



Spatial and temporal patterns of total organic carbon along the Vistula River course (Central Europe)

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ABSTRACT

Various recent trends of river organic matter concentrations and flux have been presented for Northern Hemisphere. The catchment of the Vistula River has been a place of intensive economic transformation since the 1980s, which has been accompanied by increase of extreme weather and hydrological events. The patterns of total organic carbon (TOC) has not yet been studied on Vistula River, the largest Polish river, with a basin area of 194000 km² and a mean annual flow exceeding 1000 m³s⁻¹. Annual TOC concentrations in the river mouth decreased from 10.7 mgC dm⁻³ to 7 mgC dm⁻³ between years 2000–2014; however, during a 55-year period, the TOC decrease was estimated to be 45% as a result of a large scale reduction of waste supply to Polish rivers. The Vistula River annual mean TOC export (flow normalized) was 1.54 gC m⁻² and significantly decreased, with a high inter-annual variations depending on hydrology. Gradual decreases of TOC flux were observed along the river continuum from headwaters to downstream. TOC export in wet years was 5 times higher than in dry years, indicating the important role of river flooding and droughts on TOC load to the southern Baltic Sea. Dam reservoir located on the lower part of the Vistula River course have had a large impact on the retention of terrestrial TOC load, reducing annual flux by approximately 20%.

1. Introduction

Organic carbon is an essential biosphere component and, like other elements in the ecosystem, is in constant circulation due to solar energy input and constant water movement. Part of global carbon takes place in inland aquatic systems, but fluvial system plays an important role in carbon transport, sequestration, accumulation and transformation its forms (Cole, 2007). Water is the universal solvent of substances formed during the physiological processes of plants, animals, products of the weathering lithosphere and exported substances from the soil. Thanks to gravity and solar energy forces, flowing water is a carrier of detritus transported into the oceans. The presence of dissolved (DOC) and particulate (POC) forms of carbon in water is the basis for the development of aquatic autotrophic and heterotrophic organisms (Alvarez-Cobelas et al., 2012). Organic matter (OM) is thought to be as important as nitrogen, phosphorus and silica, an important biological driver, in the functioning of water ecosystems (Williamson et al., 1999). Total organic carbon (TOC) forms occurring in freshwaters have much higher concentrations than other nutrients (N, P, Si), and their surpluses are exported from basins and conditioned by climatic (Evans et al., 2005; Sarkkola et al., 2009; Mattsson et al., 2009b), hydrological (Lauerwald et al., 2012) and, in many sites, by human activity. Organic soil leads to significant increase TOC export intensity (Wilson and Xenopoulos,

2008; Worrall et al., 2012).

Intensive studies of freshwater organic carbon began after the documented an increase in TOC concentration, changed fish structures in Scandinavian rivers and lakes affected by anthropogenic acidification (Monteith et al., 2007). The UK (Evans et al., 2006; Clark et al., 2010), the USA (Hanley et al., 2013) and Scandinavian Peninsula (De Wit et al., 2016) have described a significant increase in river DOC concentrations resulting from global climate changes in XX century. Also, many of the studies indicated that changes in atmospheric deposition and hydrology are the main driver for the water brownification (Evans et al., 2006; Erlandsson et al., 2008). In turn, the increase in organic carbon resources in small Central European streams have been explained by decreases in the ionic strength of the water (Hruska et al., 2009).

Many earlier studies on TOC export or organic matter trends pointed mainly to organic rich freshwaters (humic waters) with very heterogeneous data and were not comparable from a methodological point of view, giving quite different values and trend directions depended to catchment area (Alvarez-Cobelas et al., 2012; Filella and Rodriguez-Murillo, 2014).

Recent estimations of TOC export with rivers of continental Europe are not uniform. Most often, these estimations were taken from semi-natural catchments (Hope et al., 1997; Mattsson et al., 2009a), with a

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large share of wetlands (Kortelainen et al., 2006; Freeman et al., 2004; Worrall et al., 2012). In boreal catchments, the annual TOC flux has been estimated to be higher than 10 gCm^{-2} , which is almost twice more than the global average (Ludwig et al., 1996) and rivers of the Amazon (Salimon et al., 2013). Moore et al. (2011) reports an annual TOC export of 82 gC m^{-2} for a small tropical basin in Indonesia. Equally high values of riverine TOC export, in the range of $4\text{--}8 \text{ gC m}^{-2}$, were recorded in the 1980–90s in highly urbanized rivers of Western Europe, as well as in Amazonian rivers (Degens et al., 1991) and in small mountain rivers of Panama (Goldsmith et al., 2015). However, the largest organic matter flux from catchments in rivers were recorded in the Ganges and Mekong, with 21 gC m^{-2} and 11 gC m^{-2} , respectively (Ludwig et al., 1996). Climate specifics, high population density, cultural traditions of river water use and imperfect sewage treatment make TOC exports much higher than average values for large rivers. TOC exports from the basins of Chinese rivers have values in a temperate range ($2\text{--}8 \text{ gC m}^{-2}$), but with high shares of POC in the total organic export (Lu et al., 2012). TOC export from intensively used catchments can be significant reduce by intensive waste management despite significant climate and hydrology fluctuations (Rodríguez-Murillo et al., 2015).

Hydrological conditions increased share of forests and wetlands (Mattsson et al., 2009a; Worrall et al., 2012) are factors increasing a natural TOC export, while an increased share of lake areas and the volume of water retained in artificial reservoirs and ponds can limit TOC export (Kortelainen et al., 2006; Räike et al., 2012). The specificity of temperate rivers is the significant diversification of natural environmental conditions and the intensity of anthropogenic changes. Political and economic conditions are important in water management and pro-environmental lifestyles. The post-communistic countries of Central Europe have been subjected to rapid decrease of industrial production since the 1990s, limiting total TOC flux. In this time the significant reduction of industrial and communal waste production, the decrease in water use and changes in water and wastewater management were observed, as well as a decrease in the total amount of fertilizers used in agriculture (Majewski, 2013). Additionally, the number of intensive cattle and pig farms has also increased (Pastuszak and Igras, 2012). Therefore, the Vistula River is an appropriate basin for a biogeochemical long-term TOC study. The aim of the present study is to estimate the dynamic of TOC concentrations on the basis of direct and long-term data of TOC measurements in the first 15 years of the 21st century. I also study TOC seasonality along the course of the Vistula River as the primary and historically important river of Poland. I would like to explain what are significant factors determining TOC export from Vistula River during the significant transformations of the economy coincides with the recent climate change has impacted TOC fluxes in this river.

2. Study area

2.1. Characteristic of basin

The basin of the Vistula River (VR) has a total area of 194.424 km^2 (54% of Poland, Fig. 1), 12% of the basin area is located in the Ukraine and Belorussia (Bug River) and 1% in Slovakia (Poprad River in Dunajec River basin). It is 8-th river order with the largest-area river basin in the drainage area of the Baltic Sea. The Vistula River runs from south to north for a distance of 1041 km, with a mean catchment elevation of 270 m a.s.l. and a range of 2655 to -1.8 m a.s.l. (depression in a delta-type estuary). The mountainous section of the river is on the upper course and consists of only 10% of the river length and has a channel slope greater than 1‰. However, the rest of VR's course has a slope typical for a lowland river ($0.2\text{--}0.3\text{‰}$), with sections of braided channels or low class regulated waterways (Table 1). The theoretical time of water flow from its springs to the Baltic Sea has a mean 60 days and most of the time is spent in the Polish Lowland. Dunajec, Wisłoka, San

rivers (a, b, c in Fig. 1) are the main mountain tributaries with high amplitude of discharges. Highland part of VR basin with Nida, Pilica and Wieprz Rivers (e,f,g on Fig. 1) have a stabile water resources, caused by the high groundwater supply in total outflow from basins. Narew River and Bug River have a largest percent of active wetlands with high flow of melt waters in the spring. Drwęca and Brda rivers represent lakeland regions with low seasonal variation of discharge cause by lakes located on the river course.

2.2. Hydroclimatic conditions

With the exception of the mountain basin, most of the VR basin is located in a temperate continental climate with warm summer (Dfb), according to the Köppen classification (Peel et al., 2007), with an average temperature between 7° and 9°C (data for years 1971–2000), with monthly average values higher than 18°C in July and minimal values in January (Institute of Meteorology and Water Management data from GUS, 2015). The amount of precipitation reaching the catchment, depends on the basin's altitude, with more than 1000 mm per year occurring in the mountains, 600–700 mm in the highland and lowland lakeland areas and less than 550 mm in middle of the Vistula River course. Weather conditions during the presented investigations were highly variable, with warm conditions, poor snow winters and poor precipitation, different between years and seasons. In the years 2000–2014 in the VR basin, the mean annual air temperature was $0.7\text{--}1^\circ \text{C}$ higher than average from years 1960–2000. The mean annual sum of precipitation in the last 15 years was 20–40 mm higher than noted in the years from 1971 to 2000 (Table 2). High precipitation in summer 2010 effected on large flash floods in southern part of Vistula River basin. The reversed contrast climate conditions were noted in 2003 and 2012 as a very dry and warm.

2.3. Hydrological regime

High multiannual flow irregularity is a characteristic feature of the Vistula River as well as other Central European rivers (Gailiūsis et al., 2011), and monthly discharges at the mouth of the investigated river have changed ten times in the last 15 years (Fig. 2). The average flow at the mouth of the Vistula River was $1054 \text{ m}^3\text{s}^{-1}$ for the period from 2000 to 2014 with its maximum between May–June and its minimum between November–December (Fig. 2). This annual pattern of river discharges is typical for rivers with two periods of high water, referred to as the snowy-rain regime (Łajczak et al., 2006). Spring high waters result from spring snowmelt, and in June/July there are heavy rains. A river ice-jam flood occurs from time to time, in the lower, northern part of the river valley. The upper course of Vistula River has a water regime typical for mountainous character with two (late spring and middle summer) high water periods and low discharge in winter. In the middle course, highland rivers inflow with a high groundwater supply increase flow in winter and autumn. However, in the lower part of VR basin, the lowland plain rivers have an important role in the spring where the highest flows occur and low flows in the late summer and early autumn (Narew River).

The highland and lowland lakeland rivers have a more balanced flow than the rest of the investigated rivers, caused by high and more stable water resources in their basins. Seasonal and spatial changes along the course of the Vistula River flows are affected by artificial water retention in the Goczałkowice Dam (upper course) and in the Włocławek Dam Reservoir located in the end of middle course VR, with volume of 408 mln cubic meters and mean 5–7 days of water residence time.

2.4. Catchment and waste management

Arable area dominates the Vistula River catchment (47%), forests cover 29% of the area, wetlands cover 9.6%, and urbanized areas

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