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NUTRIENTS EXCESS IN THE DNIESTER DELTA

Recently, scientists across Europe have chronicled the little-known Nitrogen dilemma and highlighted the threats it poses to human health and our environment, namely water quality, air quality, biodiversity loss, soil quality and greenhouse gases (GHGs) [1, 2]. It is known that 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]. To date the UNEP-GEF 'Targeted Research for improving understanding of the Global Nitrogen Cycle towards the establishment of an International Nitrogen Management System (INMS)' project has 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]. 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 nutrients (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].

The aim of this study is to highlight some important aspects and consequences of N and P riverine and atmospheric inputs to the Dniester Delta ecosystem.

Materials and methods. This study was based on the data obtained within the Lower Dniester basin during 2010-2013. Locations of sampling sites of Odessa National I. I. Mechnikov University within studied region are specified below (Fig.1).

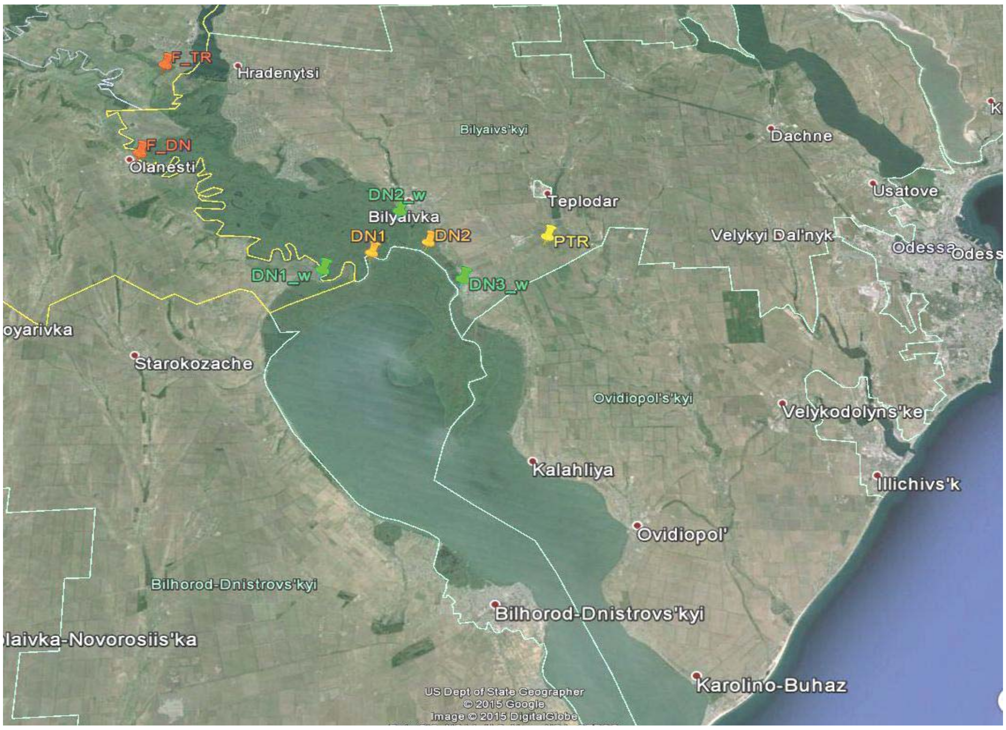

Fig. 1. The location of water mass discharge measurement stations (F_DN: Olăneşti, the Dniester River; F_TR: Nezavertailovca, the Turunchuk River), water sampling sites (DN1_w: Palanca, the Dniester River; DN2_w: Bilyaivka, the Turunchuk River; DN3_w: Mayaki, the Dniester River after confluence), atmospheric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

To assess riverine input 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) in the framework of the international data exchange process. 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 bulk deposition samples have been collected monthly/ fortnightly in three sites: cropland (PTR), garden (DN1) and natural (DN2) (Fig. 1). To estimate total N (TN) as well as 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].

In this report we presented our fieldwork results for 2010-2013, discussed the significance of riverine and atmospheric inputs as nutrient pollution sources effecting on the Dniester estuary ecosystem and propose recommendations and further actions to do. It was shown that riverine run-offs of TN and TP 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.

It was 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 highlighted for the studied ecosystem. 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" funded by Ministry of Education and Science of Ukraine as well as in-kind partnership with UNEP/GEF INMS project. The authors would like to express their gratitude to the staff of Regional Centre for Integrated Environmental Monitoring and Ecological Studies of ONU for the assistance in routine sampling.

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