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The apparent and potential effects of climate change on the inferred concentration of dissolved organic matter in a temperate stream (the Malše River, South Bohemia)

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Abstract

Long-term and seasonal changes in concentration of dissolved organic matter (DOM) and their possible drivers were evaluated for an upland stream in central Europe during 1969–2000. Two periods have been detected within this data set—years with decreased DOM until the middle of 1980s and then years with increased DOM until 2000. Temperature, hydrological regime of runoff from the catchment (namely the amount of interflow), and changes in atmospheric deposition of acidity coincided with the variations in DOM concentrations. The analysis of single runoff events confirmed the relation between the export of increased DOM concentrations from the catchment and interflow. A multiple linear regression model based on monthly averages of temperature and interflow explained 67% of DOM variability. This model suggested a 7% increase in DOM concentration under the scenarios of possible future climate change related to doubled CO₂ concentration in the atmosphere. The scenarios were based on results of several global circulation models.

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1. Introduction

The concentration of dissolved organic matter (DOM) in headwater streams reflects largely processes in the terrestrial part of the catchment ecosystems because the predominant origin of

DOM is leaching from soils. Transport of DOM from terrestrial ecosystems to freshwaters and, eventually, coastal waters is important for many biotic and abiotic processes in aquatic ecosystems (Keskitalo and Eloranta, 1999), affects quality of water resources (Vik and Eikebrokk, 1989), and represents a significant carbon flux from the global carbon store in organic soils and peat bogs to the hydrosphere and, finally, atmosphere (Freeman et al., 2001). An increase in concentrations of dis-

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solved organic matter has been described by Evans and Monteith (2001) at streams and lakes throughout the UK in the last decades. Several factors causing this increase have been suggested, including recovery from atmospheric acidification, changes in soil acidity, soil moisture content and temperature. Seasonal hydrological patterns represent the other factors that control DOM concentrations in streams.

The aim of this paper is to show that the increasing DOM trend in the recent period can be recognised also in central Europe. We have analysed seasonal and long-term variability of DOM concentrations in an upland stream draining a mixed agricultural and forested catchment and have found that a considerable part of DOM variability can be explained by variations in climate conditions (temperature, precipitation) and hydrology (runoff and its components). A simple regression model and climate change scenarios based on several global circulation models (GCMs) have been used to predict DOM in this stream in the end of this century.

2. Locality, data and methods

The Malše River catchment above the profile at Pořešín (14°32'E/48°47'N; 40.1 km upstream from the confluence of the Malše River with the Vltava River; area 438 km²; mean/maximum/minimum altitudes—705/1072/480 m above sea level) is situated at the border of the Czech Republic and Austria. The bedrock is formed by weathered paragneiss, diorite and granite. Most soils are dystric cambisols and mountainous podzols of acidic character (pH < 4.5). Approximately 32% of the catchment is used as arable land, 19% as meadows, 43% for forestry and 2% are urbanised areas. No significant changes in land use and human population (~10 000) occurred during the study period 1969–2000.

The long-term data on DOM during 1969–2000 were inferred from daily monitoring of water quality in the Malše River by the Waterworks Pořešín [the company of Water Supply and Sewerage South Bohemia, a.s. (WSS-SB)]. DOM was analysed as the chemical oxygen demand with the standardised permanganate Kubel method (COD; Hofmann, 1965). The oxidation efficiency for

DOM from natural waters is only approximately 40% in this COD method (Janicke, 1983), however, this method has a good repeatability and long term stability when applied to one type of water. The expanded uncertainty value according to ISO (1993) was $\pm 7\%$ for the concentration of 3 mg l⁻¹ (i.e. ± 0.23 mg l⁻¹; Karel Janowiak from WSS-SB, unpublished). A relatively tight correlation of dissolved organic carbon (DOC) with COD was determined for this locality in 1995–1998 as: $\text{DOC} = 1.4 + 0.67 \cdot \text{COD}$ ($n = 235$, $R^2 = 0.88$, $P < 0.001$). DOC was analysed with the Shimadzu TOC5000 analyser with expanded uncertainty of results ± 0.2 mg l⁻¹ at the 5 mg l⁻¹ concentration level.

The discharge in the Malše River was measured continuously at the gauging station at Pořešín and precipitation (daily readings) was measured at 6 stations throughout the Malše River basin, both by the Czech Hydrometeorological Institute (CHMI). Air temperature (daily means) was obtained from the CHMI meteorological station in České Budějovice, situated approximately 25 km southward from Pořešín.

Trends within the measured data and model results were evaluated by the non-parametric seasonal Kendall test that was applied to the monthly average blocks of data (Hirsch et al., 1982). This test is robust with respect to non-normality and high seasonal fluctuations of data and has been used in many monitoring programmes (e.g. Evans et al., 2001). Trend slopes were calculated by the method of Sen (1986) as the median of all between-year differences between data values. A significance threshold of $P < 0.05$ was applied to the trend tests. A second threshold of $P < 0.2$ was also used to indicate weaker, but potentially existing trends.

Runoff and its components were modelled with the Sacramento Soil Moisture Accounting Model (SAC-SMA; Burnash, 1995) coupled with the snow model of Anderson (1968); (Buchtele et al., 1996). The model was calibrated for the period 1961–1970 and validated on the 1969–2000 period. The surface (SUR), interflow (INT), primary baseflow (PRM) and supplementary baseflow (SUP) components of total runoff were calculated

with the model. With temperature and precipitation as the input variables, the model was able to describe correctly 63% of daily total runoff variability with absolute mean error of $1.4 \text{ m}^3 \text{ s}^{-1}$ (35% of the mean runoff value).

Thirty two-year daily weather series representing the changed climate conditions (see later) were prepared either by a direct modification of observed data series or by a stochastic daily weather generator. In case of the direct modification of observed weather series, the temperature was modified additively, and the precipitation multiplicatively by increments defined separately for individual months. In the case of the stochastic weather generator, the two-variate version of the Met&Roll generator (Dubrovský, 1997) was employed. The generator with parameters derived from the observed weather series was used to prepare synthetic series representing the present climate. To generate series representing the changed climate, parameters of the generator were modified in accordance with the climate change scenarios.

Climate change scenarios for the future period were based on the outputs of the transient runs of GCMs available from the web page of IPCC Data Distribution Centre (<http://ipcc-ddc.cru.uea.ac.uk/>). Three scenarios of monthly increments to the studied weather characteristics were constructed. Two of them were based on NCAR DOE-PCM (Scenario N) and ECHAM4/OPYC3 (Scenario E), which were found to be the most successful GCMs in the validation tests. The third scenario (Scenario A) was obtained by averaging the climate change scenarios based on seven GCMs (CCSR/NIES, CGCM1, CSIRO-Mk2, ECHAM4/OPYC3, GFDL-R15-a, HadCM-2, NCAR DOE-PCM). The climate change scenarios related to the doubled CO_2 concentration (666 ppm), which is expected for 2092 in the case of the IS92a emission scenario. Each of the three scenarios was defined by the pattern scaling technique (Santer et al., 1990), which consisted in multiplying the standardised regional scenario by the forecasted increment of the global average temperature, ΔT_G . The value of $\Delta T_G = 2.33$ was used according to the results of one-dimensional climate model MAGICC (Hulme et al., 2000) assuming IS92a emission scenario and the middle

climate sensitivity. Generally, the standardised regional scenario is obtained by dividing a climate change scenario for the given area and period by the increase of annual mean global surface temperature predicted for that period. In this study, the standardised regional scenario was determined as a weighted average of the series of scenarios for nine consecutive 10-year intervals within the 2010–2099 period of the GCM transient runs.

3. Results

3.1. Seasonality of DOM, climate and hydrology

DOM in the Malše River during 1969–2000 showed a distinct seasonal pattern with the lowest concentrations ($\text{COD} \sim 4 \text{ mg l}^{-1}$) during winter periods of freezing and the highest concentrations (daily values of COD 6 to $>20 \text{ mg l}^{-1}$) during summer months, and loosely followed the pattern of temperature (Fig. 1a,c). Runoff was dominated by maximum discharges after snowmelt in March and April which were followed by a gradual decrease until November but with occurrence of short, peaking flows during the summer in some years (Fig. 1b). Average monthly values of flow components in the Malše River obtained by modelling with SAC-SMA are shown in Fig. 1d. On an average basis, primary baseflow, supplementary baseflow, interflow, and surface flow accounted for 32, 48, 7 and 13%, respectively, of the total discharge. Primary baseflow was nearly constant throughout the year. Its relatively small proportion conformed to the hydrogeology of the Malše River basin which is typical with only shallow aquifers formed in the weathered zone of the bedrock up to the depths of maximum 10–30 m. The other flow components showed seasonal patterns with maxima in spring for supplementary baseflow or in spring and summer for interflow and surface flow.

The summer increases in DOM concentration occurred mainly during high runoff events. An example of DOM changes during a hydrograph is given in Fig. 2. A heavy precipitation event of frontal origin in the Malše River basin in July

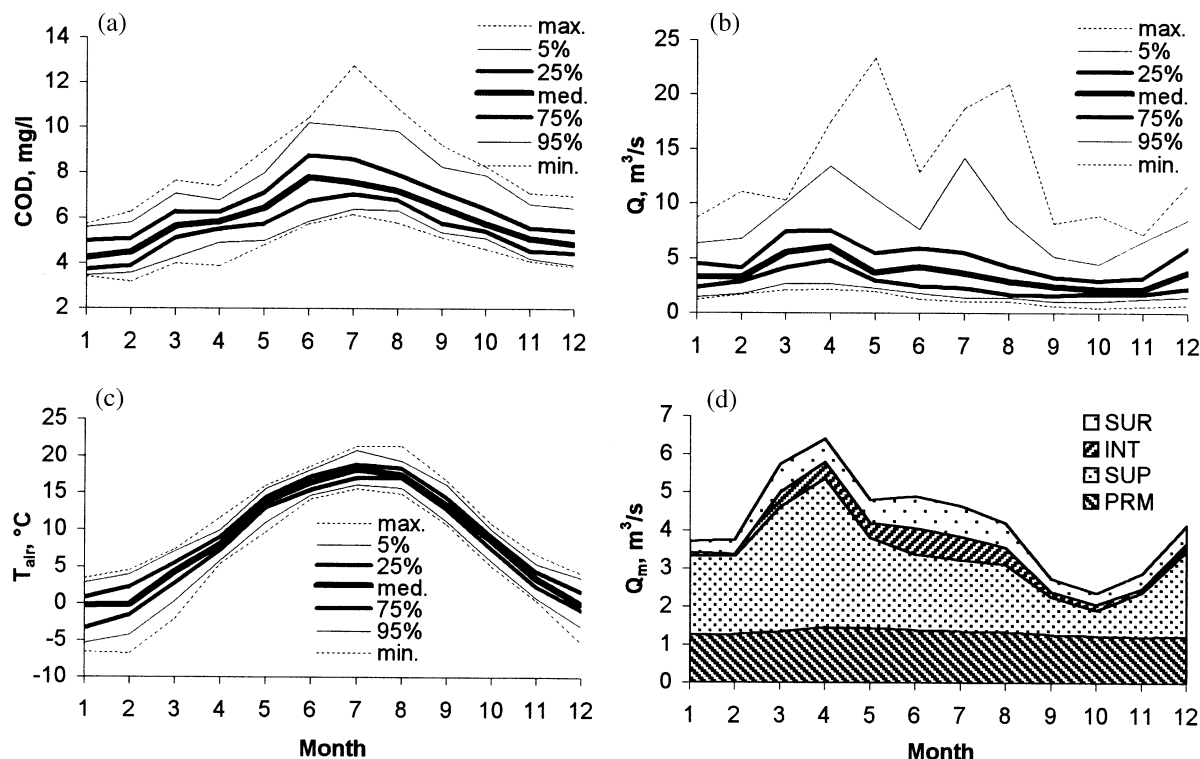


Fig. 1. Monthly averages of COD (a), discharge (b), air temperature (c), and flow components (d) in the Malše River at Pořešín during 1969–2000. The lines in figures a, b and c show minimum, maximum, median, and 0.05–0.95 percentile values.

1999 was followed by a discharge maximum which was composed of the sequence of peaks of surface flow, interflow and supplementary baseflow (Fig. 2c). The changes of DOC concentration during this event suggested that transport of high concentrations of DOM was connected mainly with interflow. The counter clockwise hysteresis (lower concentrations at equivalent water discharge during the rising stage compared to the falling stage) of both DOC and interflow (Fig. 2b,d) indicated that DOM was flushed out from the organic horizon of soil profile and transported by lateral flow into receiving water courses.

Selected results of correlation analysis are given in Table 1, indicating which hydrologic and climate parameters affected DOM in the Malše River. The strongest correlations were found for temperature, apparently due to identical seasonal courses of both parameters, and for interflow. A multiple

linear regression model (1) was calculated with these two parameters:

$$\begin{aligned} \text{COD} [\text{mg l}^{-1}] = & 4.64 + 0.140 \times \text{Temperature} [^{\circ}\text{C}] \\ & + 0.802 \times [\text{INT} [\text{m}^3 \text{s}^{-1}]] \\ (n = 384, R^2 = 0.67, P < 0.001) \end{aligned} \quad (1)$$

All coefficients of the model were statistically significant ($P < 0.001$) with the relative standard error of 1.5, 5 and 7% for the intercept, temperature coefficient and interflow coefficient, respectively. The absolute mean error and the root mean square error of the modelled monthly COD concentrations for the 1969–2000 period were 0.65 and 0.86 mg l^{-1} , respectively. The errors were evenly distributed during the year (Fig. 3). The sensitivities of the model in respect to temperature and interflow changes were 0.14 mg l^{-1} per 1 $^{\circ}\text{C}$ and 0.8 mg l^{-1} per 1 $\text{m}^3 \text{s}^{-1}$ of interflow, respectively, giving almost the same ranges of effects for

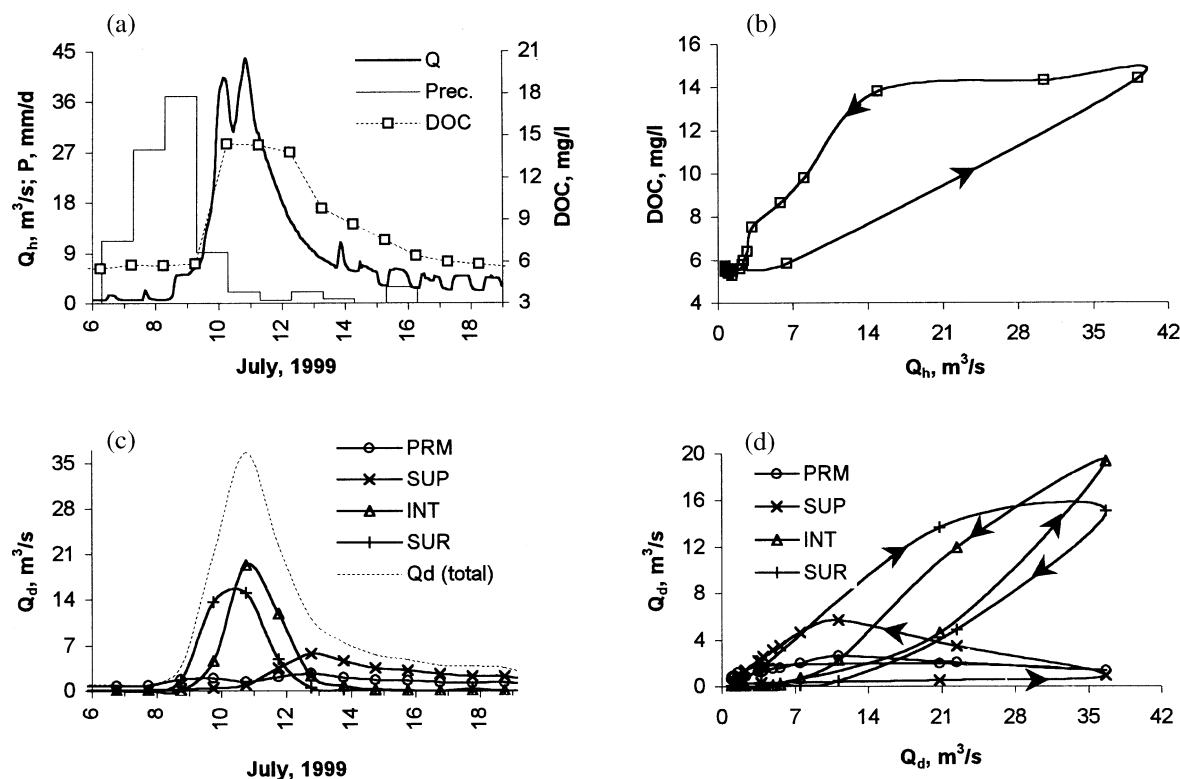


Fig. 2. Discharge, flow components, DOC, and their hysteresis in the Malše River during a runoff event during July 6–19, 1999. (a) Precipitation (P; daily averages from 6 station throughout the Malše River basin), runoff hydrograph (Q_h , hourly averages) and DOC (instantaneous samples), (b) hysteresis of DOC, (c) modelled flow components (daily averages), (d) hysteresis of flow components.

the fluctuation intervals of these parameters during the study period, i.e. 4.0 mg l^{-1} for the temperature range (-6.7 – $21.4 \text{ }^{\circ}\text{C}$) and 4.4 mg l^{-1} for the interflow range (0 – $5.5 \text{ m}^3 \text{ s}^{-1}$).

3.2. Long-term changes

Several significant trends were revealed by the seasonal Kendall test within the COD data series in spite of large fluctuations (Fig. 4, Table 2): (i) for the whole period 1969–2000 (increasing; $P < 0.05$) (ii) 1969–1984 (decreasing; $P < 0.01$), and (iii) 1983–2000 (increasing; $P < 0.01$). The changes of COD derived for these periods from the Sen's slope estimator (Sen, 1986) were 0.32 mg l^{-1} (+5%), -0.85 mg l^{-1} (–14%), and 0.56 mg l^{-1} (+9%), respectively. The existence of

increasing trend of DOM in the Malše River at Pořešín during the 1983–2000 period is supported by the increase of COD by 0.72 mg l^{-1} (+14%) determined for the same period in water abstracted from the downstream situated Římov Reservoir with an average hydraulic residence time of 0.3 year (based on unpublished data of WSS-SB).

The increases of temperature calculated from the Sen's slope were 1.0 and $0.9 \text{ }^{\circ}\text{C}$ for the 1969–2000 and 1983–2000 periods, respectively, with significance $P < 0.01$. These values are approximately twice higher in comparison with the global temperature increase during the last decades given in the latest IPCC report (Houghton et al., 2001) but correspond to other climatic monitoring stations in the Czech Republic, for example Prague (Brůžek, 2000).

Table 1

Correlation coefficients for linear relationships between monthly mean COD vs. monthly mean temperature, discharge and flow components in the Malše River during 1969–2000

Temperature, °C	Discharge, m ³ s ⁻¹	PRM, %	SUP, %	INT, %	SUR, %
0.74*	0.34*	-0.31*	-0.06	0.54*	0.46*

* $P < 0.01$

Precipitation and discharge showed significant and indicative increasing trends, respectively, but only in the latest period 1983–2000. Discharge modelled with SAC-SMA increased significantly also only during 1983–2000. Significant trends within flow components were found in 1983–2000 for primary baseflow (negative) and interflow (positive) but with very low slope, indicating almost no change.

COD concentrations calculated with model (1) showed a significant increasing trend in 1983–2000 and an indicative increasing trend in 1969–2000. The agreement between trends of measured and modelled results has justified the selection of model parameters and supported the hypothesis of temperature impact on DOM in the Malše River. On the other hand, approximately three-time smaller slope of the modelled COD trend suggested that also other, not considered factors might act in the transport of DOM from the Malše catchment.

3.3. Climate change scenarios

The $2\times\text{CO}_2$ climate change scenarios used in this study predict an increase of mean temperature by the end of this century in the range from 2.5 to 3.6 °C (Table 3). The increase in temperature was relatively uniform throughout the whole year (Fig. 5). Precipitation changes were predicted differently in each of the scenarios with the mean values of +7.2, +0.8 and -3.2% in Scenario N, A and E, respectively. The temperature and precipitation projections (as well as their ranges and seasonal patterns; Fig. 5) corresponded well with the generally accepted results of IPCC studies (Houghton et al., 2001). There were only minor differences between the scenarios based on the direct modification of observed data series and the scenarios based on the weather generator. These differences were related to the stochasticity involved in the data generating procedure. The

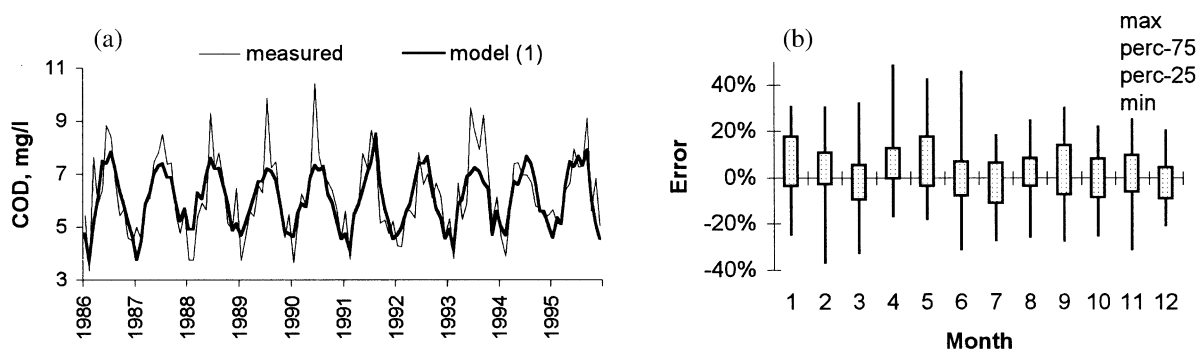


Fig. 3. (a) A comparison measured and model (1) monthly average COD concentrations in the Malše River for a 10-year period (1986–1995). (b) Selected statistics of model (1) errors during the year; minimum values, interquartile range, and maximum values are given.

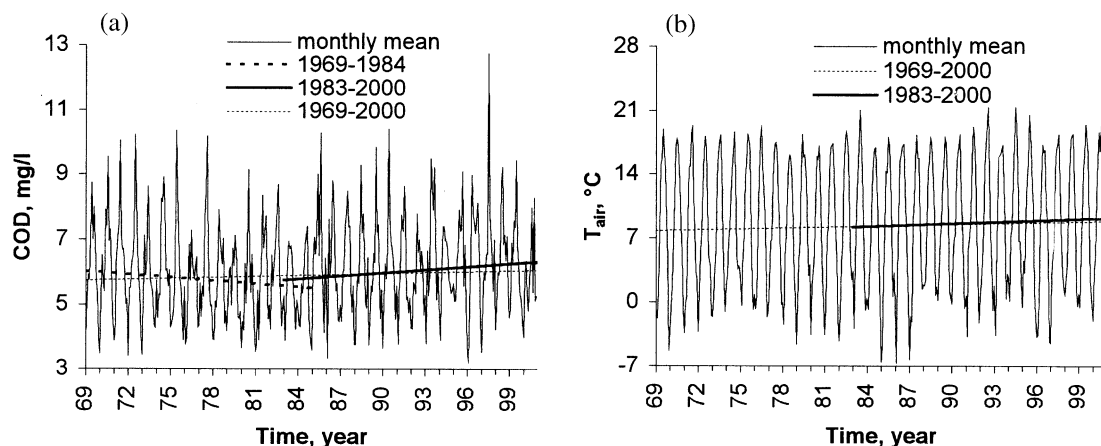


Fig. 4. Monthly average values of COD in the Malše River (a) and air temperature (b) during 1969–2000 with significant trends revealed by the seasonal Kendall test.

Table 2

Sen's slope estimates of significant trends detected by the seasonal Kendall test in COD, climate, and hydrology of the Malše River basin during 1969–2000

Parameter	Period		
	1969–1984	1983–2000	1969–2000
COD, mg l ⁻¹	–0.053**	0.031**	0.010*
COD calculated from model (1), mg l ⁻¹	–	0.011**	0.004 ⁺
Temperature, °C	–	0.054**	0.032**
Precipitation, mm	–	0.4**	–
Discharge, m ³ s ⁻¹	–	0.01 ⁺	–
Discharge modelled with SAC-SMA, m ³ s ⁻¹	–	0.06**	–
PRM, %	–	–0.2*	–
SUP, %	–0.003 ⁺	–	–
INT, %	–	0.01**	–
SUR, %	0.002 ⁺	–	–

Probability level: + <0.2; * <0.05; **0.01. Units of all slopes are per year

Table 3

Changes of temperature, precipitation, discharge and concentration of dissolved organic matter (as COD) in the Malše River based on different GCM scenarios for 2×CO₂ in comparison with the period of 1969–2000

Scenario	Temperature, °C		Precipitation, %		Discharge, %		INT, %		COD, %	
	D	G	D	G	D	G	D	G	D	G
A	3.0	3.0	0.8	0.6	–2.2	–1.8	–5	–14	6.5	6.6
E	3.6	3.7	–3.2	–3.2	–12.0	–11.3	–23	–33	7.1	7.6
N	2.4	2.5	7.2	6.6	12.6	12.4	23	25	7.1	7.1

Input daily weather data were obtained either from direct modification of observed weather series (D) or from the weather generator (G)

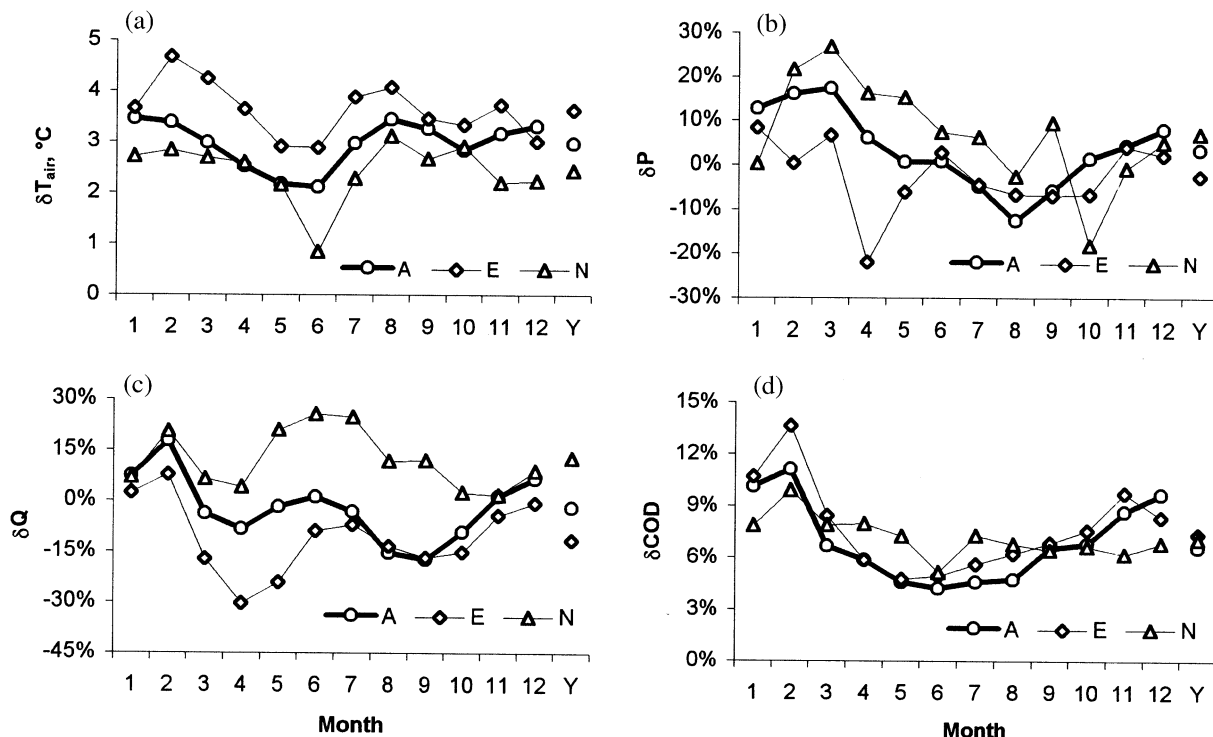


Fig. 5. Climate change scenarios for monthly average temperature (a) and precipitation (b), and related changes in discharge (c) and concentration of COD in the Malše River (d). The climate change scenarios were based on two single GCMs [ECHAM4 (E), NCAR DOE-PCM (N)], and the average over seven GCMs (A); δ denotes a difference from average value during the 1969–2000 period.

winter increases of temperature and precipitation caused in all scenarios higher discharges in the Malše River during January and February due to lesser storage of snow in the catchment and decreased discharge in March and April during snowmelt. Summer discharges and the proportion of interflow varied between the scenarios.

The above changes of climatic and hydrological conditions resulted in a similar COD increment (+7%) in all scenarios (Table 3). This increment was mostly governed by the temperature increase (from more than 85%) with a less distinct effect of interflow, changes in which contributed to the COD either positively (Scenario N) or negatively (Scenarios A and E). The seasonal courses of COD changes were also similar in all scenarios with the dominant increase in winter (Fig. 5).

4. Discussion

Potential sources of DOM in streams include: atmospheric deposition, decaying litter and humus on the soil surface, soil organic matter, wetland peat deposits, aquatic detritus, aquatic sediments and aquatic organisms. DOM from these sources may reach surface water directly or may be transported to streams as a surface flow, subsurface lateral flow (interflow), or groundwater inputs. Seasonal and long-term changes in DOM concentration in a stream reflect dynamics of individual sources and proportions in the hydrologic inputs (Cronan, 1990). Thus, DOM can be considered an indicator of overall change in hydrologic and soil conditions in the catchment.

The regression DOM model (1) that was purposely developed in this study has to be considered a crude approximation of reality for the specific conditions of the Malše River basin. However, 67% of described variability and capturing the long-term trends indicate that main controlling mechanisms have been rendered correctly. The model parameters seem to reflect dominant DOM sources and transport mechanisms from the catchment. The constant term in the model (1) corresponds with the concentration of COD during winter periods of freezing when the aquatic primary production was low and streamflow was composed largely of groundwater inputs. The term associated with temperature covers a complex of seasonally changing processes, e.g. the increase of DOM concentrations in organic horizons of soil profile during the growing season (Hoffman et al., 1980), the corresponding seasonal increases in surface and subsurface runoff, and the autochthonous in-stream production. The term associated with interflow accounts for a greatly increased DOM concentrations during periods of short but intense precipitation events.

The model (1) could not of course reproduce not-included processes. One of such processes was probably associated with the peaking acid atmospheric deposition of acidity during the studied period. Loading of soils with mineral acids is known to cause decreased leaching of DOM (Krug and Frink, 1983; Tipping and Hurley, 1988). The changes of acid deposition in the central European region were very pronounced with a gradual increase from the 1950s until the early 1980s, a flat maximum until middle 1980s, and then a rapid drop towards the end of the 1990s (Kopáček et al., 1998). This course of acid deposition is mirrored by the decreasing and increasing trends in COD during 1969–1984 and 1983–2000, respectively (Fig. 3). Although this acidification period did not result in any unequivocal decrease in alkalinity of water in the Malše River (it was masked with anthropogenic factors, for example farmland fertilisation and waste water discharges), the coincidence of the acid deposition maximum and the COD minimum suggests that the long-term course in COD concentrations in the Malše River could result from the superimposition of the

effect of peaking acid deposition upon the impact of increasing temperature trend.

It should be stressed, however, that temperature itself was probably not the main driver for the COD increase in the Malše River. It is known that on drained soils, there tends to be an inverse correlation between average soil temperature and DOM concentrations in surface soil leaches. Thus, DOM concentrations generally decrease in warmer environments (Mulholland et al., 1990). In poorly drained areas, there is a tendency for DOM concentrations to reach very high levels, independently on the climate (Cronan, 1990). The increasing COD trend together with increasing temperature in the Malše River catchment seems to contradict with this general pattern. In this case, the temperature increase acted probably together with other factors, for example elevated precipitation (Table 2), which increased moisture content of soils or diminished periods of winter freezing with low in-stream DOM concentrations.

5. Conclusions

The results of this study indicated that the DOM concentration in the Malše River is influenced by (i) climatic and hydrologic conditions, especially seasonal and long-term changes of temperature and runoff components (mainly interflow), and (ii) long-term changes in the atmospheric deposition of acidity.

The climate change scenarios for doubled CO₂ in the atmosphere suggested impacts to the streamflow and runoff components and, consequently, to DOM. The predicted increase in DOM concentrations resulted mainly from a complex of not yet fully understood processes surrogated with temperature changes and from changes in proportions of runoff components.

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