Measuring in-stream productivity: the potential of continuous chlorophyll and dissolved oxygen monitoring for assessing the ecological status of surface waters

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Abstract Continuous (hourly) measurements of dissolved oxygen and chlorophyll (determined by fluorimetry) were made for an inter-linked lowland river and canal system. The dissolved oxygen data were used to estimate daily rates of re-aeration, photosynthesis and respiration, using a process-based analytical technique (the Delta method). In-situ fluorimeter measurements of chlorophyll were ground-truthed on a fortnightly basis using laboratory methanol extraction of chlorophyll and spectrophotometric analysis. Water samples were also analysed for algal species on a fortnightly basis. The river and canal exhibited very similar rates of photosynthesis and respiration during the summer of 2001, despite much higher chlorophyll concentrations and total algal counts, indicating that benthic algae and/or aquatic macrophytes may be making an important contribution to photosynthesis rates in the river. Suspended algal populations in the canal are dominated by planktonic species, whereas the river has a higher proportion of species which are predominantly benthic in habitat. The river exhibited higher rates of respiration, reflecting a higher organic loading from external (e.g. sewage effluent) sources.

Keywords Chlorophyll *a*; dissolved oxygen; photosynthesis; phytoplankton; productivity; respiration

Water Science and Technology **Vol 48 No 10 pp 191–198**

Introduction

Continuous chlorophyll and dissolved oxygen (DO) concentrations are used to assess changes in productivity in an inter-linked river and canal system, the River Dun and the Kennet and Avon Canal in Wiltshire, England. The study sites are located within a lowland catchment system (the upper Thames basin, Figure 1) and both the canal and river are subject to eutrophication, linked to issues of nutrient supplies and climate variability, common to many lowland surface waters in the UK. In the spring of 1998, a major toxic event occurred in the Kennet and Avon Canal and the River Dun (which is fed by the Canal), resulting in the death of over 150 tonnes of fish. The following spring, a further toxic incident occurred, and these are thought to be microbial in origin and linked to the spring diatom bloom crash. Hence, there has been considerable interest in monitoring algal dynamics and productivity in the Kennet and Avon Canal/Dun system as an early warning of potential toxic problems. The development of methods of monitoring phytoplankton productivity and dynamics is also extremely important for strategic environmental management within the context of the new European Water Framework Directive (WFD; EU, 2000). Under the WFD, watercourse phytoplankton status in England and Wales may be assessed purely on chlorophyll *a* levels by the Environment Agency (EA). Presently, chlorophyll *a* is measured on a fortnightly or monthly basis by the EA, but chlorophyll *a* levels fluctuate greatly throughout the course of a year, on daily, event and seasonal time scales. Thus, the current frequency of sampling is insufficient for means, medians or other average values (whether seasonal or annual) to be an appropriate measure of phytoplankton standing crop and give strong diurnal fluctuations in chlorophyll *a*, the data may be biased according to time of collection. Continuous chlorophyll measurements (determined by fluorimetry) potentially provide a more satisfactory data source but there is a shortfall of data and information on methodologies.

Methods

Two telemetered monitoring stations were set up in February 2001 on the River Dun at Hungerford and the Kennet and Avon Canal at Dun Cottage (Figure 1). A variety of parameters have been measured using a modular monitoring and telemetry system:

- chlorophyll – YSI 6025 chlorophyll probe (fluorimeter) (YSI Environmental, European Support Centre, Farnborough, UK).
- pH, conductivity, dissolved oxygen and water temperature – "Hydrolab" multiparameter water quality monitoring system (Omnidata systems, London, UK).
- light levels (photosynthetically active radiation, PAR) – SKYE Instruments Quantum sensor (Skye Instruments Ltd, Powys, UK).

Real-time data are transmitted at hourly intervals using the Meteor Burst MCC971 H system (Meteor Communications (Europe) Ltd, Colney, St Albans, UK). Continuous chlorophyll measurements were ground-truthed on a fortnightly basis using a methanol extraction (at 4°C for 24 h) and the chlorophyll *a* in the extract was determined spectrophotometrically at two wavelengths: 655 nm (the absorbance maximum for chlorophyll *a)* and 750 nm (to compensate for background turbidity) (Pinder *et al*., 1997; Simon and Helliwell, 1998). Whereas the spectrophotometric laboratory method determines chlorophyll *a* concentrations, the fluorimetric determination measures total fluorescence intensity between 650 and 700 nm (YSI, 1999), and therefore could be measuring other chlorophyll pigments (chlorophyll *b* and *c*) as well as chlorophyll *a*. Samples were also collected for algal species identification (Lund *et al*., 1958), and classified according to taxonomy and usual habitat (predominantly planktonic, predominantly benthic or both planktonic and benthic). The continuous water quality data were compared against independent measurements made in the laboratory: the continuous readings were normalised to the accurate and independent field measurements at the successive fortnightly times of instrument interchange using linear extrapolation procedures (Neal *et al*., 1998, 2001; Williams *et al*., 2000).

Continuous dissolved oxygen (DO) measurements were used to calculate rates of net primary production. Diurnal patterns in dissolved oxygen are controlled by the interaction between primary production and respiration (linked to microbial and chemical oxygen demands in the water column or river bed sediments) and exchange of oxygen at the water surface (re-aeration) (Jarvie *et al*., 1998; Williams *et al*., 2000). Net primary production was calculated from diurnal DO curves, using the methods of Williams *et al*. (2000), based on the Delta method (Chapra and Di Toro, 1991). The relationships between net primary production and chlorophyll concentrations, light and water temperature were assessed for both the river and canal.

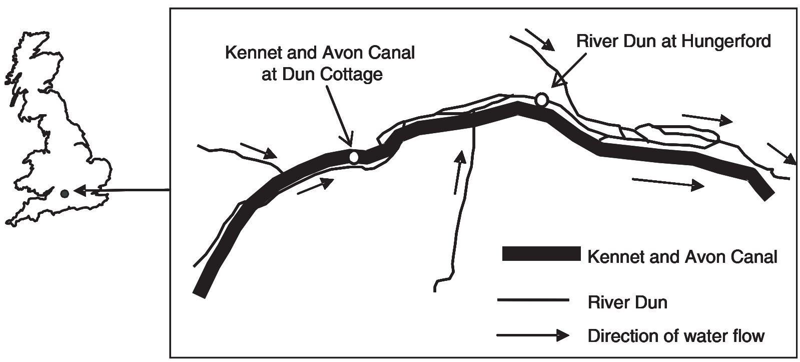

Figure 1 Location of sampling sites

Results and discussion

Both the canal and river show well-defined diurnal fluctuations of dissolved oxygen (DO) and chlorophyll (derived by fluorimetry) (Figure 2). The canal demonstrates a sudden increase in amplitude of diurnal DO fluctuations in mid-May, corresponding with a sharp increase in chlorophyll concentrations in the canal, whereas the river shows greater gradation in amplitude of DO curves and much smaller increases in chlorophyll concentrations. Greatest diurnal variability in DO in the river occurred in May, ranging from 70 to in excess of 200% saturation (off scale); whereas in the canal, the greatest diurnal DO fluctuations occurred in early June, also ranging from 70% to in excess of 200% saturation.

Maximum photosynthesis rates are frequently higher in the river than in the canal up to late May 2001 (Figure 3). After the end of May 2001, rates of photosynthesis in the canal and river are largely similar in value and show close similarity in dynamic responses. The re-aeration rate calculated in the Delta method is highly sensitive to the value re-aeration rate from the time of the minimum oxygen deficit relative to the solar noon (see Williams *et al.*, 2000). Since the data used to define the DO curve in this study are only hourly, anomalously and inappropriately high re-aeration rates can be estimated under certain conditions. This

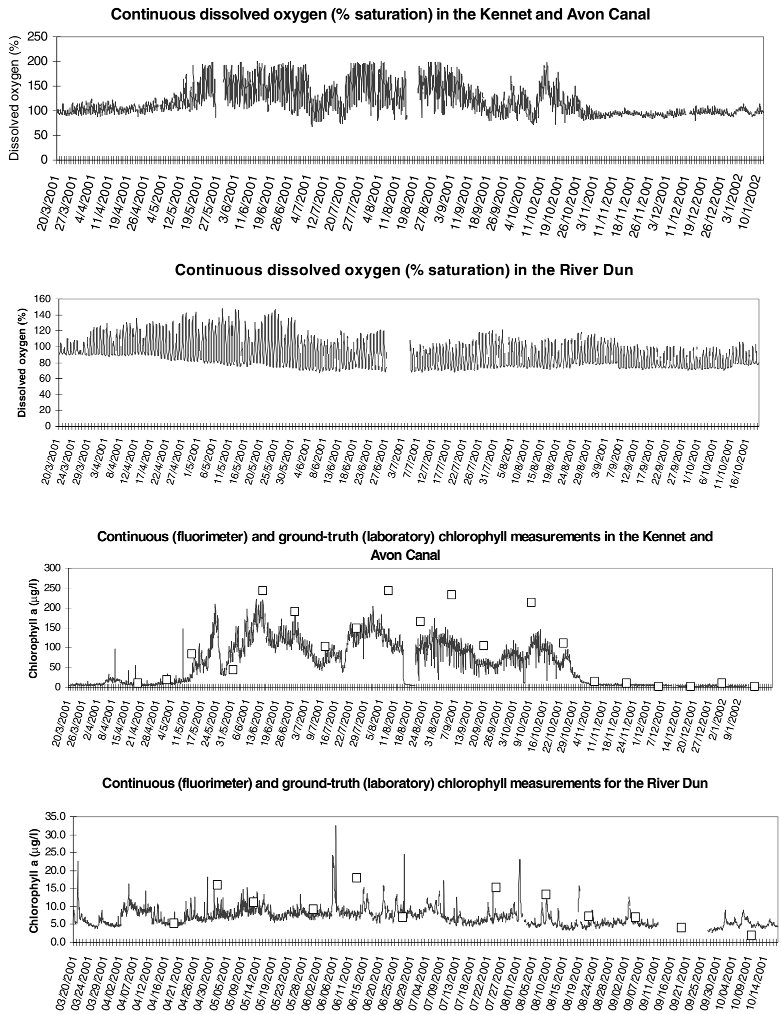

Figure 2 Continuous (hourly) measurements of dissolved oxygen and chlorophyll in the Kennet and Avon Canal (March 2001 to January 2002) and River Dun (March 2001 to October 2001)

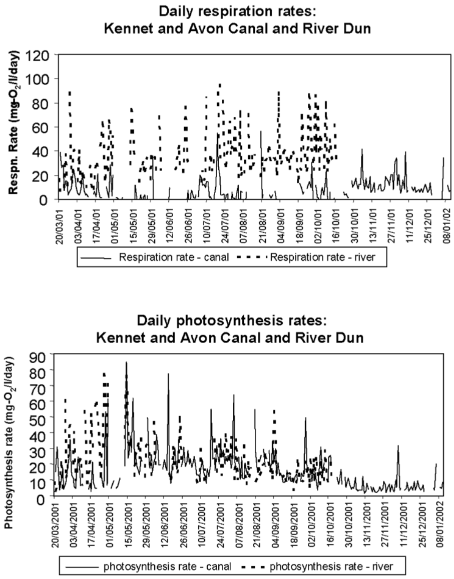

Figure 3 Calculated respiration and photosynthesis rates in the Kennet and Avon Canal and River Dun

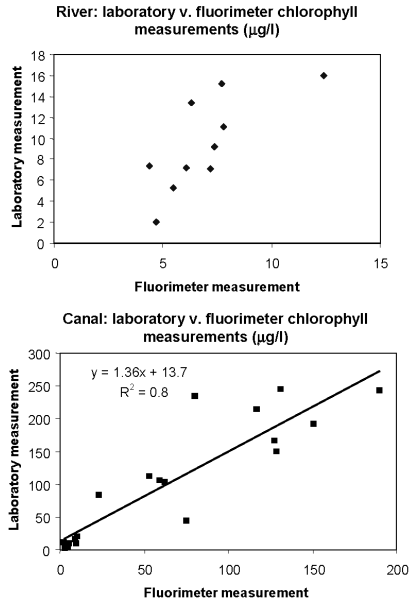

Figure 4 Relationships between laboratory-measured chlorophyll a concentrations and in-situ continuous fluorimeter-derived chlorophyll concentrations for the Kennet and Avon Canal and River Dun (note differences in scale of axes; no regression line is supplied for the River Dun owing to low concentrations and potential errors in measurement)

feeds back into estimates of photosynthesis and respiration, producing high-value spikes for these components of the cycle, which should be treated with some caution. Times when DO concentrations have gone off-scale (>200% saturation) are not included in the analysis, which is likely to cause some bias in the calculated rates of photosynthesis.

Rates of respiration are consistently higher in the river, compared with the canal (Figure 3). Odum (1956) proposed a classification of flowing water communities, based on the relationship between photosynthesis and respiration. A ratio of photosynthesis to respiration (P/R) of >1 was classified as autotrophic, whereas a P/R ratio of <1 was classified as heterotrophic. The mean P/R ratio for the Kennet and Avon Canal was 3.2, compared with a mean P/R ratio of 0.67 for the River Dun. This suggests that, on average, the Kennet and Avon canal may be classed as "autotrophic", whereas the River Dun may be classed as "heterotrophic", although it is important to consider the caveats concerning uncertainties in the calculations of photosynthesis and respiration rates outlined above.

The continuous chlorophyll (fluorimeter) concentrations in the Kennet and Avon Canal and River Dun appear to match the general dynamics of the ground-truthed (spectrophotometric) chlorophyll *a* measurements (Figure 2). Relationships between continuous fluorimeter readings and spectrophotometric measurements demonstrate positive, near-linear relationships for both the river and canal (Figure 4), although there is a higher degree of data scatter at higher chlorophyll concentrations in the Kennet and Avon Canal.

Time series showing five-day running mean values of daily photosynthesis rates, chlorophyll concentrations (measured by fluorimetry), light levels and temperature for the Kennet and Avon Canal and River Dun are shown in Figure 5.

Given the high degree of variability in daily photosynthesis rates, and uncertainties over the validity of individual high-value peaks, 5-day running means have been computed to

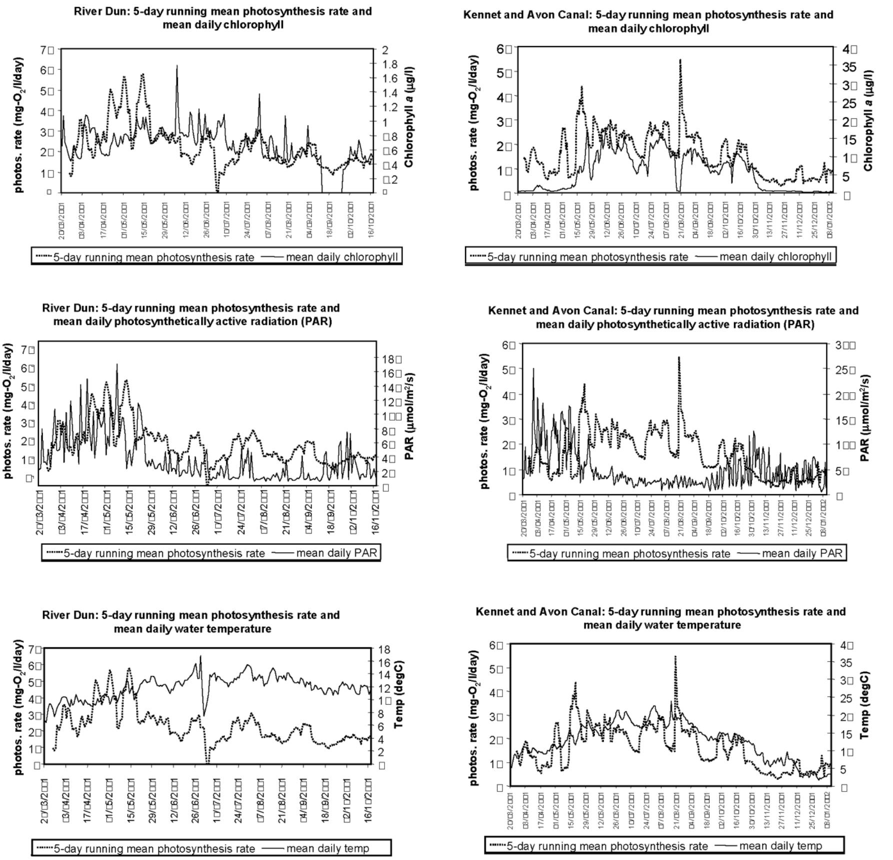

Figure 5 Time series of photosynthesis rates, chlorophyll *a* concentrations, light levels (photosynthetically-active radiation levels, PAR) and water temperature for the River Dun and Kennet and Avon Canal (NB: 5-day running means have been calculated to reduce data spikiness and aid visual inspection)

aid visual inspection of the photosynthesis time series. The River Dun does not show such a pronounced period of summer chlorophyll maxima as the canal, and chlorophyll concentrations in the Kennet and Avon Canal are typically an order of magnitude higher than those in the River Dun. Photosynthesis rates within the Kennet and Avon Canal correspond with the general dynamics of chlorophyll concentrations and water temperature. However, photosynthesis rates in the canal appear to behave independently of light levels. The lower light levels during the summer of 2001 at both sites reflects tree shading, with a reduction in solar radiation with the onset of leaf cover and an increase in solar radiation with leaf loss during autumn. In contrast to the Kennet and Avon Canal, photosynthesis rates in the River Dun show a closer linkage with light levels, but no clear relationship with either chlorophyll concentrations or temperature.

Average algal counts in the Kennet and Avon Canal are around 37 times higher than in the River Dun (Table 1). Although both river and canal waters demonstrate a similar ratio of dead to live algal species (around 1:1), the canal is dominated by planktonic species, accounting for more than 80% of the in total, live and dead counts, whereas the river has a larger proportion of benthic species, contributing around 50% of the total algal count and 83% of the dead count.

Examination of the relationships between chlorophyll measurements by fluorimetry and laboratory methods demonstrate stronger relationships between chlorophyll measurements and algal counts for the canal (Table 2), which is probably a result of (a) much higher algal

Table 1 Averages and ranges of algal types in the River Dun and Kennet and Avon Canal

		River	Canal
Total count (counts/ml)	Mean	1,436	53,213
	Max	4,237	27,7703
	Min	307	889
Live species as a % of total count	Mean	49.0	54.8
	Max	76.3	89.1
	Min	13.6	8.1
Planktonic species as % of total count	Mean	47.0	86.9
	Max	76.4	98.3
	Min	19	52.3
Planktonic species as % of live count	Mean	64.5	86.2
	Max	95.5	99.1
	Min	20.0	33.3
Planktonic species as % of dead count	Mean	25.3	83.1
	Max	50.0	96.6
	Min	12.5	54.7
Benthic species as % of total count	Mean	50.8	12.6
	Max	78.4	47.5
	Min	23.6	1.5
Benthic species as % of live count	Mean	34.3	12.5
	Max	70.0	66.7
	Min	4.5	0.6
Benthic species as % of dead count	Mean	83.1	16.9
	Max	96.6	45.3
	Min	54.7	3.4

and chlorophyll concentrations in the canal and (b) a larger number of observations. For the canal, the strongest correlations exist for the fluorimeter-derived chlorophyll concentrations, whereas for the river, the highest laboratory measurements of chlorophyll *a* provide stronger correlations with algal counts, which may indicate that the algae in the canal waters contain a wider range of chlorophyll pigments, whereas the river algae have a greater dominance of chlorophyll *a*. Chlorophyll concentrations in the canal are most strongly related to the total count and the total plankton count, whereas for the River Dun, the strongest correlation is for the total benthic count, and these correlations reflect the dominant species composition. The ratio of chlorophyll concentrations determined by laboratory methods (extraction and spectrophotometry) to fluorimetry could potentially be used to examine changes in dominant algal species, reflecting changes in the relative concentration of chlorophyll *a* to the combined concentrations of chlorophyll *a, b* and *c*. However, for the River Dun and Kennet and Avon Canal, there were no significant changes in the ratios of laboratory- to fluorimeter-derived chlorophyll measurements throughout

Table 2a Regression statistics, showing relationships between chlorophyll measurements (by fluorimetry and laboratory methods) and algal types for the River Dun (no. observations = 10)

	r^2		P-value	
Count	Fluorimeter	Laboratory	Fluorimeter	Laboratory
Total	0.1	0.4	0.36	0.05
Total live	0.12	0.31	0.33	0.09
Total dead	0.04	0.47	0.56	0.03
Total planktonic	0.03	0.25	0.63	0.15
Total benthic	0.41	0.63	0.05	<0.01
Dead benthic	0.06	0.40	0.49	0.05
Dead planktonic	0.004	0.26	0.85	0.13
Live benthic	0.63	0.31	<0.01	0.09
Live planktonic	0.04	0.22	0.6	0.17

Table 2b Regression statistics, showing relationships between chlorophyll measurements (by fluorimetry and laboratory methods) and algal types for the Kennet and Avon Canal (no. observations = 19)

	r^2		P-value	
Count	Fluorimeter	Laboratory	Fluorimeter	Laboratory
Total	0.64	0.48	<0.01	<0.01
Total live	0.56	0.39	<0.01	<0.01
Total dead	0.56	0.56	<0.01	<0.01
Total planktonic	0.63	0.47	<0.01	<0.01
Total benthic	0.27	0.28	0.02	0.03
Dead benthic	0.38	0.25	<0.01	<0.01
Dead planktonic	0.55	0.58	<0.01	<0.01
Live benthic	0.12	0.2	0.14	0.06
Live planktonic	0.55	0.38	<0.01	<0.01

the study period, probably because the algal species in both river and canal are predominantly bacillariophytes (diatoms). Neither the river nor the canal show any significant changes in the ratios of bacillariophytes to chlorophytes during the study period and no significant populations of cyanophytes have been detected.

Conclusions

The Delta method has been successfully applied to model daily rates of photosynthesis and respiration, using the hourly dissolved oxygen data from the Kennet and Avon Canal and River Dun. The results have demonstrated a high degree of similarity in absolute values and dynamics of photosynthesis rates in both the river and canal during the summer of 2001, despite chlorophyll *a* concentrations in the canal being typically an order of magnitude higher than in the river. This indicates that benthic algae and/or aquatic macrophytes may be providing a significant contribution to photosynthesis rates in the river. Between late March and late April 2001, higher rates of photosynthesis are seen in the river, which may reflect benthic algae or the effects of aquatic macrophytes which have survived the winter and which can begin photosynthesising before a significant phytoplankton crop has been established. The largely stagnant water conditions and high water residence times in the canal, compared with the high flushing rate of the river, promotes development of a larger phytoplankton standing crop in the canal, which is dominated by planktonic rather than benthic species. Shallower water in the river and thus greater light penetration, promote the growth of bottom-rooted macrophytes and the development of benthic algae, which are mobilised into the water column by the greater flow rates in the river. Photosynthesis rates in the canal are closely linked to chlorophyll concentrations and water temperature, but not light levels, whereas photosynthesis rates in the river are more closely linked to changes in light levels, but not chlorophyll concentrations or water temperature. This difference between the canal and river is probably related to the fact that productivity in the canal is dominated by phytoplankton, which respond rapidly to water temperature and largely control chlorophyll concentrations in the water column, whereas riverine productivity is controlled by benthic algae, macrophytes and phytoplankton. Although photosynthesis rates are similar in the river and canal, respiration rates are higher in the river, linked to larger loads of organic matter from external sources (sewage effluents and diffuse catchment sources).

This study has demonstrated the value of continuous measurements of DO and chlorophyll, combined with fortnightly ground-truthing and algal species identification to examine the phytoplankton status of canal and river systems. However, for a shallow river system like the Dun, information on phytoplankton dynamics provides only a partial account of in-stream ecological status. While DO measurements can provide valuable information on total in-stream productivity, the linkages with chlorophyll and phytoplankton species counts are poorer for the river, since benthic algae and/or macrophytes are clearly providing an important additional contribution to photosynthetic productivity. It might be expected that closer linkages between productivity and phytoplankton dynamics would be observed in large, deep, slow-flowing river systems (such as the main River Thames), where poor light penetration means that benthic algae and macrophytes are unable to colonise the full cross-section of the river bed.

Acknowledgements

This research was jointly funded by the Environment Agency and the Natural Environment Research Council. The views expressed in the paper are those of the authors and not necessarily those of the Environment Agency.

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