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**From heterotrophy to  
autotrophy**

T. J. S. Cox et al.

# From heterotrophy to autotrophy: a freshwater estuarine ecosystem recovering from hypereutrophication

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Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## Abstract

Increased organic matter and nutrient loads have induced major changes in aquatic systems, including hypoxia and algal blooms. In enclosed ecosystems these changes were often not gradual due to non-linear mechanisms. Here we report a 40 year record of eutrophication and hypoxia on an estuarine ecosystem and its recovery from hyper-eutrophication. We observe a paradoxical increase in chlorophyll a concentrations with decreasing nutrient inputs, and we hypothesise that algal growth was inhibited due to hypereutrophication, either by elevated ammonium concentrations, severe hypoxia or the production of harmful substances in such a reduced environment. We study the dynamics of a simple but realistic mathematical model, incorporating the assumption of algal growth inhibition. It shows an autotrophic equilibrium with low ammonia inputs, and a heterotrophic equilibrium with high ammonia inputs. At intermediate ammonia inputs it displays two alternative stable states. We conclude that the recovery of hyper-eutrophic riverine/estuarine systems can exhibit threshold-like behaviour.

## 1 Introduction

Low oxygen concentrations and harmful phytoplankton blooms are among the most severe human-induced impacts on surface waters. The degradation of allochthonous organic matter by heterotrophic organisms has made large bodies of water hypoxic and over-saturated with carbon dioxide (Vandijk et al., 1994; Heip et al., 1995; Frankignoulle et al., 1998). Increased nutrient loads have enhanced autochthonous production, resulting in harmful algal blooms and bottom water hypoxia events (Carpenter et al., 1998; Smith, 2003; Diaz and Rosenberg, 2008).

The response of aquatic systems to changes in nutrient and organic matter load can be far from gradual, and instead may reveal rich, non-linear dynamics. Most famous in this respect are shallow lakes, which have become textbook examples of ecosystems that can suddenly shift between alternative states (Carpenter et al., 1999; Scheffer

**BGD**

6, 5431–5459, 2009

## From heterotrophy to autotrophy

T. J. S. Cox et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



et al., 2001). Eutrophied coastal systems have also been suggested to show hysteresis, regime shifts and pollution thresholds (Petersen et al., 2008; Duarte et al., 2009; Conley et al., 2009). In flow-through systems, such as rivers and estuaries, the potential for non-linear dynamics received far less attention, mainly because of the assumption that their biogeochemistry is controlled by physical forcing (flow rate, mixing processes, light availability, wind speed) rather than by internal, biological processes (Dent et al., 2002). Nevertheless, biological control of biogeochemistry might in some cases be as important as physical forcing (e.g. Strayer et al., 2008).

Here we study the dynamics of the freshwater reach of a well documented, highly eutrophied estuary (Schelde, Belgium), in which nitrification and bacterial breakdown of allochthonous organic matter has caused severe hypoxia. With reductions in waste loads, a recovery of the brackish and saline estuarine reaches has been witnessed over the last two decades (Soetaert et al., 2006). From a 40 year combined data set we demonstrate that also the freshwater reach is now recovering. A paradoxical increase in chlorophyll-*a* concentrations with decreasing nutrient inputs is observed, suggesting that primary production was until recently inhibited in this hypereutrophic system. On basis of this information we develop a simple mathematical model incorporating the assumption that low oxygen and/or high ammonium concentrations negatively affect algal growth, and compare its output with the observed data. We argue that the non-linear recovery from hypereutrophication, as observed in the freshwater Schelde, could represent a regime shift.

## 2 Material and methods

### 2.1 Study area

The Schelde estuary, situated in Northern Belgium (Flanders) and the Southwest of the Netherlands, experiences significant agricultural, urban and industrial pressures, which have resulted in a notorious history of pollution, eutrophication and habitat degradation (Wollast, 1988; Meire et al., 2005; Van Damme et al., 2005; Soetaert et al., 2006).

**BGD**

6, 5431–5459, 2009

## From heterotrophy to autotrophy

T. J. S. Cox et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



The catchment area is about 20 000 km<sup>2</sup>, with approximately 240 km of tidal rivers. Following Elliott and McLusky (2002) we define the freshwater tidal reach (FW) as that part of the estuary with salinity <0.5, comprising a stretch of 35 km (Fig. 1). The average tidal range in this stretch is about 3 m.

## 2.2 Data sources

Before 1996 the water quality of the Schelde freshwater tidal reaches was not systematically monitored. The data presented in this manuscript have been compiled from a variety of sources. Data for 1967–1969 are taken from the Ph.D. dissertation of De Pauw (1975). Between 1975 and 1983 several sampling cruises were undertaken, coordinated at the Université Libre de Bruxelles (ULB) (Billen et al., 1985; Wollast, 1988). From 1977 to 1991 the Belgian Institute for Hygiene and Epidemiology (IHE) analysed a limited number of water samples every year. In 1989 a few cruises conducted by the Netherlands Institute of Ecology (NIOO-CEME) reached into the freshwater reach. Data between 1989 and 1993 were collected by the Flemish Environmental Agency (VMM). Beginning in 1996 the freshwater tidal reaches of the Schelde estuary were included in a systematic, long term monitoring campaign (OMES), coordinated at the University of Antwerp (Van Damme et al., 2005). Table 1 presents for each year the data sources and the number of available data points.

## 2.3 Numerical modelling

All numerical analyses were performed in R ([www.r-project.org](http://www.r-project.org)). Model integration and calculation of steady state solutions were performed with R-packages deSolve and rootSolve available from CRAN (Soetaert and Herman, 2009). Stable steady states were determined by varying initial conditions of steady state calculations. Unstable equilibrium points were determined manually by iteratively reducing the searched part of state space, after random generation of 10 000 states and calculating the distance to zero of the derivatives.

**BGD**

6, 5431–5459, 2009

## From heterotrophy to autotrophy

T. J. S. Cox et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



### 3 Results

#### 3.1 Water quality in the FW Schelde from the 1960s to present

Although data for the period 1968–1995 are obtained from different sources and show considerable spatial, inter- and intra-annual variability, a clear pattern emerges in the annual and FW averaged concentrations (Fig. 2). Average total ammonium concentrations (the sum of  $\text{NH}_4^+$  and  $\text{NH}_3$  concentration, hereafter referred to as ammonium) were high, typically between 250 and 1000  $\mu\text{mol L}^{-1}$ ; also average dissolved inorganic phosphorous (DIP) concentrations were high, typically between 25 and 200  $\mu\text{mol L}^{-1}$ ; average oxygen concentrations were generally below 100  $\mu\text{mol L}^{-1}$ , and average chlorophyll-*a* concentrations were typically below 60  $\mu\text{g L}^{-1}$ . This is consistent with the assessment that the upstream reaches of the Schelde estuary, until recently, were hypoxic all year around and anoxic during summer, for as long as observations are available (De Pauw, 1975; Wollast, 1988; Meire et al., 2005; Van Damme et al., 2005; Soetaert et al., 2006), with nitrification as the major oxygen consuming process (Billen et al., 1985; Soetaert and Herman, 1995).

Total dissolved inorganic nitrogen (TDIN) consistently decreased from the early 1990s. In the 1996–2007 period, average TDIN concentrations decreased further from 660  $\mu\text{mol L}^{-1}$  to 446  $\mu\text{mol L}^{-1}$ . In the same period ammonium concentrations decreased from 382  $\mu\text{mol L}^{-1}$  to 38  $\mu\text{mol L}^{-1}$ , thus changing from being the most important fraction of TDIN to the least important. Also DIP concentrations decreased during this period, from on average 26  $\mu\text{mol L}^{-1}$  in 1996 to 9.7  $\mu\text{mol L}^{-1}$  in 2007. In the mid 1990s, average oxygen concentrations started to increase. In 1996, the average oxygen concentration was 80  $\mu\text{mol L}^{-1}$ , with on average only 30  $\mu\text{mol L}^{-1}$  during May–September. By 2007, the year round average had more than doubled to 200  $\mu\text{mol L}^{-1}$ , and the May–September average quintupled to 170  $\mu\text{mol L}^{-1}$ . In 2006 over-saturated oxygen levels were observed for the first time, caused by high primary production. In the same period, chlorophyll-*a* concentrations increased from on average 18  $\mu\text{g L}^{-1}$  to

---

## From heterotrophy to autotrophy

T. J. S. Cox et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



122  $\mu\text{g L}^{-1}$ . Note that the higher average values in the 1980s and early 1990s are calculated from very few observations in these years (1–10 per year), making these data points less reliable. In 1969 and from 1996 onward, average values have been calculated from at least 50 observations each year.

5 An intriguing observation is the paradoxical decrease in nutrient concentrations and increase in oxygen concentrations, accompanied by increasing chlorophyll-*a* concentrations. This is contrary to the classical eutrophication response, from which we would expect the highest annually averaged algal biomass to coincide with the highest annually averaged nutrient concentrations (Cloern, 2001; Smith, 2006). Light limitation was important but constant, given that SPM levels (governing light penetration in the estuary, Soetaert et al., 2006) remained similar (see also discussion). However, the environmental conditions in this hypereutrophied system, may have negatively affected algal growth. There is abundant physiological evidence that extremely low oxygen concentrations negatively affect photosynthesis (Krause et al., 1985; Sundby and Schiött, 1992; Gong et al., 1993; Peckol and Rivers, 1995; Tyystjaervi, 2008) as well as metabolism (Kessler, 1974). Molecular sensors and regulatory genes related to low oxygen concentrations are present in most organisms (Wu, 2002). In such a reduced environment (Billen et al., 1988), benthic and pelagic sulfide production might have toxic effects on phytoplankton. And also elevated ammonium concentrations are known to be harmful to algae (Thomas et al., 1980; Bates et al., 1993; Kallqvist and Svenson, 2003). Therefore we hypothesize that algal growth was inhibited as a result of high organic waste and ammonia loading, leading to elevated ammonium concentrations, oxygen depletion and a strongly reduced environment.

### 3.2 A regime shift? A minimal mathematical model

25 One intuitively understands that the inhibition of algal growth may give rise to a particular ecosystem behaviour. Starting from a hypereutrophic state in which algal growth is inhibited, a decrease in ammonium input may at first not change much (we focus

**BGD**

6, 5431–5459, 2009

---

## From heterotrophy to autotrophy

T. J. S. Cox et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**From heterotrophy to autotrophy**

T. J. S. Cox et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



on ammonium inputs, as nitrification is the major oxygen consuming process in the system under study). As long as oxygen demand for nitrification forces the system to extreme hypoxia, algal growth will be inhibited, although some algal biomass (and photosynthesis) might always be present due to upstream import. However, when ammonium inputs further decrease, at a certain point photosynthetic oxygen production (in addition to surface reaeration, which is always present) could become sufficient to balance the oxygen demand, thus terminating the inhibitory processes. With subsequent increasing algal biomass and increasing photosynthetic oxygen production, the oxygen concentration might increase to a level that is distinctively higher than in the hypoxic state with only a slightly higher ammonium input.

The scenario depicted in the previous paragraph is simplified, but captures core features of potential ecosystem responses to over-enrichment with ammonium. We further explore the consequences of the inhibition of algal growth, by examining the steady states and transient behaviour of a simple mathematical model. The model consists of 3 variables: algal biomass  $B$ , dissolved oxygen  $O_2$  and ammonium  $NH_4$ , and it can be considered as a one-box model of the whole freshwater reach. The following processes are taken into account: flushing ( $R_F$ ), net primary production (NPP), the difference between gross production ( $R_{PP}$ ) and respiration ( $R_{resp}$ ), nitrification ( $R_{nit}$ ), and surface reaeration ( $R_{aer}$ ):

$$\begin{aligned} \frac{dB}{dt} &= R_F(B) + F(O_2) \cdot R_{PP} - R_{resp} \\ &= R_F(B) + NPP \end{aligned} \quad (1)$$

$$\frac{dO_2}{dt} = R_F(O_2) - O:N \cdot R_{nit} + O:C \cdot NPP + R_{aer} \quad (2)$$

$$\frac{dNH_4}{dt} = R_F(NH_4) - R_{nit} - N:C \cdot NPP \quad (3)$$

Standard formulations for all processes are used (Table 2) with parameter values that are realistic for the freshwater Schelde, based on Soetaert and Herman (1995), Ragnier et al. (1997) and Hofmann et al. (2008) (Table 3). We assume that nutrients never

limit algal growth, and in particular we assume that algae switch to nitrate as a nitrogen source at low ammonium concentrations. This assumption makes sense since TDIN and DIP levels were always higher than  $60 \mu\text{mol L}^{-1}$  and  $4 \mu\text{mol L}^{-1}$ , respectively. The feature of interest, however, is the inclusion of a factor  $F(\text{O}_2)$  that represents the adverse effect of low oxygen concentrations on photosynthesis (we leave out potential ammonium toxicity from the current analysis, and we assume that this formulation also accounts for effects of the production of harmful substances in a reduced environment). We construct  $F(\text{O}_2)$  as a Monod function of oxygen concentration, with a half saturation concentration of  $1 \mu\text{mol L}^{-1}$ . Essentially, incorporation of this factor reduces primary production continuously at decreasing low oxygen concentrations; when oxygen concentrations decreases from 10 to  $0 \mu\text{mol L}^{-1}$ , calculated primary production is reduced from 90% of maximal production to 0.

The steady states of this model depend on the upstream ammonium concentration (Fig. 3, central panel). With high upstream ammonium, the steady state ammonium concentration is higher than zero, nitrification forces oxygen to low values and primary production is inhibited. In this steady state, the calculated ratio of algal oxygen production to the sum of respiration and oxygen consumption by nitrifiers ( $P/R = F(\text{O}_2) \cdot R_{PP} / (R_{\text{resp}} + \text{O:N} \cdot R_{\text{nit}})$ ) is lower than 1, and we refer to it as the *heterotrophic state* (Garnier and Billen, 2007). Conversely, at low upstream ammonium concentration the steady state is characterized by high oxygen concentrations and algal biomass, and low ammonium concentrations. In this case the P/R-ratio is higher than 1, and we refer to this state as the *autotrophic state* (Fig. 4).

At intermediate upstream ammonium concentrations, however, the system displays both a heterotrophic and an autotrophic steady state, and between the two stable states, an unstable equilibrium is found (Fig. 4). Depending on the initial conditions, the system will evolve to either of the steady states. It follows also that with decreasing upstream ammonium concentration and equal initial conditions, the system will abruptly change from a heterotrophic to an autotrophic steady state when the upstream ammonium concentration drops below a critical threshold. As such, the model features a

---

**From heterotrophy to autotrophy**T. J. S. Cox et al.

---

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)



*regime shift* triggered by a change in ammonium input.

To link the model output to observations, we first note that the steady state calculations do not account for seasonal and spatial patterns. We might, however, reasonably expect that the most downstream observed concentrations in the FW reach, will most closely reflect the steady state conditions. We compare all May–September observations from this downstream station (plotted against total ammonium concentrations of the upstream monitoring station) with steady state model output (Fig. 3, left panel). Despite the highly simplified nature of the model, its numerical output is remarkably realistic, and its steady state characteristics seem consistent with the data (we note that no fine-tuning or calibration of parameters was performed, except for the carrying capacity ( $K$ ) of algal biomass, visually fitted to embrace all chlorophyll-*a* observations between the high and low steady state of modelled chlorophyll-*a*). With upstream ammonium concentration below  $100 \mu\text{mol L}^{-1}$ , observed ammonium concentration at the downstream station are always zero, and observed oxygen and chlorophyll-*a* concentrations are distinctly different from zero. At upstream ammonium concentrations above  $350 \mu\text{mol L}^{-1}$ , only high ammonium, low oxygen and low chlorophyll-*a* concentrations are observed. At intermediate upstream ammonium concentrations (between 100 and  $350 \mu\text{mol L}^{-1}$ ) a mixture of both situations can be observed, with a finite subset of data points reflecting the *heterotrophic state*, with high ammonium, low oxygen and low chlorophyll concentrations.

The calculated *autotrophic* steady state provides an upper limit for oxygen and chlorophyll-*a* concentration, rather than being distinguishable as an alternate state in the observations. This is not surprising, since the calculations were performed with fixed upstream boundary conditions, algal productivity and flushing rate, while in reality these quantities are not constant between May and September (Fig. 3). The model parameterisation seems to be satisfactory for conditions favouring maximal production (low discharge, high light). Moreover, a system in which the oxygen concentrations are governed mainly by the net effect of nitrification and primary production, can be expected to have short term fluctuations in oxygen concentration, responding to

**BGD**

6, 5431–5459, 2009

## From heterotrophy to autotrophy

T. J. S. Cox et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



fluctuations in discharges, incident light, boundary conditions etc. In particular, peak discharges (which cause a partial flushing out of algal biomass) and cloudy weather conditions (with lower incident light) may decrease the oxygen production below the demand for nitrification and may induce (sharp) decreases in observed oxygen concentrations.

Although the monthly sampling is probably not frequent enough to observe these (short term) fluctuations, it can be considered as random sampling of these fluctuating oxygen concentrations, and should therefore also display fluctuations. Figure 5 shows the annual pattern of oxygen concentrations at the downstream station for the 1996–2007 period. During 1996–2002, oxygen concentrations show a clear seasonal pattern, with high oxygen concentrations in winter months, and (very) low concentrations in summer and autumn. Starting from 2003, this pattern becomes more irregular, and in particular 2004–2006 oxygen concentration show large fluctuations during summer months, with maximal differences between high and low concentrations of more than  $200 \mu\text{mol L}^{-1}$ . Such an increased variability of an ecosystem state variable might be typical for ecosystems poised for regime shift (Carpenter et al., 2008).

Additional model calculations were performed to produce output comparable to the annual and FW averaged values (Fig. 2). To account for seasonal variability, we calculated model output at temperatures 5–20°C (step size 1°C) with the model extended with a classic Q10-formulation for temperature dependence of biological process rates. Since discharges and upstream oxygen concentrations are typically larger in winter, we performed the simulations at different temperatures with flushing rates and upstream oxygen concentrations based on a linear regression against temperature from the 1996–2007 dataset. Finally we calculated the 10-day average of transient model output starting from the initial conditions set equal to upstream boundary concentrations, as a proxy for the FW ecosystem average, under the assumption that the real ecosystem evolves towards steady state along the estuarine axis. The resulting proxy for annual and FW-averaged values shows a continuous, although non-linear response to decreasing ammonium inputs (Fig. 3, central panel). Again this simple approxi-

---

**From heterotrophy to autotrophy**T. J. S. Cox et al.

---

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

mation gives realistic numerical output when compared to observed data. The right panel of Fig. 3 shows observed annual and FW averaged ammonium, oxygen and chlorophyll-*a* concentrations plotted against observed annual averaged upstream ammonium concentrations, for the available data between 1968 and 2007. We note that

5 no fine-tuning or calibration of parameter values was performed, except for the choice of the integration interval of 15 days, which resulted in a visually better proxy for the observed average values than other trial intervals of 7, 10 and 20 days.

## 4 Discussion

Based on a long term data set of dissolved oxygen, total ammonium, dissolved inorganic phosphorous and chlorophyll-*a*, we demonstrate that the freshwater Schelde estuary has changed over a relatively short period of time from a heterotrophic system with persistent hypoxia, elevated ammonium concentrations and limited algal biomass, to a system with low ammonium concentrations, where hypoxia is virtually nonexistent and in which autotrophic production has become increasingly important. The paradoxical

10 increase in algal biomass with decreasing nutrient inputs is contrary to expectations from the classical eutrophication response. This stimulated us to investigate the potential causes of low algal biomass observed until the late 1990s. We conclude that it is plausible that high ammonium concentrations, persistent hypoxia or the production of harmful substances in such a reduced environment, inhibited algal growth and photosynthesis during most of the time span of our data set. We constructed a simple mathematical model that incorporates the inhibitory effect of extreme hypoxia, to explore the consequences of algal growth inhibition. This model features a regime shift, from a heterotrophic to an autotrophic state, when upstream ammonium concentrations drop below a defined threshold. At intermediate upstream ammonium concentrations, two

15 alternative, stable steady states exist. The model results are shown to be consistent with observations. This leads us to hypothesize that the recovery from hypereutrophication, as observed in the freshwater Schelde, represents a regime shift as described

20

25

**BGD**

6, 5431–5459, 2009

---

## From heterotrophy to autotrophy

T. J. S. Cox et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



by the mathematical model. Seasonal and spatial effects, however, prevent the annual, system-averaged concentrations of oxygen, total ammonium and chlorophyll-*a*, to display a pronounced discontinuous jump when plotted against time.

We have deliberately chosen a simple mathematical model to explore and highlight the core features of a system governed by the described mechanisms, although this makes direct comparison of model output to observed data more difficult. In particular, constant upstream boundary conditions, algal productivity and flushing rate, are important simplifications. Also the averaging procedure, as a proxy for annual and FW averaged values, is only an approximation to illustrate that averaged output of a model that clearly displays a regime shift, can show a continuous response. A more complex multi-dimensional model, with real forcing functions and boundary conditions, might reproduce spatio-temporal patterns, but this is outside the scope of this article and would not change the essential findings.

Documentation for a potential regime shift comes largely from the steady state calculations of the mathematical model. Although the numerical output of this model is remarkably realistic and consistent with the long-term observations, this does not prove that such a shift has occurred in the real system. However, model results indicate that, with the mechanisms described, the recovery of hypereutrophic systems can display a threshold-like, or non-linear behaviour. Whether or not the recovery can be termed a regime shift partly depends whether a more loose and pragmatic definition of “regime shift” is used (as e.g. by deYoung et al., 2008) or a more strict definition that strictly separates steep gradual responses from actual jumps between alternative stable states (as e.g. by Schroder et al., 2005). Much of the evidence for multiple steady states is drawn from mathematical or numerical model results, and it is a long standing debate whether or not multiple steady states do exist in nature, and if so whether it is possible to demonstrate their existence based on field data (Connell and Sousa, 1983; Scheffer and Carpenter, 2003). The observed change in the freshwater Schelde to increasing autotrophy over a few years, after decades of persistent hypoxia and hypereutrophication, could certainly be termed a regime shift in the loose sense. The presented

**BGD**

6, 5431–5459, 2009

---

## From heterotrophy to autotrophy

T. J. S. Cox et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



mathematical model also features a regime shift in the strict sense, but it contains the hypothesis of photosynthesis inhibition in hypoxic conditions.

At first sight, a direct adverse effect of extreme hypoxia on algal growth might seem contradictory, since algae produce oxygen through photosynthesis themselves. However, the Schelde is well mixed and light penetration is very limited (Kromkamp and Peene, 1995; Soetaert et al., 2006), consequently algal cells frequently reside in deeper, dark water masses. Thus, not only during the night, these algal cells are exposed to respiratory and diffusive oxygen loss to the surrounding hypoxic water, which they can not compensate by photosynthetic production. But also when they are exposed to low to moderate light intensities, photosynthetic production might not be sufficient to compensate the oxygen loss due to the steep inner to outer cell oxygen gradient and algal respiration taken together. As such, when extracellular oxygen concentrations are sufficiently low, algal cells will have to resort to less efficient anaerobic metabolism (Kessler, 1974), during a considerable fraction of time. A similar argumentation holds for increased sensitivity to photoinhibition under extreme hypoxia. Algal cells traveling from upper to deeper water layers might first be confronted with high light intensities inducing photoinhibition, and next be transported to dark, hypoxic water layers in which they can not recover from photoinhibitory effects (Sundby and Schiött, 1992; Tyystjaervi, 2008). Finally, a molecular oxygen sensor is probably present in all cells, and regulatory genes related to low oxygen concentrations, downregulating protein synthesis and suppressing cell growth during hypoxia to save energy for essential metabolic processes, might also be present in phytoplankton (Wu, 2002).

We have not included potential ammonium toxicity in the model calculations. A system with a well chosen ammonium toxicity function (with a steep enough response curve) would also display two alternative stable states without any inhibition by hypoxia. But to explain the low biomass state at upstream ammonium concentrations equal to or higher than  $200 \mu\text{mol L}^{-1}$ , we would have to assume an ammonium toxicity threshold of about  $100 \mu\text{mol L}^{-1}$ , as this is the steady state ammonium concentration corresponding with this upstream ammonium concentration (Fig. 3). This is at the lower

**BGD**

6, 5431–5459, 2009

---

## From heterotrophy to autotrophy

T. J. S. Cox et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



---

**From heterotrophy to autotrophy**T. J. S. Cox et al.

---

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

end of reported ammonium concentrations with inhibitory effects on algal growth, and insensitivity to much higher concentrations (up to  $440 \mu\text{mol L}^{-1}$ ) of marine algal species have also been found (Thomas et al., 1980; Bates et al., 1993; Kallqvist and Svenson, 2003). Nevertheless, a combined effect of hypoxia and ammonium inhibition remains a possibility and, since they are correlated, could reinforce each other. In general the mechanisms for inhibition of photosynthesis or algal growth by elevated ammonium concentrations and severe hypoxia are rather poorly understood. Laboratory experiments to investigate the (combined) effects of stressors on the currently flourishing phytoplankton communities, can provide more insight, but they are currently lacking.

To our knowledge, such elevated ammonium concentrations and such prolonged periods of severe hypoxia, as observed in the (freshwater) Schelde, have not been recorded in any of the major documented riverine or estuarine ecosystems. This does not mean that the described phenomena are unique to the freshwater Schelde, but published data sets of other systems might be lacking relevant periods or areas. In many regions in the world, organic matter and nutrient load to aquatic systems are still increasing (Diaz and Rosenberg, 2008). For example, in the upper reaches of the Chinese Pearl river, similar ammonium and oxygen concentrations have recently been measured, but unfortunately no information about primary production or algal biomass is available (Harrison et al., 2008).

In freshwater systems, regime shifts related to eutrophication and oligotrophication are usually studied based on dissolved inorganic phosphorus concentrations, as most freshwater bodies are P-limited (Dent et al., 2002). Although the river Schelde also showed very large changes in DIP (Fig. 3), it should be realized that ammonium is not only a nutrient like phosphorus, but also a substrate for nitrifiers, and thus directly influence oxygen consumption. In contrast, dissolved inorganic phosphorous concentrations principally depend on oxygen via redox-controlled FeP interactions.

While the presented data give indication for an adverse effect of hypereutrophication as described above, we cannot exclude other factors, such as climatic variability, playing a role in this apparent shift from heterotrophy to autotrophy. However no rela-

5 tionship between summer averaged chlorophyll concentrations, and flushing discharge and suspended matter concentration respectively, was observed for the 1996–2007 data set (Fig. 6). This indicates that the two main drivers typically invoked to justify changes in riverine and estuarine primary production, flushing rate (discharge) and light conditions (e.g. Howarth et al., 2000), are not correlated with the observed increase in average chlorophyll-*a* concentrations. When considering only the data after 2000, average summer chlorophyll *a* concentrations are negatively correlated with average summer discharge ( $r^2=0.62$ ,  $p=0.04$ ), and weakly positively correlated with average suspended matter concentration ( $r^2=0.44$ ,  $p=0.1$ ) (Fig. 6). The latter suggests that increased algal blooms is reflected in the observed suspended matter concentrations. The negative correlation with discharge for the data from 2001–2007 suggests that whereas long-term changes in chlorophyll-*a* concentrations can not be explained by the common drivers, inter-annual variability in the current *autotrophic* state is primarily determined by physical forcing, consistent with model simulations of Arndt et al. (2007).

15 Zooplankton grazing, another common controlling factor of phytoplankton biomass, likely has increased over the last decade, in accordance with the observed increasing zooplankton abundance (Tackx et al., 2005). Thus, *ceteris paribus*, we would expect a decrease rather than an increase in phytoplankton biomass. In addition, toxic pollutants are surprisingly poorly documented for the Schelde estuary. A recent study on chlorotriazines, found maximum atrazine concentrations of 736 ng/l at the downstream boundary of the freshwater Schelde (Noppe et al., 2007). This is one order of magnitude lower than concentrations with inhibitory effect on algal growth (Tang et al., 1997).

25 The freshwater Schelde has rapidly recovered from hypereutrophication, and has increasingly become autotrophic. European estuaries, including the Schelde, have been characterized as strongly heterotrophic ecosystems (Heip et al., 1995; Gazeau et al., 2005; Soetaert et al., 2006). Our results suggest that in the freshwater Schelde, this apparent heterotrophy was a result of hypereutrophication rather than light limitation of algal growth, and the partial recovery from hypereutrophication first leads to a more

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**From heterotrophy to autotrophy**T. J. S. Cox et al.

---

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[I◀](#)[▶I](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

classical eutrophic system, with large algal blooms.

With further decreasing ammonium inputs and increasing oxygen concentration, the system may develop toward a more natural foodweb and mode of ecosystem functioning, as indicated by the repopulation of the brackish and freshwater reaches by zooplankton (Appeltans et al., 2003; Tackx et al., 2005). In the future, zooplankton grazing might become a significant factor controlling phytoplankton biomass. As suggested by Strayer et al. (2008), the evolution toward a condition in which phytoplankton biomass is (partly) controlled by zooplankton grazing might also proceed rapidly, possibly inducing the next “step” in the recovery of the freshwater Schelde. In such a system also higher trophic levels, including zooplanktivorous and piscivorous fish may gain in importance, causing further changes in trophic structure and the balance between biological and physical control.

*Acknowledgements.* This research received partial funding from the Flemish project OMES, funded by W&Z NV, the Netherlands Organisation of Scientific Research (PIONIER) and the EU (HYPOX). Eric Struyf and Daniel Conley acknowledge EU Marie Curie Actions (SWAMP MEIF-CT-2006-040534, COMPACT MEXC-CT-2006-042718) for funding. Eric Struyf acknowledges FWO (Flemish Research Foundation) for his postdoc grant. This is a publication of the NIOO-KNAW Netherlands Institute of Ecology.

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**BGD**

6, 5431–5459, 2009

## From heterotrophy to autotrophy

T. J. S. Cox et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





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**BGD**

6, 5431–5459, 2009

---

**From heterotrophy to autotrophy**

T. J. S. Cox et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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**BGD**

6, 5431–5459, 2009

---

## From heterotrophy to autotrophy

T. J. S. Cox et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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**BGD**

6, 5431–5459, 2009

---

**From heterotrophy to autotrophy**T. J. S. Cox et al.

---

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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**BGD**

6, 5431–5459, 2009

---

**From heterotrophy to autotrophy**

T. J. S. Cox et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Table 1.** Data sources, number of data points (N) and average value for each year. Data sources: DP: De-Pauw (1975); W: Billen et al. (1985); Wollast (1988); A: Administration Zeeschelde; I: Belgian Institute for Hygiene and Epidemiology; V: Flemish Environmental Agency; C: Netherlands Institute of Ecology, NIOO-CEME; O: OMES project: Van Damme et al. (2005).

year	Oxygen [ $\mu\text{mol L}^{-1}$ ]			Ammonium [ $\mu\text{mol L}^{-1}$ ]			DIP [ $\mu\text{mol L}^{-1}$ ]			chlorophyll-a [ $\mu\text{g L}^{-1}$ ]		
	source	N	mean	source	N	mean	source	N	mean	source	N	mean
1967	DP	10	73	DP	2	377	DP	15	29			
1968	DP	20	69	DP	20	279	DP	46	23			
1969	DP	24	51	DP	24	490	DP	55	28	DP	50	11
1975	W	12	76	W	11	527	A	8	65			
1976	W	15	70	W	15	922	A	12	139			
1977	W, I	27	44	I, W	23	527	A, I	14	167			
1978	I, W	20	68	I, W	32	765	A, I	20	185			
1979	I	5	72	I	10	544	A, I	22	85			
1980	I	19	61	I	28	688	A, I	44	89			
1981	I	9	90	I	16	645	A, I	29	67			
1982	I, W	12	67	I, W	17	614	A, I	20	71	W	4	35
1983	I, W	10	77	I, W	15	336	A, I	23	64			
1984	I	4	79	I	8	900	A, I	16	30			
1985	I	4	48	I	8	449	A, I	17	44			
1986	I	4	66	I	8	777	A, I	17	142			
1987	I	4	43	I	8	491	I	8	158			
1988	I	5	136	I	10	424	I	10	209			
1989	I, V, C 21	81	I, C, V	35	571	I, C, V	19	107	C, V, I	7	55	
1990	I, V	19	74	V, I	30	582	I, V	31	66	I, V	6	45
1991	V, I	20	66	V, I	32	620	V, I, C	42	49	V, I	10	48
1992	V	15	79	V	24	596	C, V	39	47	V	1	56
1993	V	16	85	V	24	448	C, V	46	45	V	3	16
1995	O	7	108	V, O	31	459	C, V, O	40	20	O	6	4
1996	O	77	83	O	86	383	C, O, V	100	26	O	85	18
1997	O	77	78	O	59	389	O, C	80	25	O	70	67
1998	O	84	116	O	77	242	C, O	95	19	O	84	50
1999	O	70	86	O	75	214	C, O	87	18			
2000	O	89	141	O	90	192	C, O	95	17			
2001	O	84	164	O	84	107	O, C	95	11	O	84	59
2002	O	63	149	O	60	100	C, O	96	12	O	63	75
2003	O	67	142	O	67	100	O	67	13	O	67	117
2004	O	84	149	O	84	79	O	84	11	O	63	135
2005	O	77	160	O	77	110	O	84	19	O	77	109
2006	O	68	209	O	70	72	O	82	9	O	60	97
2007	O	77	199	O	77	37	O	83	10	O	71	123
2008	O	43	225	O	43	41	O	43	7	O	43	80

From heterotrophy to autotrophy

T. J. S. Cox et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



From heterotrophy to autotrophy

T. J. S. Cox et al.

**Table 2.** Modelled processes. Process formulations are based on Soetaert and Herman (1995), Regnier et al. (1997) and Hofmann et al. (2008).

Surface re-aeration

$$R_{aer} = r_{aer} \cdot (O_2^{sat} - O_2)$$

Nitrification

$$R_{nit} = r_{nit} \cdot \frac{O_2}{O_2 + k_{O_2}} \cdot \frac{NH_4}{NH_4 + k_{NH_4}}$$

Phytoplankton primary production, respiration and inhibition

$$R_{PP} = \mu_{max} \cdot \left(1 - \frac{B}{K}\right) \cdot B$$

$$R_{resp} = R_m \cdot B$$

$$F(O_2) = \frac{O_2}{O_2 + k_{O_2}}$$

Flushing

$$R_F([\cdot]) = \frac{Q}{V} \cdot ([\cdot]^{up} - [\cdot]) \quad \text{with } [\cdot] = B, O_2 \text{ or } NH_4$$

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Table 3.** Process and stoichiometric parameters, and upstream boundary conditions. Parameters values are taken from Soetaert and Herman (1995); Regnier et al. (1997) and Hofmann et al. (2008).

Surface re-aeration		
$r_{\text{aer}}$	=	0.05 d <sup>-1</sup>
$\text{O}_2^{\text{sat}}$	=	300 mmol m <sup>-3</sup>
Nitrification		
$r_{\text{nit}}$	=	70 mmol m <sup>-3</sup> .d <sup>-1</sup>
$k_{\text{O}_2}$	=	1 mmol m <sup>-3</sup>
$k_{\text{NH}_4}$	=	5 mmol m <sup>-3</sup>
O:N	=	1.89 mmol O <sub>2</sub> (mmol NH <sub>4</sub> ) <sup>-1</sup>
Phytoplankton primary production, respiration and inhibition		
$\mu_{\text{max}}$	=	1 d <sup>-1</sup>
$K$	=	700 mmol C m <sup>-3</sup> ( <i>fitted</i> )
$R_m$	=	0.25 d <sup>-1</sup>
O:C	=	1 mmol O <sub>2</sub> (mmol C) <sup>-1</sup>
N:C	=	0.15 mmol N (mmol C) <sup>-1</sup>
Chl:C	=	15 mg Chl (mg C) <sup>-1</sup>
$k_{\text{O}_2}$	=	1 mmol m <sup>-3</sup>
Flushing		
$\frac{Q}{V}$	=	0.14 d <sup>-1</sup>
Upstream boundary conditions		
$B^{\text{up}}$	=	50 mmol C m <sup>-3</sup>
$\text{O}_2^{\text{up}}$	=	100 mmol O <sub>2</sub> m <sup>-3</sup>

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

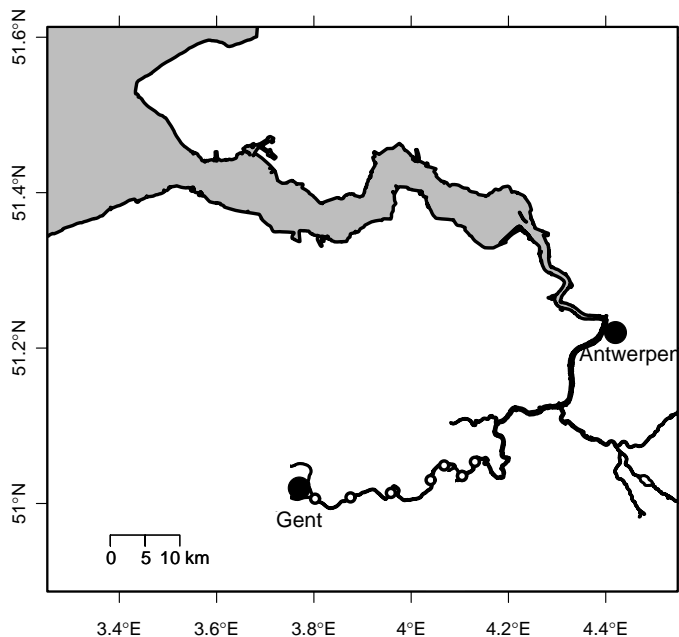
Printer-friendly Version

Interactive Discussion



From heterotrophy to autotrophy

T. J. S. Cox et al.



**Fig. 1.** The Schelde-estuary with the part of its tributaries under tidal influence. The OMES monitoring stations (1995–present) in the freshwater tidal reach are marked with a circle.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

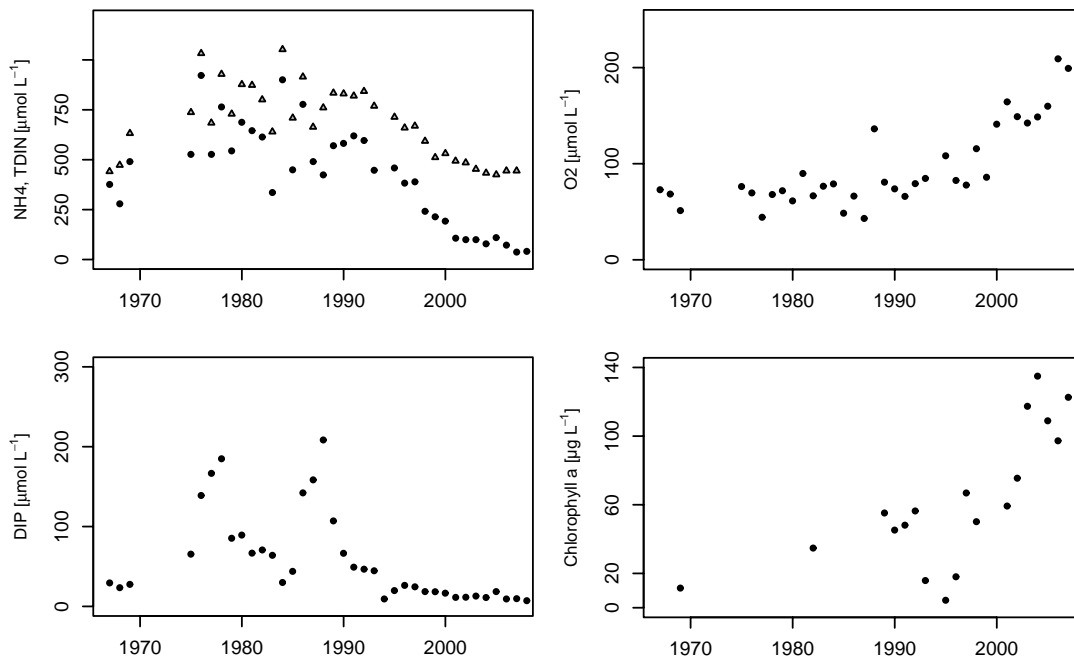
Interactive Discussion





From heterotrophy to  
autotrophy

T. J. S. Cox et al.



**Fig. 2.** Annual and FW averaged TDIN (triangles),  $\text{NH}_4$  (circles), DIP,  $\text{O}_2$  and chlorophyll *a* concentrations from 1967 to 2007. Data compiled from different sources, with different sampling frequency. Only starting from 1996 the freshwater reach has been consistently monitored, with more than 50 measurements each year (see Table 1).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

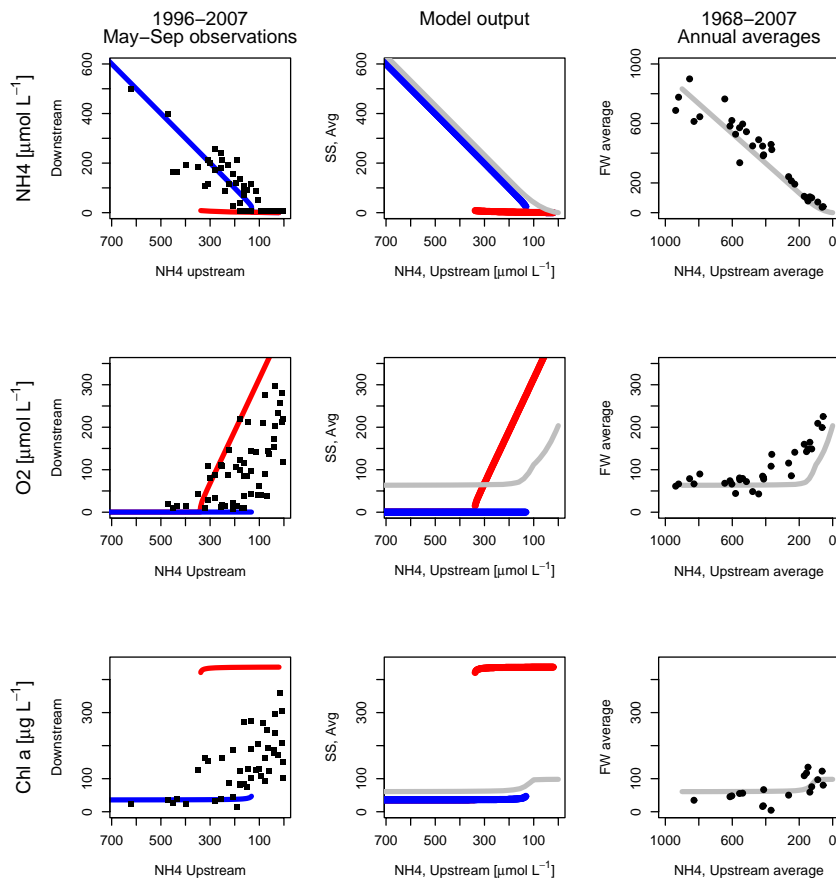
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Full Screen / Esc

Printer-friendly Version

Interactive Discussion



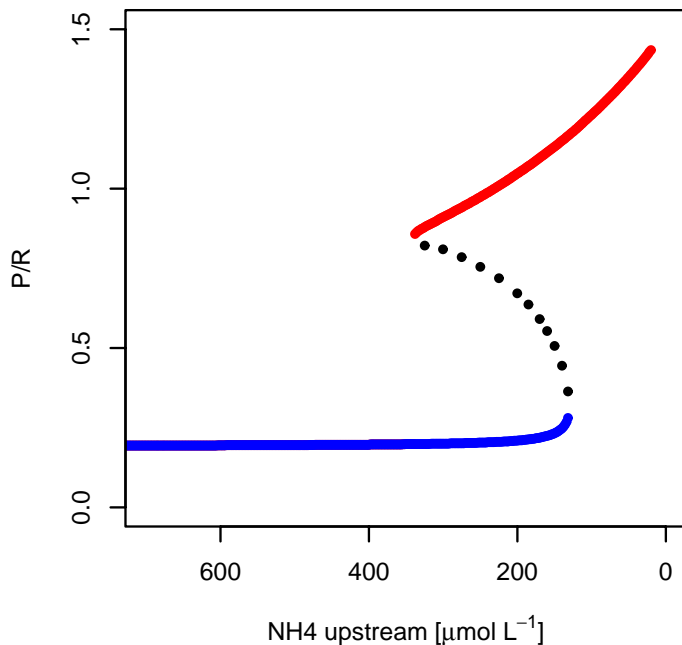


**Fig. 3.** Steady state and averaged model output (central panel). The model displays a *heterotrophic state* (high ammonium, low oxygen and low chlorophyll-*a* concentrations; blue line) at high upstream ammonium concentration and an *autotrophic state* (low ammonium, high oxygen and high chlorophyll-*a* concentrations; red line). Steady state output is compared with data from the downstream station plotted against ammonium concentrations at the upstream station for the years 1996–2007 (left panel). The calculated proxy for the annual FW average (grey line) is compared with annual and FW averaged data from 1968–2007 plotted against annual averaged upstream ammonia concentration (right panel). See text for detailed information.

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[◀](#)
[▶](#)
[◀](#)
[▶](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)


From heterotrophy to autotrophy

T. J. S. Cox et al.



**Fig. 4.** The ratio of oxygen production (algae) and consumption (respiration and nitrification) at steady state (full lines) and at the unstable equilibria of the system (dotted line).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

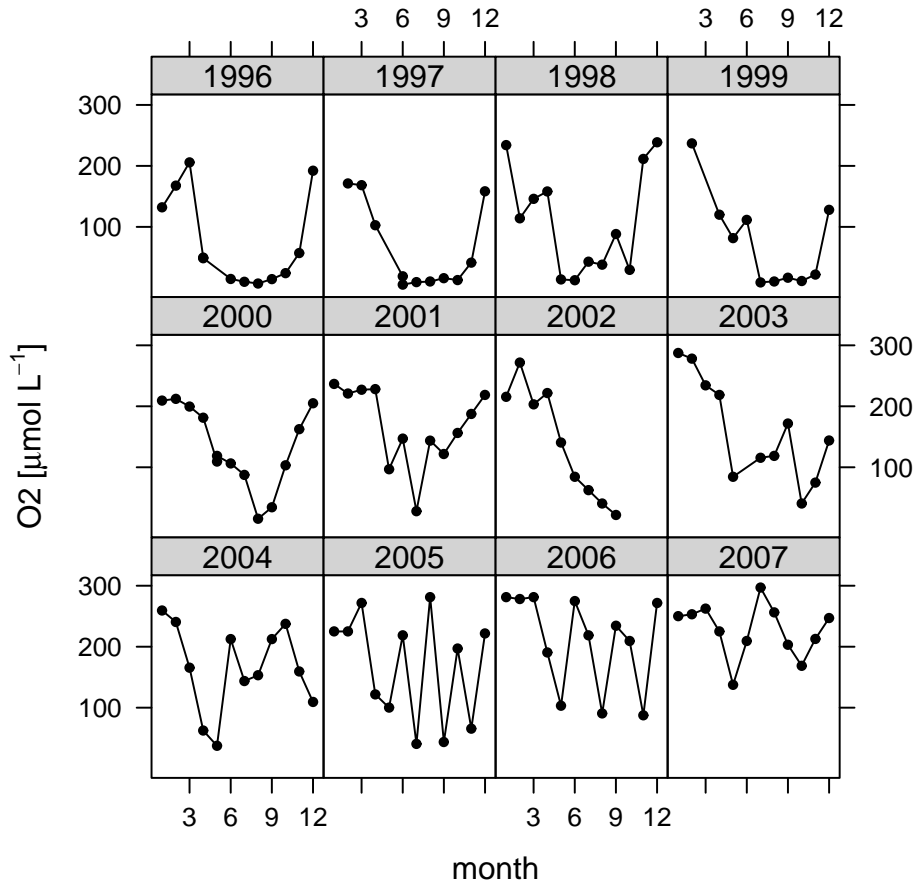
Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





**Fig. 5.** Annual pattern of dissolved oxygen at the downstream station.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

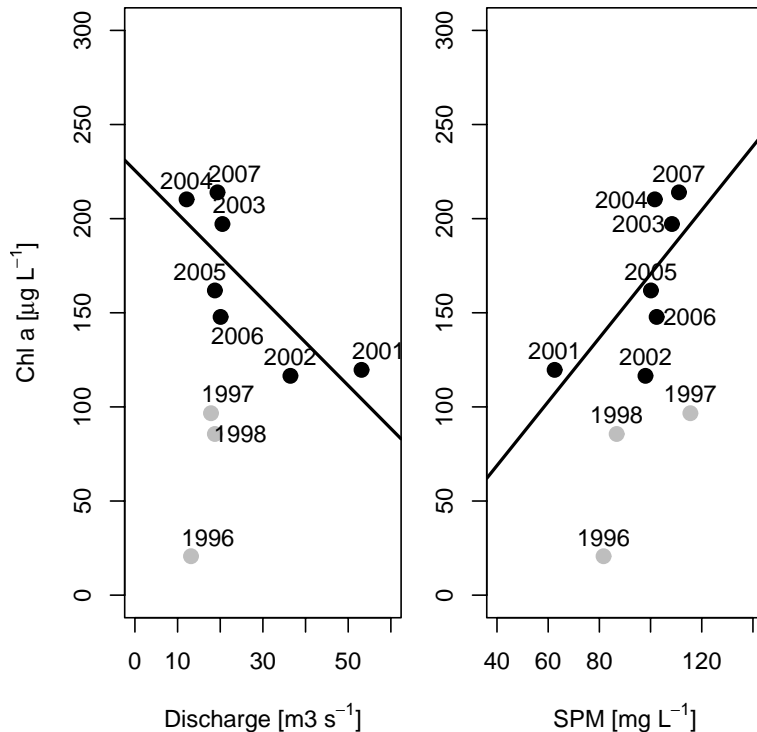
Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





**Fig. 6.** May–September and FW averaged chlorophyll-*a* concentrations versus average discharge ( $Q$ ) and average suspended matter concentration (SPM), with linear regression lines for data points after 1999. There exists no correlation for the whole 1996–2007 data set (black and grey symbols). For the 2001–2007 data set (black symbols), average chlorophyll-*a* concentration is negatively correlated with average discharge ( $r^2=0.62$ ,  $p=0.04$ ), and weakly positively correlated with suspended matter concentration ( $r^2=0.44$ ,  $p=0.1$ ).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

