A NEW APPROACH TO EVALUATING SPATIAL VARIABILITY OF PHOTOCHEMISTRY BASED ON CHARACTERISATION OF OPTICAL WATER TYPE FROM SATELLITES

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ABSTRACT

We present a novel, satellite-based approach for studying the spatial variability of photochemistry in the upper ocean to better understand the importance of DOC photodegradation processes in the context of the global carbon cycle. Our method involves investigating the hypothesis that different optical water types have characteristically different apparent quantum yields for DOC photo-oxidation. Our efforts will be guided by four primary objectives. Our first objective is to make measurements of the quantum yield for photochemical oxidation of DOC to CO_2 for a variety of optical water types in the Northwest Atlantic. The second objective is to refine our existing satellite-based optical water type classification techniques using *in situ* measurements of inherent and apparent optical properties for each water type. Once we have made detailed measurements and developed robust classifiers, the focus will be on interpreting the data in order to quantitatively assess the importance of upper-ocean DOC photo-oxidation in the carbon cycle. Our third objective is to apply our classifiers to satellite images of ocean colour for the Northwest Atlantic in order to identify the location and extent of each optical water type, describing seasonal and inter-annual variability in the boundaries between optical water types over the region. Our final objective is to map DOC photodegradation over the Northwest Atlantic by characterising the relationship between DOC photo-oxidation rate and optical water type; we plan to calculate photochemical efficiency for each pixel on the basis of correlations between quantum yields and optical water types, and produce satellite-based seasonal and annual maps of the total contribution of DOC photo-oxidation for the region. This will allow us to quantify the importance of the photochemical oxidation of DOC in the Northwest Atlantic carbon cycle, thereby contributing to a better understanding of the processes that shape global climate and environmental change.

INTRODUCTION AND BACKGROUND

Since both transient climate variations and long-term climatic trends are influenced by changes in the carbon cycle, understanding and predicting climate change relies on an understanding of carbon cycle processes, their rates, and the factors that control them. The photochemical oxidation of DOC to inorganic carbon is an important component of the oceanic carbon cycle, representing a direct loss of organic carbon that bypasses the microbial loop. Estimates of the magnitude of this DOC sink in the global ocean suggest that the yearly loss of DOC by photochemical oxidation to CO_2 may be as high as 1×10^{15} moles C/year (Kieber and Mopper 2000). Without more data on the magnitude and environmental variability of the efficiency of DOC photo-oxidation, global and regional estimates of this process remain ill-constrained. We are advancing the quantitative understanding of this important carbon cycle process by identifying relationships between the efficiency of DOC photo-oxidation and appropriate optical water types that can be distinguished from satellite observations.

Photochemical Oxidation of DOC in the Ocean

Dissolved organic carbon in the ocean represents one of the largest organic carbon reservoirs on earth. Oxidation of this organic carbon pool is a process that can exchange carbon with the atmosphere on time scales relevant to global climate change. In spite of its size and potential for impact to global carbon cycles, the majority of the oceanic DOC pool remains chemically uncharacterised. The apparently long oceanic residence times for this material along with microbial incubation data argue for an apparent inertness with respect to biological degradation of these uncharacterised DOC components. In contrast to this lack of biological reactivity, this same portion of the DOC, through its role as ***the*** most significant absorber of UV radiation in the ocean, is the most reactive in terms of marine photochemistry. The photochemical oxidation/degradation of DOC, coupled with the consequent changes these processes have on biological carbon assimilation, can strongly impact the geochemical cycling of organic carbon in the ocean. It has been suggested that photochemical oxidation in the coastal zone may provide all or part of the sink for terrestrial DOC and provides an unquantified, but possibly important, sink for DOC produced *in situ* in the open ocean (Miller and Zepp, 1995). Although there is a vast array of consequences of photochemical reactions in the ocean, most do not quantitatively impact the cycling of DOC except, perhaps, through their impact on biological rates. The singular exception to this generality is the direct "photomineralisation" of DOC to carbon monoxide (CO) and carbon dioxide (CO_2). Furthermore, the photo-production of CO_2 appears to be the largest non-biological loss process for DOC in the ocean.

We must know the efficiency by which photochemistry converts DOC to CO_2 in order to construct a quantitative model for the estimation of DOC loss due to photochemistry in the ocean that is capable of incorporating changes in the distribution and absorption of UV radiation for different waters. New work done in one of our laboratories (Johannessen and Miller 2001) describes CO_2 apparent quantum yield (AQY, moles CO_2 produced / moles photons absorbed) spectra for sea water in each of fourteen samples from the Gulf Stream, the Mid-Atlantic Bight, and Halifax Harbour, Nova Scotia. These AQY spectra represent the very first complete study of CO_2 AQY for marine waters. Additionally, the data were generated using a novel multi-spectral irradiation technique that makes the experimental determination of AQY much more rapidly than traditional monochromatic methods for AQY determination (hours vs. days to weeks). With this advantage in methodology, we also produced the first data set capable of addressing the variability of CO_2 AQY spectra with location and depth. The AQY spectra for CO_2 photoproduction are quite variable, both in shape and magnitude, indicating that the photochemical production of CO_2 in all areas of the ocean cannot be calculated accurately using a single AQY spectrum. It was possible, however, to estimate CO_2 production using a combination of three pooled spectra: one for inshore water, one for coastal water, and one for open ocean water (Figure 1). A great deal more work is needed to quantify the magnitude of each, but clearly, the open ocean water samples photo-produced CO_2 more efficiently than did either the coastal or the inshore water.

An analysis using modelled irradiance and ocean colour showed clearly that the single largest determinant in our calculations of the variability of whole water column CO_2 photoproduction is the choice of AQY from our three pooled spectra. More AQY determinations are necessary to assess the broad applicability of the pooled spectra approach. Because of the limited number of spectra available, our crude division of AQY based on salinity currently represents the best method for assigning AQY spectra to various areas of the ocean. A better classification that allows clearer definition of the water types that correspond to distinct AQY spectra will be critical for refining this approach.

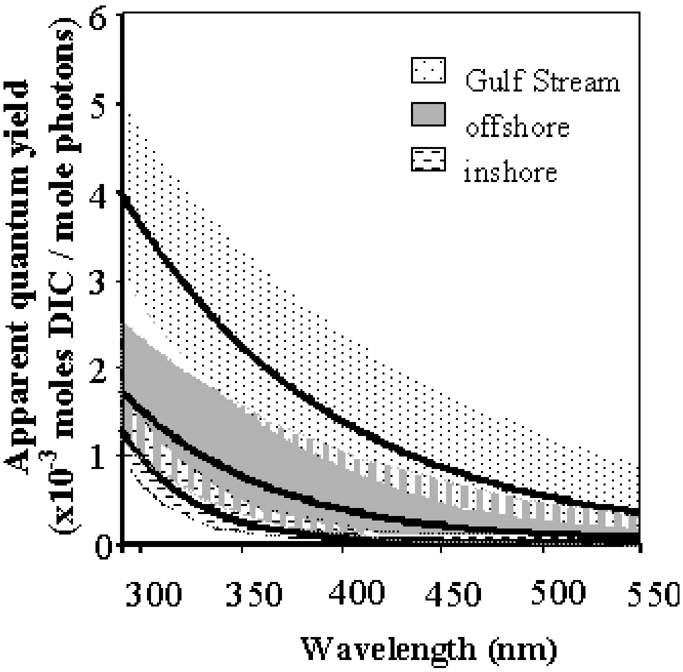

Figure 1. Zone average apparent quantum yield spectra plotted with 80% confidence intervals for waters from the Gulf Stream, the Mid-Atlantic Bight (offshore), and Halifax Harbour (inshore).

Optical Water Type Classification

The availability of remotely-sensed ocean colour data from satellite sensors such as SeaWiFS and CZCS has opened up new opportunities to study ecologically and biogeochemically important properties in the upper ocean. Satellite images of large geographic areas often reveal mesoscale reflectance features that are associated with physical, biogeochemical and biological processes in the upper ocean. Remotely-sensed ocean colour data have been exploited to help identify the scales associated with these features, and attempts have been made to correlate this data with *in situ* observations to identify the processes contributing to spatial and temporal variability. Optical water type classification approaches based on satellite data have great potential to contribute to the study of the spatial and temporal dynamics of upper ocean optical properties and their relationships with biological, physical, and chemical properties, including carbon sources and sinks in the upper water column. There have been efforts to use ocean colour data for water type identification using specialised algorithms for recognition of the unique optical properties of a particular type of phytoplankton, e.g., coccolithophore blooms (Brown and Yoder 1994) and *Trichodesmium* blooms (Subramaniam and Carpenter 1994). Identification of water types from satellite data has also contributed to understanding spatial and temporal variability of important components of the oceanic carbon cycle; e.g., Sathyendranath *et al*. (1991) used AVHRR imagery combined with local bathymetry to define water types in a study of productivity on Georges Bank. By combining satellite-based water type classification techniques with *in situ* measurements, we can begin to gather fundamental information about important carbon cycle processes in the upper ocean.

We have developed optical water type classification approaches based on remotely-sensed water leaving radiance, and applied these to the study of upper ocean ecological and biogeochemical properties (Martin Traykovski and Sosik, in press). Our focus has been on developing feature-based classifiers for the Northwest Atlantic region. Analysis of CZCS and SeaWiFS imagery revealed that pixels from several locations in this region projected into distinct clusters in single-band feature space, suggesting that these waters can be easily distinguished using a few spectral bands of ocean colour data. We have developed two different feature-based classification techniques: both the Euclidean Distance Classifier and the Eigenvector Classifier assign pixels to a class on the basis of their distance from class centroids in feature space, but they differ in the manner in which class variance is considered. We have applied these classifiers to ocean colour images of the Northwest Atlantic to elucidate the geographical location and extent of each water type. Our current emphasis is on refining and applying these water type classification approaches to advance our understanding of the relationship between the efficiency of DOC photo-oxidation and remotely-sensed optical water type.

APPROACH

Our work is aimed at examining variability in the rate of photochemical oxidation of DOC in the context of optical water types identifiable from satellite imagery. The primary goal is to develop a method to quantify the role of photochemical oxidation of DOC to inorganic carbon in the ocean component of the global carbon cycle. To accomplish this, we will test the hypothesis that different remotely-sensed optical water types are characterised by different apparent quantum yields for the photochemical oxidation of DOC. Our efforts are guided by four primary objectives. Our initial emphasis is on acquiring *in situ* data and developing classification techniques tailored to our research problem. Our focus will then shift to data analysis and application of our classification approaches to test our hypothesis. We hope to establish a relationship between measured DOC photo-oxidation rates and optical water types. Through our unique approach of combining *in situ* measurements of the efficiency of DOC photo-oxidation with time series of optical water type classification results from remotely-sensed ocean colour data, we will contribute to advances in the quantitative assessment of the role of DOC photo-oxidation in the oceanic carbon cycle.

Data Acquisition and Classifier Development

Our first objective is to measure the apparent quantum yield (AQY) for photochemical oxidation of DOC to CO_2 for a variety of optical water types in the Northwest Atlantic. Using our unique multi-spectral approach, we will make the experimental determination of AQY based on the following fundamental photochemical equation describing the production rate of CO_2, dP/dt (moles CO_2 produced $m^{-3}s^{-1}$) as:

$$dP/dt = \int E_d(\lambda)\, a_{CDOM}(\lambda)\, \phi(\lambda)\, d\lambda\ , \qquad (1)$$

where $E_d(\lambda)$ is the incident downwelling irradiance (moles photons $m^{-2}s^{-1}nm^{-1}$), $a_{CDOM}(\lambda)$ is the absorption coefficient of coloured dissolved organic matter (CDOM) (m^{-1}), λ is wavelength (nm), and CDOM is assumed to be the only UV absorbing constituent in our 0.2μm filtered samples by definition. Our method requires measurements of the incident spectral irradiance and the CO_2 production values for each sample irradiated under fourteen long-pass optical filters spaced from 280 to 480 nm. Then using these matrices with an assumed spectral shape for quantum yield, the best fit parameters (m1 and m2) are determined from all sample data simultaneously for the equation:

$$\phi(\lambda) = e^{-(m1+m2(\lambda - 290))}, \qquad (2)$$

where $\phi(\lambda)$ is apparent quantum yield (moles DIC produced/mole photons absorbed). The solution gives the one equation for the AQY spectrum that best fits all of the CO_2 production rate data from 14 samples (each pair of duplicates exposed to different spectral irradiance). This method differs from traditional monochromatic approaches to AQY determination in that the mathematical solution of matrices containing values for $E_d(\lambda)$, $a_{CDOM}(\lambda)$, and dCO_2/dt allows the entire AQY spectrum to be determined in a single irradiation lasting from 4 to16 hrs (depending on UV absorbance), allowing for replication and experimentation on fresh samples at sea. Our photochemical measurements of AQY for DOC oxidation will be associated with at-sea measurements of optical properties for the water type from which experimental samples are collected. This will provide the required context for describing observed variations in AQY spectra.

Our second objective is to refine our satellite-based optical water type classification techniques using *in situ* measurements of inherent and apparent optical properties for each water type, so that they are tailored to our investigation of the relationship between optical water types and photochemical efficiency. In the Northwest Atlantic region, we have identified six optical water types: type **A** waters are largely confined to the Gulf of Maine; water type **B** occurs mostly over Georges Bank; type **C** denotes coccolithophore and sediment-dominated waters; two water types predominate in the Central Mid-Atlantic Bight, type **D** to the north and near the coast, and type **E** farther to the south in the Gulf Stream; type **F** waters occur in the northern Sargasso Sea area. Normalised water-leaving radiances at 443 nm, 520 (or 510) nm and 550 (or 555) nm were extracted from CZCS or SeaWiFS images for 100 randomly selected pixels from each of these six locations; these data were used as a training set for the classifiers (Martin Traykovski and Sosik, in press). Mean spectra are characteristic of each water type (Figure 2).

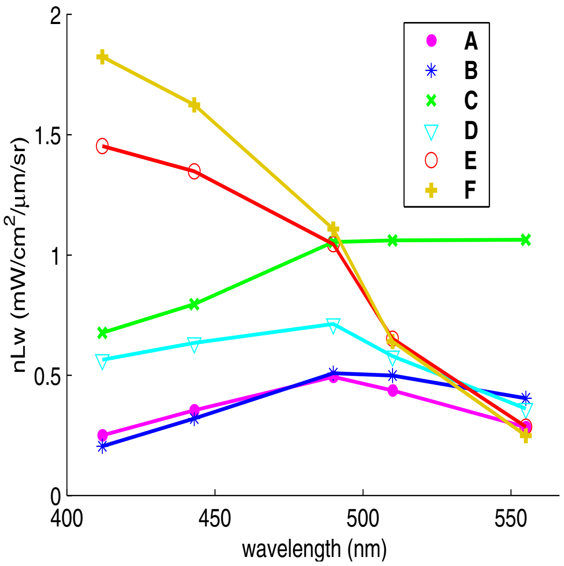

Figure 2. Mean spectra of each optical water type, based on classification of the SeaWiFS imagery from 8 October 1997. Average radiance values were computed for pixels classified in each water type class. In situ sampling of water properties in the Northwest Atlantic will contribute to our understanding of the sources of optical variability that leads to the differentiation of these water types.

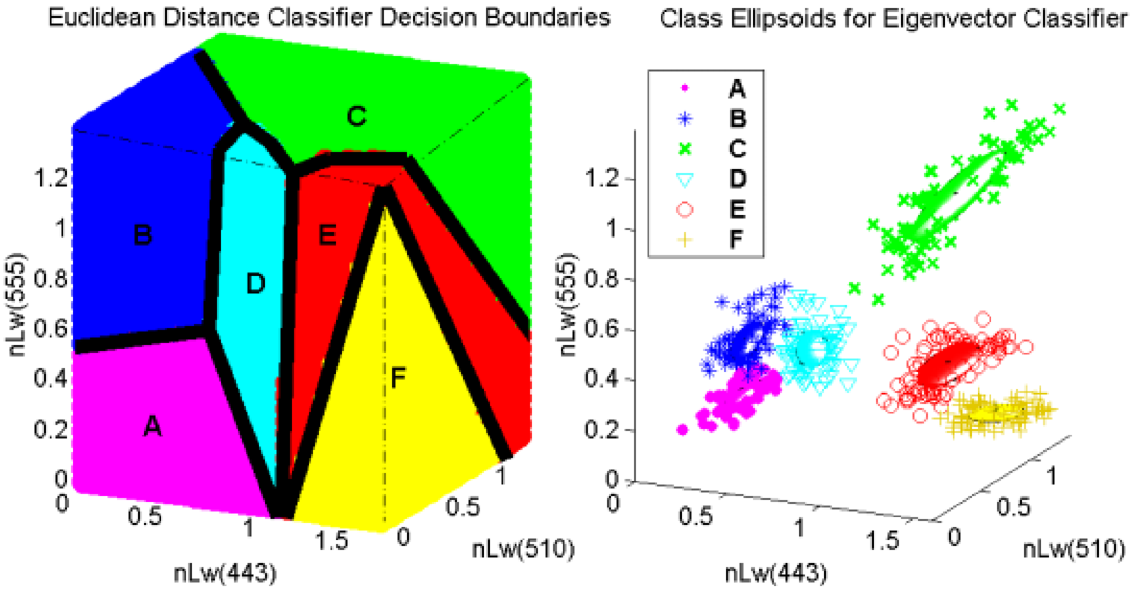

Figure 3. Decision boundaries for the Euclidean Distance Classifier (left); as a result of the Euclidean distance decision rule, the boundaries between water types are defined as planes in three-dimensional space, which project as straight lines in two dimensions. Ellipsoids defining the classes for the Eigenvector Classifier (right); each ellipsoid encompasses one standard deviation of the training data for each class. Classifier training set is shown as discrete points in feature space. Optical water types A and B are confined to the Gulf of Maine/Georges Bank area, types C, D, and E are found in the Central Mid-Atlantic Bight, and type F occurs to the south.

We have implemented two different feature-based classifiers that apply statistical decision criteria to define class boundaries and assign pixels to a particular class. For each water type class i a centroid $\mathbf{m}_i$ is computed as the arithmetic three-dimensional mean of the training data points $\mathbf{a}_{ij}$ for that class. The Euclidean Distance Classifier assigns each pixel $\mathbf{p}_j$ to a water type i on the basis of distance between that pixel and the centroid of each class. The Euclidean distance d_{euc} between a pixel $\mathbf{p}_j$ and a class centroid $\mathbf{m}_i$ is defined as:

$$d_{euc}(\mathbf{p}_j\,,\,\mathbf{m}_i) = [(\mathbf{p}_j - \mathbf{m}_i)^{\mathrm{T}}(\mathbf{p}_j - \mathbf{m}_i)]^{1/2}\,, \tag{3}$$

and the boundaries between water types are defined as planes in three-dimensional feature space (Figure 3 left). With the Eigenvector Classifier, each water type class is defined in terms of an ellipsoid in feature space, the principal axes of which are given by the three dominant eigenvectors of the covariance matrix ($\mathbf{K}$) of the training data in that class:

$$\mathbf{K}_i = \mathbf{A}_i^{\mathrm{T}}\mathbf{A}_i\,, \tag{5}$$

where each row of $\mathbf{A}_i$ is a data point $\mathbf{a}_{ij}$ from the training set for class i. The extent of each class in the three eigenvector directions is represented by the corresponding eigenvalues (Figure 3 right). The distance of a pixel from the centroid of each class is computed in terms of components along the eigenvector directions for that class, and each component is normalised by the corresponding eigenvalue.

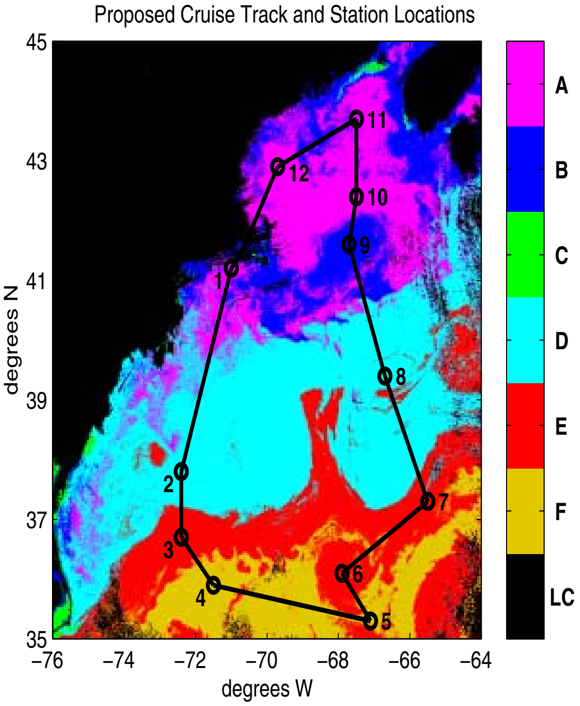

Figure 4. Example cruise track and primary station locations (numbered circles) superimposed on map of water types derived from classification of SeaWiFS data from 8 October 1997. Radiometer, CTD/inherent optical property/water collection casts will be conducted at all stations. Each water type will be sampled at least twice within two hours of local apparent noon. LC (black) indicates land or clouds.

To contribute to our characterisation of these optical water types and increase our insight into the sources of optical variability in the Northwest Atlantic, we are measuring the inherent and apparent optical properties of each water type as part of our work at sea. Our cruises will transit through the Gulf of Maine/Georges Bank region as well as extending far enough southward to cross the Gulf Stream (Figure 4). Station work is conducted within 2 hours of local apparent noon, to correspond with ocean colour satellite overpasses. Two types of profiles are conducted at each station: radiometer casts to measure apparent optical properties, and rosette/inherent optical property casts (see Table 1).

Table 1. Measurements of optical and chemical water properties to be made (with indicated spectral resolution) at stations within each optical water type.

Measured Properties	**Derived Properties**	**Spectral Samples**	**Technique**	**Instrument**
dP/dt (CO_2 photoprod.)	φ (AQY)	n/a	spectral incubations	multi-spectral irradiation system
surface E_d		7 bands[a]	continuous surface radiometry	Satlantic MVD
L_u, E_d	L_w, K_d, R_{rs}	7 bands[a]	depth profiling radiometry	Satlantic SPMR
a_p, a_d, a_{cdom}	a_{phyto}	1 nm res.	spectrophotometry	Perkin Elmer λ-18
a, c, a_{cdom}	b ,a_p	9 bands[b]	continuous depth profiling	WETLabs ac-9
a, b_b		2 bands[c]	continuous depth profiling	HOBILabs a-βeta
chl fluorescence		1 band[d]	continuous depth profiling	SeaTech trans/fluor
phytoplankton pigment conc.	chla chla+carot.	n/a n/a	calibrated fluorometry HPLC	Turner Des. 10-AU Bermuda Biol. Stn.
CO_2 photoprod.	φ (AQY)	n/a	monochromatic incubations by Kieber and Mopper	narrowband spectral irradiation system

[a] 413, 443, 490, 511, 555, 666, 683 nm; [b] 412, 440, 488, 510, 532, 555, 650, 676, 715 nm;
[c] 442, 555 nm; [d] 660 nm

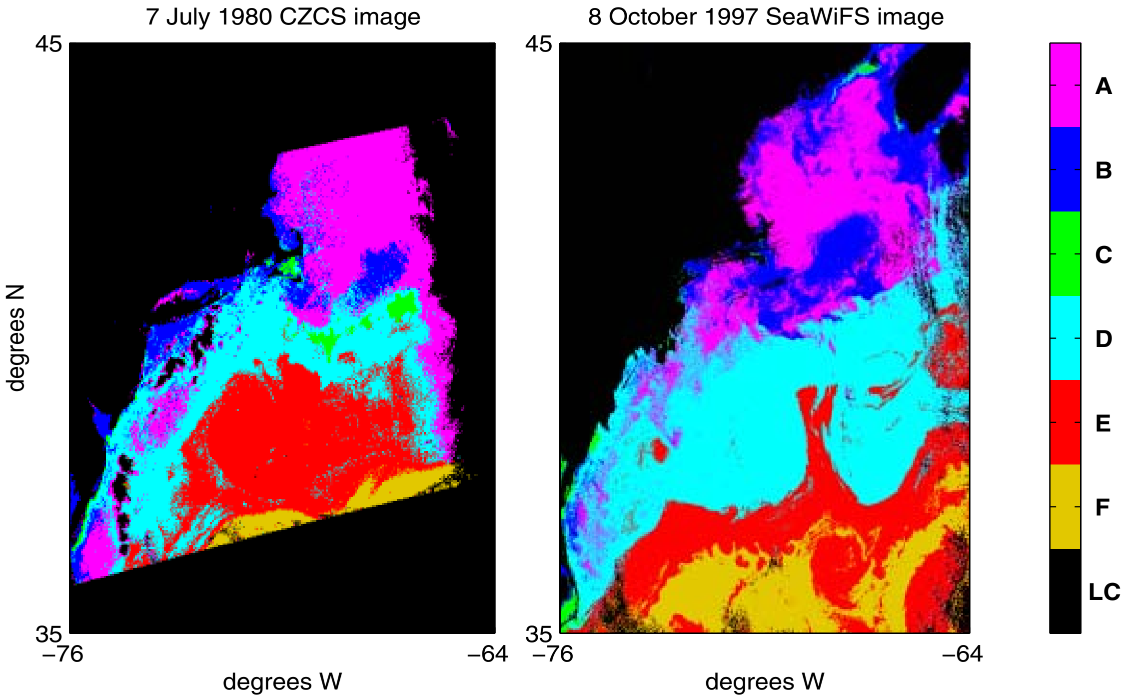

Figure 5. Classification results for the Euclidean Distance Classifier applied to the Northwest Atlantic on two different days: 7 July 1980 (CZCS image, left) and 8 October 1997 (SeaWiFS image, right). The water types are clearly distinguishable, and application of the classifier reveals that they form well-defined water masses. The distribution patterns of these water types are strikingly similar between the two scenes, 17 years apart. Mesoscale physical oceanographic features are apparent; differences may represent seasonal and/or inter-annual variability.

Data Analysis and Hypothesis Testing

Our third objective is to apply our classifiers to satellite images of ocean colour for the Northwest Atlantic region to identify the location and extent of each optical water type. The classifiers will detect water types with different optical signatures and delineate the boundaries between them, mapping the areal coverage of each water type over the time period of our study. We will characterise seasonal and inter-annual variability in the location and extent of each optical water type over the region to establish a context for quantifying the role of DOC photo-oxidation in the carbon cycle. Application of our classifiers to ocean colour imagery of the Northwest Atlantic has revealed striking patterns of water type distribution throughout the region (Figure 5). The water types in each scene are clearly distinguishable, and classifier application to images spanning 17 years reveals that waters of the same optical type form well-defined water masses that remain in the same general geographical regions over time. Once we have established maps of optical water type distribution and areal coverage over the region, we will be poised to test the hypothesis that different optical water types have characteristically different apparent quantum yields for DOC photo-oxidation.

Our final objective is to map DOC photodegradation over the Northwest Atlantic by characterising the relationship between DOC photo-oxidation rates and specific optical water types. This final aspect of the work will be accomplished in two stages. First, we will combine our AQY measurements for CO_2 from DOC photo-oxidation with our satellite-derived optical water type classification results to test our hypothesis that each optical water type has a characteristic AQY for DOC photodegradation. Once we have established a relationship between optical water type and photochemical efficiency of DOC photo-oxidation, we will quantify the magnitude of this carbon sink by using the optical water type distribution patterns resulting from the classification of ocean colour satellite images of the region to determine which AQY spectrum to use for the calculation of CO_2 photoproduction. For each pixel, the appropriate AQY spectrum will be multiplied by the incident irradiance spectrum for that location (computed on the basis of our *in situ* measurements combined with the SeaWiFS PAR product produced by NASA) to obtain the whole water column production of CO_2 from DOC oxidation. Ultimately, our aim is to examine the temporal and spatial variability of photochemical DOC oxidation over the Northwest Atlantic region. Based on the relationships we establish between AQY spectra and optical water properties, we will make predictions of the total regional loss of DOC to photochemical oxidation. This quantitative approach will provide a mechanism by which these types of calculations can be evaluated and incorporated into a new generation of process models that describe DOC cycles in the sea.

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