (2010) reported that N deposition within Europe varied in a range of 5-44 kg N ha^{-1} yr^{-1}, with the highest magnitudes in areas with intensive agriculture production. Critical N load of >15-20 kg N ha^{-1} yr^{-1} was reported for temperate grasslands and even lower threshold (>10-15 kg N ha^{-1} yr^{-1}) was found for lichens and mosses (see Bobbink et al., 2010). Bobbink and colleagues have highlighted the main effects of excessive N loads to the ecosystems, *inter alia* direct toxicity of N gases and aerosols, N accumulation and acidification.

The aim of this study was to quantify and compare the rates of atmospheric N deposition to natural and two managed areas within the Lower Dniester catchment in 2011-2019.

Methods

The study has been performed in the Lower Dniester catchment (Odesa region, Ukraine). We used custom-made accumulative samplers (see Medinets and Medinets, 2012; Medinets, 2014) to collect atmospheric bulk (dry and wet) deposition according to the recommendation of EMEP (2001). The samples have been collected fortnightly or monthly in three sites (Fig. 1). The natural wetland site (DN2) was located in the protected area ~20 m far from the river and operated over 2011-2014 only.

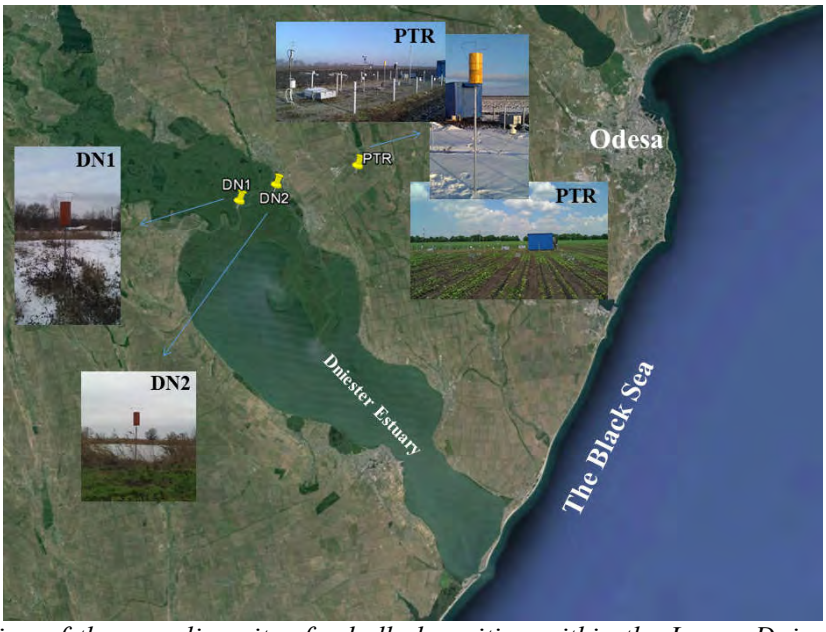

Figure 1 *Location of the sampling sites for bulk deposition within the Lower Dniester basin [DN1: garden site; DN2: natural wetland site; PTR: cropland site]*

The garden site (DN1) was situated within a private household territory ~50 m from the river, while the cropland site (PTR; see Medinets et al., 2016a) was located on the arable land at the distance of 7

km from the river; data for both managed sites covered the period of 2011-2019. Total N (TN) in unfiltered samples and water soluble total N (WSTN) in filtered (0.4 µm membrane) samples were determined using persulfate method (see Medinets, 2014). Contents of dissolved inorganic N (DIN) ions (NH_4^+, NO_3^- and NO_2^-) in the samples were determined using ionic chromatograph Metrohm IC 790 as described in Medinets and Medinets (2010, 2012). Water insoluble TN (WITN) was calculated as a difference between TN and WSTN. Water soluble organic N (WSON) was quantified as a difference between WSTN and DIN. Total organic N (TON) was roughly assessed as a difference between TN and DIN since it was presumed that WITN most probably presented by organic constituents, i.e. water insoluble organic N (WION).

Results and Discussion

We have observed similar temporal variation of TN deposition for all sites over the study period (Fig. 2). On average, 20.1±0.3 kg N ha^{-1} (range: 9.0-38.4) and 14.1±0.1 kg N ha^{-1} (range: 9.1-20.1) have been deposited to the cropland and garden sites in 2011-2019 respectively. In the meantime, the lowest annual mean TN deposition (10.0±0.3 kg N ha^{-1}) has been registered in the natural wetland, being 21-27% lower than those of the managed sites over 2011-2014 (operation period of the natural site). At all sites, the minimum of N was deposited during 2012. Meanwhile for garden and natural wetland (Fig. 2b, c) sites (located close to the river) the critical N loads (>15 kg N ha^{-1} yr^{-1}; Bobbink et al., 2010) received with deposition have been oftener registered during last 7 years of the study with the absolute maximum in 2019 (note: we assume the same pattern for the natural wetland site). The cropland site (located 7 km far from the river) has been found to be exposed to even higher N deposition loads (>20 kg N ha^{-1} yr^{-1}) in 2014 and since 2016; the absolute maximum of 38.4 kg N ha^{-1} yr^{-1} has been registered in 2019. No inter-annual dependence between annual sum of precipitation and annual TN have been found; however, we do not exclude possible relationship between the dissolved N compounds deposition and precipitation at monthly resolution (data not analysed here) as it was reported in the previous studies (Medinets and Medinets, 2012; Violaki et al., 2010; Song et al., 2017). Overall, annual rates obtained for the study sites have been in a range for Europe (5-44 kg N ha^{-1} yr^{-1}) reported by Stevens et al. (2010) and confirmed that intensity of N loading from the atmosphere to the corresponding area was closely associated with the presence and distance to local N pollution hotspots such as agricultural farms, human settlements, biomass running and industrial enterprises (Sutton et al., 2013; Song et al., 2017).

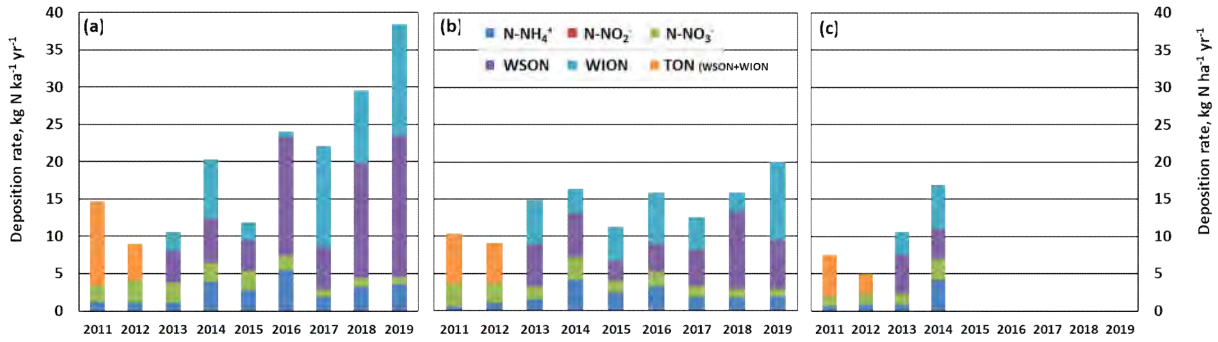

Figure 2 *Annual N deposition rates (by constituents) in cropland (a), garden (b) and natural wetland (c) sites within the Lower Dniester basin [WSON: water soluble organic N; WION: water insoluble organic N; TON: sum of WSON and WION, where those organic N fraction data were not available]*

Inter-annual DIN dynamics at study sites have not been coupled with TN trend, mainly due to a high contribution of TON (Fig.2). We have demonstrated that DIN varied significantly less between (variation coefficient (VC): 11%) and within the sites (VC: 31-34%) than TON. Mean annual DIN deposition ranged between 3.4-4.7 kg N ha^{-1} yr^{-1} across the study sites. At the same time, TON scavenging from the atmosphere had a similar pattern in the cropland and garden (and natural) sites but differed significantly in magnitudes (VC: 30%). We have concluded that DIN presented mainly by

ammonium and nitrates was likely a more stable parameter at the regional scale, while organic N appeared to be more site-specific. We have found a distinctive pattern ($p<0.01$) of steady increase of NH_4^+ and decrease of NO_3^- shares in DIN deposition over the study period for all sites. On average, ammonium share made 51-56% being increased *ca.* 2.4 times in the managed sites, while nitrate share declined 2.6-3.1 times over 9 years. Even a 4-year study (2011-2014) has shown 1.9-fold increase of NH_4^+ and 1.7-fold decrease of NO_3^- deposited onto the natural wetland. Moreover, decrease and stabilization of DIN deposition in the region have been found during 2018-2019.

Average contribution of TON to TN was 72.2±4.3% for cropland, 70.0±3.4% for garden and 66.1±4.0% for natural wetland sites over the study period, which was slightly higher than registered in the adjacent Black Sea area (Medinets and Medinets, 2012; Medinets, 2014). At the same time the WSON share in WSTN was 62.4±4.9% for cropland, 56.7±4.9% for garden and 52.6±7.6% for wetland, i.e. approximately twice higher than reported for Eastern Mediterranean (Violaki et al., 2010) and quadruple higher than reported for Chinese sites (Song et al., 2017). Such high ratios of organic fractions in N deposition might be explained by i) soil dust formation *via* wind-induced erosion of the high soil organic matter content Black soils typical for the study area (Medinets et al., 2016a), ii) impact of organic aerosols of marine origin due to closest location to the sea (Altieri et al., 2016), and iii) possibly region-specific biogeochemical condition favorable for organic compound emission to/ formation within atmosphere. Overall, the studied cropland received 53% more TON and only 16% more DIN than those of the garden site. This might be resulting from the intensive agricultural practice (fertilizer application, tillage) generating additional (machine-induced) soil dust formation containing urea, amines, macromolecules and humic-like substances (McKenzie et al., 2016).

Conclusions

We have shown that croplands in the Lower Dniester basin are recognized as a highly N polluted area being both local sink and potential source of TN acting as a local threat for the nearby natural and semi-natural ecosystems. Mean annual TN depositions have been quantified to be 20.1±0.3, 14.1±0.1 and 10.0±0.3 kg N ha^{-1} for cropland, garden and natural wetland sites respectively. We have found significant increase of reduced N and decrease of oxidized N ions during the study period with overall decline and stabilization of DIN deposition in 2018-2019. Contribution of TON (66-72%) to TN was dominant being likely region-specific. Besides, *ca.* 52-68% of water soluble TN had organic origin and can be considered as an additional easy available N source for most of organisms. Further long-term monitoring and targeted studies are urgently needed to confirm the significance and unveil the sources of high organic N content in atmospheric deposition within the Dniester basin.

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