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TOTAL ORGANIC CARBON CONCENTRATIONS AND EXPORT ALONG DANUBE RIVER COURSE IN YEARS 2010-2012

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ABSTRACT

Danube River as the second largest European river has not a detail study on total organic carbon (TOC) biogeochemistry yet. Data from Transborder National Monitoring Network from years 2010-2012 were used to characterization of TOC concentrations and flux along a distance 2500 km, from Dillingen (Germany) up to Silistra (Romania/Bulgaria border) - before Danube Delta. Although there are significant physiographic differences along the river course, a mean TOC concentrations slightly varied (2.5-4.5 mgCdm^{-3}), with the highest variability in the Alpine section and before Black Gate Gorge where there are a mouths of major tributaries of Danube Rivers. In the middle and lower part of river course were detected a differences in TOC concentrations between the near bank zone and the central part of river flow, and a mean concentrations were highest in the each of northern river bank. Multiannual hydrological variations in the lower Danube River have a more significant impact on TOC differentiation than in upper section. TOC concentrations are negatively correlated with mean water runoff from subcatchments, but annual TOC flux significant increased with runoff. TOC flux from the Alpine part of basin with values range 1.4-2.1 g Cm^{-2}y^{-1} was higher than in Silistra with mean value 1.2 gCm^{-2}y^{-1}. The recent TOC flux data show a ca.70% lower value than earlier approximations. In part it is effects of transboundary cooperation in efforts to improve the ecological status of Danube River. It remains unresolved problem of the direction and scale of organic matter load transformation on the delta area before reaching the Black Sea.

Keywords: large river, Danube River, organic carbon, flux.

1 INTRODUCTION

Natural organic matter (NOM) plays an important role in the energy and matter circulation in the basin, similar to the others ecological drivers like the nitrogen, phosphorous or silica (Williamson et al. 1999). Dissolved and particular forms of NOM occur in the rivers, an apart of hydrobionts and organic contaminants. Natural and artificial organic matter creates an autotrophs and heterotrophs structure in the rivers depending on river order, basin relief, soils, climate and the level of anthropogenic activity (Aufdenkampe et al. 2011). Biogeochemistry of NOM is related with various ions matrix in the water, type of river channel and ecohydrological conditions in the river continuum (Ludwig et al. 1996, Raymond et al. 2016). The most wide NOM studies were provided in the boreal basins where the years 80-90-th of XX century were observed effects of acidifications and recently results of global climate changes (Alvarez-Cobelas et al. 2012, Räike et al. 2012). Investigations of dynamic of total organic carbon (TOC) in the temperate rivers of Europe were more rare and not common, as well as in the Danube River basin. Only a few TOC data were presented for the selected parts of river course, mostly for Alpine region. International Commission for the Protection of the Danube River (ICPDR) expeditions (JDS3) in year 2013 has given a first more synthetic view for the summer TOC biogeochemistry (Yeh et al. 2015).

The aim of study is presentation the recent resources and seasonal dynamic of TOC along Danube River course on the basis the official published data by ICPDR. Also a regional differentiations of TOC export were investigated for evaluation of organic matter transport intensity along the large river course during the various meteorological conditions noted in years 2010-2012, a strong associated with the global climate changes.

2 STUDIED RIVER AND BASIN

Danube River is 2872 km long and its basin covering 801463 km^2 and territories of 19 states, which are located in the 9 ecoregions (ICPDR 2005). It raises in the Black Forests mountains of Western Germany and flows to Black Sea through the unique delta on the border region of Romania, Moldova and Ukraine. In the period 2010-2012 in the Dillingen (334 km from spring) mean discharge was 165 m^{3}s^{-1} and in the Silistra (375km from Black Sea) was 6000 m^{3}s^{-1} (Table 1). According to the increase of river discharge, the width and type of the river channel change, from mountain and regulated river in Germany, then braided type of river in Austria, large size meandering in Hungary or Serbia and the large river with stabile islands in the Bulgarian-Romanian border and ended large delta area. On the few gorges sections (Weltenburg Narrows, Devil Gate, Iron Gate) the river features are common, more natural, and regardless to location in the river course. In general a monthly flow of rivers have a uniform distribution over the years in the Danube water system (Wrzesiński 2013). Natural flow regime of Danube River was changed by water electricity plans in the German section, two large dam reservoirs in Slovakia and in the gorges section in the Iron Gate. Also Danube River supplies water of canals to transport and irrigation.

The arable area is dominating in the land use of total area of basin (47.4 %) and forest (33.5 %). About 83 million people live in the Danube basin. More than 20 tributaries of Danube River have a length higher than 200 km. River network contains mainly lowland and montane, large and very large rivers types, draining a siliceous sediments and rocks. Calcareous rivers are in 1/3 of all river types and only very few stream types were identified as being of organic nature. An artificial canals and waterways exist in the each part of Danube basins, as well as dam reservoirs are the significant modifier of water regime. Water of Danube River has a varied uses and services as a source of water abstraction, drinking water supply, wastewater discharge, hydropower generation, navigation, dredging and gravel exploitation, recreation, various ecosystem services (Jelev and Jelev 2012).

Meteorological conditions were various in the period of the investigations (2010-2012), because a high summer precipitations were noted in the year 2010 in the central and NE part of basin, thus annual sum was a 1/3 higher than multiannual mean of precipitation. The mean discharge in the studied stations for years 2010-2012 in the Danube River course were similar to average from long term data (ICPDR 2005). Basin and meteorological conditions in year 2010 decided that regime of unit outflow decreased from upper basin was much higher than in the middle and lower part of Danube River (Fig.1). Two periods of higher discharges were noted in January and maximal in July (110-150% of annual mean flow), but the lowest in November with a 70% of mean (Fig.2).

3 DATA COLLECTION AND CALCULATIONS

A data used in the study are originated from database of Transborder National Monitoring Network (TNMN) of Danube River coordinated by International Commission for the Protection of the Danube River (ICPDR).

TOC concentrations in river water were determinated in the samples collected monthly for period 2010-2012 on the 8 stations, where sampling was frequent and the number of data was the highest. The availability of hydrological data for the each station was a reason for the station selection too, as well as the station representativeness for the characteristic geographical regions of Danube River basin. Silistra station was last TNMN monitoring station on Danube with complete TOC data before mouth with. The missing TOC concentrations for the some stations were estimated using regression, calculated separately from data of TOC and chemical oxygen demand (CODMn) parallel provided for the each station in the investigated period. An arithmetical mean of all TOC measurements were used for stations with more frequent sampling than ones per month. The same procedure of TOC calculations were used for these stations where water samples were taken parallel from the left, middle and right parts of the river channel. The monthly discharge for each station on Danube river were taken from Hydrological Yearbook of Republic of Serbia, Hydrological service of Austria, Hungary, Germany and Romania, available on line in the internet. The average of monthly flow data were used for calculations of riverine fluxes, multiplying monthly concentrations and monthly flow. Additionally, annual average TOC concentrations were normalized using a monthly flow according to methods described in Hope et al. (1997) and Worrall and Burt (2007). Meteorological data for selected stations in the river basin were collected from database available in www.tutiempo.net. Own Basin Index BI, own authorship, was used for evaluation of catchment pressure on the hydrochemical processes occurring in the river channel and it was calculated as a ratio of the basin catchment (km^2) to the length of river in the stations along the river course.

4 RESULTS AND DISCUSSION

Topographic river profile and calculated Basin Index (BI) indicated that there are four main parts of Danube River course. Upper, Alpine part from spring to Linz in Austria (~400 km long), second from Linz to Novy Sad (~1200 km long) in Serbia, third Balkan part from Novy Sad to the river delta (~ 1100 km long) and fourth is many channels, deltaic part (~100 km long). TOC concentration varied between 7.4 and 25 mg/l Mean water retention time lasted to one month in the Alpine part with BI values not higher than 50 km^2. Due to the rapid and high water runoff from the upper basin, the TOC concentrations were quite variable and the maximal TOC reached 9 $mgCdm^{-3}$ (Table 1).

Table 1. Danube River hydrology, TOC concentrations and flux in years 2010-2012; WRT – theoretical retention time in the river according to Soballe and Kimmel (1987), n- number of data, mean* TOC – flow normalized mean

Stations	Distance form spring	Basin area	Flow	WRT	TOC [mgC dm^{-3}]				Annual export [gCm^{-2} a^{-1}]		
	km	10^3 km^2	m^{3}s^{-1}	days	n	mean*	min	max	mean	min	max
Dillingen	334	11.3	165	13	76	3.43	1.7	9.0	1.58	1.46	1.68
Jochenstein	668	77.1	1383	33	76	3.34	1.9	6.8	1.89	1.62	2.11
Wien	937	101.7	1819	38	36	2.49	1.4	4.8	1.41	1.35	1.46
Hainburg	993	130.8	1955	44	72	2.67	1.3	4.9	1.25	1.18	1.38
Szob	1165	183.3	2237	53	88	3.11	1.6	6.8	1.20	0.95	1.63
Bezdan	1437	211.5	2375	58	35	4.16	2.1	9.4	1.47	1.22	1.95
Novo Selo	2038	580.1	5306	97	98	3.70	2.1	5.5	1.07	0.69	1.69
Silistra	2497	698.6	6000	108	80	4.42	2.8	6.5	1.20	0.86	1.84

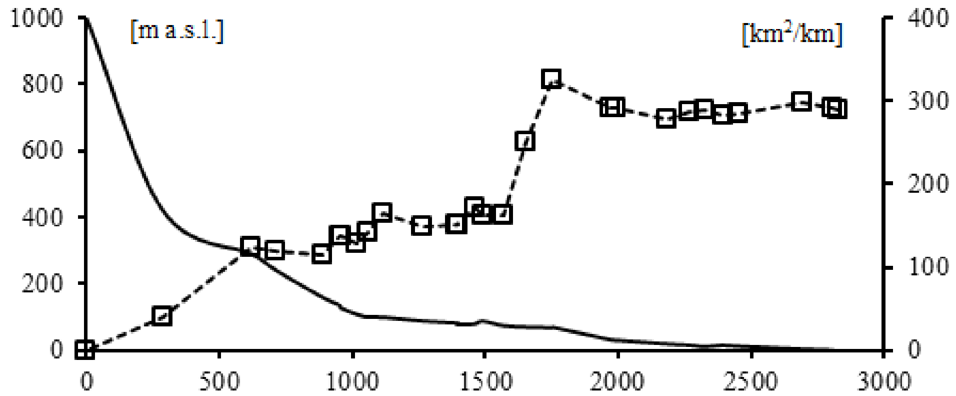

Figure 1. Elevation of Danube River course (left axis continuous line) and Basin Index (right axis, dotted line)

Although differentiated rainfall in the in the following years, annual TOC averages was almost identical (Fig.1). In the Austrian and Slovakian part of Danube River, the mean TOC concentrations decreased, reaching a lowest value in its course (Table 1). This is a probably a result of the presence of many riverbeds and related intensive utilization of organic matter by bacteria (Sieczko and Peduzzi 2014), also with the active role of the hyporheic zone (Preiner et al. 2008). This part of Danube River has a lower river slope then above, thus effected in the increase of sedimentation of organic particles (POC) in the bottom and resulted in the significant TOC decrease.

Below change of river direction (Slovakia-Hungary border) from western to south, mean TOC a concentration increased and remains on the same level in the further of Danube River course under study. Also in this stretch of river a mean TOC values were varied in the in subsequent years, not observed in the upper river course.

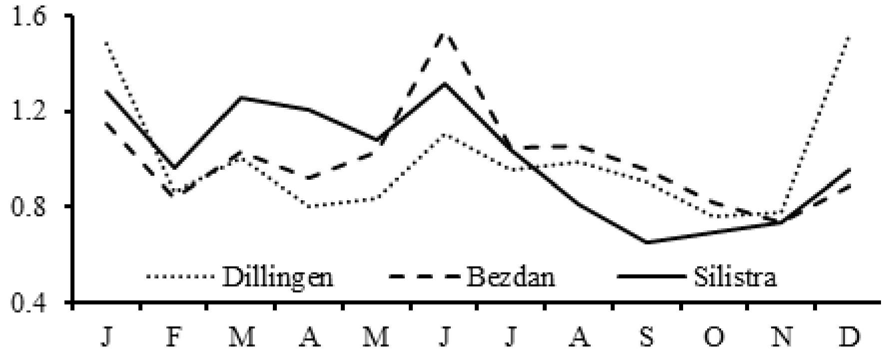

Figure 2. The mean monthly flow coefficient in the selected stations on the Danube River in years 2010-2012, representing a three main river sections

A detail data from 4 stations shows the significant statistically the differences of TOC concentrations within the river channel (Table 2). For all analysed stations an average of TOC concentrations a coefficient of variations near the left river bank were highest test points and the lowest TOC averages occurs near the right bank. The lowest TOC fluctuations were noted in the midstream locations, except a Silistra station. These differentiations within river channel regardless to type of sediment can be explained as an effects of Coriolis force on lateral erosion of the left bank of river flowing to the east direction.

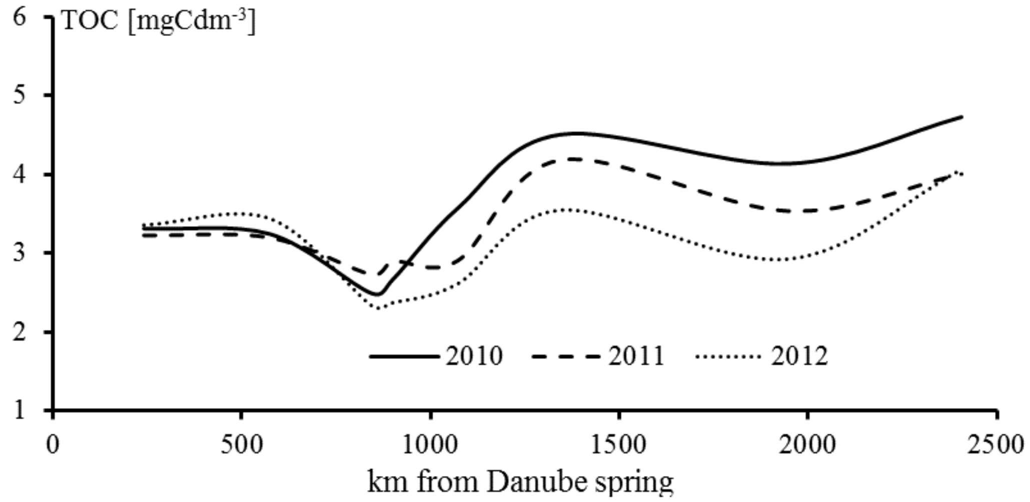

Figure 3. The changes of annual TOC concentrations in Danube River from Dillingen to Silistra in the years 2010-2012

A different seasonality of TOC concentrations was evident in the investigated stations along Danube River and was correlated with the flow regime in the following stations. Upper part of river is characterized in spring dilution and late fall increase of TOC (Fig.3). However in the Hungarian and Serbian Plains a spring time was connected with the highest TOC concentrations in the year. It is an effect of Tisza River and Sava River water supply to the Danube River in the short distance. Additionally Tisza and a few the smaller direct tributaries are richest in the organic matter from all Danube tributaries (data not presented).

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It is an effect of simultaneous a Tisza River and Sava River water supply in the short distance. Additionally Tisza and a few the smaller direct tributaries are richest in the organic matter from all Danube tributaries (data not presented). For all investigated stations in the Danube River a significant correlation between TOC and runoff exist (Fig. 4), indicated a hydrology as a dominant driver regulating the organic matter resources in the Danube system.

Table 2. Within channel differentiation of TOC concentrations (mgC dm^{-3}) in the selected stations on Danube River in years 2010-2012

station	km from spring	n	parts of river channel			average
			left	middle	right	
Bratislava	955	26	3.02±0.72	2.93±0.64	2.66±0.59	2.85±0.65
Szob	1165	26	3.42±0.92	2.93±0.55	2.93±0.62	3.05±0.74
Novo Selo	2038	32	3.67±0.77	3.48±0.70	3.38±0.74	3.52±0.77
Silistra	2497	20	4.36±0.99	4.16±1.03	4.08±0.85	4.17±0.83

In the years 2010-2012 the mean annual TOC flux was higher than 1.5 g C m^{-2} in the Alpine section and in rest of the investigated river course fluctuated in the range 1.0 – 1.5 g C m^{-2}. A depression of TOC flux was noted during a river crossing through the Iron Gate gorge, during POC sedimentation and biological utilization of organic matter in the reservoirs located in this place. Theodoru and Wehrli (2005) indicated that 55% of total suspended solids of incoming loading are accumulated in these reservoirs. The yield of TOC in

Alpine section in year 2010 was only 20% lower compare to years 2011 and 2012. In the Bulgarian-Romania section, TOC flux varied more than twofold in the analysed years (Table 1) and clear illustrated that lowest part of Danube River is more biogeochemical reactive during climate changes like upper and middle course of this river. Probably the same scale of TOC variability, hydroclimatic origin, exists in the Danube Delta waters, but detail investigations are need for evaluation this thesis.

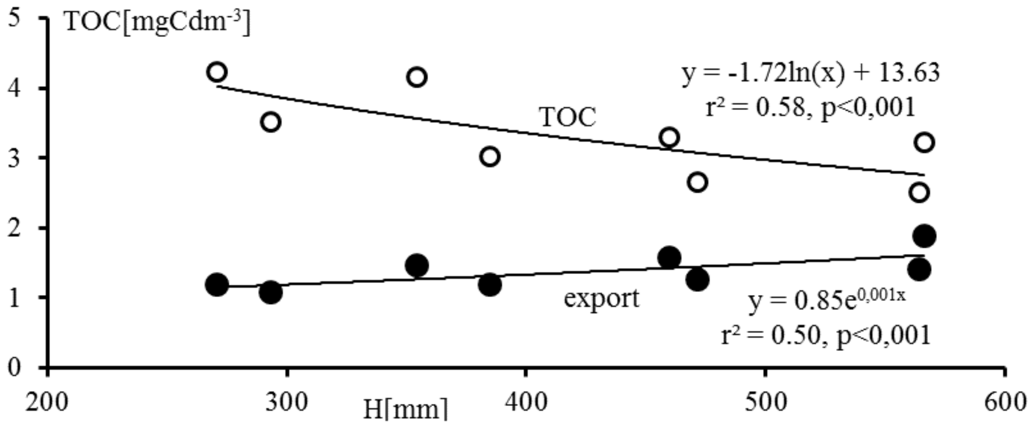

Figure 4. Relationships between runoff (H) and mean annual TOC concentrations (open circle) and TOC annual export (filled circle) along of Danube River course in years 2010-2012

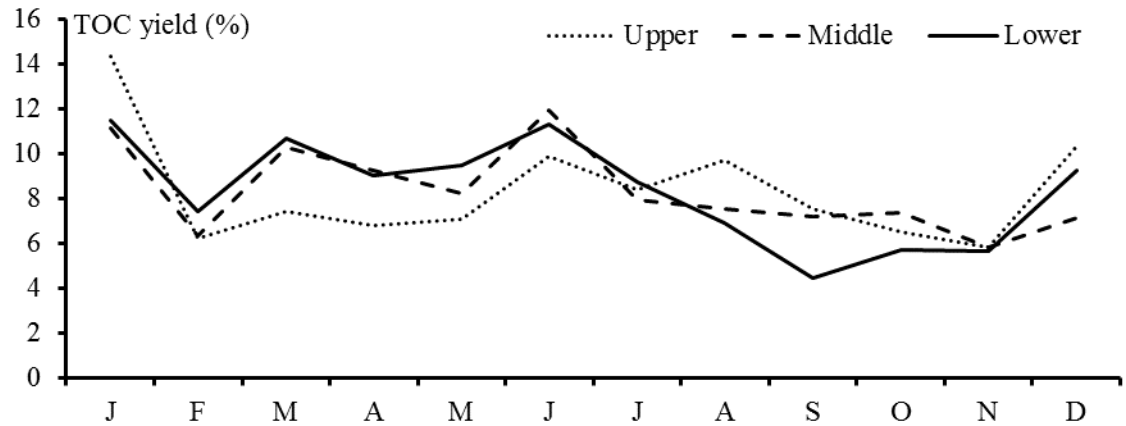

Figure 5. The mean monthly contribution on annual TOC yield in the three parts of Danube River course in years 2010-2012

The presented the recent results of TOC flux from Danube river in years 2010-2012 were much lower than those reported by Tockner et al (2009) for data from 90-th of XX century. Earlier data represented rather upper, mountain section of the river, more frequently studied than the other sections. Also differentiations between earlier published and recent data can be related to the real and intensive changes of water management in the all Danube system starting with assignation of The Danube River Protection Convention in 1994 in Sofia.

The average of monthly TOC export is fairly balanced during the year (Fig.5) and the monthly contribution in the yearly flux are in the wide range 6-9%, except January with data higher than 10%. Thus a strong seasonal the TOC export does not occur in the Danube, compare to arctic and boreal rivers where 55% of annual DOC flux occurs during snowmelt (Finlay et al. 2006). Presented small TOC export dynamics in the Danube River confirms a new "Puls - Shunt Concept" for DOM functionality in the river network proposed by Raymond et al. (2016). The large rivers metabolized organic carbon intensively in the warm season than small rivers in the low temperature and play an "active pipe" role in the DOM flux decrease, as suggested earlier by Cole et al. (2007). However the mechanisms for global change and export of organic matter from the basins are unclear and include a combination of biogeochemical and catchment responses to higher temperature and various precipitation (Sobczak and Raymond 2015).

The recent TOC flux data fits well to global relationships between basin runoff and yield of annual total organic carbon (Fig. 6). The TOC denudation is much lower than noted for a few European rivers - Rhine River, Rhone and Göta River in the Sweden, but higher than in the Dnieper River or Columbia River with high water retention in the dam reservoirs. Lakes and reservoirs can influence river DOM dynamics by influencing both hydrological and biological factors that control DOM characteristics (Hood et al. 2003).

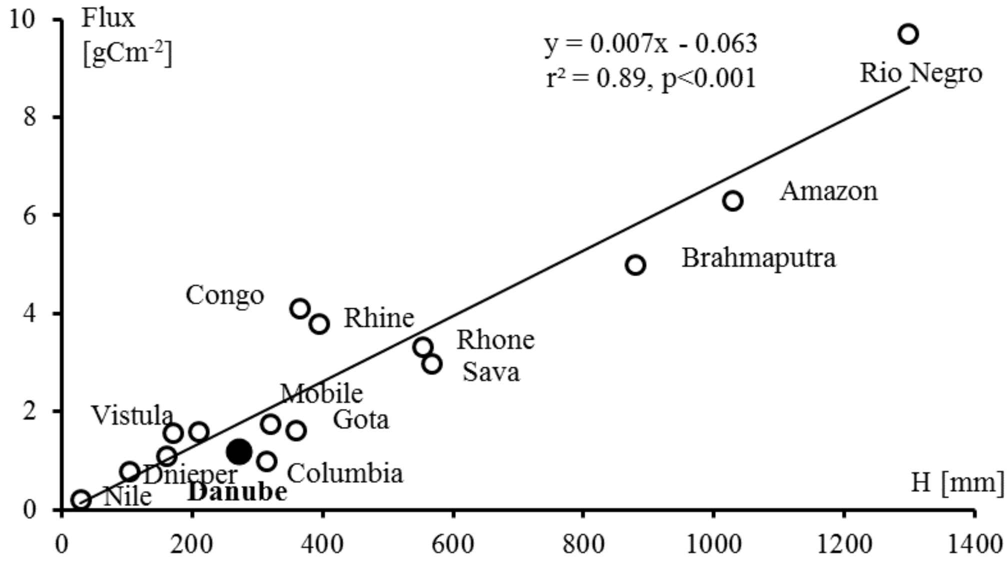

Figure 6. Correlation between runoff (H mm) of the largest rivers and annual TOC export (data from Coynel et al. 2005; Gordeev et al. 1996; Górniak in press; Kuliński and Pempkowiak 2011; Ogrinc et al. 2008; Sempere et al. 2000; Stets and Striegl 2012; Tockner et al. 2009)

Despite the short time of measurements, the presented data show an evident spatial variability of TOC and it's dynamic in the Danube River, which mainly is due the changing of the catchment features and the river channel along its course from Dillingen to Silistra. The fate of riverine TOC in the lowest parts Danube is a little known, especially in the delta area, where there are specific biogeochemical transformations of organic matter before the riverine waters inflow to the sea.

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REFERENCES

Alvarez-Cobelas, M., Angeler, D.G., Sanchez-Carrillo, S., and Almendros, G. (2012). A worldwide view of organic carbon export from catchments, *Biogeochemistry*, **107**, 275-293.

Aufdenkampe, A., Mayorga, E., Raymond, P.A., Melack, J.M., Doney, S.D., Alin, S.R., Aalto, R.E., and Yoo, K. (2011). Riverine coupling of biogeochemical cycles between land, oceans and atmosphere, *Front. Ecol. Environ.,* **9**, 53-60.

Cole, J.J., Prairie, Y.T., Caraco, N.F., McDowell, W.H., Tranvik, L.J., Striegl, R.G., Duarte, C.M., Kortelainen, P., Downing, J.A., Middelburg, J.J., and Melack, J. (2007). Plumbing the global carbon cycle: integrating inland waters into the terrestrial carbon budget, *Ecosystems*, **10**, 171-184. DOI: 10.1007/s10021-006-9013-8.

Coynel, A., Seyler, P., Etcheber, H., Meybeck, J., and Orange, D. (2005). Spatial and seasonal dynamics of total suspended sediment and organic carbon species in the Congo River, *Global Biogeochem. Cycles*, **19**, GB401. DOI:10,1029/2004GB002335.

Finlay, J., Neff, J., Zimov, S., Davydova A., and Davydov, S. (2006). Snowmelt dominance of dissolved organic carbon in high-latitude watersheds: Implications for characterization and flux of river DOC, *Geophys. Res. Lett*., **33,** L10401. DOI:10.1029/ 2006GL025754.

Gordeev, V.V., Martin, J.M., Sidorov, I.S., and Sidorova M.V. (1996). A reassessment of the Eurasian river input of water, sediments, major elements and nutrients to the Arctic Ocean, *Am. J. Sci.*, **296**, 664-691.

Górniak A. (in press). The effects of anthropogenic and climate changes on total organic carbon concentration and export of the Vistula River (Central Europe), *Applied Geochemistry* (under review).

Hood, E., McKnight, D.M., and Williams, M.W. (2003). Sources and chemical character of dissolved organic carbon across an alpine/subalpine ecotone, Green Lakes Valley, Colorado Front Range, United States, *Water Resour. Res*., **39**(7), 1188. DOI:10.1029/2002WR001738.
Hope, D., Billett, M.F., Milne, R., and Brown, T.A.W. (1997). Exports of organic carbon in British rivers, *Hydrol. Process*., **11**, 325-344.
ICPDR (2005). *The Danube River basin district. Part A, Basin –wide overview*. International Commission for the Protection of the Danube River, Document IC/084, Vienna, 175p.
Jelev, I. and Jelev, V. (2012). An ecohydrology approach to the Danube River and the "enviroGRIDS" project, *Ecohyd. Hydrob.*, **12**(2), 137-152.
Kuliński, K. and Pempkowiak, J. (2011). The carbon budget of the Baltic Sea, *Biogeoscience*, **8**, 3219-3230. DOI: 10.5194/bg-8-3219-2011.
Ludwig, W., Probst, J.L., and Kempe, S. (1996). Predicting the oceanic input of organic carbon by continental erosion, *Global Biogeochem. Cycles*, **10**, 23–41. DOI: 10.1029/95GB02925.
Preiner, S., Drozdowski, I., Schagerl, M., Schiemer, F., and Hein T. (2008). The significance of side-arm connectivity for carbon dynamics of the River Danube, Austria, *Fresh. Biol*., **2**, 238-252.
Raymond, P.A., Saiers, J.E., and Sobczak, W.V. (2016). Hydrological and biogeochemical controls on watershed dissolved organic matter transport: pulse- shunt concept, *Ecology*, **97**(1), 5-16.
Räike, A., Kortelainen, P., Mattsson, T., and Thomas, D.N. (2012). 36 year trends in dissolved organic carbon export from Finnish rivers to the Baltic Sea. *Science of Total Environment*, **435–436**, 188–201.
Sempere, R., Charribre, B., Wambeke, F., and Cauwet, G. (2000). Carbon inputs of the Rhine River to the Mediterranean Sea: Biogeochemical implications, *Global Biochemical Cycles*, **14**(2), 669-681.
Sieczko, A. and Peduzzi P. (2014). Origin, enzymatic response and fate of dissolved organic matter during flood and non-flood conditions in a river-floodplain system of the Danube (Austria), *Aquat Sci.*, **76**, 115-129.
Soballe, D.M. and Kimmel, B.L. (1987). A large-scale comparison of factors influencing phytoplankton abundance in rivers, lakes, and impoundments, *Ecology*, **68**, 1943-1954.
Sobczak, W.V. and Raymond, P.A. (2015). Watershed hydrology and dissolved organic matter export across time scales: minute to millennium. *Freshwater Science*, **34**(1), 392-398.
Ogrinc, N., Markovics, R., Kanduc, T., Walter, L.M., and Hamilton, S.K. (2008). Sources and transport of carbon and nitrogen in the River Sava watershed, a major tributary of The River Danube, *Applied Geochemistry*, **23**, 3685-3698.
Stets, E.G. and Striegl, R.G. (2012). Carbon export by rivers draining the conterminous United States, *Inland Waters*, **2**, 177-184.
Teodoru, C. and Wehrli, B. (2005). Retention of Sediments and Nutrients in the Iron Gate I Reservoir on the Danube River, *Biogeochemistry*, **76**(3), 539-565.
Tockner, K., Uehlinger, U., Robinson, C.T., Tonola, D., Siber, R., and Peter, F.D. (2009). Introduction to European rivers. In K. Tockner, C.T. Robinson, & U. Uehlinger U. (Eds.), *Rivers of Europe* (pp. 1-22). Amsterdam: Elsevier.
Williamson, C.E., Morris, D.P., Pace, M.L., and Olson, O.G. (1999). Dissolved organic carbon and nutrients as regulators of lake ecosystems: Resurrection of a more integrated paradigm. *Limnol. Oceanogr*., **44**, 795–803.
Worrall, F. and Burt, T.P. (2007). Flux of dissolved organic carbon from UK rivers, *Global Biogeochem. Cycles*, **21**(1), GB1013, DOI:10.1029/2006GB002709.
Wrzesiński, D. (2013). Uncertainty of flow regime characteristics of rivers in Europe, *Quaest. Geogr.*, **32**(1), 43-53.
Yeh, T.C., Bondar-Kunze, E., Tomas, D., Kirschner, A., Marjanovic-Rajcic, M., Welti N., and Hein T. (2015). Quality and quantity of dissolved organic matter. In I. Liška, F. Wagner, M. Sengl, K. Deutsch, and J. Slobodník (Eds.), *Joint Danube Survey 3. A comprehensive analysis of Danube water quality* (pp. 199-204), Vienna: ICPDR.