SURPLUS OF NUTRIENTS IN THE DNIESTER DELTA: WHERE DOES IT COME FROM?

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Introduction

The Dniester is a transboundary river running through the territory of two countries, Republic of Moldova and Ukraine, where lots of agricultural, industrial and domestic activities take place within the river catchment, and then flowing into the Black Sea. Intensive use of the Dniester as a valuable resource results at unintentional and sometimes even intentional environmental pollution within its basin with consequences lasting far beyond. Alongside with spontaneous microbiological (e.g. malfunctioning of municipal wastewater treatment) and chemical (*e.g.* toxic substances, heavy metals) pollution, mainly associated with point sources, the regular nutrient (Nitrogen and Phosphorus) pollution coming from nearly all diffusion and point sources and increasing in time due to constant intensification of anthropogenic activities poses the major and rather complicated issue for many river catchments. As the first two pollution types (*i.e.* microbiological and chemical, mainly presented by point sources) may cause huge human health concerns, they have high priorities and noisy publicity once identified. Meanwhile nutrient pollution often has a time delay effect on the whole ecosystem, being the main driver of eutrophication and hypoxia [1, 2]. This often impacts wetland areas throughout the river flow and the river delta (*e.g.* the Dniester Estuary), where the flow decreases dramatically. Moreover, during floods most of Nitrogen (N) and Phosphorus (P) compounds previously accumulated in sediments of wetland areas are washed out and transported downstream with further accumulation mainly in the deltaic zone and/ or carried to the Black Sea [2]. Thereby, the identification of concrete pollution sources and main processes involved in nutrient transformations with the quantification of the rates of N and P that are coming in, stored and coming out within the river basin environment is the main challenge to understand the whole picture and develop recommendations for good management practice of these nutrients, as well as mitigation measures [3]. By the way, in the autumn of 2017 the UNEP-GEF 'Targeted Research for improving understanding of the Global Nitrogen Cycle towards the establishment of an International Nitrogen Management System (INMS)' project is planned to be started [4]. The aim of the INMS is to assess the co-benefits of an overall nitrogen approach addressing better management across the N cycle to improve Economy-Wide N Use Efficiency, whilst reducing surplus that would often be wasted as pollution. In the frameworks of the INMS, the Eastern Europe demonstration region will be presented mainly with the Dniester River basin [3, 4]. A transboundary character of the demo-region is an important aspect in establishing of the N management system according to the current EU directives [5, 6].

In this study we would like to draw your attention to some important aspects and consequences of N and P riverine and atmospheric inputs to the Dniester Delta ecosystem.

Materials and methods

Study site. All investigations described here were performed in the Lower Dniester basin on the administrative territory of Odessa Oblast (Ukraine) by Odessa National I. I. Mechnikov University. Locations of concrete sampling sites for appropriate type of study are specified below (Fig. 1).

Riverine input. As a primary data we used the results of regular hydrological observations and hydrochemical analyses of water samples, conducted fortnightly during 2010-2013 at three monitoring sites: DN1_w (close to Palanca village), DN2_w (close to Bilyaivka city) and DN3_w (close to Mayaki village) (Fig. 1) [2]. To estimate water runoff of the Dniester and Turunchuk rivers we used the data, kindly provided by the Ukrainian Hydro-Meteorological Center for the Moldavian stations of Nezavertailovca (F_TR) and Olăneşti (F_DN), which were received in the framework of the international data exchange process from the Hydro-Meteorological Service of Moldova. The methods of water sampling and hydrochemical analysis are described in this study [2]. Concentrations of total organic N (TON) or P (PON) were derived as the difference between total N (TN) or P (TP) and a sum of dissolved inorganic N (DIN) or P (DIP, in a form of phosphates) compounds [2].

Atmospheric input. Atmospheric bulk deposition samples have been collected monthly/ fortnightly in three sites: cropland (PTR), garden (DN1) and natural (DN2) (Fig. 1). To assess total N (TN) as well as

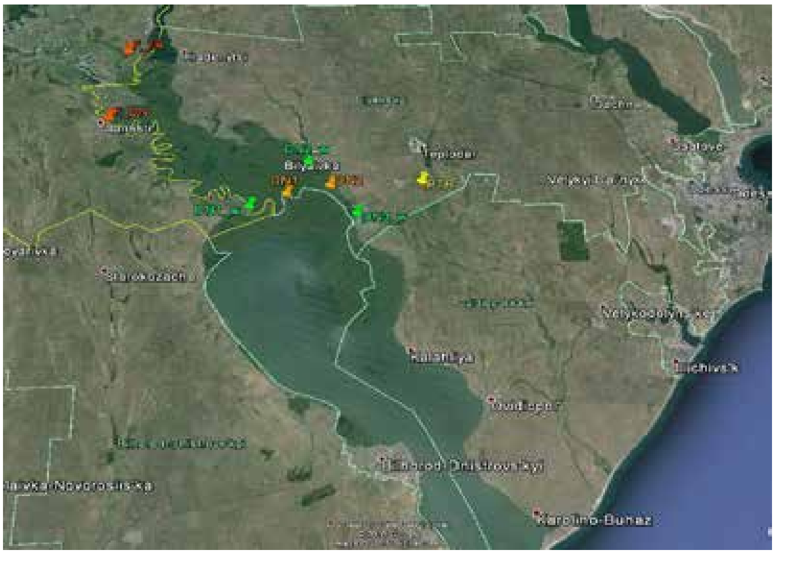


Fig. 1. The location of water mass discharge measurement stations (F_DN: Olăneşti, the Dniester River; F_TR: Nezavertailovca, the Turunchuk River), water sampling sites (DN1_w: Palanca, the Dniester River; DN2_w: Bilyaivka, the Turunchuk River; DN3_w: Mayaki, the Dniester River after confluence), atmospheric bulk deposition sites (DN1: garden; DN2: natural; PTR: cropland).

water soluble total N (WSTN) in bulk (monthly) deposition we used accumulative sampler [7, 8].

Total N in bulk deposition samples was determined using persulphate method [7, 8]. Contents of dissolved inorganic N (DIN) ions (ammonium, nitrate and nitrite) in samples were determined using ionic chromatograph Metrohm IC 790 [7, 8]. Total organic N (TON) can be roughly assessed as a difference between TN and DIN. It is suggested that TON consists of water soluble organic N (WSON) and water insoluble total N (WITN), which is presumably presented mostly by organic constituents [7, 8].

Results and Discussion

Transport of N and P with river water mass. Based on monthly data of water runoff at two stations Nezavertailovca (the Turunchuk River) and Olăneşti (the Dniester River) a total monthly runoff of the Dniester River to the Dniester Estuary has been assessed. It had been found that the annual river runoff varied substantially depending on intensity and duration of flood events [2]. An abnormal extremely high magnitude (14.15 $km^3\ y^{-1}$) was registered in 2010 mainly affected by huge flood in June – July, while over following-up 2011-2013 year the annual river runoff fluctuated in a narrow range of 6.25-9.10 $km^3\ y^{-1}$ (Fig. 2) [2]. On average the water runoff through the Turunchuk River (Nezavertailovca) was 1.5 higher than via the Dniester River (Olăneşti).

Taking into account abovementioned water runoff magnitudes the monthly N and P flow through three points (DN1_w, DN2_w and DN3_w) of sampling were estimated [2]. No seasonal variation was found, although maximal flows often registered during flooding over spring. The mean N and P flows to the Dniester Estuary (and then to the Black Sea) in 2010-2013 varied significantly and were estimated as 36.6±25.7 Gg N y^{-1} and 1.3±0.3 Gg P y^{-1} correspondingly (Fig. 3). Thus water mass contained nutrients in a ratio of N:P=28:1, *i.e.* the surplus of N was in a factor of 1.75 compared to the Redfield molar C:N:P=106:16:1 ratio [9]. Due to extreme flooding in 2010 the annual TN flow was around 2.8 times higher than in 2011 and 2013, and even 4-fold higher than in dry year of 2012. Unsurprisingly, the share of organic N constituent was larger (ca. 67%) in flooded 2010 compared to other studied years (range: 34-47%). The different pattern was observed for P constituents. We found that an increase of TP in 2010 was in a factor of 1.3-2.0 only comparing with other years. Interestingly, the flood events had a positive effect on the quantity of DIP rather than organic P constituents, thus decreasing a share of TOP in TP. Moreover, in 2013 TOP even prevailed over phosphates quantity, though the reason of this was unknown. It was shown that the Turunchuk River generally transferred 1.4 times more TN and phosphates (DIP) and even 1.6 times more TOP compared to the Dniester River before confluence with the Turunchuk [2]. That discrepancy regarding P compounds might be connected with high rates of water mass flow via the Turunchuk, as well as with volley discharges to the river from the Kuchurgansky Reservoir, the Dniester hydro-power plant and water pollution from anthropogenic activities (domestic, industrial and agricultural small/ medium enterprises) performed on its banks [2].

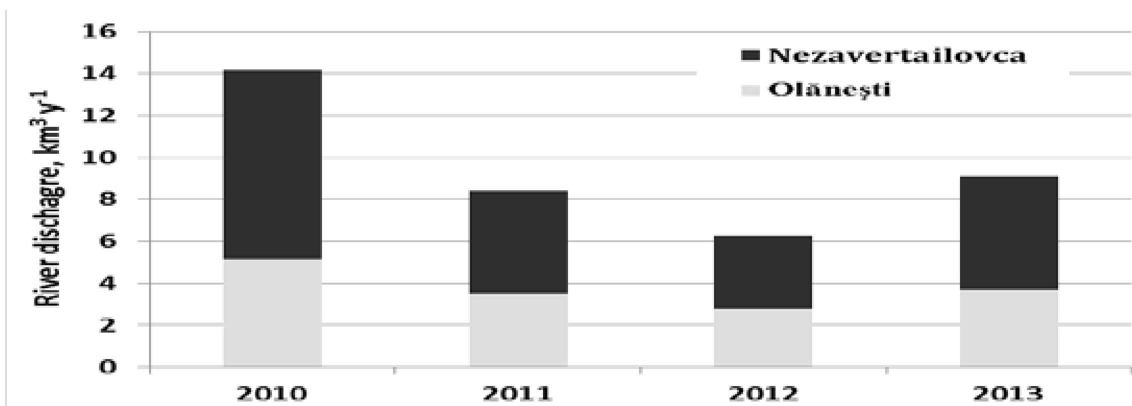
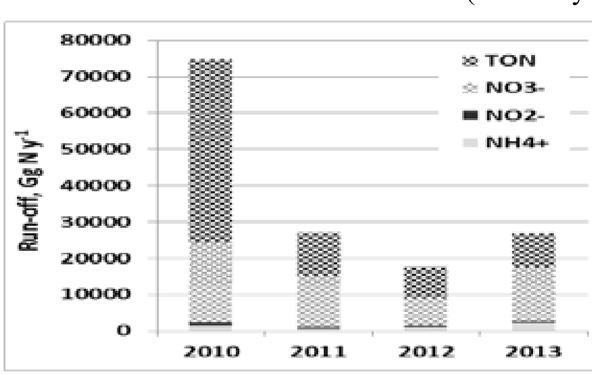


Fig. 2. The discharge of the Dniester River (near Olăneşti village), the Turunchuk River (near Nezavertailovca village) and the total estimated discharge of the Dniester River following the confluence with the Turunchuk (near Mayaki city).



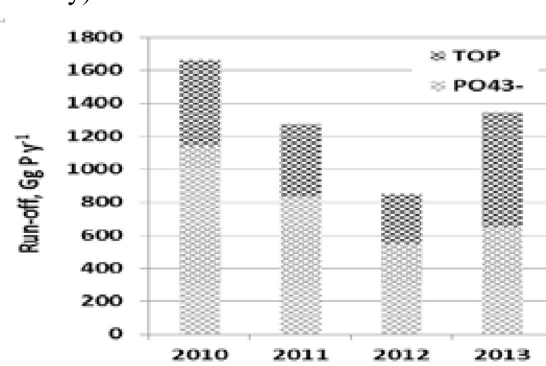


Fig. 3. Annual riverine run-off of TN and TP (by constituents) to the Dniester Estuary in 2010–2013 (adopted from Medinets et al., 2015 [2]).

Detailed studies for identification of local sources of nutrients into the area of the Turunchuk River between the Moldavian-Ukrainian border and Mayaki village are urgently needed [2, 3]. It was assessed that approximately 88% of TN and 90% of TP, entering the Dniester Estuary and then carried to the sea, had upstream origin (*i.e.* above sampling points near Palanca and Bilyaivka) [2]. It is suggested that significant part of N and P upstream may come from the territory of Moldova, i.e. areas under intensive agricultural and industrial activities. Nevertheless to confirm or contradict this assumption and localize sources of the main pollution with nutrients further long-term measurements of N and P concentration and water mass discharge are required. The rest (12% of TN and 10% of TP) were likely to have local origin, mainly as the result of surface run-off, and partially the side discharge of underground water from the Low Dniester catchment.

Atmospheric input. We found the same inter-annual pattern of TN deposition variation during study period of 2011-2013 for all sites (Fig. 4).

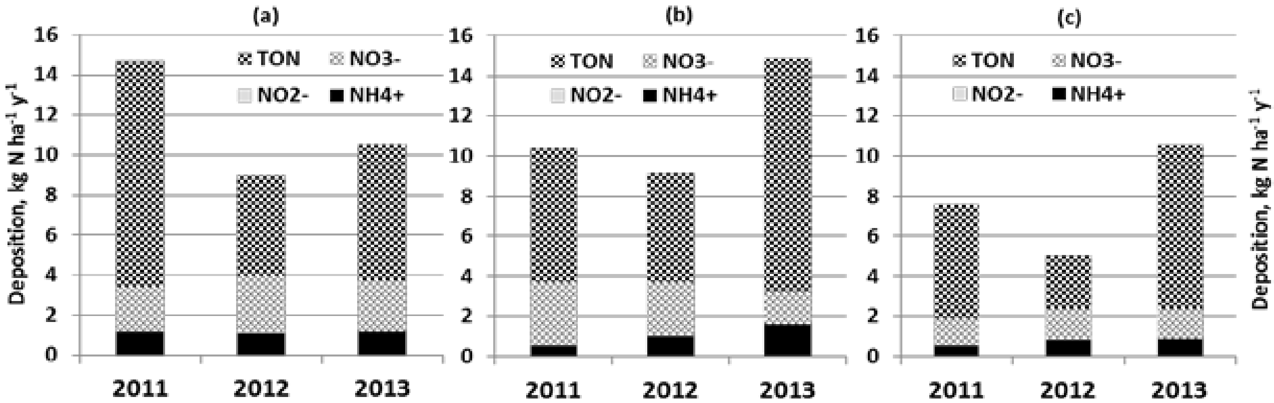


Fig. 4. Annual bulk N atmospheric deposition (by constituents) within the Dniester basin at cropland (a), garden (b) and natural (c) sites in 2011-2013.

Average annual deposition rate was estimated as 11.4 kg N ha^{-1} for cropland and garden sites, and 7.7 kg N ha^{-1} for natural site. The lowest intensity of deposited N was observed over dry year of 2012. Meanwhile for garden and natural (Fig. 4b, c) sites (located close to the river) the highest deposition rates were registered during 2013, however for the cropland site (located at 7 km distance from the river) the maximum was observed in 2011 most probably being affected by local events (*e.g.* intensive N fertilization). We showed that average TN deposition rate at natural site was in a factor of 1.5 less compared to agricultural sites. Interestingly, inter-annual DIN variation was completely uncoupled from TON dynamics. We indicated that inter-annual DIN fluctuations varied significantly less (*ca.* 8-13%) than those of TN (*ca.* 26-36%), because of a huge fraction of TON.

Agricultural sites were subjected to a greater atmospheric DIN load (in a factor of 1.6) compared to natural area. Inter-annual distribution of inorganic constituents in DIN varied between sites, however usually NO_3^- content exceeded NH_4^+ by 51-83%. More stable inter-annual distribution was observed at the natural site where NO_3^- was *ca.* 63-64% higher than NH_4^+. A strong correlation ($p<0.01$) between annual DIN deposition and precipitation sum was demonstrated for cropland ($r=0.99$) and natural sites ($r=0.96$).

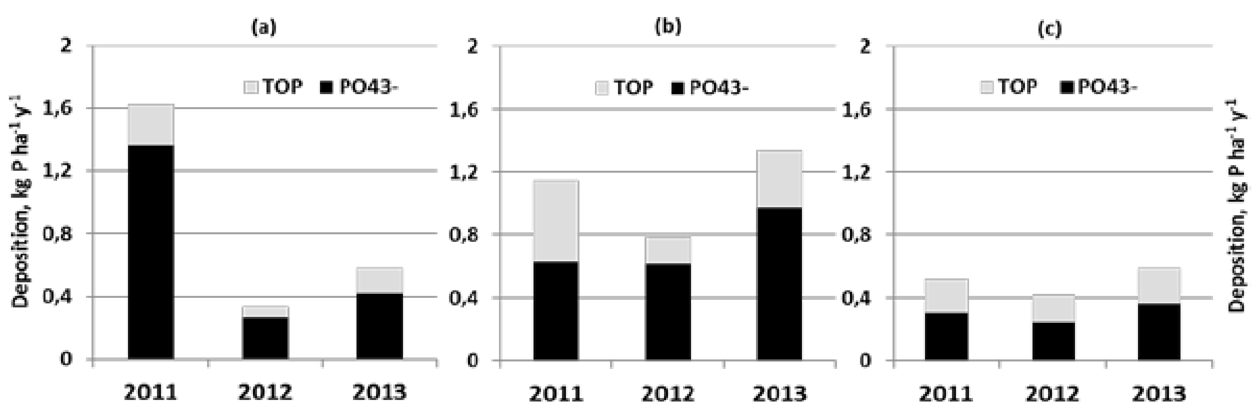


Fig. 5. Annual bulk P atmospheric deposition (by constituents) within the Dniester basin at cropland (a), garden (b) and natural (c) sites in 2011-2013.

An inter-annual pattern of TP deposition was similar to that of TN (Fig. 4). Mean annual rate of deposition was 0.82±0.29 kg P ha^{-1}, varying substantially from 0.51 kg P ha^{-1} for natural area to 1.09 kg P ha^{-1} for cropland. During the dry 2012 the lowest intensity of P deposition was registered. Phosphates significantly exceeded organic P compounds at all sites from a factor of 1.5 in natural area to a factor of 4.1 in cropland.

Surprisingly, higher inter-annual variation of TON depositions was found at the natural site compared to agricultural sites. Average contribution of organic constituent to TN and PT was 67.3% and 19.5% for cropland, 69.2% and 32.4% for garden and 71.4% and 40.5% for natural site; data was well comparable with previous studies [7, 8, 10]. Despite of weak divergence between sites we presume that it is likely that agricultural sites, subjected to higher local inorganic N and PO_4^{3-} load (e.g. mineral NPK fertilizer application), may have lower

TON:TN and TOP:TP ratios than 'clean' natural site.

To highlight the significance of atmospheric deposition we roughly assessed average annual total N and P deposition using a mean deposition rate across three studied sites (10.2±2.1 kg N ha^{-1} y^{-1} and 0.81±0.29 kg P ha^{-1} y^{-1}) to the Dniester catchment area (72 326 km^2) and found that around 73.8 Gg N and 5.9 Gg P deposited yearly to the entire basin area. Therefore, potential atmospheric input within the catchment is 2.0-fold and 4.5-fold higher than riverine transfer of N and P to the Dniester estuary correspondingly. Undoubtedly, the riverine nutrient transfer calculated here already included the upstream part (from the city of Mayaki) of atmospheric load. Meanwhile atmospheric N and P deposited to the basin area downstream should be considered as an additional source [3]. Besides, atmospheric deposition had less nutrient ratio of N:P=12.5 compared to observed fluvial (N:P=28) and conventional Redfield ratio (N:P=16), i.e. content of deposited P was in a surplus.

Additionally, to untangle a nature of 'unknown' (presumably organic) part of TN we have been performing long-term studies to separate water-soluble and water-insoluble fraction of TN (data not shown here). Further, more targeted and detailed studies are needed to discover chemical composition of deposited organic N and P and identify their main sources.

Conclusions

We showed that riverine run-offs of N and P to the Dniester estuary and the Black Sea depended on the intensity and dynamics of water mass discharge and on average made 36.6±25.7 Gg N y^{-1} and 1.3±0.3 Gg P y^{-1} in 2010-2013. On average TON made 48.2±13.8% of TN and TOP made 38.2±9.1% of TP emphasizing a large importance of organic constituents, which could be considered as an important source of eutrophication acting with a time delay. We suggested that most of the nutrients (*ca.* 90%) came to the river upstream from the sampling sites.

We found that agricultural sites regularly obtained more deposited inorganic N and P, as well as TN and TP, than natural areas obviously due to local N pollution sources related to management activity. We demonstrated that average contribution of TON to TN was more or less constant (67-71%) between sites but TOP to TP varied in a factor of 2.0 (range: 19.5-40.5%).

Imbalance of nutrient N:P ratio to N side (1.75-fold) in riverine water and to P side (1.28-fold) in atmospheric deposition according to the Redfield [9] was brought into focus.

One can conclude that significance of organic N contribution to TN in fluvial run-off and atmospheric deposition is crucial and further investigations, as well as long-term monitoring, are urgently needed.

This study illustrates that identification and quantification of the main point sources throughout the river flow and quantitative estimation of diffuse sources within the basin, as well as transparent monitoring including water bodies and terrestrial areas especially in "shadow" (not transboundary) areas, is sharply required. The big task is to pay attention and explain to stakeholders (*e.g.* farmers, businessmen, fishermen etc) how the implementation of good management practices improving the efficacy of nutrients use at a farm/ enterprise scale can be a real win-win strategy on the one hand saving considerable own funds (economic benefit) and on the other hand positively contributing to the Dniester ecosystem (environmental benefit) leading to the well-meaning consequences for future generations (invaluable benefit). Also, a high priority direction for the removal of excess nutrients from the river ecosystem is the sustainable management of natural, as well as constructed, wetlands, *i.e.* scheduled vegetation cutting for various purposes (*e.g.* pellets, sovereign goods, utilization as a green fertilizer).

The study was performed in the framework of National research project "To determine the sources and the role of Nitrogen load in the eutrophication of aquatic ecosystems of the Lower Dniester and the Black Sea". The authors would like to express their gratitude to the staff of Odessa National I. I. Mechnikov University for the assistance in routine sampling.

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