Three-parameter active $in\ situ$ optical measurements: theory, instrumentation, and results from coastal waters

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Abstract
A submersible optical instrument has been designed and constructed which simultaneously measures chlorophyll fluorescence, beam attenuation and wide-angle light scattering in sea water. A theoretical framework is presented which shows that this instrument configuration is capable of quantitatively measuring concentrations of gelbstoff, suspended particles and phytoplankton when all three components are present in a mixture, provided the relevant set of calibration coefficients are known. The inherent variability of natural materials means that the numerical values of these calibration coefficients usually have to be determined at the site of instrument deployment. However, trials in optically complex waters indicate that the instrument can be usefully employed to interpolate between chemical measurements in order to increase the spatial and temporal coverage of survey data while minimizing the resources required for sample analysis.

Keywords: Fluorometry, nephelometry, transmissometry, multiparametric analysis, coastal waters

1. Introduction

There are three naturally occurring components which significantly modify the optical properties of sea water (Kirk 1994): phytoplankton (plant cells which exist in suspension either individually or in small assemblages), suspended inorganic particles (often derived from riverine inputs) and dissolved coloured matter (yellow humic substances, or gelbstoff). Measurements of the distribution of these substances can provide information on processes of primary production, the movement of water masses and water quality which are of considerable value in monitoring areas subject to anthropogenic enrichment and contamination. Their concentrations are traditionally determined by water sampling followed by gravimetric and colourimetric analysis (Parsons *et al* 1984), but these chemical procedures are not easily adapted for implementation on automatic monitoring stations such as coastal buoys and deep water observations. There is therefore considerable current interest in the development

of alternative methods for measuring sea water composition, and optical instrumentation appears eminently suitable for this purpose. It does not involve the handling of discrete samples or the supply of chemical reagents, offers low power consumption and is easily interfaced to data logging systems. However, the general experience with optical monitoring in the marine environment has been that absolute determinations of the concentrations of sea water constituents are rarely possible. This is due partly to variations in intrinsic optical properties according to the phytoplankton species present, or to changes in the source of resuspended sediment. In addition, some of the most commonly deployed optical instruments are sensitive to more than one sea water constituent. For example, the collimated beam transmissometer can be influenced to varying degrees by gelbstoff (through absorption), suspended inorganic material (mainly through scattering) and phytoplankton (through scattering and absorption). The object of the work described here was to assess the extent to which ambiguities in optical measurements could be resolved

by measuring several parameters simultaneously. The first requirement was to identify a set of measurements which were theoretically capable of deconvoluting the overlapping optical signatures of the three sea water components of interest. It was then necessary to construct equipment capable of making these measurements *in situ*, and to assess the effectiveness of this measurement strategy under natural conditions.

2. Instrument design and calibration

Chemical variables commonly measured in routine sea water analysis include the fluorescence of acetone-extracted pigments (EPF: Parsons *et al* 1984), the mass of suspended particulate material concentrated on a filter (SPM: Strickland and Parsons 1972) and the absorption of filtered sea water at 440 nm (a(400): Bricaud *et al* 1981). EPF is considered to be an indicator of phytoplankton concentration, SPM is a function of the concentrations of both suspended sediment and phytoplankton, and a(440) is a function of gelbstoff concentration. One difficulty is the absence of a direct method of differentiating between algal and non-algal components of SPM, since standard ashing methods leave silica fustules from diatoms which are clearly biogenic in origin. In addition, the interpretation of extracted pigment fluorescence is a complex area (Krause and Weis 1991). We therefore have a set of three chemical determinants (EPF, SPM and a(440)), which act as indicator variables for phytoplankton, total particulates and gelbstoff, respectively. In order to resolve three components in a mixture, a minimum of three independent observations is required. A special-purpose three-parameter optical instrument was constructed which measures *in vivo* red fluorescence (F), wide-angle light scattering or nephelometry (N) and blue beam attenuation (c). The light source for all three sensors was a pulsed xenon flash lamp filtered to provide wavelengths between 400–500 nm. The nephelometer measured scattering at wide angles ($90 \pm 10°$) at these wavelengths, whilst the transmissometer used additional filtration to reduce the bandwidth to 440 ± 20 nm and had an angular resolution of $0.3°$ with a path length of 250 mm in water. Fluorescence emission was measured between 650–700 nm. Detailed specifications for the optics and electronics may be found in McKee (1997) and McKee *et al* (1997). For the work presented here, fluorescence and scattering signals are expressed simply in volts, while the beam attenuation signal is converted to an attenuation coefficient (m^{-1}). Calibrations in the laboratory with a variety of algal cultures, inorganic particulates and coloured solutions (including tea as a substitute for CDOM) demonstrated that the instrument response was linear over the range of concentrations tested, which exceeds that likely to occur in the sea in areas where trials have been carried out.

3. Theory

In the following treatment it is assumed that there are linear relationships between the concentrations of biogeochemical parameters and their optical characteristics. A set of constants of proportionality, k_i, therefore relates optical properties to chemical variables. If there is a linear relationship between extracted pigment fluorescence (EPF) and the signal obtained from the *in situ* fluorescence sensor (F), then

$$F = k_1 \text{EPF} \tag{1}$$

and if the approximation that the mass concentration of algal material can be derived as a linear function of the *in situ* fluorescence signal:

$$\text{SPM}_{\text{algal}} = \frac{F}{k_2}. \tag{2}$$

Next we assume that the nephelometric signal (N) is composed of components derived from both algal and non-algal material:

$$N = k_3 \text{SPM}_{\text{algal}} + k_4 \text{SPM}_{\text{non-algal}}. \tag{3}$$

Substituting equation (2) into (3) gives

$$\text{SPM}_{\text{non-algal}} = \frac{N}{k_4} - \frac{k_3 F}{k_4 k_2} \tag{4}$$

and the sum of the two SPM components can be written as

$$\begin{aligned} \text{SPM} &= \text{SPM}_{\text{algal}} + \text{SPM}_{\text{non-algal}} \\ &= \frac{N}{k_4} + \frac{F}{k_2}\left(1 - \frac{k_3}{k_4}\right). \end{aligned} \tag{5}$$

The attenuation signal (c) has three components: algal, non-algal particulate and gelbstoff:

$$c = c_{\text{algal}} + c_{\text{non-algal}} + c_{\text{gelb}}. \tag{6}$$

For linear relationships between the concentrations of algal and non-algal particulates and their contributions to attenuation:

$$c_{\text{algal}} = k_5 \text{SPM}_{\text{algal}} \tag{7}$$

$$c_{\text{non-algal}} = k_6 \text{SPM}_{\text{non-algal}}. \tag{8}$$

There should also be a linear relationship between c_{gelb} and a(440) (these two parameters would be identical in the absence of scattering by sub-0.2 μm particles)

$$c_{\text{gelb}} = k_7 \text{a}(440). \tag{9}$$

Equation (6) can now be re-expressed as

$$\text{a}(440) = \frac{1}{k_7}\left[c - \frac{k_6}{k_4}N - \left(\frac{k_5}{k_2} - \frac{k_3 k_6}{k_4 k_2}\right)F\right]. \tag{10}$$

Aggregating the k_i coefficients in equations (1), (5) and (10) then gives the following set of equations:

$$\begin{aligned} \text{EPF} &= m_1 F \\ \text{SPM} &= m_2 F + m_3 N \\ \text{a}(440) &= m_4 F + m_5 N + m_6 c. \end{aligned} \tag{11}$$

These equations represent a useful development in the interpretation of *in situ* optical data in terms of biogeochemistry. However the k_i coefficients, and the m_i values which depend upon them, are not constant within each class of material; they can vary between algal species and from one type of sediment to another (McKee 1997). As a result, in field work the set of m_i coefficients must usually be derived from multiple linear regressions between optical signals and the results of water sample analyses.
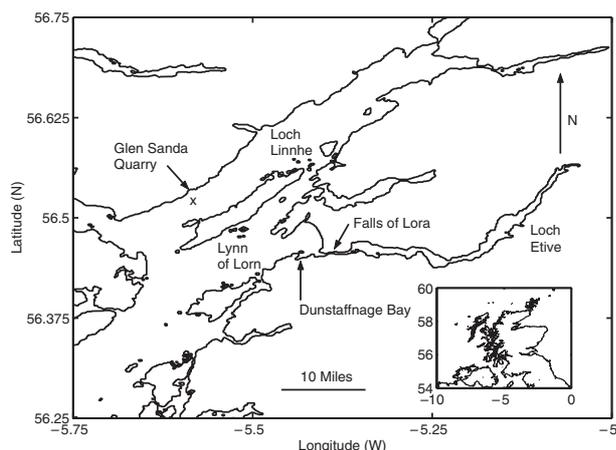
Figure 1. Map of Dunstaffnage Bay and surrounding area, including Loch Linnhe.
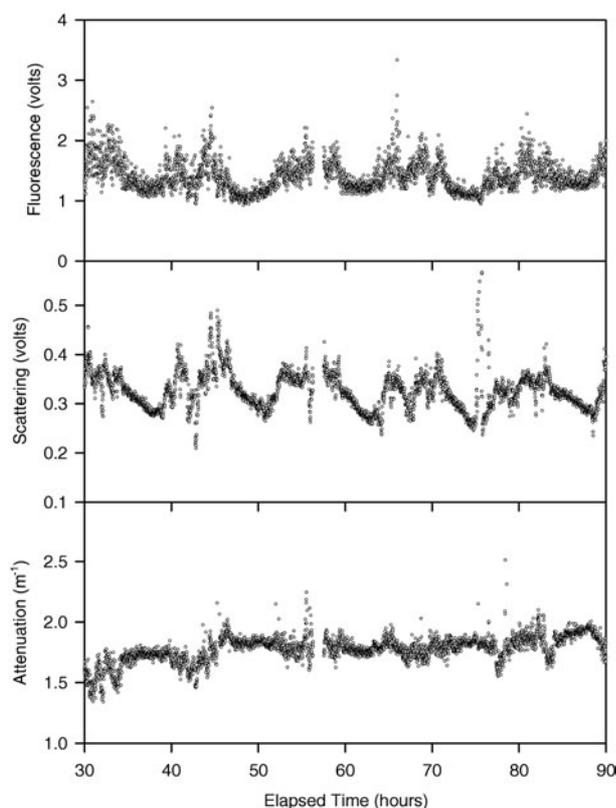

Figure 2. Optical time series in Dunstaffnage Bay. Fluorescence and scattering signals exhibit periodic fluctuations which are tidally driven. The attenuation signal, however, remains relatively stable throughout this period.

4. Results

This multiparametric approach to interpreting *in situ* optical data has been applied to two sets of observations made in Scottish coastal waters. One object was to test the usefulness of this approach in the interpretation of time series data. Several days of continuous instrument deployment were therefore carried out in June 1996 in Dunstaffnage Bay, a shallow tidal bay near Oban, Scotland (figure 1). In this location, rising tides bring water from the Lynn of Lorn which is a source of
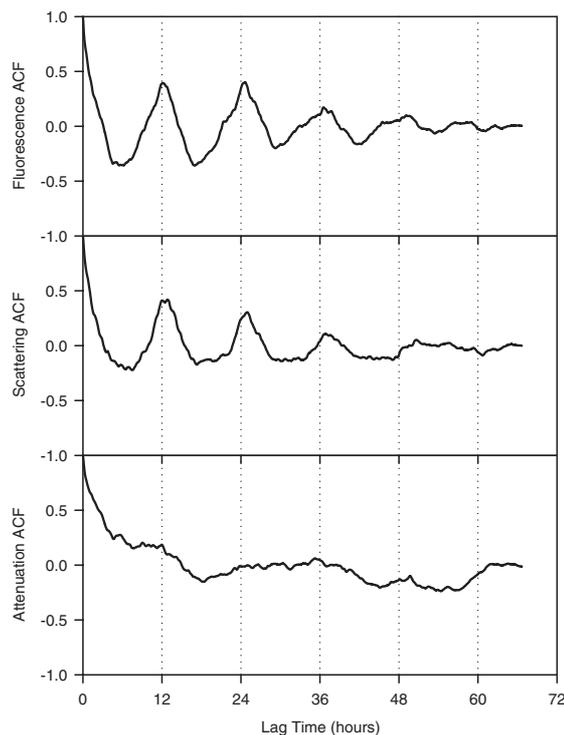

Figure 3. Autocorrelation functions for optical time series data confirm tidal periodicity in fluorescence and nephelometry signals. Attenuation shows no obvious periodicity.

well-mixed coastal sea water. Falling tides bring water from Loch Etive, which is a complex source with high freshwater input and a restricted outfall (the Falls of Lora). In addition, the pattern of current flow in the bay is known to be complex owing to the effect of the islands at its entrance. The three-parameter device was suspended at a constant depth in the water from *RV Calanus* and water samples were analysed as frequently as was practical. A typical time series is shown in figure 2. Fluorescence and nephelometric scattering exhibit pronounced periodic fluctuations in amplitude which appear to be roughly in phase with each other and have a period of approximately 12 h, but the blue attenuation signal is less obviously periodic. This analysis of the time series is confirmed by examining autocorrelation functions for each set of signals (figure 3). Both the fluorescence and scattering signals show maximum correlation coefficients when the lag time is set slightly greater than 12 h. This frequency corresponds to tidal events moving different water masses past the instrument. The attenuation autocorrelation function, on the other hand, shows little obvious periodicity. Relationships found by applying multiple linear regressions between sample chemistry values and corresponding optical measurements were

$$\mathrm{EPF} = 3.95F$$
$$\mathrm{SPM} = 0.91F + 2.78N \tag{12}$$
$$a(440) = -0.01F - 1.64N + 0.60c.$$

These equations were used to generate an estimated chemistry time series which is plotted along with measured chemical values in figure 4. Estimates of EPF and a(440) appear to match measured values reasonably well, and it is interesting to note
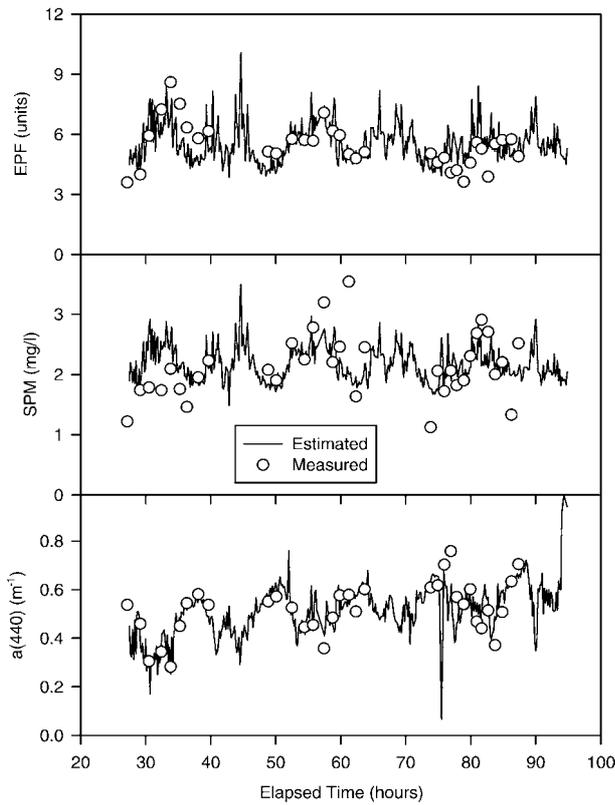
Figure 4. Estimated chemistry time series interpolates between measured values. EPF and a(440) estimates are very good. SPM estimates follow measured values less well.
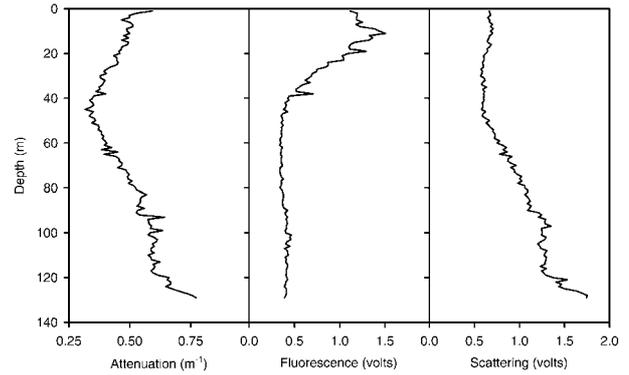

Figure 5. Three-parameter optical profiles in Loch Linnhe off Glen Sanda Quarry. The profile shows high fluorescence surface waters and high turbidity in deep water.
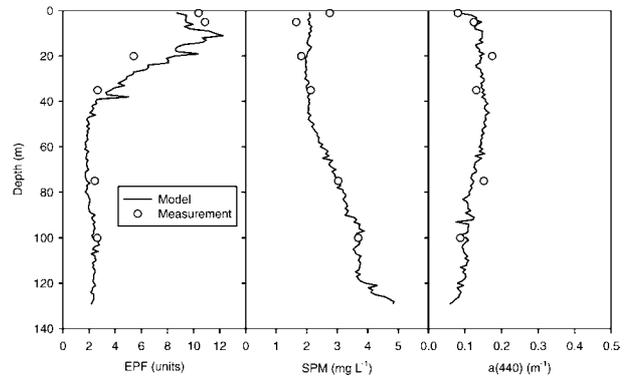

Figure 6. Modelled chemical parameters provide a reasonable match with values obtained from water samples.

that the EPF and a(440) signals appear to oscillate out of phase. This suggests that the lack of periodicity in the blue attenuation signal is due to the effects of algal and gelbstoff attenuation components cancelling each other out. SPM recovery is less successful, probably because the composition of SPM will vary depending upon the source of the water passing the sensor. Improved retrieval of SPM may be possible by determining separate relationships for different stages of the tidal cycle.

A second set of observations was taken in order to assess the usefulness of this approach in interpolating between widely spaced water samples in depth profiles. The three-parameter device was used to generate depth profiles at a station off Glen Sanda Quarry in Loch Linnhe in July 1997. Water samples were analysed from a series of depths down to a maximum depth of 100 m. The optical profiles are shown in figure 5. The water column can be clearly partitioned into near surface water with higher fluorescence and attenuation, and deeper water with higher scattering and attenuation. CTD profiles indicate that there was a pycnocline between 30 and 40 m separating these two water masses. The pycnocline occurs at the same depth as the minimum observed attenuation coefficients. Applying multiple linear regressions between optical and chemical measurements as described above gives the following set of best-fit relationships:

$$\text{EPF} = -1.38 + 9.07F$$

$$\text{SPM} = 0.71 - 0.194F + 2.41N \quad (13)$$

$$a(440) = 0.241 + 0.046F + 0.08N - 0.439c.$$

Note that an offset has been introduced into this set of equations to accommodate slight instrumental offsets in the relationships between optical and chemical parameters. Figure 6 shows a comparison of measured and modelled chemical parameters for this station. In general, there is good agreement between measured and modelled parameters in deeper water. However, there is poor retrieval of EPF and SPM close to the surface. A common factor linking these two estimates is the use of fluorescence. When fluorescence is plotted against attenuation for this station (figure 7) there is a clear bifurcation centred on the base of the pycnocline at 40 m. Above 40 m there is a tight linear relationship between fluorescence and attenuation except for the readings from 1 m. It would appear that either the fluorescence from surface waters shows signs of solar inhibition or there is enhanced attenuation near the surface perhaps due to scattering by air bubbles. This reading has been used in the linear regressions, and is probably responsible for much of the deviation of the modelled data from the measured values. Again it appears that improved results might be obtained by partitioning the data set by water mass before applying regressions.

5. Discussion

A three-parameter optical instrument has been constructed which is theoretically capable of resolving the concentration of individual components in sea water containing a mixture
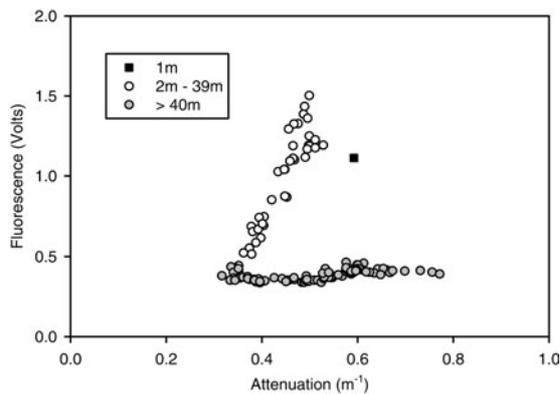
Figure 7. A plot of fluorescence versus attenuation shows a clear bifurcation centred around 40 m. The reading from 1 m deviates from the rest of the surface water data, perhaps indicating fluorescence inhibition at the surface, or enhanced scattering from air bubbles.

of phytoplankton, suspended sediment and gelbstoff. Natural variability in the optical characteristics of these three materials means that validation of optical measurements by direct chemical analysis of representative samples is usually required. Nevertheless, over limited time periods, or in geographical locations where the optical characteristics of the water body are known, it is often possible to obtain useful information from optical observations. In areas where the range of materials in suspension or solution is restricted, or where one source dominates, the burden of calibration may be reduced. Suitable examples include sites near industrial outlets and in the deep sea, where multiparameter optical measurements appear to offer a cost-effective alternative to intensive sampling by traditional methods. Potential applications of this approach include the determination of water quality in coastal waters and estuaries, the detection of algal blooms, measurements of tidal mixing and sediment resuspension, and monitoring of the effects of subsea engineering and drilling operations.

Acknowledgments

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