Assessment of riverine loads of nitrogen and phosphorus to the Dniester Estuary and the Black Sea over 2010-2019

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SUMMARY

Purpose of the work was to quantify riverine nitrogen (N) and phosphorus (P) loads to the Dniester Estuary and estimate their contributions to the Black Sea over 2010-2019. Methodology. The data on monthly water discharge and monthly N and P compounds concentrations in surface water monitored in-situ were used. Results and Discussion. Mean annual riverine water discharge to the estuary was 7.9±0.2 km^3 (range: 5.6-14.2 km^3). Higher variation of water discharges was found in the Turunchuk River (variation coefficient of 38%), 1.7 times higher than in the Dniester River before confluence. Annual TN loads to the estuary varied from 10.8 GgN (2016) to 74.6 GgN (2010), the mean was 25.7±5.8 GgN/year. Mean annual TP load was of 1.16±0.08 GgP/year (range: 0.95-1.66 GgP/year). On average, the shares of organic N and P were 48% and 43% respectively. Nitrates dominated in DIN contributing 84±2%. Conclusions. Dniester water discharge and thus water supply for its deltaic area are strongly dependent on climatic and anthropogenic factors, both affected by climate change. We have found that 25.7±5.8 GgN/year and 1.16±0.08 GgP/year are entering the Dniester Estuary annually. Mean riverine total N and total P loads to the Black Sea made 23.1±5.2 GgN/year and 1.04±0.07 GgP/year.

Introduction

Aquatic ecosystems both freshwater and coastal, being a valuable resource of ecosystem services for local population wellbeing and regional economy (e.g. tourism, aquaculture, hydropower generation, drinking water from freshwater systems) are the most vulnerable to the anthropogenic impacts (*Sutton et al., 2011*). Surface stream waters (e.g. rivers and estuaries) being considered as both local sink (from agriculture, industry, municipal and domestic activities and atmosphere) and source of reactive nitrogen (N) and phosphorus (P), mainly function as a transporter/ carrier of received nutrients (and other substances) through to the stream within catchment and further to the sea (*Rouholahnejad et al., 2014; Medinets et al., 2017*). In this study, we have considered the Dniester River system, the surface water of which is known to be an important source of drinking and irrigation water for the south-western Ukraine and the large part of Moldova with totally around 4 mln population (*Efros, 2018*). The main driver of ecological concerns in this river catchment is excessive nutrient load of anthropogenic origin resulting mainly from agriculture, wastewater, households not connected to sewage system, atmospheric deposition (*see Medinets et al., 2016, 2017*), which leads to a significant increase of phytoplankton triggering eutrophication events in the lakes, deltaic areas and the Dniester Estuary (*Dereziuk, 2019; Kovalova et al., 2018, 2019*). On top of this, N (and P) pollution of the north-western Black Sea via Dniester discharge to the coastal waters is increasing (*Kovalova et al., 2010; Rouholahnejad et al., 2014*), particularly in Odessa Bay, which is already exposed to high nutrient load from the land-based hotspots and atmospheric deposition (*Medinets, 2014; Medinets et al., 2017*). Besides, biodiversity issues are of high importance in the Lower Dniester, where national parks, Ramsar and Natura 2000 sites are located to protect wild life (*Zakorchevna, 2019*).
The aim of this study is to quantify fluvial N and P loads from the Dniester River to the Dniester Estuary and estimate their flows to the Black Sea over 2010-2019.

Methods

The Lower Dniester area from Nezavertailovca village to the Dniester Estuary was in focus for this study. We calculated monthly water discharges derived from daily flow rate data kindly provided by Hydrological and Meteorological Service of Ukraine for Nezavertailovca and Olăneşti stations in the framework of the international exchange with the Hydrometeorological Service of Moldova (2010-2014) and from the Moldavian colleagues for Nezavertailovca and Bender stations (2015-2019). As regular measurements at Olăneşti station have been officially stopped by 2017, we further estimated the water discharge for this station as the difference between Bender and Nezavertailovca stations. Water samples were regularly taken on bi-weekly/ monthly basis during 2010-2019 at three stations near Palanca village (PS), Bilyaivka town (BS) and Mayaky village (MS) according to the methods described in Kovalova et al. (2010) and Medinets et al. (2015). All the samples were analysed using ion chromatography to determine NO_3^-, NO_2^-, NH_4^+ and routine chemical methods to determine PO_4^{3-}, total P (TP) and total N (TN) as described in the previous studies (*e.g. Medinets and Medinets, 2010, 2012*). Concentrations of organic components of N or P were calculated as the difference between their total contents and the sum of dissolved inorganic N (DIN) or PO_4^{3-} respectively. We used monthly water discharges and monthly concentrations of nutrient compounds in surface waters to quantify riverine N and P loads to the Dniester Estuary and further to the Black Sea.

Results and Discussion

Based on daily water flow rate we have accurately calculated monthly and then annual water discharges from two main tributaries, the Dniester River near Olăneşti village and the Turunchuk River near Nezavertailovca village, before the confluence into the common Dniester River and then estimated total water discharge into the Dniester Estuary. Over ten years of study, mean annual river water discharge into the estuary was 7.9±0.2 km^3 varying from 14.2 km^3 in 2010, an extremely wet year, to 5.6 km^3 in 2016, a very dry year (Fig. 1). Magnitudes of water discharge from the Dniester, a precipitation-fed river system, are directly dependent on amounts of snowfalls and rainfalls over the year deposited to the catchment (data not shown here; see also Loboda and Melnyk, 2018). During last decades the tendency of precipitation decrease was observed in the upper part of the Dniester basin (OSCE, 2005) and Carpathian region (*Cheval et al., 2014; Spinoni et al., 2015*). Besides, the change of rainfall pattern has been observed over last decades (*Zolina et al., 2012*) and supposed to be aggravated in the near future (*Loboda and Kozlov, 2020*); the duration of water deficit periods substantially increased in southern part of the basin (*Mihăilă et al., 2019*). In dry years the Lower Dniester received even much less water than it naturally should owing to a highly regulated flow upstream (*Efros, 2018*). There are four large water storage reservoirs (Dniestrovske, Buferne, Dubossarske and Kuchurganske) in the Dniester catchment, operating of which has a high priority and where the frequency and amount of water releases from storages are often less than minimally required (*OSCE, 2005; Efros, 2018; Andreev et al., 2019*). All this leads to a vast of environmental concerns impacting ecosystem state and quality of ecosystem services downstream (*Medinets et al., 2017; Efros, 2018; Andreev et al., 2019*). Higher fluctuations of water discharges have been found in the Turunchuk River (near Nezavertailovca) with the variation coefficient of 38%, 1.7 times higher than in the Dniester River (near Olăneşti).

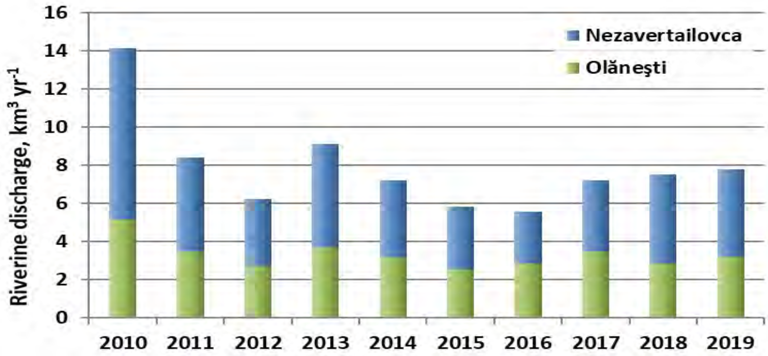

Figure 1 *Annual water mass discharges of the Dniester river (Olăneşti station) and of the Turunchuk river (Nezavertailovca station) forming total discharge to the Dniester Estuary in 2010-2019*

According to our estimates on the average 57.9% (range: 48.5-63.6%) of total water discharge of the Dniester went through the Turunchuk River over 2010-2019, which coincided well with previous studies (*OSCE, 2005; Medinets et al., 2015*). The highest flowrate (9.0 $km^3\ yr^{-1}$) was observed in 2010, while the minimal water discharged (2.7 $km^3\ yr^{-1}$) through Nezavertailovca station - in 2016 affecting wetland flushing potential and water level in that area.

According to the results of N and P compound concentrations in surface waters sampled near Palanca (PS), Bilyayivka (BS) and Mayaki (MS) at bi-weekly/ monthly basis, the monthly and annual fluvial loads of dissolved inorganic N (DIN; as sum of NH_4^+, NO_3^- and NO_2^-), organic N (ON), phosphate (PO_4^{3-}) and organic P (OP) to the Dniester (PS), the Turunchuk (BS) and further to the Dniester Estuary (MS) have been estimated over 2010-2019 (monthly data not shown here; see also Medinets et al., 2015). Annual load of TN to the Dniester Estuary significantly varied from 74.6 Gg N in 2010 to only 10.8 Gg N in 2016 with the mean of 25.7±5.8 Gg N yr^{-1} for the study period (Fig. 2a). We have shown that in 2018 and 2019 the share of ON, typically associated with flood events (both spring and flash floods), substantially increased and contributed 75 and 60%, respectively. On average, the share of DIN in TN over the study period was above 52±5%, of which NO_3^- made ca. 84±2% (Fig. 2a). The increased share of NH_4^+ content (20-25%) in DIN was observed over low-water years (2015-2017). This might be associated with domestic and industrial wastewater loads: either increased input of untreated/ insufficiently treated water mass or decrease of wastewater plants efficiency to convert/ remove NH_4^+ (*Medinets et al., 2017*). Mean annual flow of TP was of 1.16±0.08 Gg P yr^{-1} varying in the range of 0.95-1.66 Gg P yr^{-1} for 2010-2019 (Fig. 2b). On average the share of OP was ca. 7% lower than that of PO_4^{3-}, however we observed the opposite pattern for 2018, the year characterized with the highest organic shares of both P (58%) and N (75%) over the study period.

According to our assumption based on previous study (Medinets et al., 2015) ca. 90% of N and P entered to the Dniester Estuary may form the riverine N input to the Black Sea. Whereas, on average the Black Sea received around 23.1±5.2 Gg N yr^{-1} and 1.04±0.07 Gg P yr^{-1} over period the of 2010-

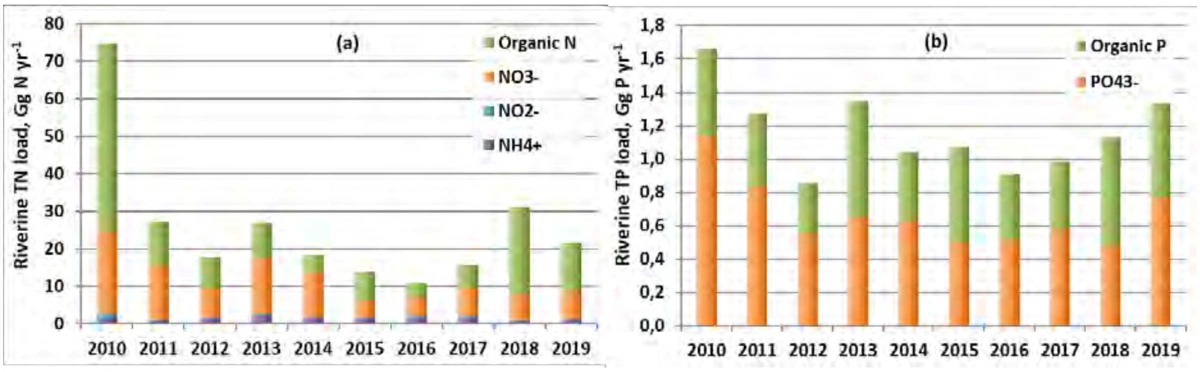

Figure 2 *Annual loads of total N and P (by main constituents) from the Dniester River to the Dniester Estuary in 2010-2019*

2019; the absolute annual magnitudes were strongly dependent on precipitation regime, i.e. highly affected by climate change (*Loboda and Melnyk, 2018; Kis et al., 2020*). Despite the mean magnitude of fluvial TN input from the Dniester to the sea was much lower (>15-fold) than that of the Danube for the same period (ICPDR, 2020), it still had a significant influence on the physicochemical properties of the coastal waters and sediment transport impacting both biodiversity and ecosystem services quality in the Odesa Bay (*Kovalova et al., 2010; Cherkez et al., 2020*).

Conclusions

Water discharge from the Dniester catchment and thus water supply for its deltaic region are strongly dependent on climatic and anthropogenic factors, both being highly affected by climate change. We have found that 25.7±5.8 Gg N yr^{-1} and 1.16±0.08 Gg P yr^{-1} were annually discharged to the Dniester Estuary from the Dniester watershed in the period of 2010-2019. On average the shares of ON and OP have been observed to be 48% and 43%, respectively. All the time NO_3^- has been dominating across DIN compounds contributing 84±2%. The share of NH_4^+ has reached 20-25% over the low-water 2015-2017. Mean riverine TN and TP loads from the Dniester to the Black Sea made 23.1±5.2 Gg N yr^{-1} and 1.04±0.07 Gg P yr^{-1} over the study period affecting the quality of coastal water and ecosystem services in the Odesa Bay.

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