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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 km^2 and a mean annual flow exceeding 1000 m^3s^{-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 4–8 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 (2–8 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 (Rodriguez-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 (0.2–0.3‰), 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 0.7-1° 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 (Gailiusis 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 m^{3}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

Fig. 1. Vistula River catchment, tributaries and stations of water sampling. Number of stations as in Table 1. Meteorological stations (A–G) as in Table 2. Tributaries: a - Dunajec River, b- Wisłoka River, c- San River, d- Przemsza River, e – Nida River, f- Pilica River, g- Wieprz River, h- Bzura River, j- Bug River, k- Narew River, l- Drwęca River, m- Brda River.

compose approximately 4% of the catchment. The mean basin population density is low (135 ind./km^2) with maximal values, 350 ind./km^2, in the Cracow-Silesia Conurbation (SW part of basin) and minimum values, below 50 ind./km^2, in the subbasins of the Narew River (NE part) and San River (SE part). The main river valley's direction, from south to north, provides an important transcontinental corridor for seasonal bird migration. The most natural and largest Central European wetlands are located in the northeastern subbasins (Narew River, Biebrza River). Additionally, in the SE part of the catchment – the Przemsza River subbasin, an intensive and long history of mining activity has had a significant impact on the water quality of the VR over a relatively long part of its course (loads of wastes with high salinity and artificial mineral seston of coal origin) (Buszewski et al., 2005). However, in the rest of the VR catchment after 1990, wide and intensive national and local activity significantly increased water quality (Majewski, 2013). Starting from 1989, political and economic transformations, especially after EU access, changed the system of water management and resulted in a two-fold decrease in total water and waste volume production (Kowalkowski et al., 2012). In the Vistula River basin during years 2000–2014 changes of water and waste management were effective after introduction a large number of new a wastewater treatment plans. Thus, a decrease in the water volumes used in industrial plants and consumed in households was evident (GUS, 2015). Therefore, the Vistula River's recent hydrochemical state is completely different than that described earlier (Niemirycz, 1997; Tockner et al., 2009).

Table 2
Hydroclimatic data for Vistula River catchment in the investigated period 2000–2014 against climatic data 1971–2000 (IMWM data from GUS, 2015). Stations location there are in (Fig. 1).

Stations	Elevation (m a.s.l)	Air temperature (°C)		Precipitation (mm)	
		1971–2000	2000–2014	1971–2000	2000–2014
A- Nowy Sącz	292	8.2	9.0	737	776
B- Katowice	284	8.2	8.9	717	736
C- Lublin	238	7.4	8.3	597	618
D - Kielce	260	7.4	8.2	650	645
E- Warszawa	106	8.1	9.0	505	579
F- Białystok	148	6.9	7.6	594	607
G- Toruń	69	8.1	8.9	526	563

3. Methods

3.1. Sampling and data collection

Data used in this study were collected by the National Water Monitoring Program (NWMP) and provided by the Provincial Environmental Protection Inspectorates in Cracow, Rzeszów, Lublin, Warszawa, Bialystok, Toruń, and Gdańsk. In the years from 2000 to 2014, monthly or biweekly water sampling was conducted at seven stations located along the Vistula River (Fig. 1, Table 1). Water temperature, pH, and conductivity were measured in the field, and TOC concentrations were determined in Regional Environment Protection.

Laboratories by automatic high-temperature oxidation methods

Table 1
Morphological, hydrological features along the Vistula River course, hydrological averages from period 2000–2014.

Stations		Distance from spring	Catchment area	River order	Average discharge	Average outflow	Type of river channel
		(km)	(km^2)		(m^{3}s^{-1})	(mm)	
I	Strumień	56	445	4	9.1	648	mountain river
II	Nowy Bieruń	110	1780	5	21.2	376	canalizated waterway
III	Annopol	405	51515	7	455	278	braided river in the gap
IV	Warszawa	618	84630	7	588	219	canalizated in urban area
V	Płock	735	168845	8	951	178	braided channel
VI	Włocławek	781	171764	8	939	172	canalizated below the dam reservoir
VII	Kieżmark	1036	193923	8	1053	171	canalizated in delta – type estuary

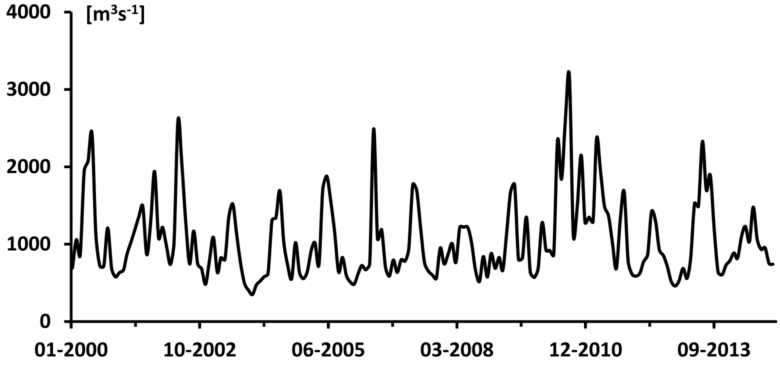

Fig. 2. Mean monthly discharge of Vistula River in the mouth (station VII) in years 2000–2014.

according to the PN-EN 1484 standard method. This method was officially introduced in 2004 by the Polish Water Monitoring Program (PWMP); earlier organic matter resources were determined as a chemical oxygen demand (CODMn). For five stations in the period from 2000 to 2004, when TOC was not measured directly, concentrations were estimated using linear regression, calculated separately for each station from data of parallel TOC and CODMn determinations provided after 2004. Most of the regressions have a high correlation value with r^2 higher than 0.7–0.8. Similar TOC - CODMn correlations were found in Finnish waters by Kortelainen (1993) and Sarkkola et al. (2009). For a 15-year period (2000–2014), 1450 TOC data from seven stations along the Vistula River course were collected. Results of TOC concentrations earlier than 2000 for the Vistula River were recalculated from CODMn archival data (annual average concentrations) from Kieżmark (station VII) using a TOC- CODMn relation for this stations from period 2000–2014. In this stations (VII), a national river monitoring was provided from 1961 with a few breaks (Niemirycz, 1997), thus data represent period of 53 years.

3.2. Calculations and statistics

Most PWMP stations were located close to hydrological stations of the Institute of Meteorology and Water Management, where daily river flow was determined. The average monthly flow data were used for calculations of riverine fluxes (multiplying monthly concentrations and monthly flow). In the absence of TOC data from the whole year in a station series, the missing values of annual TOC fluxes (calendar year) were calculated separately for each station using an equation from the data of annual TOC flux and annual mean flow (all had r^2 values greater than 0,8, $p < 0,001$). Additionally, annual average TOC concentrations were normalized using a monthly flow according to methods described in Hope et al. (1997). Using the difference yearly load data between stations V and VI, the TOC retention in Włocławek Reservoir was calculated. For trends analysis (annual data) I have used the non-parametric test Mann-Kendall, which documents a significant long-term trend of parameter ($p < 0.05$).

4. Results

4.1. River hydrochemistry

The annual average water temperature of the Vistula River was similar at each of the stations, with a range of 10.8–12 °C, and a statistical significant differentiation between stations occurred for in the period of May–August. The riverine water contained temperate amounts of dissolved mineral components and at most of the investigated stations, conductivity ranged from 300 to 700 μS cm^{-1}, total phosphorous 0,1–0,2 mgP and total nitrogen (TN) 2,5–3,1 $mgNdm^{-3}$ (Table 3). However, below the Przemsza River inflow to VR (Station II) an artificial water salinization was observed in the short stretch of headwater (Table 3). Water with pH in the range 7.5–8.5 was typical in the VR course and nutrients had moderate concentrations, decreasing gradually from the middle to lower parts of the river course (Table 3). Seasonality of riverine water chemistry with course refers to the discharge regime; therefore, high spring runoff gives a different level of water softness, and autumn low water represents mainly groundwater chemistry, as appropriate for the catchment geology.

4.2. TOC concentrations

TOC concentrations in the VR in the period from 2000 to 2014 ranged from 1.1 to 29.3 mgCC dm^{-3}, and average values for the studied stations along the river varied in a smaller range from 6 to 9 mgC dm^{-3}. But in the first 60 km long mountain river course mean concentrations were two times lower than in the rest part of river (Table 4). A significant increase in TOC concentrations below the inflow of the polluted Przemsza River (Station II) and Narew River (Station V) was observed. The middle and lower courses of the Vistula River have an aligned TOC source, and only a slight, 10% decrease in the TOC average was noted after water passage through the Włocławek Dam Reservoir (Station VI) and a 40% reduction in the TOC concentration's variability (Table 5). TOC seasonality was clearly marked except in the headwaters, and the monthly averages of TOC for most stations were lower in the winter and larger in the summer, except for at Station II where there exists a high anthropogenic modification of the river channel and in the basins of its tributaries (Table 5).

Seasonal differences between the mean summer and winter TOC concentrations were higher in the upper course than in the middle and lower courses of the Vistula River. Differences of mean annual TOC concentrations in wet (2010) and dry (2012) years show that in the middle part of the Vistula River course, high water flows significant increased TOC, but not observed at other stations (Fig. 3). The average values of TOC concentrations along the VR course were significantly correlated with runoff, which is an important factor determining the organic matter richness in rivers (Fig. 5). A gradual decrease in TOC concentrations and the flux of the VR was observed over the 15 years, but as a Mann-Kendall shows this trend is not statistically significant (for example for station III test results were following; $S = -39$, $Z = 1.88$, $p = 0.061$) (Fig. 3A). TOC fluctuations were higher in headwaters than in downstream.

The long-term data, starting from 1960 indicated more clear decreasing trend of TOC concentration in the mouth of Vistula River (Fig. 4). The Mann–Kendall test for 48 annual data shows statistically significant negative trend for TOC ($p < 0.0001$), however for a mean annual discharges was not exist.

4.3. TOC export

Annual TOC flux during the 15-year period (2000–2014) from the Vistula River catchments was 302 Gg yr^{-1} ($Gg = 10^9$ g), corresponding to a mean annual areal export of 1.57 gCm^{-2} (Table 4). This value was the lowest of all stations under investigation, because areal TOC export

Table 3
Basic water components concentrations along course of Vistula River in years 2000–2014, data from NWMP.

Stations	Distance from spring (km)	EC (μScm^{-1})	pH	TP (μgdm^{-3})	TN (mgdm^{-3})	N-NO$_3$ (mgdm^{-3})
I	56	243 ± 60	7.5 ± 0.2	104 ± 49	2.48 ± 0.8	1.66 ± 0.8
II	110	5189 ± 4232	7.4 ± 0.1	356 ± 290	4.85 ± 1.7	1.97 ± 0.8
III	405	761 ± 258	8.2 ± 0.3	125 ± 51	2.49 ± 0.8	1.27 ± 0.7
IV	618	692 ± 193	8.3 ± 0.4	182 ± 99	3.09 ± 1.2	1.43 ± 0.8
V	735	578 ± 159	8.1 ± 0.4	152 ± 120	2.46 ± 1.1	1.24 ± 1.1
VI	781	640 ± 153	8.0 ± 0.8	165 ± 83	2.63 ± 1.1	1.30 ± 1.0
VII	1036	751 ± 152	8.1 ± 0.3	186 ± 84	2.51 ± 0.9	1.33 ± 0.9

decreased with small non-regular fluctuations starting from 2.4 to 3.0 gCm^{-2} and ending with values 50% lower at Station VII near river mouth. A significant high TOC export was observed only in Station II, below inflow of Przemsza River from coal mine Silesia region. In the wet years TOC flux in the upper, mountain part of catchment increased higher (st. I, III) than in lowland part (st.V,VI,VII) (Table 5, Fig. 6A). A long term data from station VII indicated that export slowly increase up to the first years of 80-s and after deep reduction in years 1983–1990, the next smaller than earlier TOC export maximum has placed. In the XX century TOC export in lower VR was stabile with values near 1.0–1.1 gC m^2 and only in one year 2010 (flood period) high value of TOC export was noted.

Seasonality of TOC export closely follows the seasonality of river runoff at each station, with the lowest monthly load below 5% of the yearly flux in the coldest period (December–January) and the highest values in May or June (Fig. 7). Spring months (March–April) are characterized by a greater TOC load in the lowland part of the river than in the mountain or highland parts of the Vistula River course. The situation is reversed in the late summer and autumn (August–November).

As my calculation shows (see section Methods), difference between annual flux in stations VI and VII (Fig. 1) (before and downstream of the Włocławek Dam Reservoir) is statistically significant (Kruskal-Wallis test, H (chi2) = 4.92, p = 0.026). Near 68 × 10^{3}t of TOC per year (20% of the total annual riverine TOC load) is accumulated and metabolized in this reservoir, especially in April and June. In the period 2000–2014, only in two years (2001, 2002) input and output of organic carbon to reservoir was practically the same in situation of low water inflow to reservoir (Fig. 8). Thus the biogeochemical role of this reservoir in TOC load reduction from a whole VR catchment is important.

5. Discussion

5.1. Beneficial impact of improved basin management

The presented TOC data clear show that for the Central European freshwaters, the last 20 years was a time of slow return to an ecological state of rivers, not observed when monitoring series started. Intensive economic transformations from a communist to free market economy forced also changes in water management in the Vistula River catchment. A significant "revolution" in water management in the last 15 years (2000–2014) was made, that accompanied increasing industrial and agricultural activity. A decrease in the water volumes used in industrial plants and consumed in households was the most important change (Majewski, 2013; Pastuszak et al., 2012), as well as an increase in the amount of wastewater treatments (GUS, 2015). More effective waste treatment (higher levels of phosphorus removal and an increase in the share of the population using the wastewater network increase from 51.5% in 1999 to up to 71.3% in 2014 (GUS, 2015). In the last 15 years a significant changes were observed in the Polish rural areas, where length of sewage network increased 5 times and share of village population served by sewage network increased 3 times (GUS, 2015). These changes particularly affected N and P fluxes and the organic matter transport (Pastuszak et al., 2012). Recent TOC concentrations in the Vistula River, with annual values 7–8 C dm^{-3}, are below the mean concentrations of running water (Ludwig et al., 1996) and have become more typical of seminatural, temperate large rivers, with values comparable to those presented for the Daugava River (Kokorite et al., 2012). Therefore, long-term trends in TOC concentrations observed in the Vistula River have resulted mainly from economic and pro-environmental activity at the basin scale, including strong increase number of new and modern waste treatments plants together with sewage network and also new water usage fee rules. In the same time there are not any significant trend in average of annual discharge and

Table 5
The average flow normalizated TOC concentrations along the Vistula River course in the wet year 2010 and dry year 2012; w/d-ratio of values from wet and dry years.

Stations	SQ (m^{3}s^{-1})			TOC (mgCdm^{-3})			Export (gCm^{-2})		
	wet	dry	w/d	wet	dry	w/d	wet	dry	w/d
I	16.5	7.0	2.4	3.46	2.96	1.2	4.04	1.88	2.2
II	42.9	14.9	2.9	7.83	4.54	1.7	5.95	1.20	5.0
III	851.0	290.3	2.9	3.73	4.40	0.84	1.94	0.78	2.5
IV	1057.3	379.0	2.8	7.82	8.18	0.95	3.08	1.16	2.7
V	1568.0	687.8	2.3	12.2	10.2	1.2	3.57	1.31	2.7
VI	1580.7	699.1	2.3	8.51	7.97	1.1	2.47	1.02	2.4
VII	1663.2	798.0	2.1	9.80	7.82	1.3	2.65	1.01	2.6

Table 4
Total organic carbon concentrations in the Vistula River and flux in the years 2000–2014; n-number of TOC samples. Station as in Table 1 and Fig. 1; 1- average flow-adjusted values.

Stations	n	TOC concentrations							Annual TOC export (gCm^{-2})
		range	average[1]	V	winter	spring	summer	autumn	
		(mgC/dm^3)		(%)	Dec–Feb	Mar–May	Jun–Aug	Sept–Nov	
I	159	1.1–8.1	3,76	33,9	3.0 ± 1.1	3.0 ± 0.9	4.3 ± 1.2	4.5 ± 1.1	2.38
II	146	2.0–26.6	6.94	39.4	7.5 ± 5.8	6.2 ± 1.9	7.6 ± 3.5	6.3 ± 2.2	2.97
III	136	2.2–29.3	7.05	49.1	5.6 ± 2.2	6.7 ± 2.7	9.3 ± 4.9	6.6 ± 2.7	1.99
IV	274	3.4–17.9	8.36	31.0	6.9 ± 2.0	8.3 ± 2.3	9.9 ± 2.7	8.4 ± 2.6	1.86
V	164	4.4–25.5	9.61	40.7	8.0 ± 3.3	9.5 ± 4.1	10.9 ± 3.5	9.9 ± 4.4	1.79
VI	145	5.1–14.0	8.77	22.1	7.8 ± 1.6	8.9 ± 2.2	9.4 ± 1.5	8.8 ± 1.7	1.47
VII	269	3.9–14.8	9.15	23.4	8.1 ± 1.6	9.6 ± 1.8	9.8 ± 2.2	8.4 ± 2.2	1.57

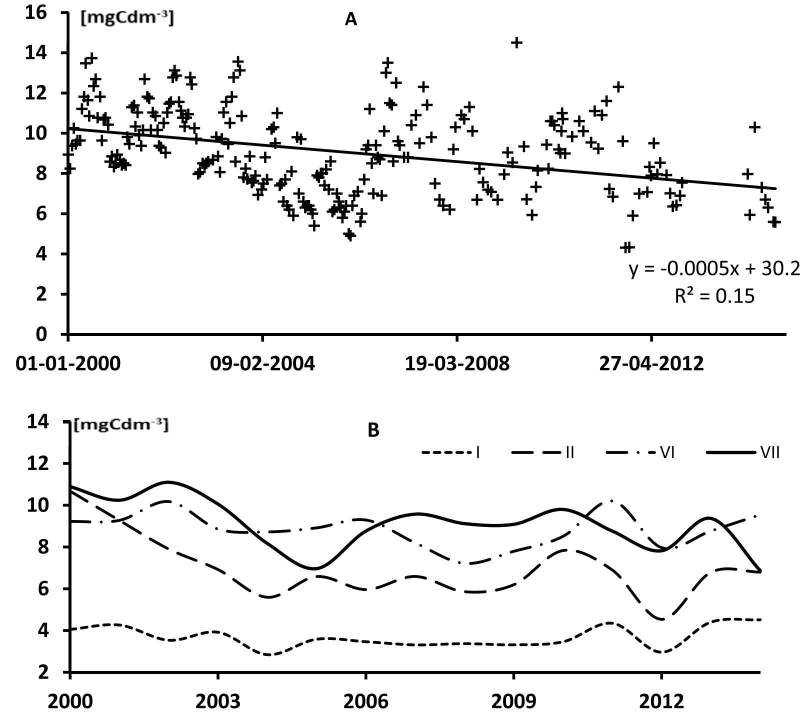

Fig. 3. Monthly TOC concentrations (A) in the station VII and yearly data (B) for selected monitoring stations along Vistula River course in period 2000–2014; station numbers as on Table 1.

clear show that TOC changes effected non-natural origin.

The anthropogenic decrease of TOC concentrations occurred regardless of the values of river flow, both in years with high and low water. This study shows that earlier estimates for TOC concentrations in the Vistula River were too high (Niemirycz, 1997; Kuliński and Pempkowiak, 2011) and represent more past situation than present time. Recent TOC concentrations in the VR are much lower than those observed in boreal Swedish (Erlandsson et al., 2008) and Finnish rivers (Räike et al., 2012) but higher than those observed in Swiss mountain rivers (Rodriguez-Murillo et al., 2015), the Drava River (Ogrinc et al., 2008) and the Danube River (Górniak, 2016). More detail comparison data from VR with results from other studies are very difficult caused by large range of analytical methods used and different data treatment method applied (Filella and Rodriguez-Murillo, 2014).

The specific TOC abundance in the Vistula River is connected to the structure of its catchment, an especially high proportion of hydrochemical active wetlands in the lowland tributaries (Narew River, Bug River), located in the northeastern part of the basin. This type of basin, typical for boreal landscapes, largely determines TOC riverine resources (Räike et al., 2012; Winterdahl et al., 2014) and also has important effects on Central European rivers, not only in VR but also in Neman or Daugava Rivers.

Low-order rivers are strongly biochemically and hydrologically connected with catchment drainage and organic carbon resources refer to landscape characteristics. A six order and higher order temperate rivers TOC resources are more under basin hydrological control than landscape type which they across (Raymond et al., 2016) and become more transit than autochthonic. Biogeochemical processes in channels of high order rivers become autochthonic and are not always typical of processes existing in their tributaries (Tockner et al., 2009).

Organic matter of wetland origin introduced into the river net is a very resistant, causing an aromatic structure in humic substances (Mattsson et al., 2009a), not easily utilized by freshwater microorganisms. However, anthropogenic organic matter from waste and surface runoff is more effectively used by bacteria and fungi and provides a short residence time of TOC in the surface water when conditions are favourable (Stanley et al., 2012). Location of the Włocławek Dam Reservoir in the lower part of the VR course determines that part of the organic matter exported from the wetland part of basin is effectively used in limnic processes. TOC concentrations in the VR below the dam are decreased, which is advantageous from the point of view of the Baltic Sea waters. The effect of TOC reduction occurs in the temperate dam reservoirs only with short water retention time when the retention time is lower than 30–40 days. Longer water retention time of

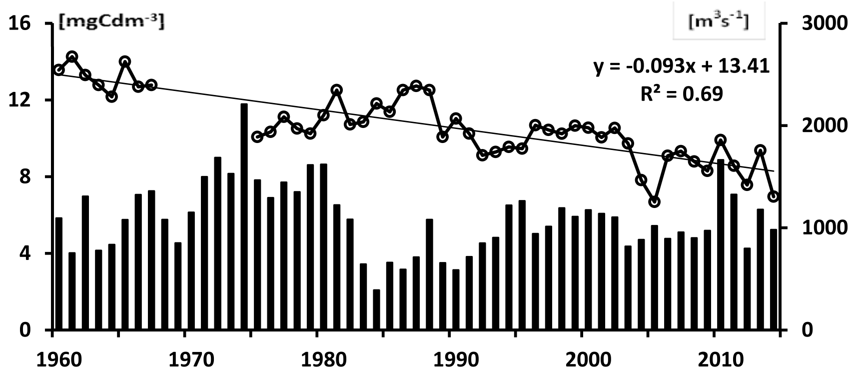

Fig. 4. Long-term TOC concentrations trend in Vistula River in station VII in years 1960–2014 (left axis) and average of yearly discharges. For period 1969–1975 lack of data.

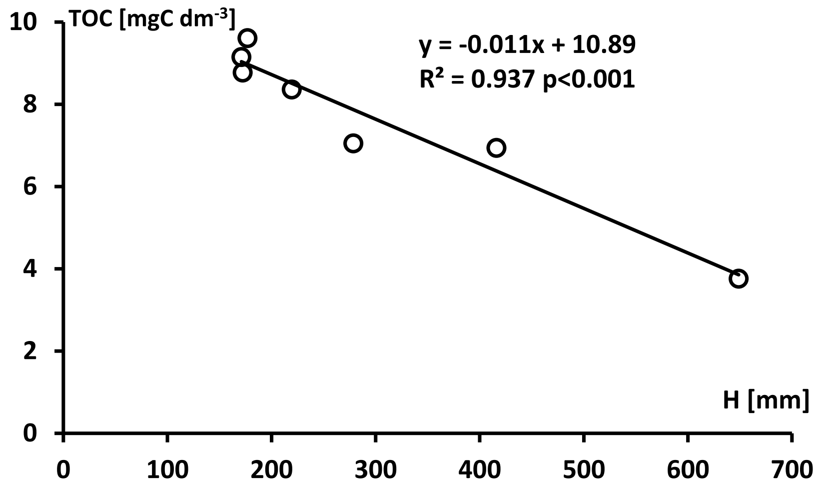

Fig. 5. Relationships between water runoff (H) and TOC concentrations along the Vistula River course; mean data from years 2000–2014 for each stations.

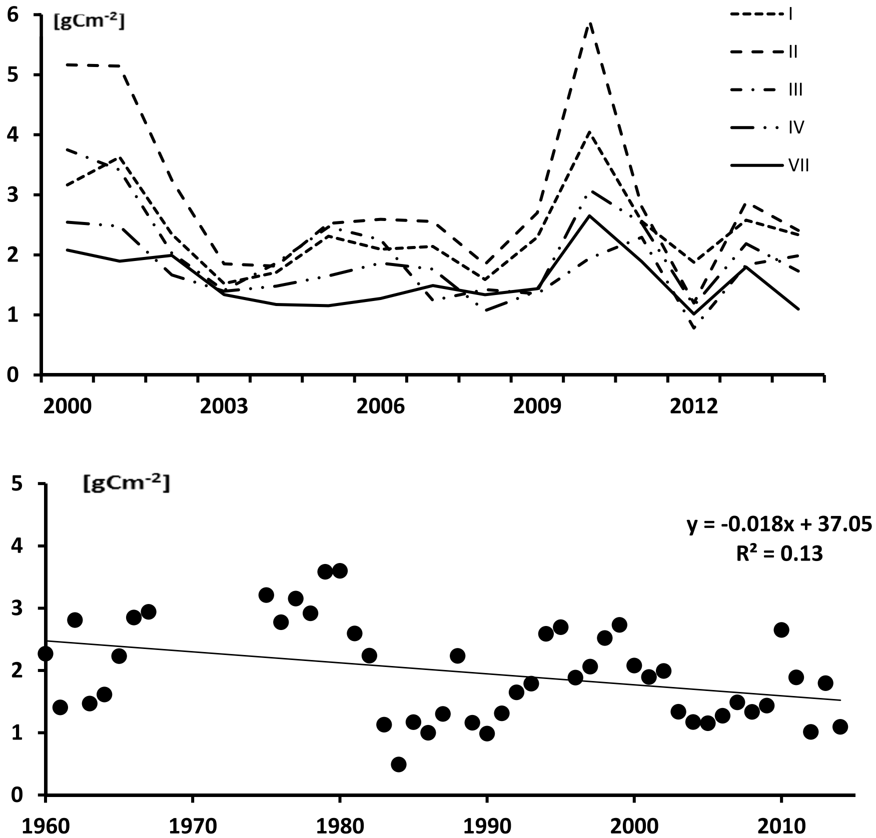

Fig. 6. Yearly TOC flux along Vistula River course in period 2000–2014; station numbers as on Table 1(upper panel) and in period 1960–2014 for station VII (lower panel).

reservoirs affected a significant increase in TOC concentration occurs due to progressive water eutrophication. Lauerwald et al. (2012) estimated organic carbon loss occurs in the fluvial network of North America rivers near 20% of DOC export from land to marine system. TOC concentrations along the VR course are significantly correlated with runoff (Fig. 3c). Thus areas of Central Europe with high runoff, mainly mountain rivers, have lower TOC concentrations than lowland rivers with low values of runoff.

5.2. Flood and drought

The more important, global regularity that we have found between the runoff and TOC export rate, regardless of climatic zone (Fig. 9), shows that recent catchment hydrological situations influence riverine TOC resources. This is important in situations of increasing precipitation differentiation between particular years in temperate climate zones resulting from global climate changes. Additionally, increases in precipitation will decrease the water quality impounded in the reservoirs, where increases in TOC concentrations will be observed. Also artificial changes in the catchment water cycle will lead to increases in total runoff and in effect increase TOC export, especially in agricultural and urbanized catchments (Mattsson et al., 2009b; Stanley et al., 2012).

These relationships are well explained by differences in long-term TOC export in the VR (Fig. 5b). High runoff values in 2010 resulted in an increase in yearly TOC concentrations, not at every station, but the annual TOC export was 60–120% of the average in period 2000–2014.

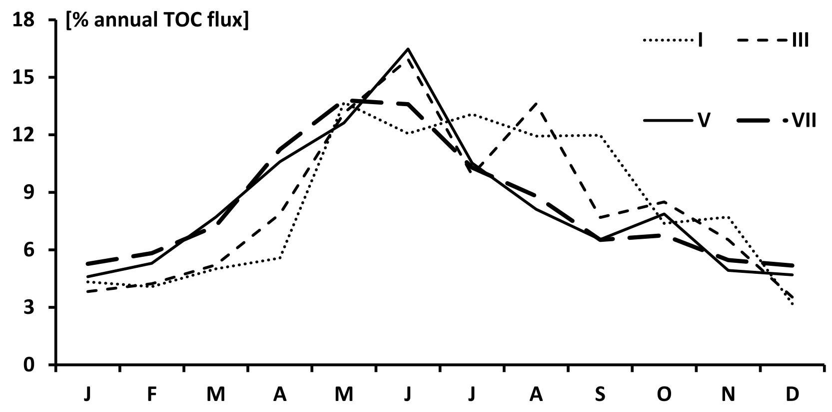

Fig. 7. Seasonality of TOC flux along Vistula River course in years 2000–2014 (station numbers as in Table 3 and Fig. 1).

During more frequent floods, the basin organic matter losses were relatively high, decreasing organic carbon resources, which was unfavorable for the preservation of ecological balance and biodiversity. Severe drought associated with global changes could be a significant factor controlling the TOC flux in rivers. Worrall and Burt (2007) have not observed effects in fluxes and concentrations of DOC in British rivers. However, in the small rivers of northeastern Poland, drought resulted in a 30% decrease in DOC concentration (Zieliński et al., 2009). A very dry year 2012 in Central Europe with a long hydrological drought resulted in a 5–35% decrease in TOC concentrations along the VR river course, with higher declines upstream.

6. Conclusions

The presented study clearly shows that recent changes in the hydrochemical features of the Vistula River have been very improved, leading to a restoration of more natural river conditions as a consequence of national political activity in large-scale water management and sustainable development. The observed decreasing trend in TOC export by Central European rivers can in part be associated with effects of decreasing of air pollution emissions noted in Scandinavian countries in last decade of XX century (Erlandsson et al., 2008). The same significant decreasing trend for atmospheric sulphur deposition, but removed in time, was observed in southern Poland and for example annual concentrations of SO_2 in Cracow have decreased by 70–80% between 1970s and 2006 (Bokwa, 2010). Evans et al. (2006) suggested that reduced air pollution was the main driver for water brownification which is developing in changes of seasonality of water cycle in the boreal zone. I can suppose that river catchments in Central European are subject of distinct hydroclimatic changes resulted in slowly decrease TOC flux with increase of multiannual variability.

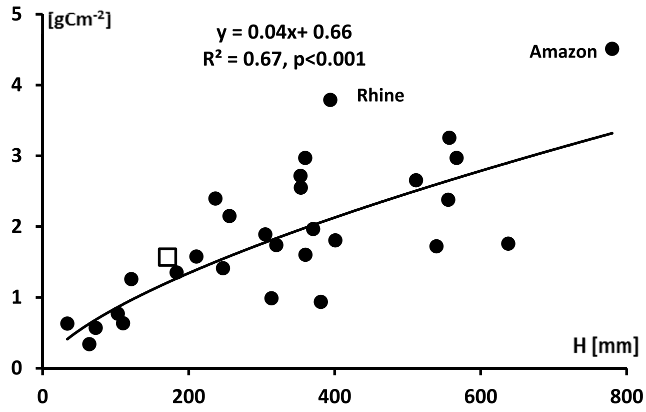

Fig. 9. Relationships between mean runoff and riverine TOC flux selected 29 basins larger than 80000 km^2 from the different world climatic zones. Square-Vistula River from this study. *Data from*: Degens et al., 1991, Kokorite et al., 2012, Kuliński and Pempkowiak, 2011, Probst et al., 1994, Ran et al., 2013, Wu et al., 2007.

River flow dynamics were presented in earlier studies as the dominate driver of TOC changes in rivers. The recent study indicate that in last 50 years was a period of significant reduction in supply of organic pollutants into the Vistula River and its effects were probably more significant than hydroclimatic changes which in the future will stay a dominant driver of riverine TOC concentrations dynamic. Therefore, global changes of water balance in the temperate zone are expected to modification of organic matter resources in surface waters. In Vistula River case, these effects on the riverine organic carbon biogeochemistry can be various compare to natural basins.

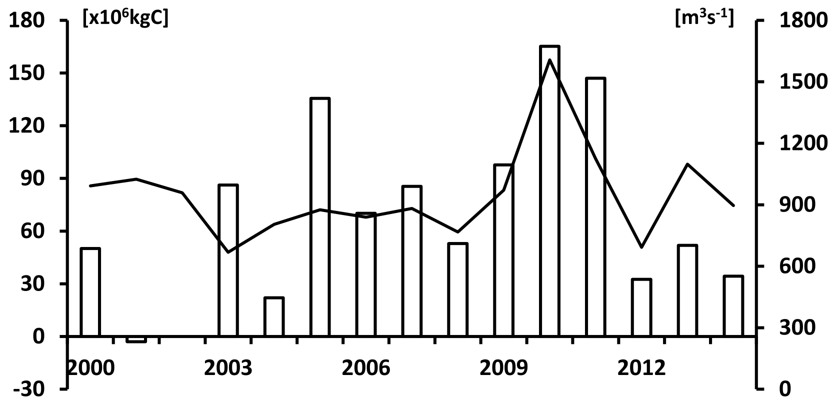

Fig. 8. Efficiency of Włocławek Dam reservoir in the reduction of annual TOC load (bars) transported by Vistula River in period 2000–2014. Line present annual discharge of Vistula River below reservoir (right axis).

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