Chemical Characteristics of Wetlands of Middle (Hungarian) and Lower (Bulgarian) Danube River

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Abstract: Several physicochemical variables of wetland water bodies of Middle and Lower Danube including nutrients (N- and P-forms) were measured and analyzed. The application of multivariate redundancy analysis (RDA) showed that variables reflecting the degree of wetland connectivity (isolation) to the main river and the macrophyte development are among the main and common factors for Middle and Lower Danube responsible for spatial variations of relationships between chemistry variables, ratios between nutrient concentrations in wetlands and the river and ordination of wetland sampling sites. However, in the Lower Danube the morphological type of wetlands related to their limited or absent connectivity to the river seems to have stronger influence, while in the Middle Danube factors related to existing connectivity like flow availability and its direction are of significant importance.

Key words: chemistry, nutrients, trophic status, wetlands, multivariate analysis.

Introduction

In recent times besides the primary function to sustain biodiversity the wetlands are performing new additional and important functions helping to mitigate the anthropogenic pressure coming from land and river. These new functions and the wetland ecological status are related to great extend to their physicochemical characteristics, which measurement is of fundamental importance. Thus depending mainly on their hydrology i.e. connectivity wetlands might act either as sources or as sinks for nutrients (BONDAR *et al.* 2007, HEIN *et al.* 2005). The alternation of wet and dry phases in wetlands may favor either denitrification or mineralization of nitrogen (VENTERINK *et al.* 2002). According to SAUNDERS, KALFF (2001) owing to the processes of denitrification, uptake by aquatic plants and sedimentation the wetlands are superior to lakes and rivers in retaining nitrogen. However, when studying the wetland importance for large rivers like the Danube we have to consider it as much as possible as a whole and to account for wetland peculiarities in different river reaches, moreover the old differences between Middle and Lower Danube are extended or altered by strong local and global anthropogenic pressures. In this first attempt we are going to evaluate and compare the main factors influencing the chemical composition and potential ability for nutrient retention as well as the trophic character of selected wetlands from Middle and Lower Danube.

Materials and Methods

The Middle Danube part is presented by the Gemenc floodplain area, which extends between 1469 and 1498 km of the River. Five different wetland subunits from this large territory – the Grébec-Holt Danube abbreviated as GDU, Rezéti-Holt Danube (RDU), Vén-Danube (VDU), Nyéki-Holt-Danube (NYHD) and Mocskos Danube (MDU) were investigated (Fig. 1).The selected samples originated from July 2009 and included measurements of water temperature (^oC), pH**,** conductivity [µS/cm] *in situ* by WTW Multi 403i meter; Na, K, Cl, Ca, Mg, NO_2-N and SO_4 ions in [mg/l] by DX-120 ionchromatograph (Dionex); TOC (total organic carbon, non-filtered), DOC (dissolved organic carbon, filtered)), TIC (total inorganic carbon, non-filtered) DIC (dissolved inorganic carbon, filtered) TC (total carbon, non-filtered) DTC (dissolved total carbon, filtered) TN (total nitrogen, non-filtered) DTN (dissolved total nitrogen, filtered) in [mg/l] determined by TOC analyzer (Elemetar-

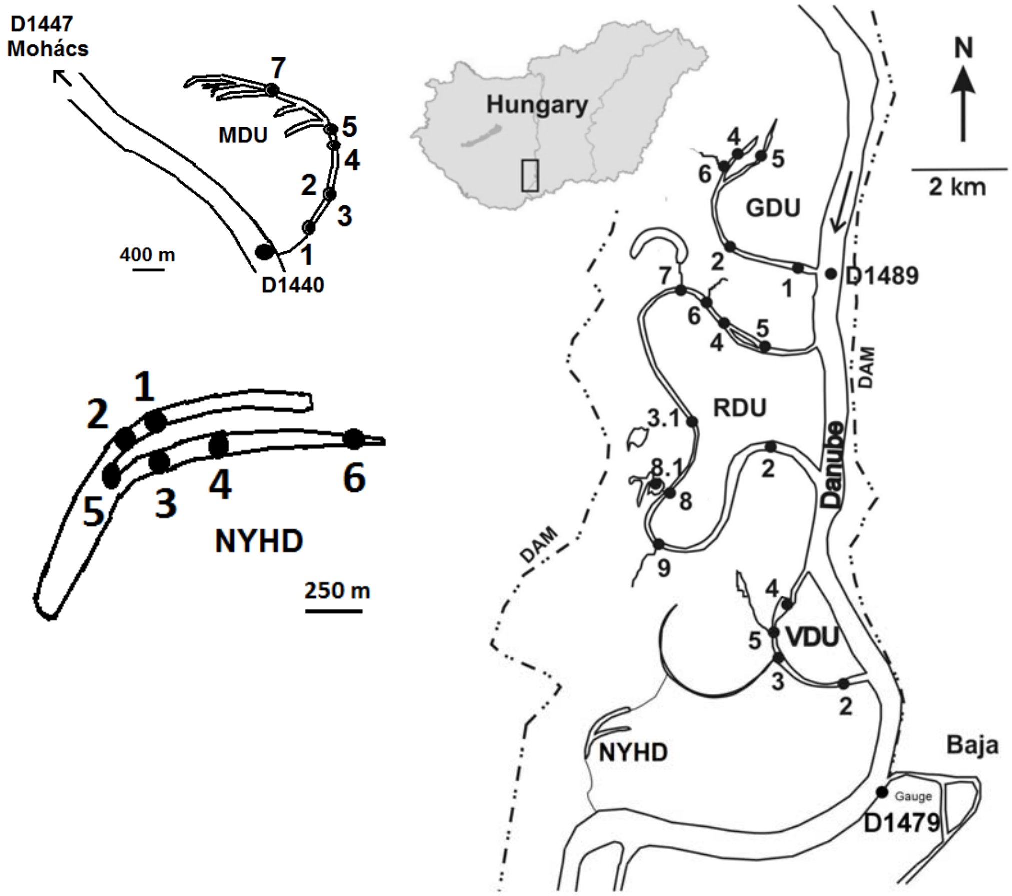

Fig. 1. Location of sampling sites of Gemenc and Béda-Karapancsa floodplain area, between 1440 and 1489 river km, with indications of five wetland regions GDU, RDU, VDU, NYHD and MDU and numbering of sampling sites. For the meaning of applied abbreviations see the "materials and methods" part

liqui-TOC); HCO_3, SPM (suspended particular matter), m-alkalinity and NO_3-N in [mg/l] and NH_4-N, PO4-P, DTP (dissolved total phosphorus), TP (total phosphorus), Chl-a (chlorophyll-a) in [µg/l] were determined in the laboratory by standard analytical methods (GOLTERMAN *et al.* 1978).

The Lower Danube is presented by 3 marshes (Murtvo blato, Peschin and Dyulova bara) located on Belene island and 3 other wetlands (Kalimok canal, Kalimok marsh and Brushlen canal) belonging to Kalimok-Brushlen protected area (Fig. 2). Additionally samples taken from the middle of the side arm located opposite to Belene town (Fig. 2) were used for comparison with the Danube River. The samples were taken one per season (spring, summer, autumn) starting from autumn 2009 and finishing in spring 2012. The water temperature [^{o}C], pH, conductivity [µS/cm] and oxygen concentration [mg/l]were measured in *situ* either by WTW - Multi 1970i or by GMH 3510, or Greisinger electronic (pH) and Winkler titration (oxygen).The NO3-N, NO2–N, NH4-N, SiO2, PO4-P and Fe in [mg/l] all filtered and TN, TP, COD (chemical oxygen demand) in [mg/l], turbidity at 550 nm as absorbance all not filtered, were determined colourimetrically by Nova photometer 60 and kits of Merck. The chlorophyll-a samples after filtering through 0.7 µm glass fiber filter and stored in liquid nitrogen were analyzed in the laboratory after ISO 10260 standard. Some additional characteristics of wetland sites like water depth, distance to the main river, availability, and direction of flow or its absence, degree of connectivity defined by eu-, para-, plesio- and paleopotamal categories, percentage of water surface covered by macrophytes etc. were composed and applied as environmental variables in the subsequent statistical analyses.

In order to find out whether the wetlands are potential sources or sinks for nutrients we calculated the ratios of sum of inorganic nitrogen compounds (N-inorganic), PO4-P, TN and TP concentrations in wetlands to those in

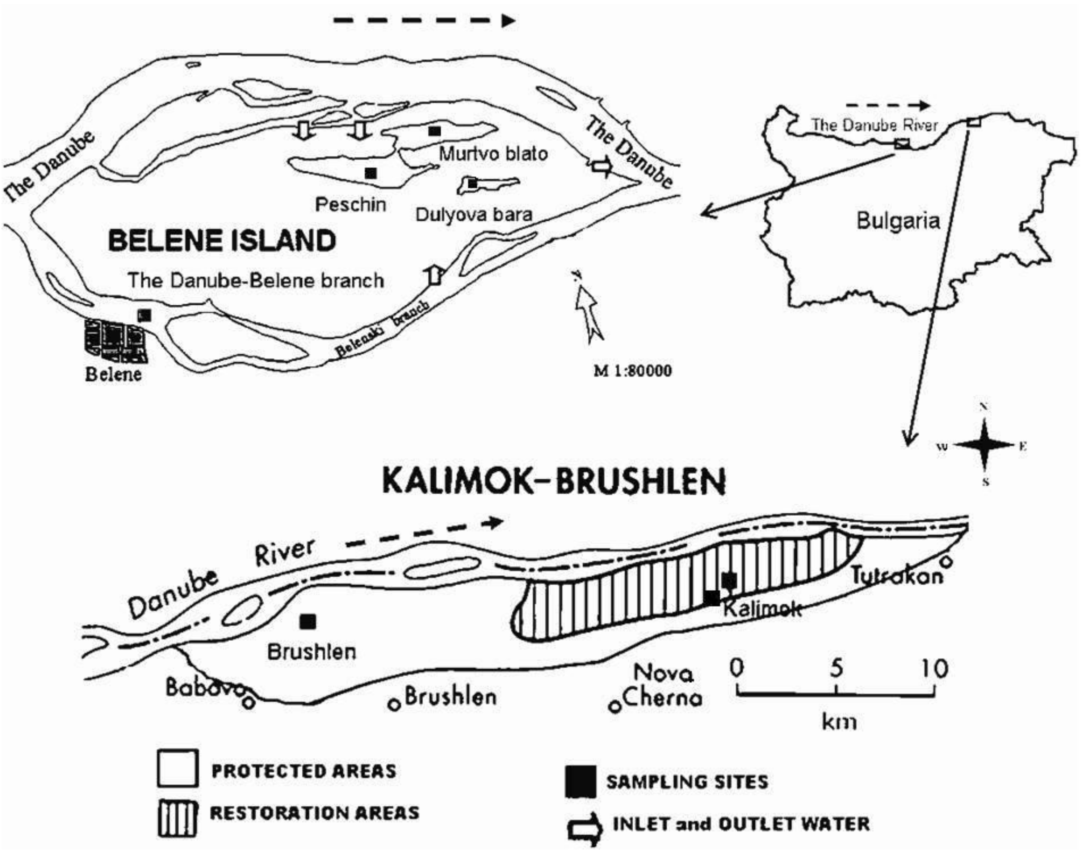

Fig. 2. Location of studied wetland sites on Belene island (river km 561 -576): Murtvo blato, Peschin and Dyulova bara marshes; in Kalimok-Brushlen area river km 440-465 : Kalimok canal, Kalimok marsh, Brushlen canal. The dotted arrow indicates the flow direction in the river

the river. The statistical treatment includes application of multivariate detrended correspondence analysis (DCA) and redundancy analysis (RDA) by Canoco 4.55 after TER BRAAK, ŠMILAUER (2002). By means of RDA we analyzed the spatial variations of chemistry data, which in the case of Bulgarian data was done by the partial RDA performance.

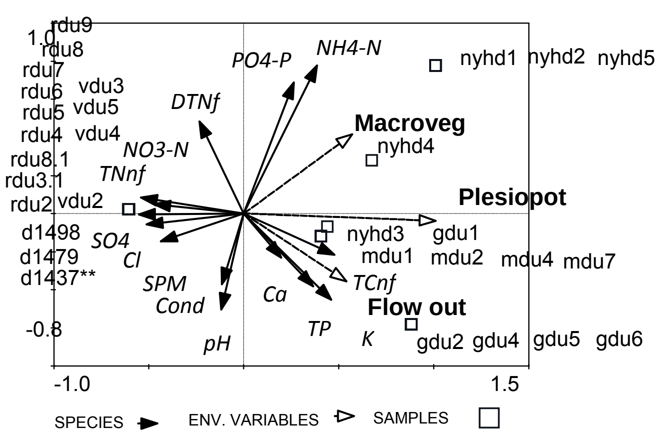

Fig. 3. RDA ordination of chemical variables from the Hungarian Danube as response variables (species) and % covered by macrophytes, Plesiopotamal and availability of "Flow out" water movement as explanatory variables (env variables). The eigenvalues of the first canonical axis (0.451, significant for P=0.002) and of second axis (0.111) together are explaining 56.2% of total variation. All canonical axes are also significant for P=0.002. The applied subscripts "f" and "nf" indicate data of filtered and non-filtered samples; for the meaning of the other abbreviations see "material and methods" part

Results and Discussion

Before applying the multivariate analyses the number of available numerous chemical variables were reduced by removing those of them which were highly correlated (R≥0.80). Thus the RDA of Hungarian data clearly separates the more isolated regions GDU, NYHD and MDU which are ordered to plesiopotamal type from RDU and VDU sites whose samples coincided completely with those from the Danube river sites (Fig.3). Obviously the almost simultaneously sampling of all sites (with one week difference) at times of river high water levels (about 500 cm) is responsible for close resemblance between river and RDU and VDU sites. This resemblance increased at high and decreased at low water levels as previously indicated by SCHÖLL *et al.* (2008), ÁGOSTON SZABÓ *et al.* (2013). Besides the plesiopotamal degree of isolation the macophytes and the outwards flow of water as explanatory variables also contributed to the presented site separation (Fig. 3). The river, RDU and VDU sites were distinguished by high SPM, SO4 and nitrogen (NO3-N, TN, DTN) concentrations, while the

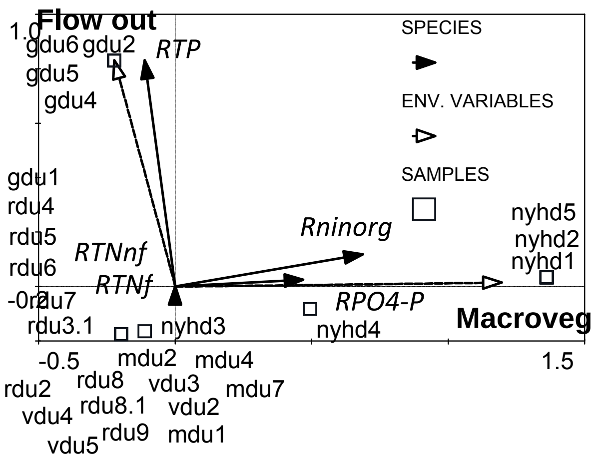

Fig. 4. RDA ordination triplot of wetland to river ratios of nutrient concentrations from the Hungarian Danube as response variables (species) and % covered by macrophytes, and availability of "Flow out" water movement as explanatory variables (env variables). The eigenvalues of the first canonical axis (0.249, significant for P=0.002) and of second axis (0.124) together are explaining 37.3% of total variation. All canonical axes are also significant for P=0.002. The applied subscripts "f" and "nf" indicate data of filtered and non-filtered samples; for the meaning of the other abbreviations see the "materials and methods" part

more isolated sites were rich in TP (GDU), PO4-P and NH4-N (NYHD) concentrations, which might have allochthonous (from the catchment) or autochthonous (from sediments rich in nutrients) origin.

This separation of sites is partly confirmed by ordination of ratios of nutrient concentrations between wetlands and the Danube River on Fig. 4. The average values of ratios of PO4-P (1.94) and of sum of inorganic N-compounds (N-inorganic, 6.33) in wetlands covered by macrophyte (NYHD sites) and TP ratio of the GDU sites (1.74) are higher than unity, what means that they are potential sources of the corresponding kind of phosphorus. The MDU sites despite their different chemical composition shown by their separate site ordination from the Danube sites (Fig. 3) their ordination according to nutrient ratios coincided with Danube sites (Fig. 4). Therefore the MDU sites seem not to be a potential source of phosphorus (ratio average value for PO4-P 0.97 and for TP 1.05). Obviously the isolated sites have lower total nitrogen concentrations than the river (ratios for GDU 0.81 and 0.73 and for NYHD 0.76 and 0.90 for TNnf and TNf), and therefore they may act as nitrogen sinks in comparison to less isolated RDU, VDU and MDU wetland sites. However the RDU and VDU sites with ratio averages of 0.67 and 0.57 are showing considerably lower values for N-inorganic than the Danube (Fig. 4).

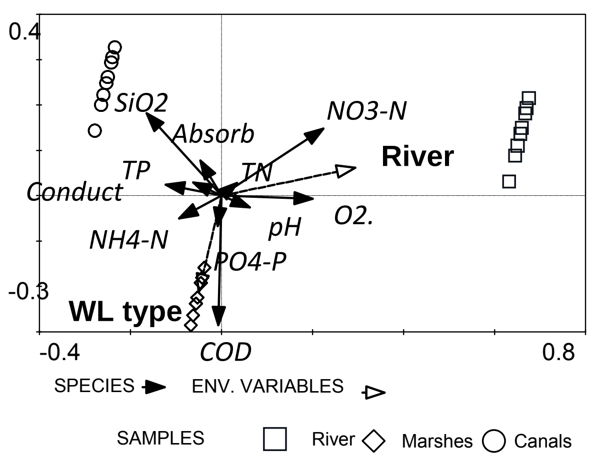

Fig. 5. Partial RDA ordination tripolot of chemical characteristics from the Bulgarian Danube as response variables (species) and kind of sites presented as "river" and type of wetlands (WL type) as "canal or marshes" as explanatory (env variables). The eigenvalues of the first canonical axis (0.095, significant for P=0.002) and of second axis (0.049) together are explaining 18.1% of total variation. All canonical axes are also significant for P=0.002. For the meaning of the other abbreviations see the "materials and methods" part.

The RDA spatial ordination for chemistry data of Bulgarian wetlands shows clear separation between the sites, due to their belonging to different water body type – river, drainage canals or marshes, which are selected by analysis as explanatory variables (Fig.5). These sharp differences originate from the low or absent connectivity between river and wetlands. The marshes of Belene Island are connected to the Danube by ground and partly by surface water which flowing through wetlands is regulated by man and is possible only for short intervals during times of high water levels. The Kalimok canal and marsh are also connected by ground waters and periodically are inundated by surface waters but without flowing trough effect, while the Brushlen drainage canal is serving the collection of ground waters and its pumping back to the river. Therefore the Bulgarian wetlands differently from Hungarian are able to function predominantly as sinks for nutrients. The only explanatory variable which level of significance is close to the significance border is the percent coverage by macrophytes (Fig.6). The averages of PO4-P (2.03) and TP (2.14) ratios for all Bulgarian wetlands were higher, than unity and than those of TN (0.87) and N-inorganic (0.84), what indicates that the Bulgarian wetlands predominantly retain nitrogen compounds but might act as sources of phosphorus if connected to river. The macrophytes seem to have negative effect on nitrogen and no effect on the phosphorus ratios (Fig. 6) and as a result the wetlands from the Kalimok-Brushlen region have lower nitrogen based ratios than those of Belene Island.

The comparison on Fig. 7 shows, that the Bulgarian wetlands have slightly higher TP concentrations than the Hungarians, which in their turn are distinguished by higher TN concentrations. However, according to their TP values both wetlands seems to have passed the hypertrophy boarder, but according to TN all Hungarians are clearly situated in the hypertrophy area, while two of wetlands and the river site from Bulgarian territory are close to or bellow the hypertrophy boarder. The lower nutrient concentrations might be explained on one hand by stronger macrophyte development (Kalimok marsh site) and on the other by more frequent occurrence of anoxic conditions, which should favor the denitrification ((VENTERINK *et al.* (2001), SAUNDERS & KALFF (2001), HEIN *et al.* (2005)) despite the temporary character and complete drying of some of Bulgarian wetlands in the summer and autumn seasons during low water years like 2011.

Surprisingly, the Hungarian wetlands being of permanent character should stimulate more intensively the denitrification processes and should have lower nitrogen concentrations than the Bulgarians, which are of temporary character and their dry periods should promote the nitrogen mineralization. However, the lower TP and high TN concentrations in Hungarian wetlands especially during the studied summer period of high river waters might be explained by the flushing effect the flowing water has on wetlands by washing out the nutrient rich sediment layers and preventing oxygen shortage (SCHÖLL *et al.* (2008). On contrary, the flushing effect of flowing water on Bulgarian wetlands is minimized or is completely absent for some of them. Therefore they are functioning predominantly as nutrient sinks, which leads to accumulation of sediments rich in phosphorus, but low in nitrogen due to frequently occurring anoxic conditions favoring denitrification. This obviously did not seem to be compensated by the occasional drying events. The strong macrophyte development observed during both the

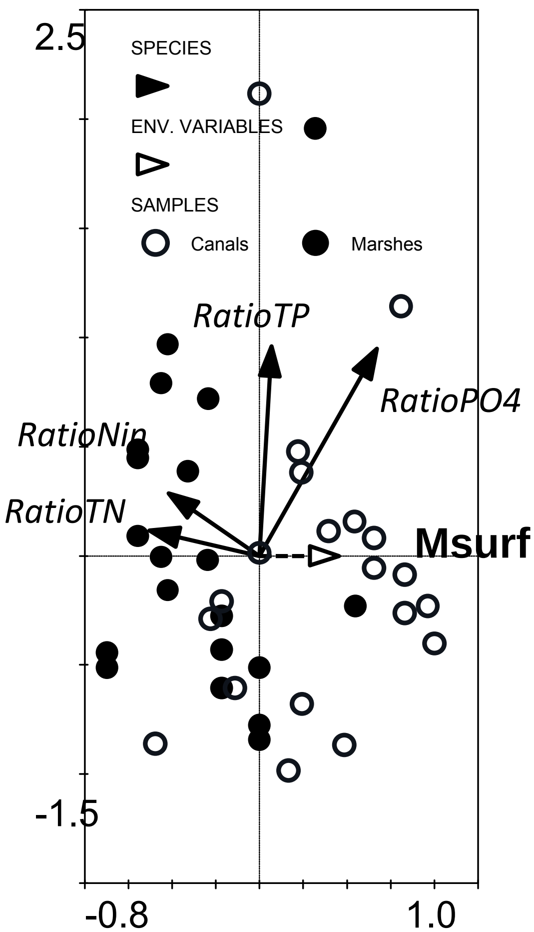

Fig. 6. Partial RDA ordination of sites and ratios between nutrient concentrations from wetlands and river from the Bulgarian Danube as response variables (species) and % covered by emerged macrophytes, as explanatory variables (env variables). The eigenvalues of the first canonical axis (0.032, significant for P=0.057e explaining 5.7% of total variation. For the meaning of the abbreviations see the "materials and methods" part

aquatic and dry periods on territory of Bulgarian wetlands additionally contributes on one hand to nitrogen uptake and on the other by providing organic matter for decomposition to more severe oxygen shortage during aquatic phase and acceleration of denitrification.

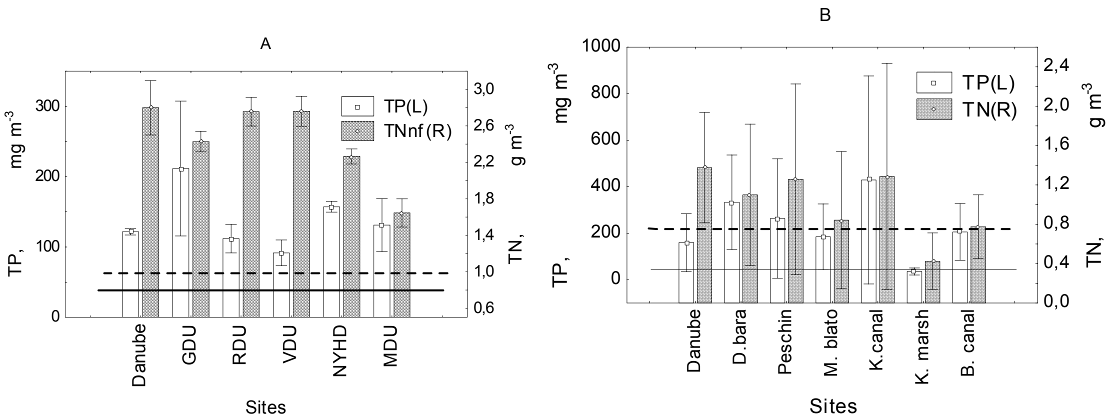

Fig. 7. The averages and standard deviations of total phosphorus (TP) and total nitrogen (TN) concentrations from wetlands and river sites of Hungarian (A) and Bulgarian (B) Danube parts. The solid line indicates the lower hypertrophy border for TP and the dotted line for TN concentrations after Likens (1975). For applied site abbreviations see the "materials and methods" part

The main differences of the Lower Danube wetlands in comparison with the Middle Danube summarized as lower connectivity, lower flow through effect, stronger macrophyte development, sink function, anoxic conditions and denitrification are to great extend result of reservoir constructions in the upper river sections. The accumulation of water in the reservoirs and the deeper river bed are acting in one and the same direction - reducing probability and duration of inundation by cutting off the water peaks or of laying dry in wet years and in dry years correspondingly in lower situated wetlands.

Acknowledgments: This study was funded by the National Scientific Fund of Bulgaria within the project DO 02-352, by the Deutsche Bundesstiftung Umwelt, AZ 24050 project and by the Hungarian Academy of Science. We are also very grateful to Buzetzky Győző for his help in the fieldwork, to Gábor Horváth and Bernadett Garad for the chemical analyses to Mr. D. Terziyski for the help with multivariate analyses and the reviewer for the valuable suggestions.

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