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Temporal trends in organic carbon content in the main Swiss rivers, 1974–2010

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HIGHLIGHTS

- High-quality organic carbon data used to study long-term trends in Switzerland
- A statistically significant decrease in TOC and a less clear increase in DOC observed
- Trend change in all rivers: upward until 1999, stronger downward 1999–2010
- Riverine OC fluxes should be taken into account in carbon budgets of the country

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ABSTRACT

Increases in dissolved organic carbon (DOC) concentrations have often been reported in rivers and lakes of the Northern Hemisphere over the last few decades. High-quality organic carbon (OC) concentration data have been used to study the change in DOC and total (TOC) organic carbon concentrations in the main rivers of Switzerland (Rhône, Rhine, Thur and Aar) between 1974 and 2010. These rivers are characterized by high discharge regimes (due to their Alpine origin) and by running in populated areas. Small long term trends (a general statistically significant decrease in TOC and a less clear increase in DOC concentrations), on the order of 1% of mean OC concentration per year, have been observed. An upward trend before 1999 reversed direction to a more marked downward trend from 1999 to 2010. Of the potential causes of OC temporal variation analysed (water temperature, dissolved reactive phosphorus and river discharge), only discharge explains a significant, albeit still small, part of TOC variability (8–31%), while accounting for barely 2.5% of DOC variability. Estimated anthropogenic TOC and DOC loads (treated sewage) to the rivers could account for a maximum of 4–20% of the temporal trends. Such low predictability is a good example of the limitations faced when studying causality and drivers behind small variations in complex systems. River export of OC from Switzerland has decreased significantly over the period. Since about 5.5% of estimated NEP of Switzerland is exported by the rivers, riverine OC fluxes should be taken into account in a detailed carbon budget of the country.

1. Introduction

Inland waters have often been disregarded as relevant parts of the carbon cycle. However, the rate of burial of organic carbon (OC) in inland water sediments exceeds OC sequestration on the ocean floor and dissolved organic carbon (DOC) is now recognized as a significant supplier of carbon to oceans (Battin et al., 2009). In addition to their native (i.e., produced in situ) OC (autochthonous organic matter), rivers and lakes integrate OC from soils, terrestrial vegetation and anthropogenic sources (allochthonous organic matter). Rivers and lakes are active agents of OC transformation (respiration, burial), and not merely transporters (Cole et al., 2007; Battin et al., 2009). The role of inland waters in the carbon cycle depends on changing environmental parameters and can, therefore, change in response to global change. The increase in DOC concentrations that has often been reported in rivers and lakes of the Northern Hemisphere over the last few decades (Evans et al., 2005; Clark et al., 2010 and references therein) is an extensively studied example of such potential change. However, although observations of increasing OC trends in the Northern Hemisphere surface waters are dominant, they are not general (Filella and Rodríguez-Murillo, 2014), and the mechanisms driving this increase are poorly understood (i.e., observed changes have been attributed to a myriad of different drivers such as runoff, air temperature, solar radiation, precipitation, soil moisture, timing of ice break-up and snowmelt,

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length of seasons, land use, atmospheric CO_2 increase, and atmospheric deposition chemistry) (Evans et al., 2005; Clark et al., 2010; Sucker and Krause, 2010 and references therein).

Since most of the temporal series studied correspond to boreal, humic rich ecosystems or to systems recovering from acidification and many correspond to small catchments, broadening the range of rivers and lakes studied to other climatic and edaphic zones is desirable in order to elucidate whether the increase in DOC is a general trend in inland waters and, if so, which environmental or anthropogenic drivers underlie the temporal trends observed. Switzerland is an interesting case study because: (i) it has a network of hydrological stations, belonging to the Swiss National River Monitoring and Survey Programme (NADUF) (www.bafu.admin.ch/hydrologie/01831/01840/index.html?lang=en), which holds long series of many physical and chemical parameters, including OC concentrations; (ii) it is the head of five separate European drainage basins; two of the main rivers in Western Europe (Rhine, Rhône) originate in the Swiss Alps, known as Europe's "Water Tower". The NADUF data set has been evaluated a number of times (e.g., Jakob et al., 2002), and in particular for temporal trends between 1974 and 1998 by Zobrist et al. (2004). The Swiss Rivers are also an interesting case study because they combine an Alpine origin – with high water discharge regimes – with running in populated areas little distant from their sources and have large catchments. To our knowledge, no other systems with these characteristics have been looked at so far in long-term OC temporal trend studies.

In the present work, we apply non-parametric techniques to the study of the temporal change of DOC and total organic carbon (TOC) concentrations and loads in the main Swiss rivers from 1974 to 2010. To identify possible drivers for the long-term variations observed, we investigate the dependence of OC on other measured parameters and explore the impact of acid deposition and anthropogenic OC inputs.

2. Methods

2.1. Study sites

This study includes data from seven measuring stations, which have been in operation for over 25 years, selected from the 31 stations regularly monitored as part of the NADUF programme. The remaining stations have shorter measuring periods, regular interruptions in the series of measurements or smaller water discharges. The seven stations selected are situated in the Rhine, Rhône, Aar and Thur rivers and cover about 90% of the river discharge leaving Switzerland. Their main characteristics as well as the time periods under examination are shown in Table 1, while their location is shown in Fig. 1. All data can be retrieved from: www.eawag.ch/forschung/wut/schwerpunkte/chemievonwasserresourcen/naduf/datendownload.

2.2. Analytical methods

The physical and chemical parameters examined in this study are organic carbon (TOC and DOC) concentrations, discharge, water temperature, TSS (total suspended solids) and DRP (dissolved reactive phosphorous) concentrations, and TOC and DOC loads. Although some measurement devices have changed slightly over the years, the methods of measuring water's physical and chemical parameters are similar in all stations. In brief, the water level and water temperature are measured directly in the river with a sensor and discharge is calculated from water level readings. All other parameters are measured in water-discharge proportional integrated samples. Over two weeks, a collective sample is taken in 1 mL parts from a river water flow throughput container (size 25 L, water flow 50–150 L min^{-1}) in the station. The flow proportional sampling device is regulated in such a manner that a 1–3 L sample is obtained per period. Collected samples are stored at 4 °C and transported in cooled containers to the analytical laboratory at the Swiss Federal Institute of Aquatic Science and Technology (Eawag). Immediately after arrival, samples are filtered (washed cellulose-nitrate filter, 0.45 μm) and stored at 4 °C. TOC samples are homogenised and then stirred just before injection. For TOC and DOC analyses, samples are acidified and purged with nitrogen gas to eliminate the inorganic carbon. Organic carbon determinations are always performed by high-temperature combustion with infrared detection of the CO_2 produced. The best OC analyser (a home-adapted for low OC concentration Beckman, Elementar, Shimadzu) available at the time was always used. Potassium phthalate serves as the calibration reagent. The limit of detection is 0.5 mg C L^{-1} and the reproducibility for TOC and DOC are 0.5 and 0.2 mg C L^{-1}, respectively. The OC analytical method, as well as the methods used for other parameters looked at here, are in line with ISO methods for water analysis. The methods applied and their history are summarized in www.eawag.ch/forschung/wut/schwerpunkte/chemievonwasserresourcen/naduf/index. All data are subject to a strict quality control procedure before storage in the data bank.

2.3. Data treatment methods

Many water variables are not normally distributed and, therefore, it is not generally appropriate to evaluate temporal trends using parametric methods such as linear regression. What is more, water parameters are often influenced by other factors such as outliers, serial correlation and seasonality (Hirsch and Slack, 1984; Helsel and Hirsch, 2002). For these reasons, non-parametric data treatment methods were used in this study. Initially, seasonality in time series was always tested by the Kruskall–Wallis (KW) test calculated with the XLSTAT package (www.xlstat.com). Depending on the results, time trends were calculated using the non-parametric Mann–Kendall (MK) test, when no seasonality exists, or by the Seasonal Mann–Kendall (SMK) test otherwise (Gibbons and Coleman, 2001). For this purpose, ktaub and sktt functions developed by Jeff Burkey for MATLAB package (www.mathworks.com/matlabcentral/fx_files/22389/7/sktt.m, www.mathworks.com/matlabcentral/fileexchange/11190-mann-kendall-tau-b-with-sens-method-enhanced/content/ktaub.m) were modified to fit our needs. The magnitude of the trends was estimated either by the Sen's slope (Sen, 1968) or the SMK slope estimators,

Table 1

Sampling stations studied. Water discharge, TOC, DOC and DOC/TOC are average values in the period considered.

River	Station[a]	Catchment area / km^2	Average catchment altitude / m.a.s.l.	Water discharge / $m^3\ s^{-1}$	TOC / mg C L^{-1}	DOC / mg C L^{-1}	% DOC	Period	Number of bi-weekly periods
Rhône	Porte du Scex	5220	2130	188	2.4	1.0	42	1974–2010	943
	Chancy	10,294	1580	355	2.5	1.5	60	1977–2010	776
Rhine	Diepoldsau	6119	1800	231	2.9	1.1	38	1984–2010	704
	Rekingen	14,718	1260	452	2.9	2.0	69	1975–2010	928
	Village-Neuf/Weil	36,472	1100	1084	3.3	2.2	67	1977–2010	886
Thur	Andelfingen	1696	770	48	5.5	2.9	53	1981–2010	766
Aar	Brugg	11,750	1010	324	3.9	2.6	67	1974–2010	955

[a] Information about station coordinates and station elevation is available at www.hydrodaten.admin.ch/en/.

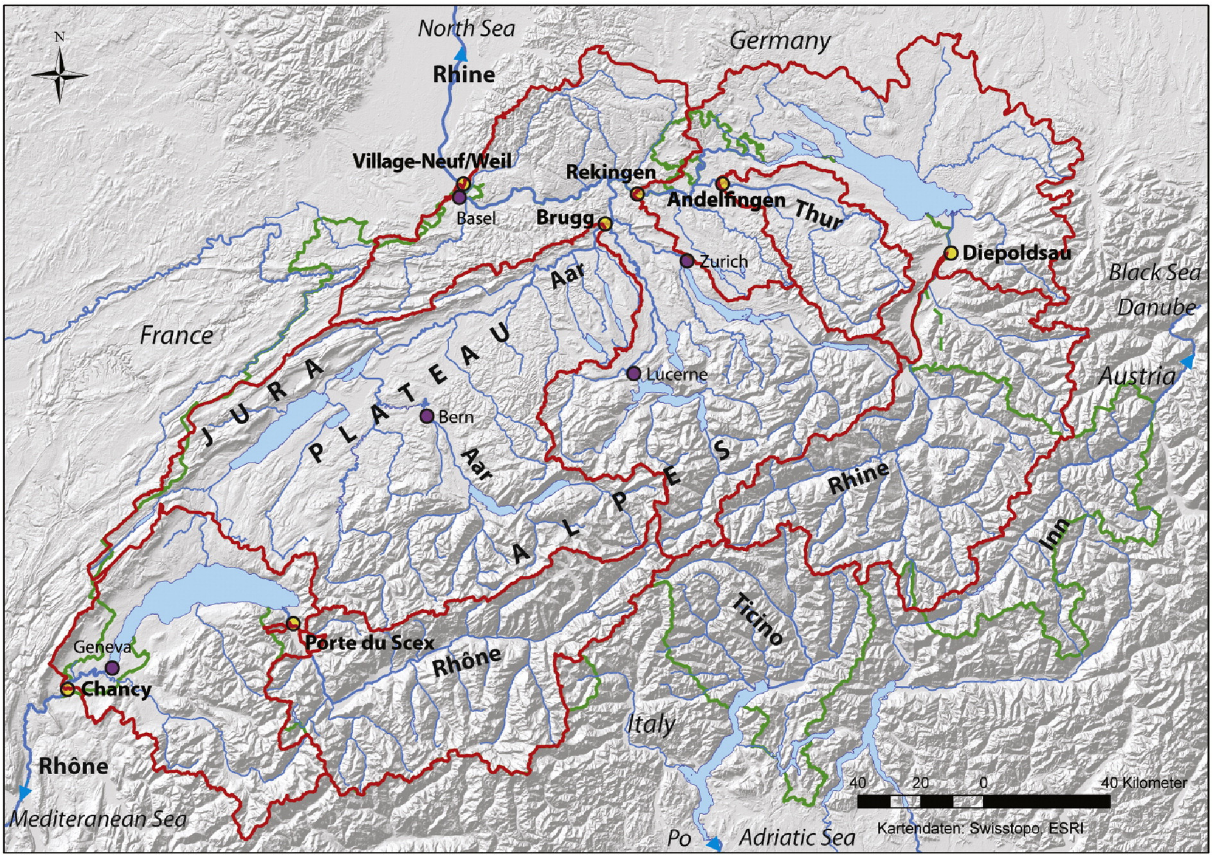

Fig. 1. Map of Switzerland with the location of the stations chosen for the present study. River basins are delimited by red lines and Swiss frontiers are shown in green.

with a higher slope value indicating a stronger trend. The statistical significance of the trend is indicated by the corresponding *p*-value, as it usually accepted. However, the current blind use of *p*-values is being increasingly challenged (Nuzzo, 2014), even more in the case of tiny effects (Siontis and Ioannidis, 2011). For these reasons, we have chosen to show all trends, whether significant or not, and to consider also other criteria, such as internal consistency, in our discussion.

MK tests were also applied to 3-year moving averages of annual means of DOC and TOC concentrations. Calculation of moving averages is one of the simplest techniques for smoothing out high frequency fluctuations and facilitating the discovery of long-term trends in data series (Subramanya, 2008).

The strength and the statistical significance of the relationships of TOC and DOC with discharge, water temperature, DRP and TSS were examined by calculation of Sen's slopes of correlations between variables using the above mentioned MK MATLAB function. The LOWESS (LOcally, WEighted Scatterplot Smoothing) regression method (Helsel and Hirsch, 2002) was used to calculate the correlation coefficients (explained variability) of DOC and TOC with each of the above mentioned variables. LOWESS describes the relationship between variables using an iterated weighted least squares procedure (Cleveland, 1979) and was calculated with XLSTAT (www.xlstat.com). LOWESS has also been used to graphically represent relationships between some variables (i.e., OC versus discharge). The order of the polynomial locally fit to each point was set equal to 1, the weight function was the tricube, and the degree of smoothing, 0.5. A parametric multiple least squares regression (STATGRAPHICS Plus) was applied to calculate the correlation coefficients (and thus the explained variability) of DOC and TOC with several variables (discharge, water temperature and DRP). Although, as mentioned above, linear regression cannot be strictly applied to water variables, the use of multiple linear regressions is a common practice due to the lack of non-parametric alternatives.

3. River and catchment characteristics

Tables 1 and 2 characterize rivers discussed in this study as well as their catchments. All catchments are situated in a temperate-humid climatic zone with somewhat more precipitation in summer than in winter; the average rates in catchments studied vary from 1260 to 1430 mm y^{-1}. As a result, the water-discharge of the rivers is high, averaging between 0.85 and 1.2 $m^3\ m^{-2}\ yr^{-1}$ (Aar in Brugg, Rhine at Diepoldsau), compared to large lowland European rivers; for instance the water discharges of the Elbe, Seine, Danube and Rhine into the sea, all around 0.2 $m^3\ m^{-2}\ yr^{-1}$ (Stanners and Bourdeau, 1995). Part of the sources of the rivers studied lie in alpine and pre-alpine regions which are covered by snow in the winter, therefore water discharges peak in summer (Schädler and Weingartner, 2010). The water discharge of rivers situated downstream of the perialpine lakes (the Rhône in Chancy, Rhine in Rekingen, Aar in Brugg and Rhine in Village-Neuf/Weil) only reacts smoothly to heavy rainfalls. In contrast, alpine rivers (Rhône in Porte-du-Scex, Rhine in Diepoldsau) and the pre-alpine river Thur in Andelfingen show clear short time peak flows. Nowadays, all rivers are channelized and their beds exhibit a moderate slope (about 1‰ on the Swiss Plateau) resulting in a distinct water flow velocity in the range of 1 $m\ s^{-1}$. In consequence, tributaries mix quickly and the re-aeration rate is high.

The bedrock and the unconsolidated zones governing the geochemical water composition of rivers and groundwater consist mainly of calcareous minerals (calcite, dolomite and anhydrite/gypsum). Minor zones with siliceous rocks also exist in some alpine headwater areas of the rivers looked at here. Due to glaciation, most soils around the Alps, i.e. in the largest part of catchment in this study, are relatively young (<12,000 years B.P.). The most developed soils are Cambisols and Luvisols covering drained and rather stable areas.

Table 2
Land use and population in catchments.

River	Station[a]	Land use in % [a]				Inhabitants (estimated for 2010)
		Intensively used agricultural land	Extensively used vegetation covered land	Dense forest	Barren land	
Rhône	Porte du Scex	6	33	17	41	290 000
	Chancy	14	24	24	31	1 700 000
Rhine	Diepoldsau	8	46	23	20	340 000
	Rekingen	29	16	26	13	2 700 000
	Village-Neuf/Weil	30	22	29	12	7 500 000
Thur	Andelfingen	46	18	26	1.5	380 000
Aar	Brugg	34	20	28	11	2 100 000

[a] The addition of the percentages of different land uses does not make up to 100% because the minor contribution of urban land has not been considered.

Land uses in the different catchments vary considerably (Table 2). Areas under intensive agriculture, e.g. heavily fertilized land, make up little of the alpine catchments (6–8%) but occupy near the half of the Thur catchment. These areas contribute significantly to non-point inputs of nitrogen and phosphorus into rivers (Zobrist and Reichert, 2006). Relatively high concentrations of OC in the Thur compared to the other rivers also indicate a distinct input of organic materials from intensive agriculture. Unfertilized areas which are covered by vegetation but nonetheless extensively used, such as alpine grasslands, bushlands and parks, are more common in alpine catchments (accounting for 46% in the alpine Rhine against 18% in the Thur). The percentage of barren land (no vegetation and surface waters) varies considerably from 2% in the Thur catchment to 42% in the alpine Rhône. Dense forests, a mix of deciduous and coniferous trees depending on altitude and forest management, are a distinct part of the large catchments. The area they cover does not vary strongly (17% alpine Rhône to 28% Aar). Inputs from these three types of land (vegetated and extensively used, forest and barren) cover the natural input of nutrients and OC. Over the last 30 years, changes in land use were limited. Urban land, which represents a minor fraction, has increased at the cost of agricultural land.

On the other hand, population has increased by an average rate of 0.8% y^{-1} (www.bfs.admin.ch/bfs/portal/de/index/themen/01/02/blank/key/bevoelkerungsstand.html). The potential pollution impact of the population can be expressed as a percentage of wastewater related to the water discharge. It varies from 0.5% in the alpine Rhône to 2.8% in the Thur, assuming 300 L of wastewater per capita and day. About 70% of the inhabitants in 1975 and nearly 100% of the inhabitants in 2010 were connected to sewage treatment plants (Siegrist, 2013).

4. Results

4.1. Temporal trends

Visual inspection of all bi-weekly DOC and TOC concentration values considered in this study (Fig. 2) reveals few interruptions in the series of measurements, no obvious monotonic trends, and TOC concentrations with much higher variability than DOC.

First, data seasonality was tested by applying the KW test to the temporal series of DOC and TOC concentrations in the seven stations. Clear seasonality is observed in the majority of the time series (nine out of 14), with a $p < 0.0001$ (probability of error in rejecting the hypothesis that monthly data come from the same population). The SMK test was therefore applied in all 14 cases, and, in the five 'less seasonal' series, normal MK was also applied for comparison. The remaining variables (river discharge, water temperature, DRP and TSS concentrations) as well as TOC and DOC loads, were treated as seasonal without performing the KW test, with the exception of the time series of 3-year moving averages of TOC and DOC concentrations. These were studied directly using the MK method, as no seasonality can be present. Sen's slopes of SMK non-parametric regressions were also calculated. Sen's slopes for TOC and DOC concentrations and loads versus time are also shown in Fig. 3 to facilitate their understanding (i.e., they provide an instant picture of the results).

Bi-weekly TOC concentrations were observed to decrease significantly in five out of seven cases (Table 3). Calculated trends in Porte du Scex and in Rekingen were non-significant. Decreases in TOC concentrations are small (less than 1% of mean TOC concentration per year). Bi-weekly DOC concentrations show a less clear picture. Temporal decreases are observed in four cases but none are significant, and of the observed increases (Rekingen, Chancy and Diepoldsau), only the first two are significant.

Moving 3-year averages of annual means of DOC and TOC concentrations were calculated (Fig. 4a and b) to highlight long-term trends by smoothing shorter (yearly) fluctuations. TOC moving averages show statistically significant decreases at three stations — the same ones where decreasing trends in bi-weekly values were statistically significant. Conversely, DOC moving averages tend to increase in all stations except Brugg, with those in Rekingen, Chancy, Diepoldsau and Porte du Scex being statistically significant.

However, the most interesting point is that TOC and DOC moving averages are non-monotonic in time. A decrease after the mid to end 90s is clear at all stations. DOC moving averages of three of the longer time-series (Porte du Scex, Village-Neuf/Weil and Brugg) display two maxima, suggesting the existence of two cycles in the temporal change of DOC concentrations.

In order to ascertain possible changes in the directions of the trends, we divided our data into two periods: from the beginning of the measuring campaigns to 1998 and from 1999 to 2010. The split was chosen both because of the observed change in Fig. 4 and because it allowed our time trends to be directly compared with those reported in the NADUF study (up to 1998) (Zobrist et al., 2004) obtained by a sinusoidal linear regression analysis. In this study (1974–1998), the authors found statistically significant increases of TOC concentrations over time in five of the seven stations studied here, with no significant decrease at any station. Similar tendencies were reported for DOC concentrations but with decreases at two stations.

Temporal trends of DOC and TOC concentrations were different before and after 1999 (Table 4 and Fig. 5). Before 1999, the dependence of TOC versus time was weakly, albeit significantly, positive, except in Village-Neuf/Weil, Andelfingen and Brugg. This is in line with results in the NADUF study. From 1999 to 2010, the dependence of TOC versus time became statistically significantly negative in all stations, with higher slopes than in the first period considered. The temporal change of DOC concentrations is less clear but follows a pattern similar to TOC. Before 1999, DOC concentrations increased significantly with time at four stations and indicated a decreasing tendency at two, generally mirroring the NADUF study. From 1999 onwards, DOC temporal change is significantly negative at all stations. This is in broad agreement with the existence of a phase of decreasing DOC (and TOC) concentrations from the mid-late 90s observed in the 3-year moving average.

DOC and TOC loads follow the temporal trends observed in DOC and TOC: TOC loads decrease statistically significantly with time at three out of seven stations, while DOC load does so at four stations.

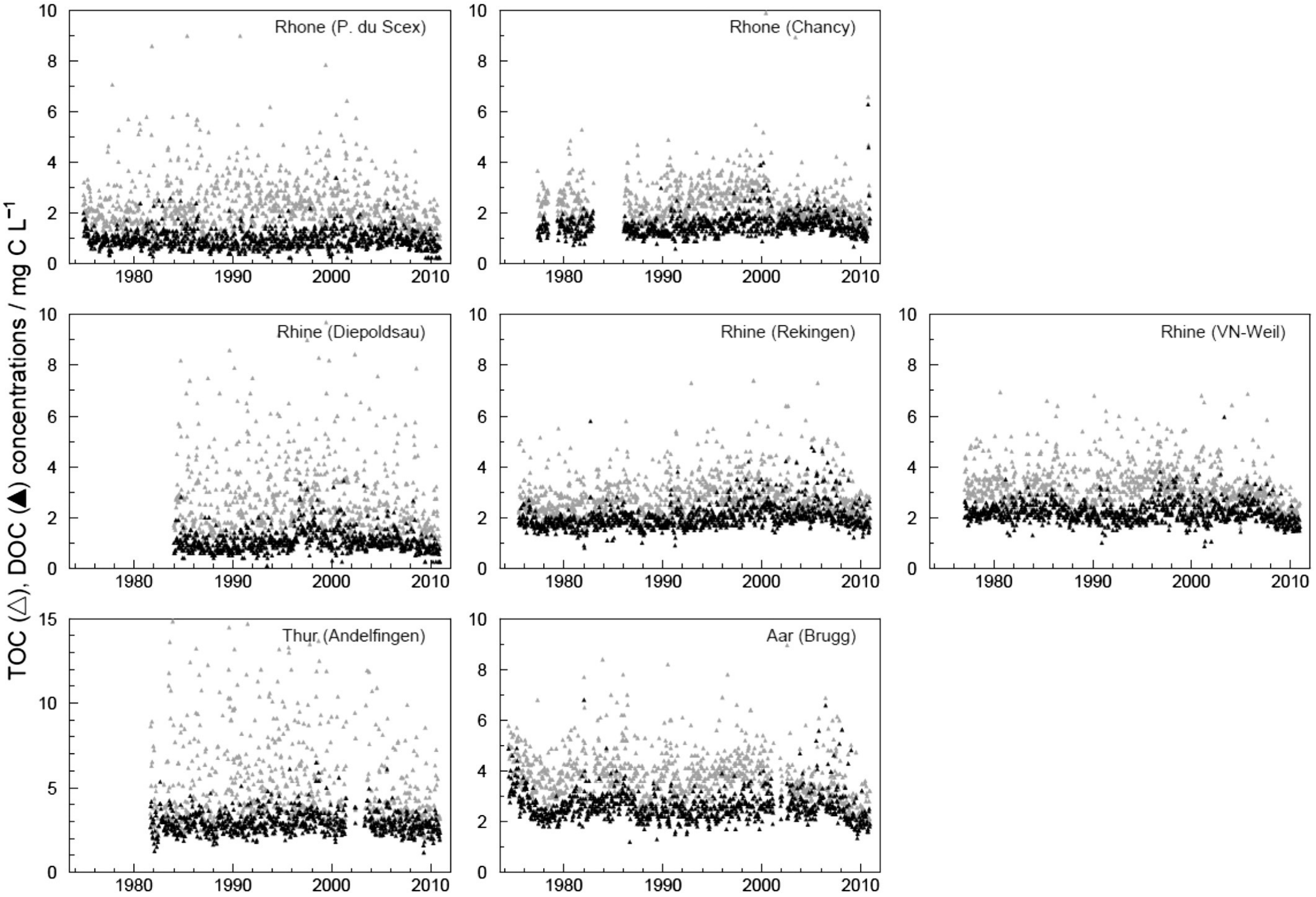

Fig. 2. Time series of bi-weekly TOC (grey triangles) and DOC (black triangles) concentrations (mg C L^{-1}).

Temporal trends of parameters that could help to explain OC behaviour have also been studied over the whole period (Table 3), as well as before 1998 and for 1999–2010 (Table 4). River discharges decrease in six out of seven cases but only in Chancy do so significantly. Discharge decays are less than 1% per year. A decrease in discharge values was also observed during the period studied in the NADUF study, which they suggest could be due to less precipitation and/or higher evapotranspiration caused by increasing temperatures. When treating data in two groups, the tendency toward smaller discharges is observed to increase during 1999–2010. During this period, discharges decrease in all stations with time (non-significantly in Brugg, Village-Neuf/Weil and Andelfingen) while before 1998 only Chancy and Village-Neuf/Weil showed significant decreases.

Water temperature usually exhibits a rapid and direct response to climate forcing. It is the parameter that shows the clearest temporal behaviour, increasing very significantly in every station studied. Increases

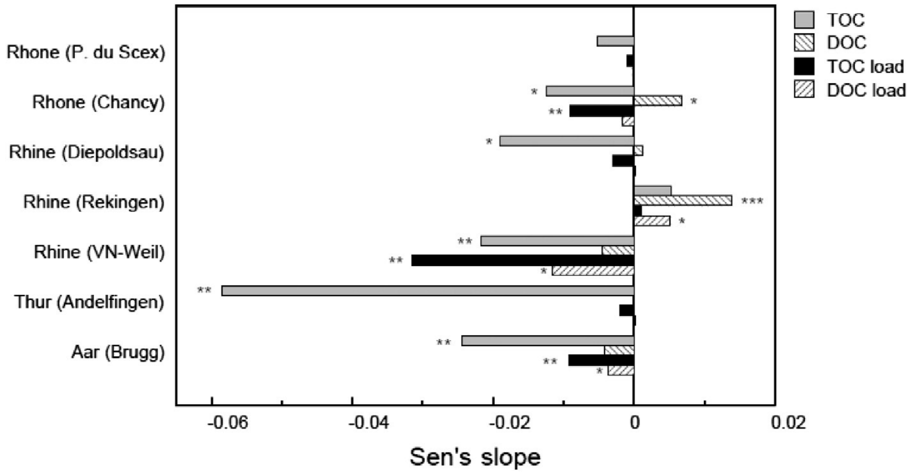

Fig. 3. Time trends for the time series of TOC and DOC concentrations (mg C L^{-1}) and loads (kg C s^{-1}) for the whole period examined. Bars are Sen's slopes of non-parametric regressions (SMK test) of these parameters versus time. Slope units are expressed as magnitude per year. Stars indicate the significance of the temporal trend: (*): $0.1 > p > 0.01$; (**): $0.01 > p > 0.001$; (***): $p < 0.001$.

Table 3
Time trends (SMK test) for the time series of TOC and DOC concentrations, water discharge, water temperature, TSS and DRP concentration, and TOC and DOC Loads. All values calculated from bi-weekly data except when otherwise stated. Numbers are Sen's slopes. A positive sign means increase, a negative sign means decrease. NS: non-significant trend ($p > 0.1$); (*): $0.1 > p > 0.01$; (**): $0.01 > p > 0.001$; (***): $p < 0.001$.

River	Station	TOC / 10^{-3} mg C L^{-1} yr^{-1}	DOC / 10^{-3} mg C L^{-1} yr^{-1}	TOC / 10^{-3} mg C L^{-1} yr^{-1} 3-yr average	DOC / 10^{-3} mg C L^{-1} yr^{-1} 3-yr average	Discharge / m^3 s^{-1} yr^{-1}	Water T / °C yr^{-1}	TSS / mg L^{-1} yr^{-1}	DRP / 10^{-3} mg L^{-1} yr^{-1}	TOC load / g C s^{-1} yr^{-1}	DOC load / g C s^{-1} yr^{-1}
Rhône	Porte du Scex	−5.2 NS	0 NS[a]	+10 NS	+3.4 (*)	−0.193 NS	+0.020 (***)	+0.170 NS	−0.4 (***)	−1.0 NS	−0.22 NS
	Chancy	−12 (*)	+6.8 (*)	−25 (*)	+17 (***)	−2.88 (**)	+0.041 (***)	−0.123 (*)	−1.0 (***)	−9.1 (**)	−1.7 NS
Rhine	Diepoldsau	−19 (*)	+1.3 NS	−40 (**)	+9.5 (*)	−0.114 NS	+0.023 (**)	+0.55 (**)	−0.27 (***)	−3.0 NS	+0.18 NS
	Rekingen	+5.2 NS	+14 (***)	+8.3 NS	+22 (***)	−0.498 NS	+0.038 (***)	−0.037 NS	−2.3 (***)	+1.1 NS	+5.1 (*)
	Village-Neuf/Weil	−22 (**)	−4.5 NS	−26 (***)	+0.53 NS	−3.07 NS	+0.053 (***)	−0.177 (***)	−2.7 (***)	−32 (**)	−12 (*)
Thur	Andelfingen	−59 (**)	0 NS	−75 NS	+8.2 NS	+0.0579 NS	+0.021 (*)	−0.161 NS	−5.1 (***)	−1.9 NS	+0.22 NS
Aare	Brugg	−24 (**)	−4.2 NS	+1.1 NS	−4.5 NS	−0.722 NS	+0.035 (***)	−0.026 NS	−2.2 (***)	−9.3 (**)	−3.6 (*)

[a] Seasonal Kendall test and slope "not valid". Result of normal MK test is negative, NS trend, too.

are calculated to be 0.02 to 0.05 °C per year, which represent less than 1% of mean water temperatures per year. Changes in water temperature in the NADUF study were positive and significant, like ours, but annual increases (0.3–0.8%) were higher (0.2–0.4%).

TSS concentrations increased in two cases but only significantly in one, and decreased in five cases (significantly in two, Chancy and Village-Neuf/Weil). Except in Diepoldsau and Porte du Scex, the trend in TSS change is the same as the trend in TOC change. DRP concentrations decreased very significantly in all stations. In all, except Chancy, the decrease in DRP concentrations is faster over the first time period (until 1999) than in the second one (1999–2010).

4.2. Parameter dependence

TOC and DOC concentration dependency on some parameters (water temperature, DRP, TSS and discharge) has been investigated applying the MK test to bi-weekly data and calculating the corresponding Sen's slopes. Correlation coefficients between TOC, DOC and the presumed driving variables have been obtained through LOWESS regression, and a classical multiple regression approach (Table 5).

TOC increases very significantly with water temperature at all stations, except in Village-Neuf/Weil and Brugg. DOC concentrations decrease significantly with water temperature at three stations and increase at four (significantly at three). The dependence of TOC and DOC on water temperature has found to be small using LOWESS (results not shown): only in Diepoldsau and Porte du Scex is R^2 for TOC and water temperature correlation higher than 10%, DOC dependence on temperature being generally less than 5%.

The relationship between DRP and TOC or DOC are positive at four stations, negative at two stations (Chancy and Rekingen) and opposite between TOC and DOC at Porte du Scex. LOWESS regression of TOC and DOC concentrations with DRP (values not shown) showed low R^2 (only DOC concentration in Rekingen has an R^2 higher than 10%).

TOC is strongly and positively related to TSS in all stations. DOC dependence on TSS is weaker and only statistically significant at four stations.

TOC concentrations increase with discharge very significantly at all stations. In contrast, DOC concentrations decrease with discharge in four out of seven cases and increase in three (all significantly). TOC dependence on discharge was found to be positive and modest (8–31%), but significant, in every station by LOWESS regressions (Table 5; Fig. 6 shows two stations as examples). DOC dependence on discharge is very small (less than 3%), positive or negative depending on the system.

Even if not being strictly rigorous, we applied a classical multiple linear regression approach to TOC and DOC concentration variations with discharge, water temperature, and DRP concentrations for the seven sites (Table 5). Significant relationships ($p < 0.1$) were obtained, except for DOC at Diepoldsau, but explained variability remains small, particularly for DOC. Besides, in several cases, temporal changes in discharge before 1999 are in the opposite direction of temporal changes in TOC and DOC concentrations. Of the tested drivers, the main control factor for TOC is discharge (explaining 7–30% of TOC variability) with water temperature and DRP not being relevant. Only in Village-Neuf/Weil and Brugg, does inclusion of DRP seem to improve the correlations, while in Andelfingen, the variable that improves the correlation is water temperature.

5. Discussion

5.1. Temporal trends

Most of the papers published on OC temporal trends in surface waters point to a general increase in OC concentrations over time (Monteith et al., 2007) in the systems studied. Our analysis of data for Swiss rivers does not support these previous observations: TOC concentrations have decreased in six out of the seven Swiss rivers considered in

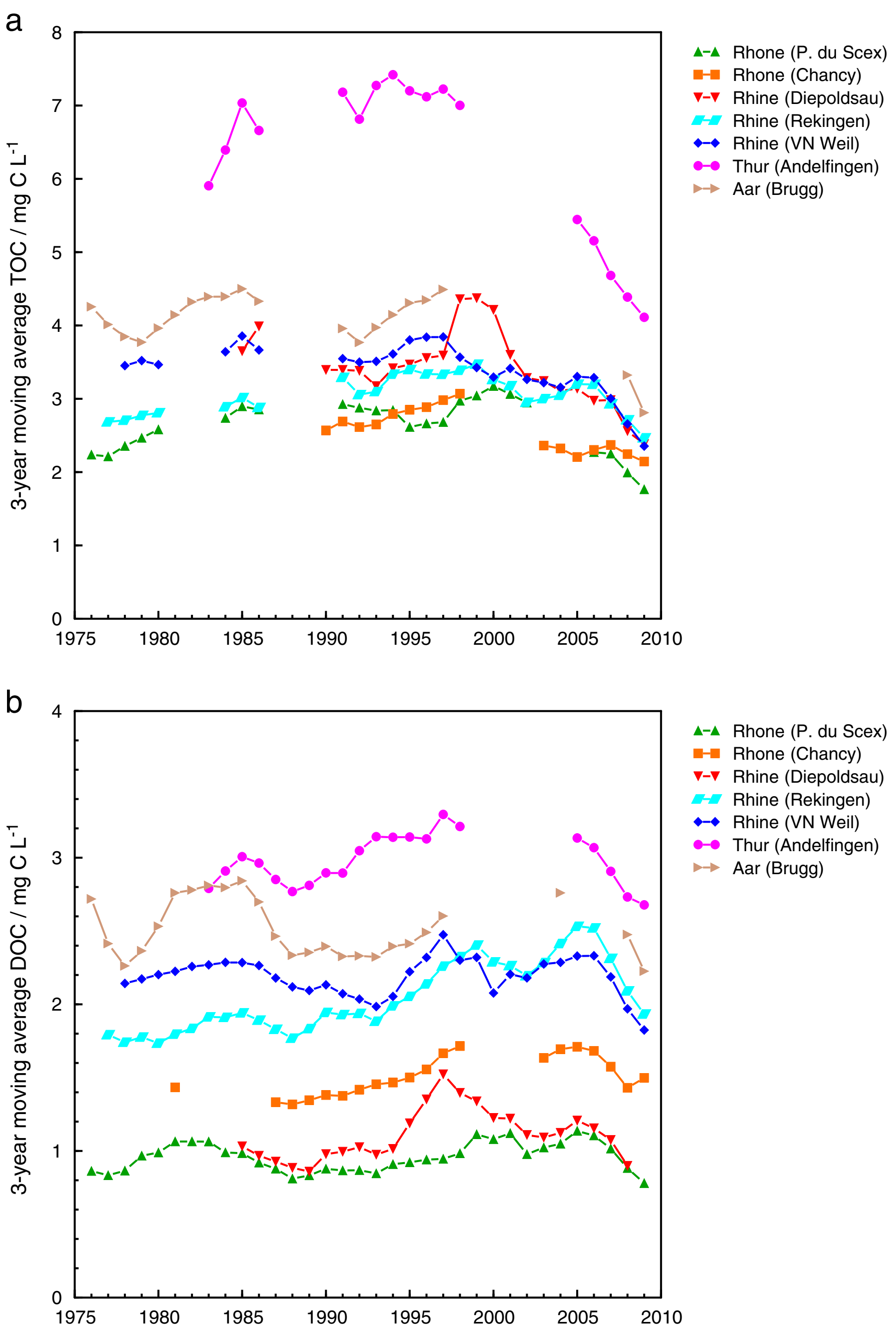

Fig. 4. Three-year moving averages of TOC (a) and DOC (b) concentrations (mg C L^{-1}). Yearly averages having not at least 80% of data per year are not included.

the study period (dates differ depending on the river, see Table 1) up to 2010, a decrease which is even more marked when only the period 2000–2010 is considered. DOC concentrations show mostly non-significant changes except in the two stations downstream of large lakes (Chancy and Rekingen) where they increase significantly. Three-year moving averages show essentially similar trends but, in the case of DOC, detect significant, though weak, increases in other stations (Porte du Scex and Diepoldsau). It is very important to stress that the strength of the observed trends (either TOC decreases or the cases with DOC increases) is weak compared to most of those reported in the literature (Filella and Rodríguez-Murillo, 2014). When comparing our results with previously published results, it is important to keep in mind that most of the existing data come from humic rich ecosystems and, in the case of rivers, often from headwater waterflows, which is not our case.

A change of tendency is apparent in all the rivers studied in the present work, from an upward trend until 1999 to a stronger tendency to decrease from 1999 to 2010. It is possible that such a change is simply part of a cyclical behaviour. Cyclicity has been found in other temporal series (Hejzlar et al., 2003; Gruau et al., 2004; Worrall and Burt, 2007; Monchy and Gruau, 2010; Zhang et al., 2010) and points to a climate related driving factor. It would be interesting, but not easy, to be able to distinguish between these relative short-term cycles and the existence of possible underlying longer term trends — revealed by Sen's slopes and possibly related to long term climate or environmental changes.

To our knowledge, this is the first time that a simultaneous study of DOC and TOC temporal trends has been carried out in rivers. Sun et al. (2010) also found different dynamics for DOC (increasing) and particulate organic carbon (POC) (decreasing) concentrations in the Xijiang River during the last 50 years, but their DOC and POC values

Table 4
Time trends (SMK test) for the time series of TOC and DOC concentrations, discharge and DRP concentrations in the two studied periods. All values calculated from bi-weekly data. Numbers are Sen's slopes. A positive sign means increase, a negative sign means decrease. NS: non-significant trend ($p > 0.1$); (*): $0.1 > p > 0.01$; (**): $0.01 > p > 0.001$; (***): $p < 0.001$. "+" means positive relationship; "−" means negative relationship.

River	Station	TOC / 10^{-3} mg C L^{-1} yr^{-1} (until 1998)	TOC / 10^{-3} mg C L^{-1} yr^{-1} (1999–2010)	DOC / 10^{-3} mg C L^{-1} yr^{-1} (until 1998)	DOC / 10^{-3} mg C L^{-1} yr^{-1} (1999–2010)	Discharge / m^3 s^{-1} yr^{-1} (until 1998)	Discharge / m^3 s^{-1} yr^{-1} (1999–2010)	DRP / 10^{-3} mg L^{-1} yr^{-1} (until 1998)	DRP / 10^{-3} mg L^{-1} yr^{-1} (1999–2010)
Rhône	Porte du Scex	+21 (**)	−115 (**)	−0.074 NS	−29 (*)	+0.262 NS	−1.91 (*)	−0.47 (**)	0 NS
	Chancy	+23 (*)	−44 (***)	+8.9 (*)	−32 (*)	−3.71 (*)	−6.16 (*)	−0.16 NS	−1.7 (***)
Rhine	Diepoldsau	+46 (*)	−96 (**)	+33 (**)	−40 (**)	+0.837 NS	−5.34 (*)	−0.24 (*)	−0.13 (**)
	Rekingen	+27 (**)	−65 (*)	+14 (**)	−36 (*)	−2.35 NS	−9.57 (*)	−2.3 (***)	−0.20 NS
	Village-Neuf/Weil	+12 NS	−89 (*)	0 NS	−27 NS	−9.53 (*)	−20.8 NS	−4.5 (***)	−0.20 NS
Thur	Andelfingen	+62 NS	−115 (**)	+25 (*)	−57 (*)	−0.213 NS	−0.818 NS	−6.7 (***)	−1.5 (*)
Aar	Brugg	0 NS	−122 (**)	−8.9 NS	−55 (*)	−1.51 NS	−4.78 NS	−3.1 (***)	−0.52 (*)

were deduced by regression equations from discharge and TSS data; they did not actually measure OC concentrations over the 50 year time-span. TOC concentrations include a DOC fraction plus a fraction usually known as POC. Although the distinction between POC and DOC is entirely operational (i.e., in reality a continuum of sizes exists), it nonetheless reflects differences in chemical composition, origin and behaviour. In many of the previous studies where temporal trends were studied, TOC and DOC had been taken as being the same (Hongve et al., 2004; Vuorenmaa et al., 2006; Hruška et al., 2009; Haei et al., 2010). This might well be the case in waters with high humic content, such as those in the lakes and rivers that have been the most extensively studied ecosystems, but it is not what is observed in Swiss rivers. As shown in Table 1, DOC represents variable percentages of TOC, and the results obtained show that DOC and TOC follow different temporal trends: since TOC predominantly decreases and DOC increases (albeit not always significantly), the proportion of DOC is increasing with time, and thus the POC fraction is decreasing.

5.2. Drivers

The temporal trends observed for OC concentrations are broadly similar for most of the rivers considered and it is tempting to think that a common cause lies at their origin. It is common practice, when trying to explain observed variations in long-term studies, to deduce a cause or causes on the basis of significant correlations between variables linked to stressors. However, this approach can prove to be of low explanatory value when, as in our case, temporal trends are weak, and possible drivers are multiple and not independent. Natural organic matter in aquatic systems is a particularly complex issue, with the effects observed being the combined result of interactions between multiple processes operating on different time scales, and only rarely stemming from a single, well-defined cause. For instance, the observed long-term trends might be the result of interactions between climate-related effects (e.g., CO_2 increase affecting vegetal production, water productivity, and soil processes; temperature increase affecting runoff, permafrost melting, glacier dynamics, weathering, soil and water productivity, etc.) and directly anthropogenic ones (e.g., changes in land cover and use; river and lake regulation for hydroelectric production, flood protection, irrigation; eutrophication or oligotrophication; deposition of sulphur and nitrogen oxides; nutrient input to the rivers, wastewater discharges, etc.). The poor explanatory power of the usual climatic variables (water temperature and discharge) and one anthropogenic variable (DRP concentrations) observed in the study is a perfect, albeit somewhat frustrating, example of how the complexity of natural processes cannot always be reduced to single causes. The observed effects and caveats of the different drivers are discussed below.

5.2.1. Water temperature

Temperature has frequently been invoked as a factor in increasing OC concentrations in waters (Evans et al., 2005). However, air temperature can affect many different interconnected processes related to OC production and consumption in both soils and waters, therefore not always producing a net positive or negative effect on OC concentrations (e.g., higher air temperature can increase DOC concentrations in soils by increasing plant production and organic matter decomposition (Evans et al., 2005); increasing evapotranspiration, reducing runoff and affecting discharge and, consequently, OC input into rivers (Clair and Ehrman, 1996); influencing water productivity and organic matter mineralisation; or influencing discharge–DOC relationships (Raymond and Saiers, 2010)). The lack of a clear net effect probably explains why some studies suggested temperature increase to be a minor direct driver of DOC changes (Tranvik and Jansson, 2002; Monteith et al., 2007). Water temperature is an excellent proxy for air temperature and a good proxy for average soil temperature, data that are not available as time series. A strong relationship between air and water temperature has been reported in Switzerland (www.meteosuisse.admin.ch/web/

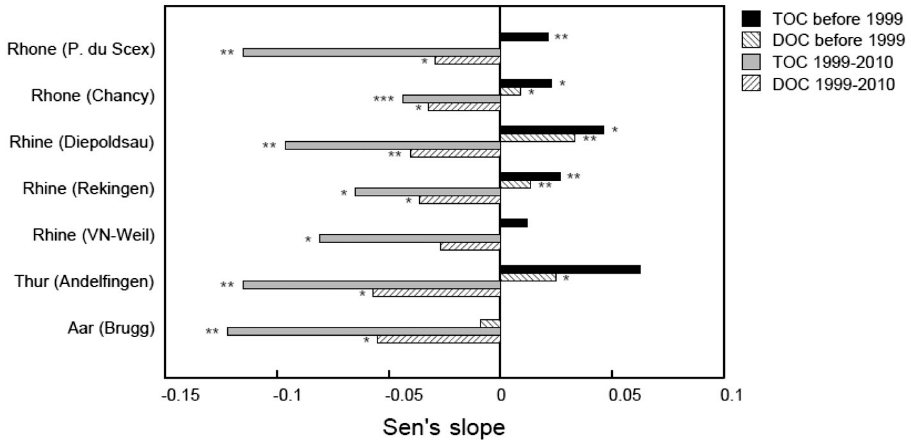

Fig. 5. Time trends of the time series of TOC and DOC concentrations (mg C L^{-1}) before 1999 and from 1999 to 2010 examined. Bars are Sen's slopes of non-parametric regressions (SMK test) of these parameters versus time. Slope units are expressed as magnitude per year. Stars indicate the significance of the temporal trend: (*): $0.1 > p > 0.01$; (**): $0.01 > p > 0.001$; (***): $p < 0.001$.

en/climate/climate_today/trends_in_switzerland.html). As expected from air temperature trends, water temperature increased with time over the period studied but a weak positive correlation of TOC to temperature is observed even if TOC decreases in most of the rivers studied. On the other hand, the dependence of DOC on temperature is positive or negative, depending on the site, but always weak.

5.2.2. Dissolved reactive phosphorus

'Re-oligotrophication' processes are a common feature of many rivers and lakes in Europe, which were heavily polluted in the 50s and 60s, and which, following the widespread establishment of wastewater treatment plants and enforcement of antipollution regulations (i.e., reducing phosphate input to the water bodies), began a process of recovery. The same happened in Switzerland where the NADUF study (Zobrist et al., 2004) shows a steep decrease of DRP concentrations over the period covered. This decrease is bigger in rivers with higher anthropogenic loads, i.e., those with densely populated and/or heavily farmed drainage basins, as are found in the Swiss Plateau (i.e., the Thur and lower sections of the Rhine and Aar rivers), and smaller in less impacted rivers (i.e., Diepoldsau in the alpine Rhine, and Porte du Scex and Chancy in the Rhône). Our study confirms that the change over time of DRP concentrations is monotonically negative in the two time periods at all stations. This change contrasts with the differentiated time trends observed for DOC and TOC concentrations at different sampling stations. Moreover, the dependency of DOC and TOC concentrations with DRP ones is weak and DRP added small additional significance to the DOC and TOC variability explained by discharge only (Table 3), which points to a non-significant effect of DRP and probably of 're-oligotrophication' processes in OC trends in Swiss rivers.

On the other hand, this apparent lack of effect of DRP decrease on riverine OC concentrations does not allow to point either to a predominant soil-origin of organic matter inputs because of the intricate links between DRP, trophic status, production and respiration. Studies are scarce: changes in the trophic status of continental waters have been put forward as an explanation of time tendencies in OC concentrations in some lakes (e.g., Bertoni et al., 2010) but more rarely in rivers (Sun et al., 2010). At the same time, preliminary results have shown no clear indication of change of OC concentrations with phosphate in perialpine lakes located North of the Alps (Rodríguez-Murillo and Filella, 2013). Since phosphate does not necessarily keep a direct relationship with autochthonous primary production, it would have been preferable to have data on river production changes but, unfortunately, long-term (more than 10-year) records of production in rivers are scanty. Of the rivers in the present work, such data are available only for the Thur (Uehlinger, 2006). According to this author, gross primary

Table 5
Dependences (MK test) of the time series of TOC and DOC concentrations on discharge, water temperature and DRP. Determination coefficients R^2 of TOC and DOC concentration dependence on discharge (from LOWESS) and of multiple linear regression on discharge, water temperature and DRP concentrations. Parameter units as in Tables 1–4.

River	Station	Sen's slopes (MK), units are mg C L^{-1} per unit of discharge, temperature or DRP [a]								LOWESS R^2 [b]		Multiple regression R^2 [c]	
		TOC vs water T	DOC vs water T	TOC vs DRP	DOC vs DRP	TOC vs discharge	DOC vs discharge	TOC vs TSS	DOC vs TSS	TOC vs discharge	DOC vs discharge	TOC	DOC
Rhône	Porte du Scex	+0.152 (***)	−0.0123 (**)	−9.61 (***)	+4.57 (***)	+0.00448 (***)	$-7.84x10^{-4}$ (***)	+0.00580 (***)	0 NS	0.15	$7.2x10^{-4}$	0.15	0.015
	Chancy	+0.0185 (***)	+0.00463 (*)	−1.75 NS	−0.633 (*)	+0.00176 (***)	$-2.78x10^{-4}$ (***)	+0.0147 (***)	0 NS	0.075	0.016	0.079	0.045
Rhine	Diepoldsau	+0.161 (***)	+0.00129 NS	+74.3 (**)	+2.86 NS	+0.00685 (***)	$+2.15x10^{-4}$ (*)	+0.00890 (***)	$+3.52x10^{-4}$ (***)	0.31	0.025	0.31	0.0020 (NS)
	Rekingen	+0.0255 (***)	+0.0113 (***)	−1.72 (*)	−4.52 (***)	+0.00155 (***)	$+1.53x10^{-4}$ (**)	0.0265 (***)	+0.00377 (***)	0.084	0.0042	0.084	0.084
	Village-Neuf /Weil	−0.00658 NS	−0.0113 (***)	+4.97 (***)	+1.39 (***)	$+5.59x10^{-4}$ (***)	$-1.21x10^{-4}$ (***)	+0.0282 (***)	0 NS	0.091	0.0097	0.13	0.020
Thur	Andelfingen	+0.0895 (***)	+0.0279 (***)	+7.18 (***)	+0.884 (**)	+0.0328 (***)	+0.00233 (**)	+0.0288 (***)	+0.00329 (***)	0.11	NC.	0.22	0.098
Aar	Brugg	−0.0111 (*)	−0.0209 (***)	+6.47 (***)	+2.60 (***)	+0.00133 (***)	$-7.19x10^{-4}$ (***)	+0.0250 (***)	−0.00171 (*)	0.098	0.023	0.14	0.061

[a] NS: Non-significant trend ($p > 0.1$); (*): $0.1 > p > 0.01$; (**): $0.01 > p > 0.001$; (***): $p < 0.001$. "+" means positive relationship; "-" means negative relationship.

[b] NC: Not calculable; statistical significance of LOWESS relationships are assumed to be the same as for Sen's slopes of TOC and DOC vs discharge.

[c] For all R^2 values, $p < 0.001$, except for DOC in Diepolsau ($p = 0.22$).

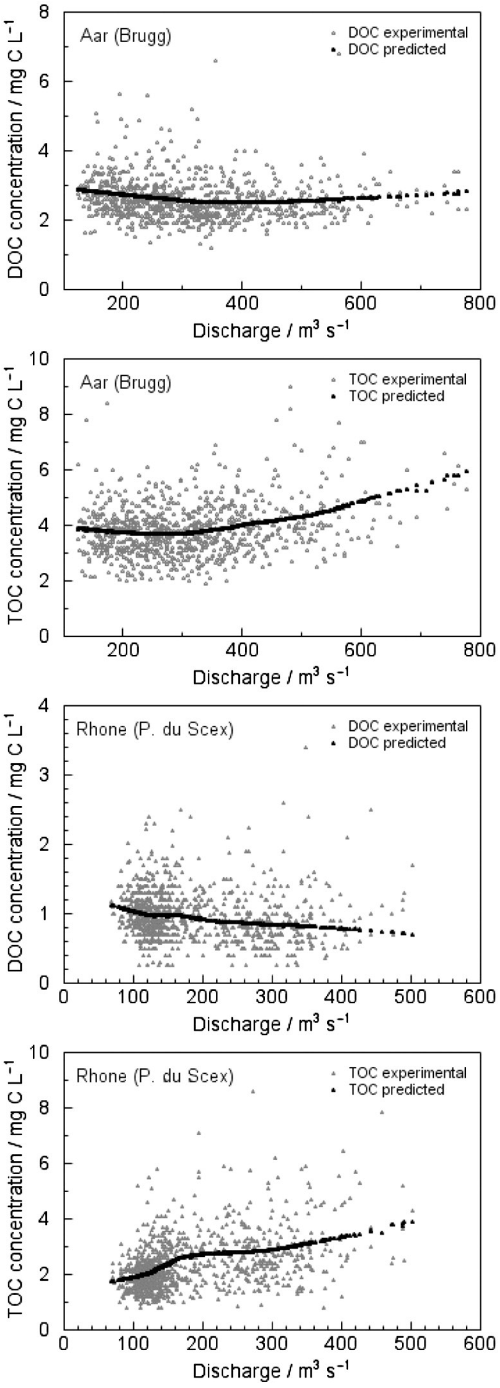

Fig. 6. Non-linear regressions (LOWESS) of DOC and TOC concentrations (mg C L^{-1}) versus discharge (m^3 s^{-1}). Empty dots are measured DOC and TOC concentrations and filled dots are concentrations predicted by LOWESS. Only two stations are shown as examples: Porte du Scex (Rhône River) and Brugg (Aar River).

production (GPP) in this river remained constant from 1986 till 2000, whereas ecosystem respiration (ER) decreased 50% over the same period, probably due to the decrease in the biodegradable organic loads from wastewater treatment plants.

5.2.3. Discharge

Many studies have documented correlations of DOC concentrations in streams with discharge, particularly with temporal high discharge events, such as storms or spring snowmelt, typically resulting in big increases in DOC concentrations (e.g., Buffam et al., 2001; Inamdar et al., 2006; Eimers et al., 2008; Raymond and Saiers, 2010). However, when DOC concentrations and discharge values in our data series were analysed by the MK and LOWESS tests, weak and variable (positive and negative) dependencies of DOC on discharge were obtained. This is not surprising, as the effect of discharge on DOC concentrations in streams and rivers is highly complex. As pointed out by Evans et al. (2005), several processes may co-exist which could lead to opposite effects (e.g., increase of discharge without change in DOC flux entering the river leads to decreased river DOC concentration merely by dilution; increasing discharge due to greater water runoff may increase DOC flux by transporting organic matter present in enriched surface soil horizons either through overland flow or shallow subsurface flow). DOC quality could depend on discharge (Maurice et al., 2002; Hongve et al., 2004); chemical composition of DOC changes during events with observations showing event DOC is more labile (Buffam et al., 2001), with a high aromaticity (Vidon et al., 2008) and from a different source than non-event DOC. This means that a change in OC quality could affect its 'lifetime', thus changing its concentration in the rivers. In our study, continuous and water discharge proportional sampling over two weeks quench the reported effects of flood events over measured concentrations.

The dependence of TOC concentration on discharge differs from that observed for DOC concentrations: a positive and significant correlation of TOC versus discharge is always observed, despite the fact that only a minor part of TOC variability is explained by discharge variability (a maximum of 30% and a minimum of 8%). Discharge explains even less of DOC variability (2.5% in the best case). Differences in TOC and DOC behaviour point to a different origin of the POC fraction that is confirmed by the different dependencies of TOC and DOC on TSS concentrations: TOC concentrations are closely related to TSS's, which suggests a dominant local terrestrial source for river POC, which is not the case for DOC. These results confirm previous observations (Kempe et al., 1991; Sun et al., 2010).

It should be mentioned that a change in trends is also apparent in discharge, with a steeper decrease from 1999 onwards, mirroring TOC and DOC behaviour. Yearly average precipitations in Switzerland (mean of 12 pluviometric stations) have increased slightly (non-significantly) from 1975–1999 and have decreased markedly (but again non-significantly) from 2000–2011 (www.meteoschweiz.admin.ch/web/en/climate/swiss_climate/tabellen.html). This fact agrees with the observed decrease of discharge.

5.2.4. Anthropogenic organic carbon

Although in some systems they can be comparable in magnitude to 'natural' OC inputs, direct OC discharges into rivers coming from human activities have rarely been invoked (Sun et al., 2010) and have never been taken into account in studies on long term river OC trends. In the last 30 years, the OC input per capita to rivers and lakes from sewage plants has dropped by approximately a factor of 2. Today sewage inputs are about: 2.8 ± 0.7 g C per capita and day for DOC and 5.0 ± 1.0 g C per capita and day for TOC (Siegrist, 2013). From this data, and knowing the inhabitants corresponding to each catchment, we have estimated that DOC and TOC loads from sewage inputs amount to a few per cent of the measured OC loads in the alpine Rhône and Rhine rivers, 12% in the Thur and up to 20% in the rest of the rivers studied. Improvements in wastewater treatment has outweighed population increase in the last 30 years.

It must be pointed out that these estimated values of DOC and TOC load inputs from sewage represent an upper limit for the sewage OC load that effectively arrives at each station because an unknown, but probably non negligible, fraction of the calculated OC will be mineralized or deposited before attaining the sampling station.

The possible contribution of the decrease in sewage OC loads over the last 30 years to the decrease in measured DOC and TOC loads has also been estimated. It represents a small percentage at the alpine stations of the Rhine and Rhône rivers as well as at Chancy. However, in the others rivers, which drain more populated areas, a higher proportion, 12 to 25%, – with a maximum value, up to 50% in the Thur – , of the measured OC decrease could be attributed to improved wastewater treatment.

From these estimations, we can conclude that OC inputs from treated sewage represent a countable part of the OC in rivers and that decreases in sewage OC have probably played a role in the observed long-term trends of OC in rivers.

5.2.5. Acid deposition

Acid deposition has been a common feature of the drainage basins of many rivers and lakes known to experience increases in OC concentrations (Monteith et al., 2007). In many (but not all) places (see Hudson et al. (2003)), an increase in DOC has occurred at the same time as a decrease in sulphate deposition. DOC in the soil solution generally decreases with soil acidification, as does DOC in lakes due to increased DOC photodecomposition in acidic lakes (Gennings et al., 2001). So the recovery from acidification experienced in the Northern Hemisphere could be a cause of the widespread DOC increase in continental waters. Nitrogen oxide (NO_x) and especially sulphur dioxide (SO_2) deposition have decreased considerably since the mid 80s across much of Europe and North America thanks to emission control policies. This has also been the case for Switzerland. However, in the area studied, the acidification potential from atmospheric deposition is predominantly governed by the nitrification of deposited reduced nitrogen (ammonia and ammonium) and this part of deposition has not changed as significantly in the last 30 years as that of sulphur species (Augustin and Achermann, 2012). A decade of monitoring (1995–2007) in Switzerland has shown that soil solution in forests was relatively little influenced by the recent changes in throughfall deposition or that the trends were too small to be detected (Pannatier et al., 2011). These facts, and the lack of a significant change in the alkalinity trends in the stations studied, has led us to consider that acid deposition is not a driver of TOC and DOC change over time.

5.3. Swiss riverine export

Export of TOC from Switzerland (including a minor fraction from adjacent countries situated in the catchment studied) have decreased significantly over the period studied (1980–2010) as a result of decreasing TOC concentrations and river discharges. In the Rhine (Village-Neuf/Weil), the decrease is of 2 kg C s^{-1}, which means an approximate 45% decrease in TOC export since 1980. In the Rhône River (Chancy), the decrease is about 0.58 kg C s^{-1}, which is a 47% decrease from 1980 levels. These decreases have been calculated as the difference between 3-year average values at the beginning and at the end of the period. The two rivers account for about 92% of the mean output water discharge from Switzerland. In 2010, $2.08.10^4$ t C were exported through the Rhône, and $7.54.10^4$ t C through the Rhine. This could be compared with Switzerland's forests net ecosystem production (NEP), which was $1.8.10^6$ t C yr^{-1} in the 90s (Bellassen et al., 2011). It is important to emphasize that the OC transported, respired and accumulated in freshwaters is not accounted for in such estimates of NEP. About 5.5% of estimated NEP, a sizeable proportion, was found to be exported by rivers. This is comparable to the case of Sweden (Weyhenmeyer et al., 2012). One could speculate that a comparable or higher amount of carbon sediments settles, principally in lakes, and is respired (Battin et al., 2009). Riverine carbon fluxes should thus be taken into account in a detailed carbon budget of Switzerland.

6. Summary and conclusions

This is the first time that a long-term change in both riverine DOC and TOC concentrations and loads has been reported with actual measured data in large catchments. TOC values showed significant decreases at most stations and no significant temporal increase. Significant temporal trends are similar for 3-year moving averages. DOC values show no significant trends except increases at two stations located downstream of large lakes (Chancy and Rekingen). Moving averages confirmed these increases and also detected positive increases in two additional sites on alpine rivers (Porte du Scex and Diepoldsau). The absolute strength of the temporal trends is always weak and generally much smaller than most reported trends in the literature. However, it is important to remember that, as systems, Swiss rivers differ considerably from most of those studied previously: they are characterised by high-discharge regimes – due to their Alpine origin – and run through highly populated areas.

A change in tendency is apparent in the OC concentrations in all the rivers studied, from an upward trend until 1999 to a stronger downward trend from 1999 to 2010. The calculation of 3-year moving averages from the original bi-weekly data has helped to reveal long term trends, pointing to the possible existence of cycling behaviour in OC concentrations overlaying a long-term temporal trend. The period studied is not long enough to ascertain whether the recent decrease is a part of a cycle or a change in the underlying trend.

Possible drivers for the observed temporal trends in OC have been explored but results are inconclusive. Our study clearly exemplifies the inherent difficulties associated with the search for simple causality mechanisms behind weak trends in complex systems. The main control factor on the temporal change of TOC concentrations is discharge, yet it explains no more than a maximum of 31% (and a minimum of 8%) of TOC variability and no more than 2.5% of DOC variability in the best case. DRP concentrations and water temperature do not significantly increase the explained variability of either TOC or DOC concentrations. Estimated anthropogenic (sewage) TOC and DOC loads delivered to the rivers could account for 4–20% of the observed temporal trends in load depending on the river. The decrease of OC in waste water inputs has a clear influence in the observed riverine OC trends but it is not an overwhelming factor.

TOC exported from Switzerland has decreased significantly over the period studied (1980–2010) as a result of decreasing TOC concentrations and river discharges. About 5.5% of estimated NEP is exported by the rivers, which is a sizeable proportion. Riverine carbon fluxes should thus be taken into account in a detailed carbon budget of Switzerland.

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