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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/.