Variation in Organic Matter and Water Color in Lake Mälaren during the Past 70 Years

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Received: 16 November 2008 / Revised: 5 May 2009 / Accepted: 11 August 2009 / Published online: 28 April 2010

Abstract Interest in long time series of organic matter data has recently increased due to concerns about the effects of global climate change on aquatic ecosystems. This study presents and evaluates unique time series of chemical oxygen demand (COD) and water color from Lake Mälaren, Sweden, stretching almost seven decades (1935–2004). A negative linear trend was found in COD, but not in water color. The decrease was mainly due to installation of sewage works around 1970. Time series of COD and water color had cyclic pattern. It was strongest for COD, with 23 years periodicity. Similar periodicity observed in air temperature and precipitation in Sweden has been attributed to the North Atlantic Oscillation index and solar system orbit, suggesting that COD in Lake Mälaren is partly derived from algae. Discharge influenced water color more than COD, possibly because water color consists of colored substances brought into the lake from surrounding soils.

INTRODUCTION

Interest in long time series of organic matter (organic carbon) data has recently increased (Worrall and Burt 2004; Evans et al. 2005), mainly due to concern about the effects of global climate change on aquatic ecosystems (Freeman et al. 2001), and associated changes in raw water quality for waterworks (Eikebrokk et al. 2004). Studies of surface waters in parts of Sweden (Löfgren et al. 2003; Forsberg and Petersen 1990; Erlandsson et al. 2008; Hongve et al. 2004; Forsberg 1992) and in parts of Europe and North America (Worrall and Burt 2004; Evans et al. 2005, 2006) indicate that organic matter concentration has increased during the last two decades.

The concentration of organic material in surface water depends on climate, soil, and vegetation in the catchment

area, but is also influenced by internal processes in the water system, such as sedimentation and mineralization (Wetzel 2001). Water color and chemical oxygen demand (COD) are two methods to estimate the concentration of organic matter (Birge and Juday 1934; Åberg and Rodhe 1942). Water color is a measurement of aquatic humic substances, but is also influenced by other factors, for example iron and nitrate concentration, differences in pH and iron redox (Åberg and Rodhe 1942; Hutchinson 1957). COD constitutes all matter oxidizable by permanganate, such as carbon, sulfur, nitrogen and iron (also chloride at high levels). Autochthonously derived organic matter can contribute to COD without much influence on measured water color (Birge and Juday 1934; Åberg and Rodhe 1942).

Climate change has an impact on the quality and quantity of organic matter in surface waters. Scenarios for future climate change in Scandinavia indicate increasing average temperatures and shorter winters in coming decades. Precipitation will increase/decrease depending on the specific region in Sweden, and this will influence the discharge and watertable (Rummukainen et al. 2003). Changes in the dominant terrestrial water flow pathways (due to changes in the watertable) could generate organic matter of different quality in the surface water. Raw water with more color and higher concentrations of organic matter and/or different quality could require new and better treatment at waterworks.

Stockholm waterworks supplies fresh water to 1.5 million inhabitants in Stockholm, Sweden, and this water originates from Lake Mälaren (Fig. 1). Lake Mälaren water chemistry has been evaluated previously (Wallin et al. 2000; Weyhenmeyer 2004; Weyhenmeyer et al. 2004; Willén 2001), using environmental assessment data collected at different sites in the lake since around 1965, and one site since 1940 (Löfgren et al. 2003). In 2001, one of the

Fig. 1 Map of Sweden (*right side*), the Lake Mälaren catchment at the outlet at Norrström, Stockholm, with the Lovö waterworks and Mörbyfjärden bay

Stockholm water treatment plants, the Lovö waterworks (Fig. 1), had problems reducing organic matter in raw water to acceptable levels and investigations showed that the concentrations had significantly increased since the 1970s.

This study presents and evaluates trends in time series of water color and COD from 1935 to 2004 in the raw water at Lovö waterworks and in discharge from the outlet of Lake Mälaren. It also evaluates the impact of the discharge on water color and COD during the period 1944–2004.

STUDY AREA

Mörbyfjärden bay (Fig. 1) is the raw water supply for the Lovö waterworks (N59°19', E17°48'). The Lake Mälaren catchment area is 22,063 km² and comprises forest (70%, mostly coniferous forest), arable land and meadows (20%) and lakes (10%) (Wallin et al. 2000). The lake area, including islands and islets, represents 1617 km², of which the total water surface area is 1096 km². The mesotrophic Lake Mälaren is lobate and rich in islands, and consists of five clearly defined basins (Wallin et al. 2000). Basin E, from which the Lovö waterworks collects its raw water, has an estimated hydraulic retention time of 0.4 years, a mean depth of 14 m, and an area of 96.5 km² (Wallin et al. 2000). The theoretical hydraulic retention time of the entire lake is 2.8 years (Wallin et al. 2000). Hydraulic retention time has an influence on water quality, as longer retention time allows sedimentation and breakdown of particles and aquatic humic substances (Wetzel 2001).

In Lake Mälaren, there are two main directions of water transport; west-east and north-south. The catchment area

for north-eastern Lake Mälaren comprises relatively nutrient-poor glacial till, overlain in some areas by carbonate rich-clay, and peat distribution is low. Hence, the inlet watercourses to the north-eastern part of the lake are generally low in water color but high in nutrients. The soil in the north-west of the catchment area is low in carbonate and nutrients and peat land is more abundant, so the runoff to the western part of the lake is more colored and less nutrient-enriched than that to the eastern part (Wallin et al. 2000). Water from both parts is mixed and reaches the inlet to the Lovö waterworks. Mean annual air temperature (1930–2002) at nearby Uppsala (Fig. 1) is ~6°C, with mean monthly temperature of –4°C in January and 15°C in June. Mean annual precipitation is about 550 mm (Uppsala, 1930–2002) (Johansson 2003). From October to April, the precipitation can occur as snow.

Information about total area of arable and forest land in the provinces located in the Lake Mälaren can be obtained from national statistics (SCB 1958, 1983, 1993). Province area does not completely coincide with catchment area, but the differences were considered negligible. The total area of arable land decreased by 22% from 1937 to 1992 in five of six provinces in the catchment area, but in the province of Uppsala it increased by 3%. The area of forest land increased in all provinces except Stockholm (30% decrease). However, total forest area has only increased by 0.5%. This increase was most evident in Uppsala province (43%) and occurred mainly during the period 1956–1981 (38% increase). In the same period, the area of forest in Stockholm province decreased by 24%. Area with more (coniferous) forest could contribute more organic matter, and more colored organic matter, to nearby surface water.

METHODS

Data Collection

Data describing raw water quality back to 1935 were available at Lovö waterworks. All chemical analysis has been performed at Lovö waterworks, by their staff. The authors have not taken part in the chemical analysis. The discharge at the outlet of Lake Mälaren has been measured as total discharge per month (Mm³) at Norrström in Stockholm since 1944 (data from Stockholm municipal community office).

Water color, COD, and pH in the raw water were analyzed approximately once a week during the period 1935–2004. However, water color values for 1992 were missing. Alkalinity has been analyzed since 1944. The raw water tubes collect water from 5, 10, 15 and 23 m depth, sometimes from only one depth but also as a mixture of all these depths. No seasonal or yearly trend was observed in water collection depths. The inlets are situated in the pelagic; during periods with stratification (the lake is dimictic), water is taken beneath the thermocline.

Since 1935, the analytical method used for determining the amount of organic matter has varied, mainly due to legislative demands (Wilander 1988). Before 1997, organic matter was determined as COD (chemical oxygen demand, analyzed according to KMS122) and from 1997 as TOC (total organic carbon, analyzed according to SS-EN 1484 using high temperature combustion method). For 2 years, 1997–1998, organic matter was analyzed using both methods. The following relation was found: COD = 0.85 × TOC [$n = 34$, coefficient of variation = 5%, (Blomberg 1998)]. The methods were analyzed in parallel during a short period of time and no detailed statistical analyses were carried out. Generally the COD method, based on permanganate, gives poor information about the concentration of total organic carbon in Swedish lakes and streams (Meili 1992). TOC was introduced in the end of the study period (1997–2004) and at this point it is too early to evaluate how the shift in methods influenced the time series of Lake Mälaren.

Water color (unfiltered) was measured according to SS-EN ISO 7887, which is an ocular analysis method. Alkalinity was measured according to end-point titration with HCl (0.025 M) to pH 5.6 (SS 02 81 39) and pH according to SS 02 81 22. The methods for analyzing water color and alkalinity have not changed during the study period.

Trend Analysis of Times Series

The time series for water color, COD and discharge were tested for monotonic linear trend, stepwise trend and cyclic trend (Helsel and Hirsch 1992). The quality of organic

matter was estimated as the ratio of water color to COD, which is an indicator of the fraction of compounds rich in aromatic moieties, often referred to as hydrophobic organic matter (Dilling and Kaiser 2002). Trends in this ratio were also evaluated.

In order to evaluate how installation of sewage works (mainly during the late 1960s–early 1970s) influenced organic matter content in Lake Mälaren, the stepwise trend was tested using a binary variable containing zeros until the breakpoint, and thereafter ones. The stepwise trend was assumed to occur somewhere between 1965 and 1975 (Fölster and Wilander 2002), and the binary variable with a breakpoint that had the best correlation with time series of color and COD was used.

Long-term cyclic trends have been observed in time series of temperature, evaporation and water chemistry in Sweden (Fölster and Wilander 2002; Eriksson 1981; Moberg 1996). To test cyclic trends, sine and cosine function (Eq. 1) was adjusted to yearly median values of water color, COD and color/COD, using JMP 7.02 (SAS Institute Inc.), according to the formula:

$$C = k \cdot \text{BreakPoint} + B + A \cdot \text{Sine}\left(\frac{(T - t_0) \cdot 2\pi}{p}\right) + D \cdot \text{Cosine}\left(\frac{(T - t_0) \cdot 2\pi}{p}\right) \quad (1)$$

where C , T and BreakPoint have known values, C is median year value of color, COD and color/COD, T is a running time variable, in year, BreakPoint is a dummy variable with zero before 1970 and 1 after 1970. Unknown values were calculated by Newton–Raphson iterations ($\alpha = 0.05$ and convergence criterion was set to 0.00001); k is the factor for the break point, t_0 is the start year of the sine function, p is the periodicity of the sine function, A is the amplitude of the sine function, B is the base line of the sine function, and D is the amplitude of the cosine function.

Only the sine function was significant in (Eq. 1), so for all further results the cosine part of the equation was omitted. Values every second year (even years) were used to build the model, and values in uneven years were used to validate the sine function by regression. The cyclical behavior in time series of discharge was too weak and no sine function could be adjusted.

Impact of Discharge on Organic Matter

The impact of discharge on COD and water color was regarded as an estimate of allochthonously derived organic matter. The correlations between discharge in Lake Mälaren and time series of water color, COD and color/COD ratio, respectively, were studied.

In order to detect any trends in water chemistry not related to changes in discharge, the median values of water color, COD and color/COD were normalized for discharge (Helsel and Hirsch 1992). Since the retention time in Lake Mälaren is 2.8 years (Wallin et al. 2000), the time series were normalized using discharge (Q) with three time lags; $Q(t)$, $Q(t - 1)$, $Q(t - 2)$ and $Q(t - 3)$. The normalization was performed according to Eq. 2 (Helsel and Hirsch 1992).

$$y_{\text{norm}}(t) = [y(t) - [a + b_1 \times Q(t) + \dots + b_n \times Q(t - n)]] + y_{\text{median}} \quad (2)$$

where y_{norm} is the concentration normalized for discharge at time t , $y(t)$ is the observed concentration at time t , $Q(t)$ is the observed discharge at time t , y_{median} is the median of the series of observations, and $a + b_1 \times Q(t) + \dots + b_n \times Q(t - n)$ is the equation of regression using one or more time lags in discharge (yearly sum).

The discharge-normalized time series for water color and COD were tested for monotonic linear trend and stepwise trend (Helsel and Hirsch 1992). The breakpoint was assumed to occur somewhere between 1965 and 1975.

Quality Control of Results

For all statistical analyses the coefficient of determination was adjusted for differences in degrees of freedom (r_{adj}^2). Residual analyses were performed to confirm statistical analyses. The regression was considered as significant if p -value was lower than 0.05. In all the cases with a significant regression result ($p < 0.05$), the regression between residuals was also significant in all cases except one (test of a stepwise and cyclic trend in water color values). R_{adj}^2 - and p -values for all statistical analysis are presented in Tables 1, 2, or in a few cases, directly in the text.

Table 1 Results of regression analysis for water color, COD, ratio color/COD and discharge at year (t) or antecedent year ($t - 1$)

Y	X	Time	r_{adj}^2	p	df	Residuals (r_{adj}^2/p)
Color (t)	Color ($t - 1$)	1935–2004	0.36	<0.001	66	0.34/<0.001
	COD (t)	1935–2004	0.51	<0.001	67	0.49/<0.001
	Discharge ($t - 1$)	1944–2004	0.42	<0.001	59	0.43/<0.001
COD (t)	COD ($t - 1$)	1935–2004	0.63	<0.001	68	0.54/<0.001
	Discharge ($t - 1$)	1944–2004	0.33	<0.001	60	0.38/<0.001
Color (t)/COD (t)	Color ($t - 1$)/COD ($t - 1$)	1944–2004	0.37	<0.001	66	0.37/<0.001
	Discharge ($t - 1$)	1944–2004	0.18	<0.001	59	0.19/<0.001
Discharge (t)	Discharge ($t - 1$)	1944–2004	0.052	0.042	60	0.050/0.045

r_{adj}^2 the coefficient of determination was adjusted for differences in degrees of freedom (df)

Table 2 Trend analysis on time series of water color, COD and discharge

Parameter	Trend test	Equation	Time	r_{adj}^2	p	df	Residuals (r_{adj}^2/p)
Color	Linear trend	$142 - 0.0597 \text{ Year}$	1935–2004	0.040	n.s.	68	–
	Stepwise trend	$25.5 - 3.06 B^a$	1935–2004	0.074	0.014	68	–
	Step and cyclic	$-0.2 + 0.970 \text{ Sine_Color}^b$	1935–2004	0.12	0.028	33	0.055/n.s.
COD	Linear trend	$45.1 - 0.0196 \text{ Year}$	1935–2004	0.20	<0.001	69	–
	Stepwise trend	$7.04 - 1.13 B^a$	1935–2004	0.42	<0.001	69	–
	Step and cyclic	$-0.288 + 1.04 \text{ Sine_COD}^c$	1935–2004	0.61	<0.001	34	0.52/<0.001
Color/COD	Linear trend	$0.30 + 0.00172 \text{ Year}$	1935–2004	0.000	n.s.	68	–
	Stepwise trend	$3.62 + 0.143 B^a$	1935–2004	0.004	n.s.	68	–
	Step and cyclic	$0.566 + 0.820 \text{ Sine_Ratio}^d$	1935–2004	0.21	0.004	33	0.26/0.001
Discharge	Linear trend	$17371 - 6.3 \text{ Year}$	1944–2004	0.000	n.s.	60	–
	Stepwise trend	$5294 - 532 B^e$	1944–2004	0.014	n.s.	60	–
	Step and cyclic	No cyclic trend	1944–2004		n.s.		

Step and cyclic means stepwise and cyclic trend. B is a binary variable containing zeros until the breakpoint and thereafter ones. Breakpoint years in brackets. For more details see “Methods” section

n.s. non significant

^a Breakpoint occurred in 1970–1971, ^b Equation 3, ^c Equation 4, ^d Equation 5, ^e Breakpoint occurred in 1968–1969; $p \geq 0.05$

RESULTS

During the period 1935–2004, incoming water to the Lovö waterworks had the highest water color (>35 mg Pt l^{-1}) in the years 1937, 1945, 1986 and 2001 (Fig. 2a). Low water color (<20 mg Pt l^{-1}) was observed during the beginning of the 1970s and 1990s. From 1935 to 1970, the levels of COD were higher (median 7.1 mg l^{-1} , $n = 1823$) than during the period 1971–2004 (median 5.8 mg l^{-1} , $n = 1737$) (Fig. 2b). Comparing same time periods as for COD, water color had median of 25 mg Pt l^{-1} for the first time period (before 1970) and 21 mg Pt l^{-1} for the second period (after 1970). The water color/COD ratio had a median of 3.6 in both periods. The water color/COD ratio was high (>4) during 1945, the 1980s and 2001 (Fig. 2c), while low ratios (<3) were observed during the beginning of the 1960s. The median pH during the period 1935–2004 was 7.6 ($n = 3510$, 5th and 95th percentiles were 7.2 and 8.2, respectively), and median alkalinity was 0.98 meq l^{-1} ($n = 3077$, percentiles 0.82 and 1.2). The yearly median of total discharge per month from the outlet of Lake Mälaren

was low (<300 Mm^3) during the beginning of the 1970s and 1990s, and high (>400 Mm^3) during 1944, 1967 and 2000 (Fig. 3).

During the period 1935–2004, yearly median of COD was strongly related to the median in the preceding year, $r_{\text{adj}}^2 = 0.63$ (Table 1). This inter-year correlation was weaker for color, but still obvious, $r_{\text{adj}}^2 = 0.36$. The correlation between yearly median water color and COD for the whole period was $r_{\text{adj}}^2 = 0.51$ (Table 1).

Trend Analysis of Time Series

A significant negative linear trend was observed in time series of COD, $r_{\text{adj}}^2 = 0.20$ (Table 2). No linear trend was observed in time series of water color, color/COD ratio or discharge (Table 2).

Using a binary variable, a stepwise trend was achieved in time series of COD between the years 1970 and 1971, which decreased by a factor of 1.13 mg l^{-1} in 1971, $r_{\text{adj}}^2 = 0.42$ (Table 2). A weak but significant stepwise trend was found in time series of water color, $r_{\text{adj}}^2 = 0.074$

Fig. 2 Yearly median (with 5- and 95-percentiles) of **a**) water color, **b**) chemical oxygen demand (COD) and **c**) color/COD ratio for water (1935–2004) at the inlet of the Lovö waterworks, Lake Mälaren, Sweden, based on approximately one sample per week. Sine function adjusted to yearly median. See “Methods” section and Table 2 for more details

Fig. 3 Yearly median (with 5- and 95-percentiles) discharge at the outlet of Lake Mälaren during 1944–2004, based on total sum of each month (Mm^3)

(Table 2). No stepwise trend was detected in color/COD ratio or discharge (Table 2).

The following sine functions (based on Eq. 1, but without the cosine part) were found in time series of water color (Eq. 3), COD (Eq. 4) and water color/COD ratio (Eq. 5):

$$\text{Color} = -3.17 \cdot \text{BreakPoint} + 26.0 + 2.05 \cdot \text{Sine}\left(\frac{(T - 1943) \cdot 2\pi}{13.3}\right) \quad (3)$$

$$\text{COD} = -1.02 \cdot \text{BreakPoint} + 7.00 + -0.481 \cdot \text{Sine}\left(\frac{(T - 1942) \cdot 2\pi}{22.9}\right) \quad (4)$$

$$\frac{\text{Color}}{\text{COD}} = 0.213 \cdot \text{BreakPoint} + 3.63 + -0.375 \cdot \text{Sine}\left(\frac{(T - 1937) \cdot 2\pi}{17.1}\right) \quad (5)$$

Best fit of periodicity in time series of water color, COD and color/COD ratio was 13, 23 and 17 years, respectively (Fig. 2). No cyclic pattern was found in time series of discharge. Validation of the sine function adjusted to median values of COD showed a strong significant cyclic trend in time series of COD, $r_{\text{adj}}^2 = 0.61$ (Table 2). A significant cyclic trend was also found in time series of water color, $r_{\text{adj}}^2 = 0.12$, and color/COD ratio, $r_{\text{adj}}^2 = 0.21$ (Table 2).

Impact of Discharge on Organic Matter

Discharge correlated better to water color and COD when a one-year time lag was used, while no lag or longer lags gave poorer correlations. The yearly sum of total discharge

1944–2004 was related to yearly median COD the following year, $r_{\text{adj}}^2 = 0.33$ (Table 1). The relation to water color was stronger, $r_{\text{adj}}^2 = 0.42$. When monthly medians were used instead of yearly medians, the correlations of discharge with COD and water color during 1944–2004 were lower. The correlations were best, but still low, when a time lag of 6 months was used (for COD: $r_{\text{adj}}^2 = 0.068$, $p < 0.001$, degree of freedom (df) = 731 and water color: $r_{\text{adj}}^2 = 0.12$, $p < 0.001$, df = 709).

During 1944–1968, COD values corrected for discharge were above the median value for the whole period (6.3 mg l^{-1}). Flow-normalized COD values were highest during the 1940s, late 1960s and in the early 2000s (Fig. 4b). Flow-normalized water color had a different pattern, fluctuating around the median value of $25 \text{ (mg Pt l}^{-1}\text{)}$, and were highest during the 1940s, early 1980s and in 2000 (Fig. 4a). The ratio of flow-normalized water color to flow-normalized COD median of 3.6 and reached its lowest value in 1960, and was high in the early 1980s and 2000s (Fig. 4c).

A negative linear monotonic trend was observed in flow-normalized COD for the whole period ($r_{\text{adj}}^2 = 0.39$, $p < 0.001$, df = 60). A weak trend was observed in flow-normalized water color ($r_{\text{adj}}^2 = 0.055$, $p = 0.039$, df = 59) and no trend was found in flow-normalized color/COD ratio. Using a binary variable, a stepwise trend was achieved in time series of flow-normalized COD between 1970 and 1971, which decreased by a factor of 0.98 mg l^{-1} in 1971 ($r_{\text{adj}}^2 = 0.57$, $p < 0.001$, df = 60). No stepwise trend was found in flow-normalized water color or color/COD ratio.

DISCUSSION

When evaluating the effects of global climate change on aquatic ecosystems organic matter, the time period is an important factor. This study evaluates organic matter in Lake Mälaren during a period of 70 years and it is obvious that the choice of time period affects the result of a trend analysis. If only data from the beginning of the 1970s are used for comparison, COD and water color have increased (Fig. 2a–b), but for the whole time series there are negative trends, especially for COD. High values of organic matter were observed during the 1940s, 1980s, and 2000s, and the values during the 1970s were low in general (Fig. 2). Similar time series patterns have been observed for other long Swedish time series since the 1940s (Löfgren et al. 2003), and for shorter time series (beginning around 1965) at environmental assessment sites in Lake Mälaren (Wallin et al. 2000; Weyhenmeyer 2004; Weyhenmeyer et al. 2004; Willén 2001). Long-term negative trends in organic matter since the 20th century have been found in four other Swedish lakes using TOC reconstruction from full sediment cores (Cunningham et al. 2009).

Fig. 4 Flow-normalized a) water color, b) COD and c) ratio of normalized color to normalized COD (1944–2004) for the inlet of the Lovö waterworks, Lake Mälaren, Sweden

Acidification and land use changes can influence the amount and character of lake organic matter (Evans et al. 2005, 2006), but Lake Mälaren had stable pH and alkalinity during 1935–2004. The land-use changes seem only to have a minor impact on the organic matter in basin E of Lake Mälaren (see “Study area” section).

This study indicates that hydrology to a large part determines the temporal variation in organic matter. Water color and COD in raw water at Lovö waterworks correlated best to discharge at the outlet of Lake Mälaren (Norrström) when a one-year time lag was used (Cunningham et al. 2009). A one-year time lag seems reasonable since it falls between 0.4 and 2.8 years (Wallin et al. 2000), the estimated hydraulic retention time in Lake Mälaren and basin E, respectively. When monthly medians were used instead of yearly medians, the correlations between discharge and COD or water color were weaker. The best correlation gave a time lag of 6 months, agreeing with the hydraulic retention time of 0.4 years in basin E. Other studies (Weyhenmeyer et al. 2004) support the observation that water color

in Lake Mälaren is influenced by inter-year variations and that long-term trends in color are easier to detect.

Discharge had a stronger correlation with water color than with COD, possibly because water color consists of colored organic matter, iron and manganese mainly brought into the lake from surrounding soils (Wetzel 2001). Strong correlation between water color and discharge has also been found in Swedish rivers (Forsberg 1992). During periods with low discharge, as in the 1970s and in part during the 1990s, the water color in Lake Mälaren was low. Consequently, periods with increasing discharge have higher water color. Peaks in color were observed after high precipitation during autumn of the preceding year, when there was much rain during October to December (Johansson 2003). After the vegetation period, large amounts of organic matter are stored in the soil (Moore 2003). Rain in the autumn raises the watertable, resulting in more allochthonously derived organic matter in the surface water (Fölster and Wilander 2002; Bishop et al. 2004). Higher watertables thus give surface water with higher concentrations of

organic matter and this organic matter is more colored (Bishop et al. 2004).

This study also indicates flow-independent trends in COD and water color values, 1944–2004. The flow-normalized COD values (Fig. 4b) during the period 1944–1968 were above the median value for the whole period (6.3 mg l^{-1}), and a negative stepwise trend between 1970 and 1971 with a factor of 0.98 mg l^{-1} was observed. The decrease can be explained by the installation of sewage works around Lake Mälaren, which started in 1968 and was fully completed 5 years later (Willén 2001). The concentration of organic matter in the lake began to decrease before the sewage works were completed, an effect attributed to low discharge during that period (Ahl 1973). The concentration of phosphorus and nitrogen decreased after the installation of sewage works, and the decrease was most evident in 1970–1971 in the part of Lake Mälaren from which the Lovö waterworks takes its water (Wallin et al. 2000). Decrease in inorganic nutrients indirectly reduces the production of autochthonous organic matter in the lake (Wetzel 2001), but the installation of sewage treatment plants properly also reduced direct input of anthropogenic organic matter. Earlier, it has been shown that most of the anthropogenic input of COD (before 1973) into Lake Mälaren seemed to be uncolored (Ahl 1973). In this study, only a weak stepwise trend was found in flow-normalized water color and it confirms that anthropogenic input did not affect water color as much as COD.

Cyclical trends in organic matter have been attributed to climate factors (Löfgren et al. 2003). The stepwise trend together with a cyclical trend with a frequency of 23 years could explain about 60 per cent of the variation in COD concentration in Lake Mälaren (Fig. 2; Table 2). Cyclical variation with a frequency of 23 years has also been observed in time series of air temperature (Moberg 1996), precipitation data (Eriksson 1981) and in water chemistry in watercourses (Fölster and Wilander 2002) in Sweden. Similar to the time series of COD (Fig. 2b), the cyclical variation in water chemistry had a minimum in 1972 (Fölster and Wilander 2002). Possible causes of these variations are the North Atlantic Oscillation (NAO) index, which is the difference between the two pressure centers around the Azores and Iceland (Visbeck et al. 2001), and the solar system's 22-year orbit (Eriksson 1981; Moberg 1996). Studies in aquatic ecosystems have shown that NAO index clearly affects lake physics (Straile et al. 2003). A higher NAO index indicates that Scandinavia is more influenced by the Gulf Stream, manifested in higher air temperature, more wind and more precipitation (as rain). These three factors act to shorten the period with ice on Lake Mälaren, enhancing the light regime in the lake (Straile et al. 2003). A positive influence of NAO index on algal biomass (Blenckner and Hillebrand 2002; Straile and

Adrian 2000) can perhaps explain the 23 year cyclical pattern in COD.

In this study, water color had a weaker cyclical pattern (lower correlation with the sine function) than COD and the frequency was shorter (Fig. 2). The inter-year correlation was stronger for COD than for water color, confirming the smoother, more cyclical pattern in the time series of COD. An explanation is that autochthonously derived organic matter, as algal biomass, can contribute to COD without much influence on measured water color (Birge and Juday 1934; Åberg and Rodhe 1942). No cyclical trend was observed in the time series of discharge indicating that the cyclical trend in COD and water color was not related to variation in discharge.

The fact that the cyclical trend in water color had a period of 13 years is hard to explain. Due to the weak cyclical pattern in color values, the reliability of a 13 years' frequency should be questioned. The cyclical trend in color/COD values was probably influenced by the cyclical trend in color and COD values, giving a frequency of 17 years, i.e. in between 13 and 23 years.

When the time series of water color were corrected for discharge, the values in 2001 and 2002 were still notably high (Fig. 4a). Other sources (Weyhenmeyer et al. 2004) show that parts of Lake Mälaren supported by water from the western catchment area experienced extreme water chemistry conditions during 2001 as a result of unusually high precipitation in late 2000. The water color/COD ratio during 1935–2004 reached its highest value in 2001 (Fig. 2c). This indicates that in 2001 Lake Mälaren received the highest amount of allochthonously derived organic matter of the period (1935–2004). The water color/COD ratio value in 2001 is based on TOC, while the older ratios (1935–1996) are based on COD directly, so a slight precaution is needed when comparing the ratio (see the “Methods” section). The conversion of TOC to COD is not stable and depends on seasons, point sources, etc. (Meili 1992).

According to current scenarios, the future climate in Scandinavia will be warmer, receive more precipitation and experience more extreme weather events (Rummukainen et al. 2003). Simulations on nearby Lake Vänern indicate higher discharge during winter periods (Andréasson et al. 2002). This study showed that discharge is the driving force for water color and COD in Lake Mälaren and more runoff during winter could result in higher water color. The raw water at the Lovö waterworks could be harder to clean in the future. Autumns with high rainfall increase water color in the following year, and also water color/COD ratio. The differences observed in concentrations in 2001 (and 2002) in spite of discharge-normalization could be caused by a combination of extreme weather conditions, both higher temperature and precipitation (Temnerud and Weyhenmeyer 2008).

Acknowledgements Our thanks to Stockholm Water Company for funding parts of this study and to all those involved in the sampling and analysis of the water. Olle Svedberg provided detailed information on the Lovö Waterworks, while Anders Lindsjö prepared Fig. 1. Kevin Bishop, Stefan Löfgren, Gesa Weyhenmeyer and Anders Wilander are acknowledged for valuable discussions and comments on earlier drafts of this paper.

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