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PROCEEDINGS OF THE WORKSHOP ON

"CARBON STORAGE IN THE COASTAL ZONE"

Prince George Hotel
Market Street, Halifax, Nova Scotia, Canada

16-17 October 2001

Convened by:

Paul Kepkay
Ocean Sciences Division
Bedford Institute of Oceanography
P.O. Box 1006, Dartmouth, Nova Scotia

October 2001

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Foreword

The purpose of this proceedings is to archive the activities and discussions of the meeting, including research recommendations, uncertainties, and to provide a place to formally archive official minority opinions. As such, interpretations and opinions presented in this report may be factually incorrect or mis-leading, but are included to record as faithfully as possible what transpired at the meeting. No statements are to be taken as reflecting the consensus of the meeting unless they are clearly identified as such. Moreover, additional information and further review may result in a change of decision where tentative agreement had been reached.

Avant-propos

Le présent compte rendu fait état des activités et des discussions qui ont eu lieu à la réunion, notamment en ce qui concerne les recommandations de recherche et les incertitudes; il sert aussi à consigner en bonne et due forme les opinions minoritaires officielles. Les interprétations et opinions qui y sont présentées peuvent être incorrectes sur le plan des faits ou trompeuses, mais elles sont intégrées au document pour que celui-ci reflète le plus fidèlement possible ce qui s'est dit à la réunion. Aucune déclaration ne doit être considérée comme une expression du consensus des participants, sauf s'il est clairement indiqué qu'elle l'est effectivement. En outre, des renseignements supplémentaires et un plus ample examen peuvent avoir pour effet de modifier une décision qui avait fait l'objet d'un accord préliminaire.

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ABSTRACT

The coastal zone is a global sink for carbon fixed by terrestial plants as they draw down CO_2 from the atmosphere. The fixed carbon discharged annually by rivers into the global coastal zone outweighs the carbon stored in deep-ocean basins by a wide margin. In addition, the carbon transport by rivers to Canada's coastline (one of the largest coastal zones on earth) is, by itself, 30% of the carbon stored in deep ocean basins. An international consensus has been building among scientists in Europe, the U.S. and Canada for targeted modelling and field studies to define just how much of this river carbon is stored rather than recycled to CO_2 in coastal regions. Members of the Canadian scientific community concluded that a workshop was needed to coordinate research focussed on the Canadian coastal zone.

The Workshop was held in Halifax during October 2001. National and international experts were invited to give presentations highlighting the challenges of research in the coastal zone. An executive working group was then formed to identify major questions posed by the challenges and develop a research plan to address the questions. These proceedings summarize the presentations made at the Workshop and the final research plan developed by the working group.

RÉSUMÉ

La zone côtière est un puits planétaire du carbone fixé par les plantes terrestres, qui absorbent du CO_2 de l'atmosphère. La quantité de carbone fixe déversée chaque année par les rivières dans la zone côtière planétaire dépasse de loin la quantité de carbone stockée dans les bassins océaniques profonds. Le transport de carbone par les rivières vers la côte du Canada (une des plus vastes zones côtières de la planète) représente à lui seul 30 % du carbone stocké dans les bassins océaniques profonds. Un consensus international s'est formé parmi les scientifiques d'Europe, des États-Unis et du Canada dans le but de procéder à la modélisation et à des études in situ ciblées, permettant de définir exactement quelle quantité de ce carbone transporté par les rivières est stockée au lieu d'être recyclée en CO_2 dans les régions côtières. Les membres du milieu scientifique du Canada ont conclu qu'un atelier était nécessaire pour coordonner les recherches axées sur la zone côtière canadienne.

L'atelier en question a eu lieu à Halifax en octobre 2001. Des experts nationaux et internationaux ont été invités à faire des présentations soulignant les défis de la recherche dans la zone côtière. Un groupe de travail a ensuite été constitué pour mettre en évidence les principaux enjeux associés à ces défis et pour élaborer un plan de recherche connexe. Le présent compte rendu fait état des présentations faites à l'atelier et du plan de recherche final élaboré par le groupe de travail.

EXECUTIVE SUMMARY

The Canadian coastline is one of the longest on earth. The biogenic or fixed carbon that is exported by rivers to this northern coastal zone is at least 30% of the carbon stored in deep ocean basins. This makes the Canadian coastal zone a carbon sink of global proportions. What is missing is a reliable combination of data and models that define the seasonal impact of carbon production and degradation on the exported carbon discharged. As many global planning documents have pointed out, variations in the amount and rate at which carbon is stored in coastal systems can explain long-standing discrepancies between data-based and model-based estimates of CO_2 draw down by land and ocean.

In October 2001 a Workshop was held, allowing Canadian researchers to take advantage of knowledge obtained during recent international programs, develop working relationships with international colleagues and put together a research plan that would meet the requirements of the DFO climate program while enhancing Canadian/international collaborations.

The goals of the Workshop were:

- To review existing knowledge on the processing and storage of carbon in the coastal zone and identify major knowledge gaps.
- To engage biological oceanographers with modellers, river discharge experts, photochemists and benthic biologists in the planning of coastal zone research.
- To aid coordination between current and planned regional and international research programs.
- To develop a research plan focussed on the Atlantic Canada Coastal Zone (ACCZ).

After reviewing the state of knowledge apparent in seven key presentations, an executive working group identified major gaps in our understanding of how the coastal zone operates and outlined a research plan (Appendix III) which included objectives related specifically to carbon processing in the ACCZ.

The working group involved scientists from two government departments as well as national and international centers of coastal zone research. The approach taken by the group followed the format and recommendations of recent UNESCO (IGCP) meetings, eg. "**New Horizons in the Study of the Global Carbon Cycle**" (held in Rome during October 2000).

IGCP has been successful in pinpointing key knowledge gaps in our understanding of the planet's carbon cycle. One of the main observations made during the Rome meeting was that "**variation in riverine transport of carbon in coastal systems must be considered a significant unknown**." The Workshop based its development of a research plan on this IGCP observation.

The plan targeted 4 major topic areas:

- Seasonal carbon discharge by rivers in the Atlantic Canada Coastal zone (ACCZ).
- Seasonal estimates of the photochemical degradation of coastal zone carbon.
- Seasonal estimates of carbon production by coastal phytoplankton and biodegradation of coastal carbon by respiration.
- Estimating carbon respiration and storage in sediments.

The Workshop concluded that with a modest investment, the unique combination of expertise available in DFO, Environment Canada and at Canadian and U.S. universities would provide key information on carbon storage in the ACCZ. This information would be directly applicable to North American and global coastal carbon storage. The research plan required to obtain the information appears in Appendix III.

INTRODUCTION

Even though it is generally accepted that fossil-fuel combustion has resulted in ever-increasing concentrations of CO_2 in the atmosphere, projections of its impact on climate are not certain. One of the greatest uncertainties is the role the world's coastal zone plays in fixing and releasing CO_2.

Deep Ocean Carbon Storage and Carbon Export by Rivers

On a global scale, the ability of ocean plants to fix CO_2 into biogenic carbon has been estimated to be a minimum of $5x10^9$ tonnes carbon per annum. This marine CO_2-fixing capacity is about equal to current estimates of annual fossil fuel emissions (5 to $7x10^9$ tonnes carbon). Even so, there is still uncertainty involved in evaluating the smaller fraction of biogenic carbon (~$1x10^7$ tonnes per annum) that survives burnoff to CO_2 by respiration and photo-oxidation and is stored at depth. Added to this is the far greater uncertainty involved in determining the capacity of coastal zones to store the terrestial carbon exported by rivers. Some estimates (Degens et al 1991) suggest that $34x10^7$ tonnes of carbon per annum are discharged; more recent estimates (Probst 2001) suggest that river export is three times higher (at $100x10^7$ tonnes).

Even though these data suggest that coastal systems are subject to terrestial and marine carbon loads that outweigh deep ocean carbon by at least a factor of 34 - 100, the coastal zone has largely been ignored in models of carbon cycling (Aumont et al. 2000). This oversight should be corrected, especially in light of the fact that Canada has one of the longest coastlines on the planet (Smith and Hollibaugh 1993).

Carbon Storage in the Atlantic Canada Coastal Zone (ACCZ)

Research to date on nearshore carbon dynamics has been focussed on the seaward transport of carbon across the outer margins of continental shelves. Very little to no attention has been paid to carbon in the coastal zone. Rivers draining onto the margins of the Atlantic Provinces carry a high carbon load (Clair and Ehrman 1996). This export of carbon into the Atlantic Canada Coastal Zone (ACCZ) has been extrapolated Canada-wide (Clair et al 1999) and amounts to $14x10^6$ tonnes of carbon per year - about 40% more than the $1x10^7$ tonnes stored in deep ocean basins. This is a globally significant carbon reservoir and certainly merits the attention of the Canadian scientific community.

Expertise on Canada's Atlantic Coast

Research by DFO on Canada's East Coast has been focused on the fixing of CO_2 into biogenic carbon by marine plants and the recycling of the fixed carbon by respiration in water and sediment. All of the expertise developed during this research is of direct relevance to coastal zone work. Added to this is the focus of research in Environment Canada on carbon export by rivers and work at Dalhousie University on photochemistry and its regulation of coastal carbon pools.

In response to this unique collection of expertise, a proposal to hold a workshop was put forward in November 2000 to bring the experts together and also invite international experts to give their global perspective on carbon in the coastal zone - a missing sink of carbon storage at the interface between land and sea.

The issues addressed at the Workshop were centered on 2 questions:

- Is the Atlantic Canada Coastal Zone (ACCZ) a region of net carbon storage ?
- What is the seasonal range of carbon export and degradation in the ACCZ ?

The extended abstracts of the seven key presentations detail how these questions could be answered by data-based and model-based analysis of the ACCZ.

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EXTENDED ABSTRACTS OF PRESENTATIONS

LOICZ Global Modelling of Biogeochemical Processes in the Coastal Zone - A Matter of Scale

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The Land Ocean Interactions in the Coastal Zone (LOICZ) is an on-going project of the International Geosphere-Biosphere Programme (IGBP). One of its aims is to study the global flux of carbon, nitrogen and phosphorous (CNP) from the land, through the coastal zone and into the deep waters of the World's oceans.

The goal is to develop a "Globally Applicable" method of flux estimation that must:

- work with secondary data;
- meet minimal data requirements;
- be widely applicable, uniform methodology;
- be robust; and
- be informative about processes of CNP flux.

The approach is to use water, salt, and "stoichiometrically linked" nutrient budgets to track the fluxes. The steps are:

1. Water and salt budgets are used to estimate water exchange in coastal systems.
2. Departure of nutrient budgets from conservative behavior measures "system biogeochemical fluxes."
3. Nonconservative DIP flux is assumed proportional to (primary production – respiration).
4. Mismatch from "Redfield expectations" for DIP and DIN flux is assumed proportional to (nitrogen fixation – denitrification).

The nutrient (Y) budgets deal only with the internal **dissolved** nutrient net sources or sinks (?Y) to conserve Y.

Calculations are based on simple system Stoichiometry that sssumes:

- Redfield C:N:P ratio of 106:16:1
- (production - respiration) = -106 x ??DIP
- (Nitrogen fixation - denitrification) = ??DINobs - 16 x ?DIP

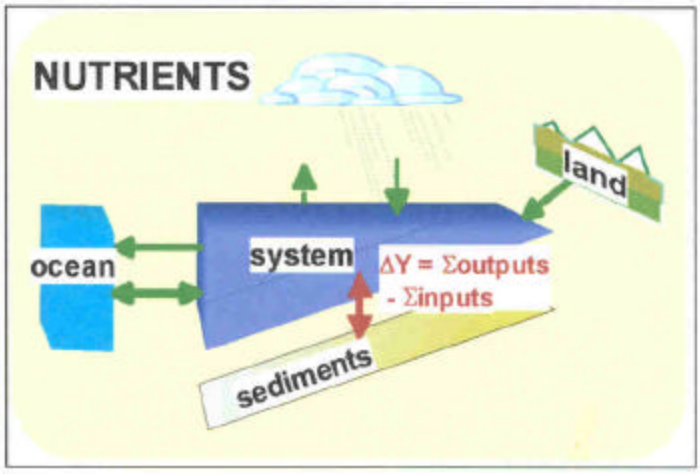

Figure 1. Schematic of LOICZ nutrient budgeting approach.

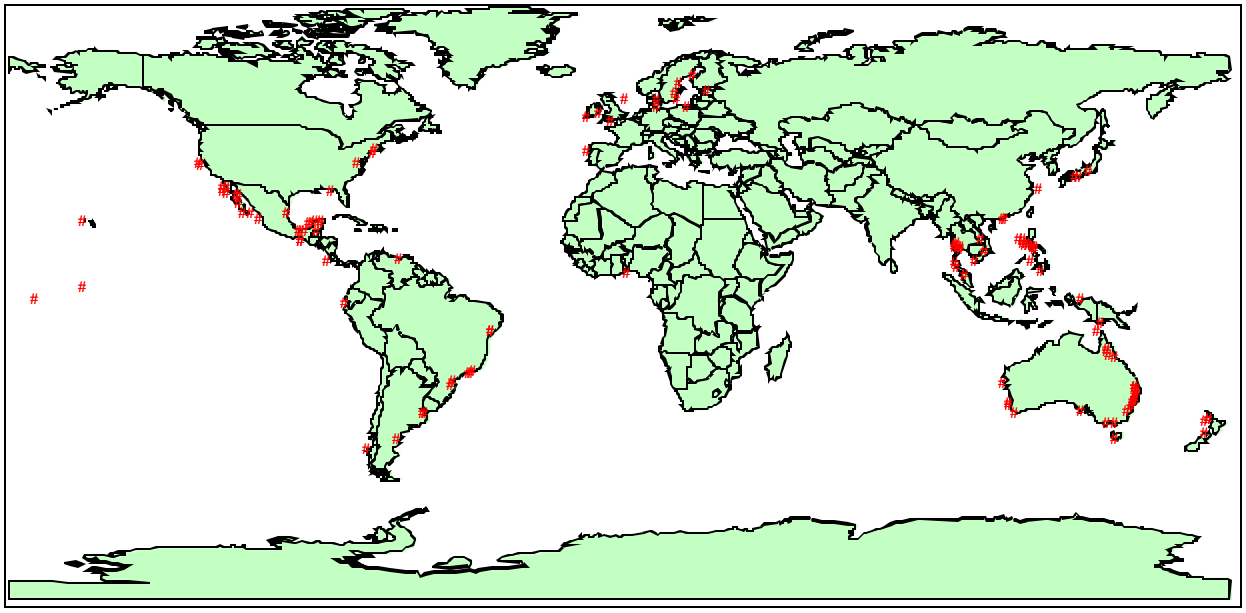

Figure 2. World map showing LOICZ budget sites.

More than 100 sites have been budgeted with this simple robust methodology with the help of many researchers around the world. Numerous workshops have been held to present the LOICZ approach and methodologies, solicit input and assist researchers in developing the budgets. Guidelines, a tutorial, and individual site budgets at: **http://data.ecology.su.se/MNODE/**. The objective of this portion of the LOICZ research is to acquire information for around 200 sites.

To upscale the results from the 100-200 biogeochemical sites to a useful global estimate of CNP fluxes, LOICZ is using typology. This is the study of types, as in systematic classification. The objective is to identify patterns that will allow the limited number of sites with budgets, to estimate the overall function of the World's coastal zone. Global databases, such as rainfall, elevation, agricultural land use, etc., are used to generate values for all sites that can be compared and studied in relation to the budget sites. Much of this information is available from remote sensors.

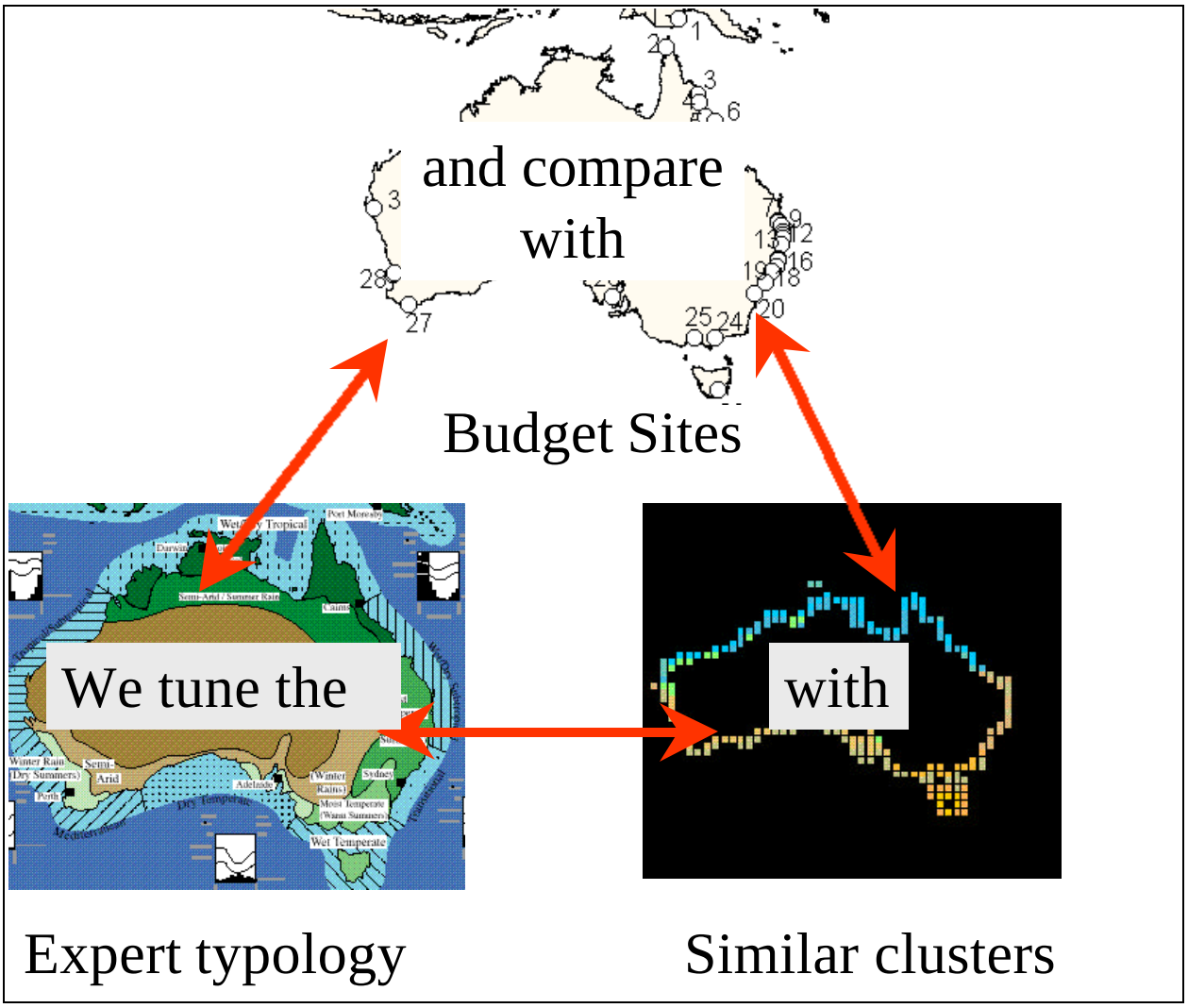

Figure 3. Using expert knowledge and budget sites for upscaling through typology.

The work is still in progress with two major workshops planned:

1) a North American budgeting workshop in association with the ERF Conference in early November; and

2) a major typology workshop scheduled for University of Kansas in mid-November.

LOICZ has begun work on a summary document that will be published in 2002. It will summarise the biogechemical budgeting results and provide a framework for continued LOICZ efforts for the next five years.

Quality and Quantity of Freshwater Carbon Contributed to Estuaries in Atlantic Canada

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To better appreciate the terrestrial contribution of carbon to estuaries in eastern Canada, it is important to clearly define how C is described by limnologists, as well to describe its various forms in lakes and rivers. I summarize the results available in the literature to show the importance terrestrial C export on a global context. Freshwater carbon, especially in the acidic waters of Atlantic Canada can either be in inorganic form as CO2 gas or HCO3-, particulate organic form, or dissolved organic. The particulate and dissolved forms are separated operationally by filtration through a 0.46um GF filter. Freshwater DOM has been characterized in a number of ways. I describe a number of methods for separating and characterizing FW organic C and identify their advantages and disadvantages.

I then report on results of studies done in Atlantic Canada which quantified the amounts of DOC which are exported from Atlantic Canada Rivers. Using data previously published, I show that DOC and dissolved organic nitroogen (DON) can be predicted using two simple regression equations:

$$\text{DOC Export (kg ha}^{-1}\text{ yr}^{-1}\text{)} =$$
$$-54+0.00045(\text{area in km}^2) + 104.7\ (\text{slope in m km}^{-1}) + 0.068(\text{pptn in mm yr}^{-1})$$
$$n=24,\ R^2 = 0.45,$$

and

$$\text{DON Export (kg ha}^{-1}\text{ yr}^{-1}\text{)} =$$
$$0.5 - 0.03\ (\text{slope in m km}^{-1}) + 0.3(\text{pptn in mm yr}^{-1})$$
$$n=24,\ R^2 = 0.3$$

Molar C/N ratios in these waters are very high compared to values from elsewhere due to the poor nature of soils and forests of the region. The median C/N ratio of 24 rivers was 82, with few values below 70 (Figure 1).

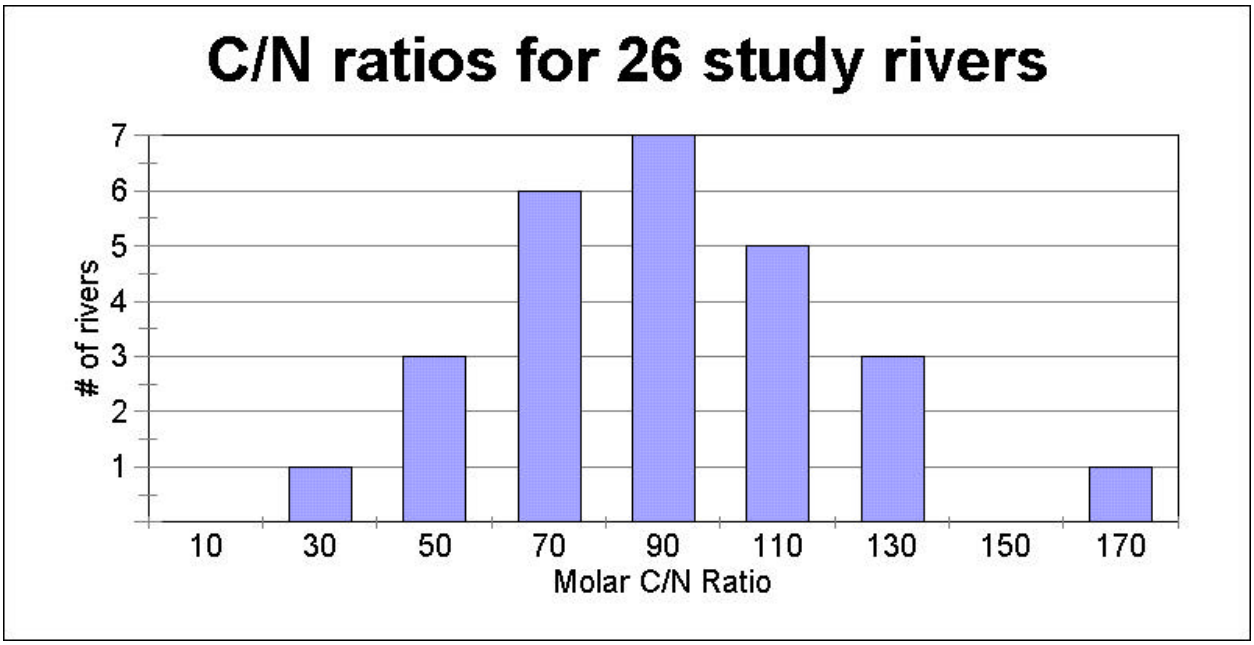

Figure 2. C/N ratios in regional rivers.

In order to get a good picture of the dynamics of DOC and DON losses from terrestrial to aquatic systems, I isolate a case study from 24 Atlantic Canada rivers which were sampled monthly for a 10 year period from January 1983 to December 1992. The Roseway River, located in southwestern Nova Scotia exported 6500 tonnes of DOC and 90 tonnes of DON on average during this study period (Figure 2). Despite the fact that DOC and DON concentrations are greatest in the summer, the greatest exports of both substances is greater in the winter and spring when water flows are greatest (Figure 3).

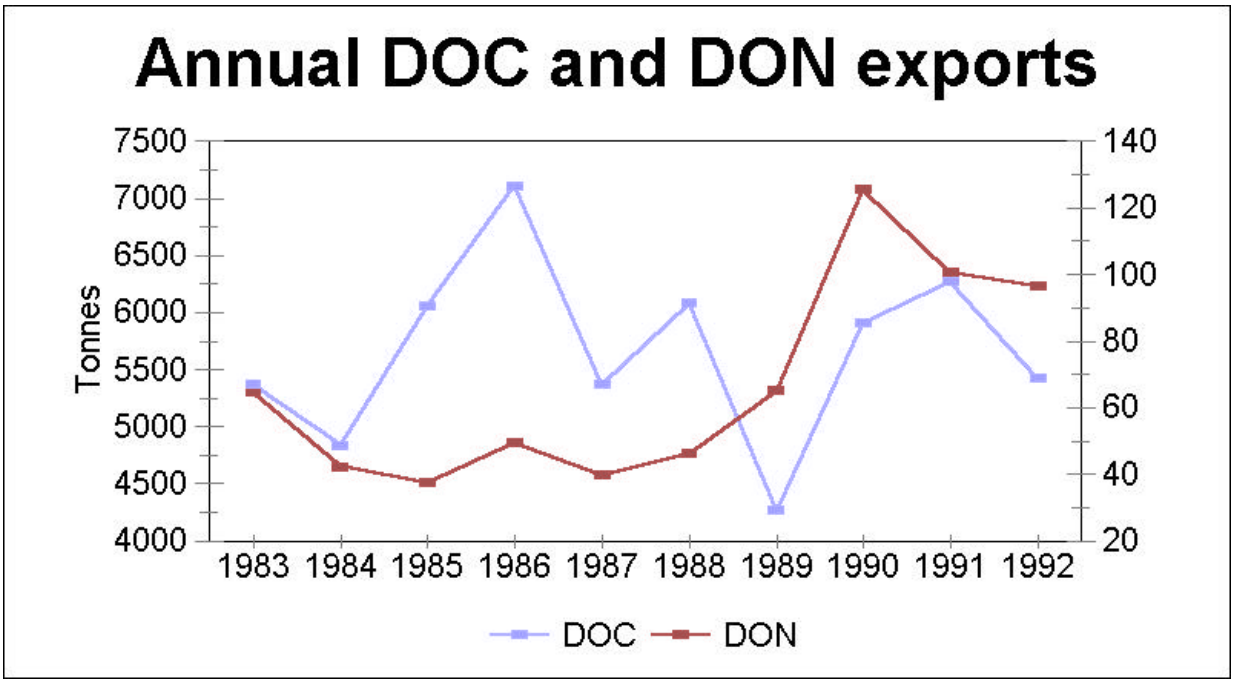

Figure 3.

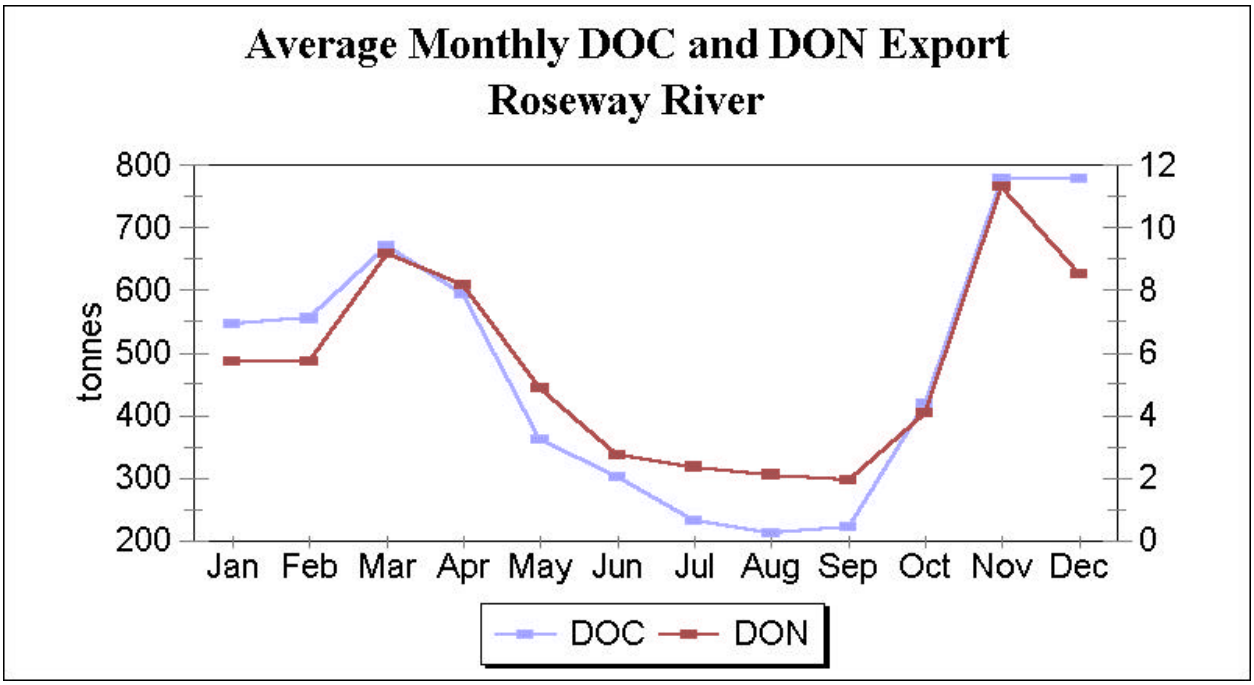
Average Monthly DOC and DON Export
Roseway River
tonnes
800
700
600
500
400
300
200
12
10
8
6
4
2
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec
DOC
DON

Figure 4.

Photochemical Remineralization of Dissolved Organic Matter in the Coastal Zone and its Impact on Carbon Cycling

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Physical and biological processes are historically considered to be the most important factors affecting the carbon cycle in the ocean. Specific processes include air-sea exchange of carbon dioxide, mixing, phytoplankton growth, microbial formation of carbon dioxide, calcium carbonate particle formation, and settling of organic and inorganic carbon particles to the sea floor. Recent studies now suggest that sunlight-initiated (photochemical) processes also affect the carbon cycle in the sea, both directly through formation of dissolved inorganic carbon (DIC) and carbon monoxide (CO) and indirectly through coupled photochemical and biological pathways. To quantify the relative importance of these pathways, we conducted experiments on two cruises (on the R/V Endeavor): the first in the Gulf of Maine and northwest Sargasso Sea (July, 1999) and the other in a transect from the Delaware Bay to the northwest Sargasso Sea (June-July, 2000).

Photochemical production rates of DIC were $\geq$ 50 nM/hr in surface waters at coastal stations in the vicinity of the Gulf of Maine, while rates at the open ocean seawater station (E) were almost a factor of three lower (Fig. 1). Similar results were obtained in the coastal transect during the 2000 Endeavor cruise (data not shown). For both cruises, photochemical production rates of CO ranged from 2-5 nM/hr. Both CO and DIC production rates were strongly correlated to the amount of organic matter in the water, as indicated by its absorbance at 300 nm (Fig. 2). Using solar filters, we determined that approximately 80% of DIC production occurred in the ultraviolet portion of the solar spectrum between 320-400 nm, although some production was also seen between 290-320 nm and at visible wavelengths greater than 400 nm. Based on our results from coastal seawater, we calculated that approximately 1.5% of

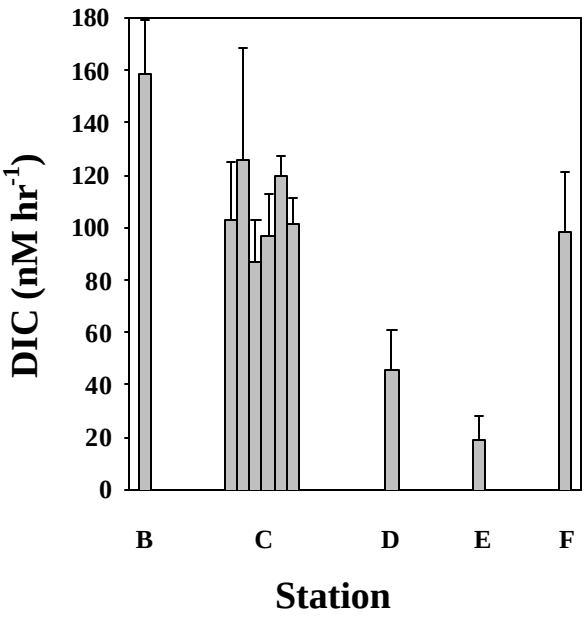

Figure 1. Photochemical production rate of DIC in seawater. Coastal stations B, C and D were in the Gulf of Maine. Open ocean station E was in the continental slope (Oceanographer's Caynon). Coastal Station F was south of Martha's Vineyard, MA.

dissolved organic carbon is directly converted to CO and DIC daily. Thus, approximately 50 % of organic carbon is converted to inorganic carbon in approximately 50 days in surface coastal seawater. This estimate reduces to approximately 25 days when microbial utilization of light-produced substrates is also taken into account. Combining measured CO and DIC photoproduction with measured sunlight-enhanced microbial carbon uptake (production + respiration) yields a total photochemical conversion rate of organic to inorganic carbon of about 3-5 µM-C/day in coastal waters. Based on these results, we suggest that photochemical degradation has a major impact on carbon cycling in coastal waters. On a global scale, we estimate that the photochemical carbon flux is about 5 % of the average for total algal production, and is more than an order-of-magnitude larger than global estimates for carbon settling to marine sediments. Even though our preliminary results indicate that this photochemical carbon flux is large, the quantitative importance of photochemistry in the coastal carbon cycle is not well established. A comprehensive field study is needed to parameterize spatial and temporal variations in DIC photoproduction because conversion rates of dissolved organic carbon into CO and DIC will be important for quantifying how fast non-living organic matter is converted to inorganic carbon in the oceans.

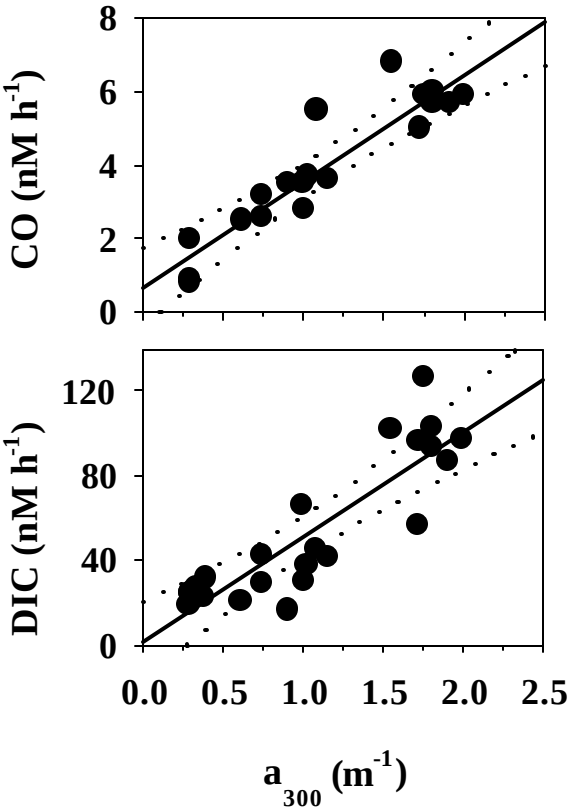

Figure 2. Photochemical production of CO and DIC in sewater as a function of seawater absorbance at 300 nm. The solid line is the best linear fit of the data, and the dashed lines are the 95 % confidence interval.

Evaluating Marine Organic Photochemistry from Space

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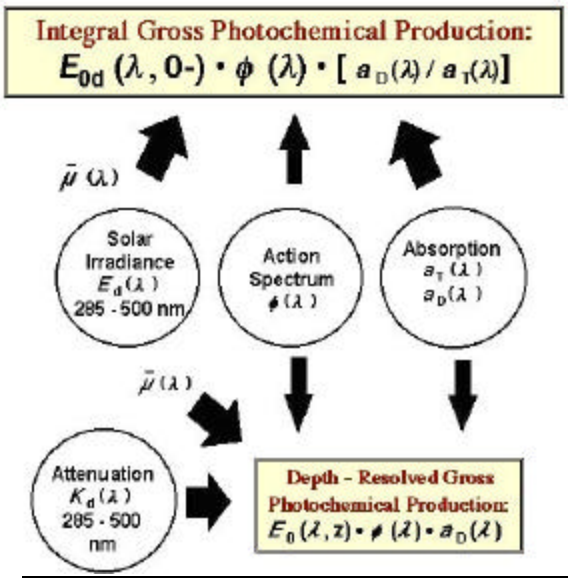
Dissolved organic carbon in the ocean represents one of the largest organic carbon reservoirs on earth. Oxidation of this organic carbon pool represents a process that can exchange carbon with the atmosphere on time scales relevant to global climate change. In spite of its size and potential for impact to global carbon cycles, only about 25% to 50% of the oceanic DOC pool is chemically characterised with the remainder made up largely of heteropoly-condensates derived from *in situ* sources (Lee and Wakeham 1992). 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, the same uncharacterised portion of the DOC, through its role as *the* most significant absorber of UV radiation in the ocean, is the most reactive with respect to marine photochemistry.

The photochemical oxidation of dissolved organic carbon (DOC) is undeniably an important process for carbon cycling in the ocean. A review by Mopper and Kieber (2000) affirms that photochemical oxidation and/or 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 in the sea (Kieber *et al.*, 1990; Miller and Zepp, 1995; Moran and Zepp, 1997). Although there is a vast array of consequences of photoreactions in the ocean (trace metal reduction, O_2 radical production, nutrient generation, reactive trace gas production, loss of UV absorptivity by DOC, etc.), most do not quantitatively impact the cycling of DOC except, perhaps, through their impact on biology.

The singular exception to this generality is the direct "photomineralisation" of DOC to carbon monoxide (CO) and carbon dioxide (CO_2). The direct photoproduction of both CO and CO_2 from DOC represents a mineralisation pathway that bypasses the microbial loop and acts as an independent sink for DOC. Miller and Moran (1997) have shown that CO_2 production averages fifteen times that of CO production for coastal marsh water. The photoproduction of CO_2 appears to be the largest non-biological loss process for DOC in the ocean.



The theoretical relationships shown at left in Figure 1 (symbols defined inside circles; λ = wavelength, 0 = surface, T = total, D = dissolved, d = downwelling) can be used to define photochemical rates in the ocean. To evaluate the significance of CO and CO_2 photoproduction in the coastal zone, this approach can be used if the photochemical efficiencies are defined and if optical relationships

can be established. The action spectra for CO and CO_2 are becoming available. Further, the strong absorbance of coloured dissolved organic matter (CDOM) that drives photochemical reactions in the ocean has been used to establish empirical optical relationships such as those shown below in Figure 2.

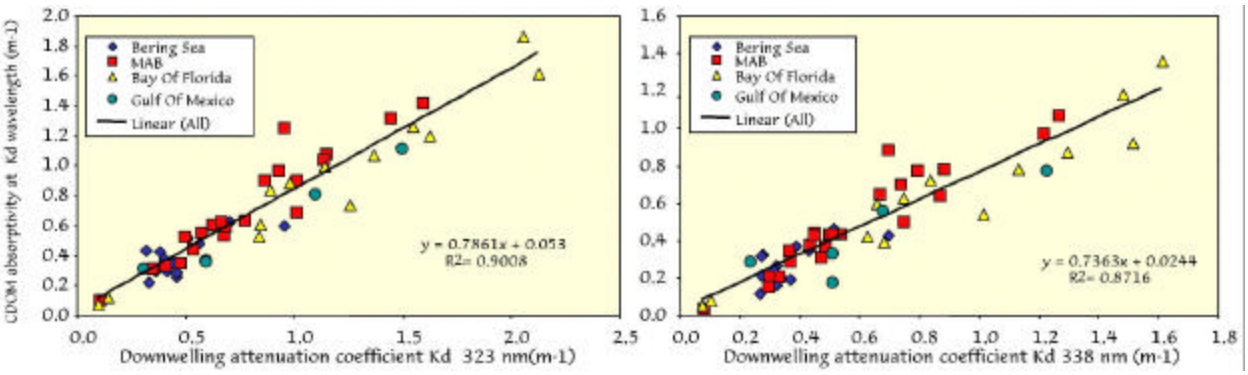


Figure 2. Optical relationships between measured total attenuation and the CDOM absorbance of 323nm and 338 nm radiation in diverse samples.

Accordingly, with data on solar irradiance, ocean optics, and photochemical efficiency, one can directly calculate photochemical reaction rates. Extrapolating from CDOM data contained in SeaWiFS ocean colour data, these rates can be estimated over regional and global spatial scales and over time scales not possible with other sampling approaches. Figure 3 below shows an example of this approach using CO photoproduction.

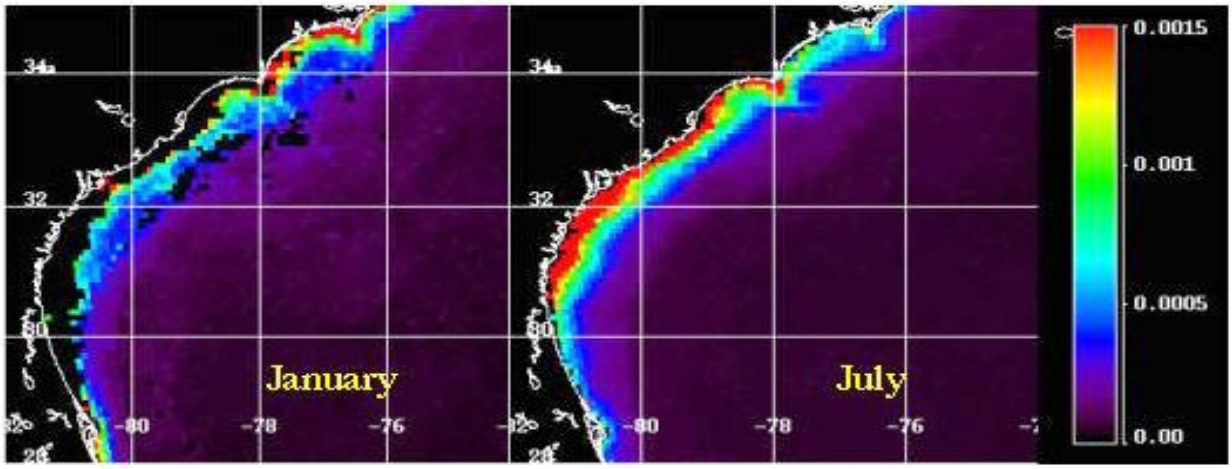


Figure 3. Surface ocean carbon monoxide photochemical production rates (moles C m^{-3} $month^{-1}$) in the Georgia Bight, U.S.A. calculated from SeaWiFS data.

In relation to photochemical processes that control the fate of organic carbon in the coastal ocean, and consequently the storage of terrestrial carbon in the nearshore, accurate optical and solar irradiance data can go a long way toward predicting photochemical rates. The least well-defined parameter in this model is the spectral efficiency data for photochemical oxidation of DOC. Once these action spectra are obtained and examined for their variability, the quantitative

significance of photochemical processes in DOC cycles will become available on every temporal and spatial scale for which remotely sensed data is available. This would represent a great leap in our ability to look at this important process with regard to carbon storage in the sea.

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Interaction of Biological and Photochemical Processes in the Degradation of Terrestrial DOM in the Coastal Zone

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The fate of terrestrial dissolved organic matter (DOM) exported to the coastal ocean is still not well understood, although both biological and photochemical degradation processes are thought to play critical roles. Biological degradation is mediated primarily by bacterioplankton that use the labile components of the DOM pool for growth and respiration. Photochemical processes mineralize DOM to gaseous organic and inorganic photoproducts, including CO and CO_2. There is also evidence of synergistic interactions between these processes, in which DOM is converted from refractory material to biologically labile photoproducts (BLPs) via sunlight, and then removed from the DOM pool by bacterial degradation (Fig. 1).

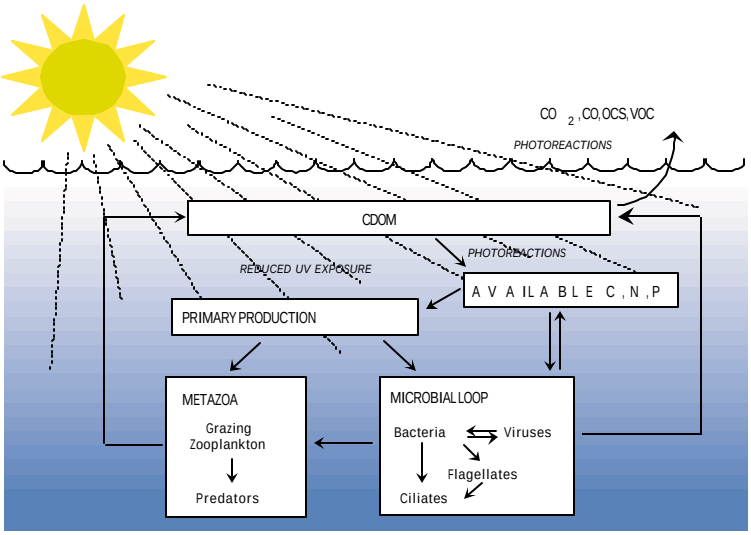

Figure 1. Pathways for biological and photochemical degradation of DOM (from Moran and Zepp 2000)

A survey of recent literature suggests that we don't yet understand enough about the formation of BLPs to predict the chemical identity of the labile photoproducts produced by irradiation of DOM. Of the nineteen identified BLPs formed in freshwater and marine DOM, only 5 have been found in both types of ecosystems, and no clear patterns can be found to explain the distribution pattern of the remaining 14 BLPs. Nor can we easily predict the flux of BLPs in aquatic ecosystems; some sources of DOM do not yield BLPs in measurable concentrations, and still others show net negative effects of irradiation on bacterial activity, suggesting that DOM is made into more refractory forms, rather than more labile forms, upon exposure to sunlight. Current literature suggests, however, that terrestrial DOM, including that exported to coastal oceans, typically forms BLPs.

Predicting the importance of BLP formation for the turnover of DOM in the coastal ocean is made difficult by the complex changes in irradiation regime that occurs horizontally (i.e., with latitude) and vertically (i.e., with depth) in the ocean. Quantum yield spectra are critical tools to deal with this complexity, since they provide information on photoproduct formation rates on a per-wavelength basis. However, no quantum yield spectrum has been available for biologically labile photoproducts before now.

An apparent quantum yield (AQY) spectrum was recently calculated for two coastal ecosystems in the southeastern U.S. using a cut-off filter method to model spectral dependence and bacterial respiratory activity as a bioassay for BLP formation (Fig. 2). Applying the AQY to continental shelf waters of the southeastern U.S., BLP formation was estimated to be 3.2 M C d^{-1} on a clear summer day, a rate potentially sufficient to supply 80% of the bacterial carbon demand. BLP formation rate is calculated to decrease rapidly with depth, however, due to the absorption of UV-A and UV-B radiation in the water column; at a depth of 4 m the rate is only 1/20th that of the surface. By assuming a similar AQY for all terrestrial DOM, the global distribution of BLP formation in coastal waters can be modeled. Using this approach, BLP formation was estimated to be highest in tropical and subtropical regions of the globe (where irradiance is high) as well as at northern latitudes (where continental shelf area is great).

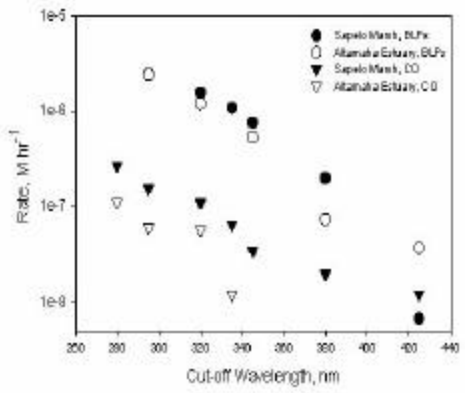

Figure 2. Spectral dependence of DOM photoproduct formation rates in a southeastern U.S. coastal marsh (from Miller et al. 2002).

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Plankton Production and Respiration:
A Comparison of Open Ocean and Coastal Environments

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A Need to Define Ecosystem Productivity - Gross versus Net Production:

The primary (light-driven) production of biogenic carbon by the phytoplankton is the basic driving element of any marine ecosystem. The carbon is food for zooplankton in the water column and for animals in and on the sediment. Nearly all estimates of carbon production by the phytoplankton are based on standard measurements of total or gross primary production.

Unfortunately, gross production is not an accurate measure of the carbon that is actually available to the ecosystem. Another process - plankton respiration - has to be taken into account because it drastically reduces available carbon loads. In results obtained from the Gully on the Eastern Scotian Shelf (Fig. 1), respiration not only reduces production by at least a factor of 4, it also leads to a different distribution of net versus gross production (Kepkay et al., 2001). This is an important ecological issue because net production is the ecologically useful parameter - defining the carbon made available rather than the total carbon produced.

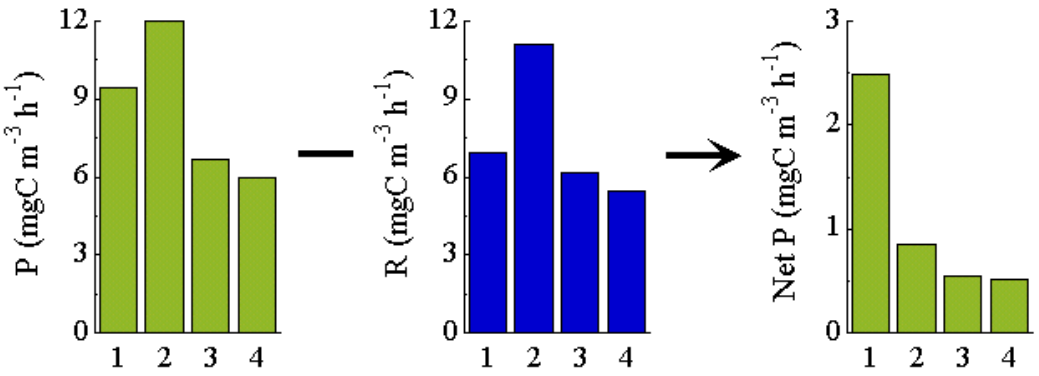

Figure 1. Relationship between gross and net production (green) in surface waters from a transect of 4 stations in the Gully marine protected area. Note the effect of respiration (blue) as it reduces the carbon generated by gross production to the carbon made available to the ecosystem as net production.

The Labrador Sea - A Seasonal Succession of Production and Respiration:

Production and respiration in this climate-sensitive region of the world's ocean follow a seasonal succession (Kepkay and Bugden 2001). High productivity during May at the beginning of the growing season gives way to respiration by October (Fig. 2). A five-fold decrease in production during this transition is accompanied by a three-fold increase in respiration. This means that an environment dominated by net production in May gives way to an environment dominated by the net consumption of carbon by October. Production and respiration are not always (if ever) "in balance". As a result, the seasonal transition from production to consumption of carbon can be far greater than year-to-year variations in production.

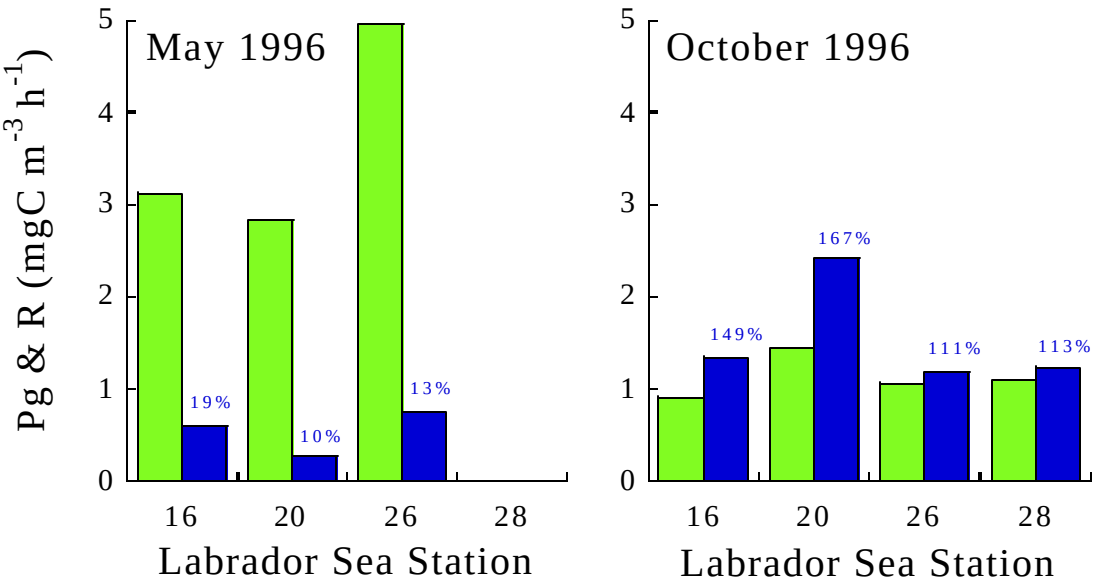

Figure 2. Gross production and respiration on the AR7W section in the Labrador Sea. Note the seasonal transition from an environment of net production during May (where respiration is 10-19% of production) to an environment of net consumption during October (when respiration is 111-167% of production).

Coastal Oxygen Depletion and Biological Oxygen Demand:

In coastal regions, such as those associated with finfish aquaculture in the Bay of Fundy, respiration can outstrip gross production by a wide margin (Fig 3) as the coastal ecosystem is exposed to terrestial and man-made carbon loads (Kepkay, 2001). The biological oxygen demand (BOD) created by this high respiration then becomes a critical issue to the point where it can seasonally-deplete oxygen concentrations in the water column to levels where fish development and growth is compromised (Page and Martin 2000).

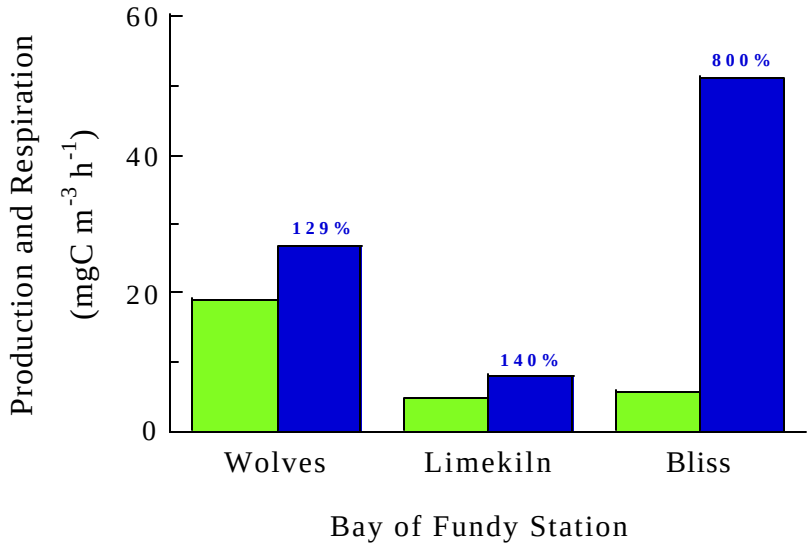

Figure 3. Gross production (green) and respiration (blue) at a coastal control station (the Wolves) and in coastal sites (Limekiln Bay and Bliss Harbour) associated with salmon aquaculture in the Bay of Fundy. Note the predominance of respiration (outstripping production by as much as 800%) as the coastal plankton in surface waters adapt to the riverine and man-made carbon loads. These coastal BODs are a good deal higher than those found in the Gully and the Labrador Sea.

Biological Oxygen Demand - A Major Consumer of Carbon in the Coastal Zone:

Together, the data from offshore and coastal ecosystems suggest that respiration by the planktonic ecosystem can change by at least a factor of 60 in response to changes in phytoplankton production and terrestial carbon loads. However two additional coastal zone processes should be taken into account:

1) Photochemical oxidation, which should be at least as important as respiration in the consumption of terrestial loads carried by rivers.

2) The BOD of sediments which, again, should be at least as important as plankton respiration in the processing of rapidly-settling carbon loads.

With carefully-coordinated, seasonal measurements of planktonic, benthic and photochemical oxygen demand, it should be possible to accurately define the amount of terrestial carbon that remains after passing through these 3 consumption processes to be stored in the coastal zone.

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Benthic Metabolism and Carbon Storage in Coastal Sediments

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Energy flux through natural biological systems can be measured as either synthetic (anabolic) or degradative (catabolic) processes. Organisms use diverse methods to accumulate energy thus total production by all organisms in a natural community is difficult to measure. Energy release, however, occurs through a series of aerobic or anaerobic metabolic processes that are more directly measured. All catabolic reactions involve exothermic biochemical reactions and thus heat production (measured by calorimetry) can be used to quantify total metabolism. O_2 uptake and CO_2 release (respirometry) can also be used to estimate oxidative (aerobic) and anaerobic ($SO_4^{=}$ and $NO_3^{=}$ reduction and denitrification) respiration.

Measurements of respiration in ecological systems can be used to test the idea that mature ecosystems are organized to maximize community respiration (Washida 1995). The Maximum Respiration Hypothesis (MRH) asserts that the development of ecological systems follows two thermodynamically-based principals: (1) as ecosystems mature they increase total energy dissipation, develop more complex structures and increase in diversity, and (2) ecosystems develop an organizational structure that maximizes community production and respiration.

Measurements of respiration (O_2 and CO_2 flux across undisturbed sediments) have been used to determine metabolic rates of integrated benthic communities in sediments (Hargrave 1980, Graf 1992). The method quantifies how sedimented products from pelagic production are utilized through aerobic and anaerobic respiration by an entire benthic community and what fraction of settled organic carbon is buried (Figure. 1)

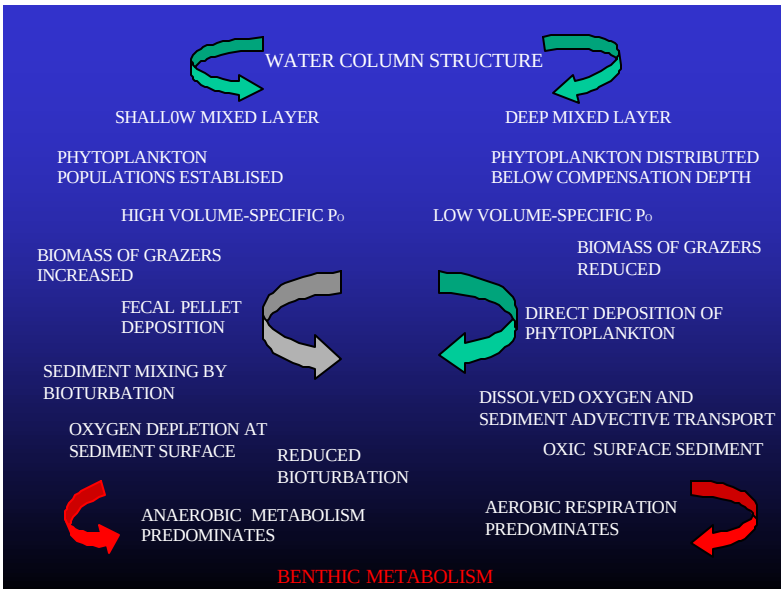

Figure 1. Relationships between processes affecting the supply and metabolism of particulate matter in sediments (from Hargrave 1980). Benthic metabolism (decomposition of organic matter by aerobic and anaerobic processes in sediments) is coupled to pelagic production by physical and biological properties in the water column. Potential transport by DOC and vertically migrating organisms are not shown.

A complete description of carbon cycling between sediment and water requires knowledge of cycling of both dissolved and particulate organic matter (Roden and Tutle 1996). However, organic carbon fluxes to sediments are usually only determined for particulate organic carbon. Thus, benthic carbon fluxes may be underestimated if consumption of dissolved organic matter is not considered.

Total benthic metabolism is also estimated if reduced by-products of anaerobic respiration accumulate in sediments (Mucchi et al. 2000, Silverberg et al. 2000). Thus profiles of H_2S and FeS and organic matter in core profiles are required to interpret measured gas fluxes. Some reduced sulfide can diffuse to the sediment surface to be oxidized by downward oxygen diffusion. Respiratory and burrowing activity of benthic macrofauna and tidal pumping also cause pore water advection and in many cases this is of equal importance to molecular diffusion for transport of dissolved substances across the sediment-water interface (Shum and Sundby 1996). Observations in some studies have shown that calculated (advective plus diffusive) fluxes from gradients within sediments measured with micro-electrodes are similar to observed *in situ* rates measured with benthic (bell jar) chambers (Silverberg et al. 2000).

Annual estimates of organic matter supply from sedimented products of phytoplankton primary production, benthic O_2 uptake and CO_2 release and organic matter (carbon) burial have been made in different aquatic coastal systems. Comparisons of results, in the form of mass balance calculations, show that decomposition and burial of organic carbon within surface sediments is not linearly related to rates of particle flux (sedimentation) or with primary production in surface waters (Emerson et al. 1985).

General empirical relations between phytoplankton production, particulate organic carbon sedimentation and the degree of degradation and remineralization at the sediment-water interface can be made using published data from various coastal and offshore ocean areas (Parsons et al. 1984). The empirical equation

$$C_s = 27\ [PP_o / Z]^{0.935} \qquad (1)$$

summarizes estimates of annual sedimentation (C_s)(g C m^{-2} y^{-1}) and the ratio of phytoplankton production (PP_o): water column depth (Z)(m). Organic carbon supply to coastal sediment would be expected to be greater than that at deeper depths due to respiration in the water column of material during sedimentation and the empirical data quantifies this relationship. C_s would amount to approximately 5 to 20% of annual phytoplankton production over the continental shelf off eastern Canada.

Depending on location within the coastal zone, on the continental shelf or beyond the shelf break, total benthic metabolism (respired carbon) may amount to from 5 to 20% of phytoplankton production (Parsons et al. 1984). The empirical expression

$$C_o = 55\ [C_s / Z_m]^{0.39} \qquad (2)$$

derived from published data shows from that benthic oxygen consumption (C_o)(l O_2 m^{-2} y^{-1}) is inversely related to mixed-layer depth (Z_m) (depth of the thermocline (*m*) during stratification),

and directly correlated with annual phytoplankton production (organic carbon supply through sedimentation) (C_s)(g C m^{-2} y^{-1}).

These empirical relationship suggest that organic carbon supply and consumption are closely linked in continental shelf environments. The efficient utilization of organic matter that reaches sediments is consistent with ecosystem structure that maximizes respiration and the observation supports the MRH described above. The test that this is the case is to determine if carbon storage (burial) in sediments is a small fraction of the total sedimented onto the seabed.

Empirical relationships between organic carbon sedimentation (C_s) and seabed oxygen consumption (C_o) (Müller and Suess 1979, Parsons et al. 1984, Emerson et al. 1985) have been described to show that both variables decrease with increasing depth and are positively correlated with phytoplankton production. The empirical expression

$$C_B = 8.4\ [PP_o / Z]^{1.37} \qquad (3)$$

describes the general relationship between organic carbon burial (C_B)(g C m^{-2} y^{-1}), phytoplankton primary production (PP_o)(g C m^{-2} y^{-1}) and water column depth (Z)(*m*). Direct observations of carbon accumulation in sediments using ^{210}Pb dating to determine the carbon burial rate and the fraction of sediment organic carbon preserved (Müller and Suess 1979) can be compared with organic carbon burial determined indirectly as the difference between annual organic carbon sedimentation and benthic respiratory demand. Most of the organic carbon deposited on the seabed is degraded. A small fraction (usually <a few percent percent of annual sedimentation in oxic shelf environments) is refractory to consumption and is buried within the sediment. The observations support the MRH by confirming the efficient respiration of deposited organic carbon.

Sampling carried out at several stations along the Halifax section, Scotian Shelf between 1987 and 1990 (data from various sources summarized in Fig. 2) provides observations to compare measured organic carbon flux into sediment traps, benthic respiration, macrofauna biomass (and calculated production from production:biomass ratios), and organic carbon in surficial sediments that can be used to test the generality of these empirical equations by application to the Scotian Shelf continental shelf and slope.

Measurements of phytoplankton production for the Scotian Shelf and slope regions are available from various sources (Fournier et al. 1977, 1979, Mills and Fournier 1979, Perry et al. 1989, Mousseau et al. 1996). These data show that organic carbon flux into sediment traps (5 to 15 % of PP_o) is within the range of values predicted from equation (1). Measured POC flux from the water column is less than estimated values for benthic respiration at shallow (110-150 m) and deep (1000-1500 m) ends of the transect (Fig. 2). POC supply and benthic respiration are approximately balanced at mid-shelf depths (depths of 275 to 500 m), while flux greatly exceeds benthic demand at the 700 m station. With the exception of the higher value at the 700 m station, macrofauna production (calculated from standing crop biomass) and POC in surface sediment show an inverse trend with increasing depth at depths >275m.

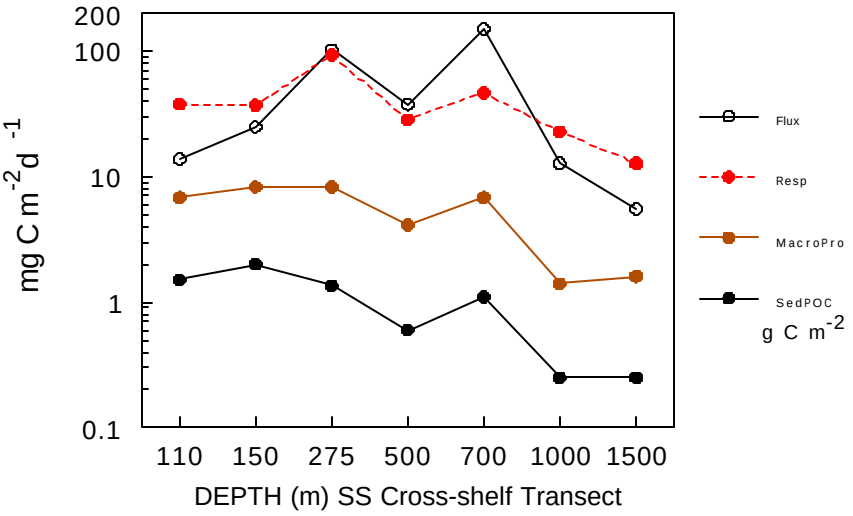

Figure 2. Cross-shelf transect (Halifax section), Scotian Shelf (SS) of measured or estimated particulate organic carbon vertical flux (250 to 500 m), benthic oxygen consumption and macrofauna production (mg C m^{-2} d^{-1}) and storage of organic carbon in sediment (upper 5 cm) (g C m^{-2}). The logarithm scale on the y-axis allows data for different variables to be combined on one graph. Data summarized from (Boudreau and Merrett 1993, Boudreau et al. 1998, Desrosiers et al. 2000, Emerson et al. 1986, Grant and Schwinghamer 1987, Grant et al. 1987, Grant et al. 1991, Grant et al. 1999, Grehan et al. 1994, Hargrave and Peer 1973, Hargrave 1974, Hargrave 1980, Hargrave 1984, Hargrave 1995, Mills 1980, Mills and Fournier 1979, Mucchi et al. 2000, Pocklington et al. 1991, Romero et al. 2000, Shum and Sundby 1996, Silverberg et al. 2000, Stewart et al. 2001, Wildish et al. 1989).

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APPENDIX II – WORKSHOP AGENDA

TUESDAY, 16 OCTOBER 2001

09:00 - 09:15 - Introduction - Overview of the Workshop's aims and schedule

09:15 - 10:00 - Paul Boudreau (DFO,BIO) - LOICZ global modelling of biogeochemical processes in the coastal zone - a matter of scale

10:00 - 10:30 - BREAK

10:30 - 11:15 - Tom Clair (Environment Canada) - Quality and quantity of freshwater carbon contributed to estuaries in Atlantic Canada.

11:15 - 12:00 - David Kieber (State University of New York) - Photochemical remineralization of dissolved organic matter in the coastal zone and its impact on carbon cycling.

12:00 - 13:00 - LUNCH

13:00 - 13:45 - William Miller, Sophie Johannessen and Cedric Fichot (Dalhousie University) - Evaluating marine organic photochemistry from space.

13:45 - 14:30 - Mary Ann Moran (University of Georgia) - Interaction of biological and photochemical processes in the degradation of terrestrial DOM in the coastal zone.

14:30 - 15:15 - Paul Kepkay, Glen Harrison and Jay Bugden (DFO, BIO) - Plankton production and respiration: A comparison of open ocean and coastal environments.

15:15 - 15:30 - BREAK

15:30 - 16:15 - Barry Hargrave (DFO, BIO) - Benthic metabolism and carbon storage in coastal sediments.

WEDNESDAY, 17 OCTOBER 2001

09:00 - 10:00 - General Discussion of the Key Elements that need to be applied to the Canadian coastal zone

10:00 - 10:30 - BREAK

10:30 - 12:00 - Development of a Research Plan based on 2 main questions:

1. Is the Atlantic Canada Coastal Zone (ACCZ) a region of net carbon storage ?

2. What is the seasonal range of carbon export and degradation in the ACCZ ?

12:00 - 13:00 - LUNCH

13:00 - 14:30 - Initial presentation and discussion of the project elements required for an ACCZ Research Plan.

14:30 – 15:00 - BREAK

15:00 - 16:00 - Presentation of a Summary Science Plan for research in the ACCZ.

APPENDIX III - SUMMARY SCIENCE PLAN FOR RESEARCH ON CARBON STORAGE IN THE ATLANTIC CANADA COASTAL ZONE (ACCZ)

MAJOR QUESTIONS AND RESEARCH GAPS

The Workshop Executive was presented with two questions. Their answers to the questions were summarized to highlight research gaps and develop a science plan for research on carbon processing and storage in the ACCZ. The questions and associated research gaps are outlined below:

1. Is the ACCZ a region of net carbon storage ?

- If it is assumed that only 1% of the carbon exported by rivers into the ACCZ survives photochemical and biological degradation in the water column and at the sediment surface, there are still 6000 tonnes C per year that could potentially be stored in sediments.
- Despite this potential for carbon storage, there is no information on the actual storage of carbon in the sediments of any one river basin in the ACCZ that can be linked to carbon export to the same basin.

2. What is the seasonal range of carbon export and degradation in the ACCZ ?

- Estimates suggest that seasonal river carbon export can vary by as much as 600 tonnes C per month.
- There is good evidence for strong seasonal variations in phytoplankton production and respiration in the open ocean. There are no equivalent seasonal measurements in the ACCZ
- Global estimates also suggest that the photo-oxidation of terrestial C is important. Yet there are no seasonal estimates of photo-oxidation.
- Carbon export, production, respiration and photo-oxidation work together to regulate carbon storage. However, the four processes also follow seasonal cycles that are not in phase, making it an impossible task to predict their combined effect without actual measurements. As a result, seasonal co-ordinated measurements of export, production, respiration and photo-oxidation are required in a representative river estuary that can be scaled up to the ACCZ.

RESEARCH PLAN

In order to fill the research gaps highlighted by the workshop, a three-year research plan was developed to establish the magnitude of carbon storage and establish the main processes that regulate storage in the ACCZ. The research would, by necessity, require the co-ordinated efforts of biological, photochemical and benthic oceanographers.

Year 1 - Identify Type River and Quantity/Quality of Carbon Export

- Existing data utilized to identify a river that is typical of the ACCZ watershed and is also typical of the carbon exported to the ACCZ.
- Total carbon, C:N, watershed characteristics (drainage area, particle load, agricultural input) and a river classification system used to define the type river.
- Type river sampled for carbon, nitrogen, nutrients, ions and UV absorbance (colour) on weekly to monthly intervals.

- Multibeam (EM3000) acoustic survey to identify the depositional basins associated with sediment deposition by the type river.

Year 2 - Seasonal Variations of Photo and Bio-Processing of Carbon

- Seasonal measurements of carbon processing in the type river during spring (April), Summer (July), Fall (October) and Winter (January)
- River flow sampling at weekly (spring), monthly (summer), weekly (late fall) and monthly (winter) intervals for carbon, nitrogen, nutrient, ion and UV absorbance measurements.
- Carbon-processing measurements - including production, respiration, photochemical degradation, biologically-labile photoproducts (BLPs) and photochemistry optics (inwater and surface spectral irradiance).
- Year-long incident light measurements (at a station established on the type river).
- Sediment sampling in depositional basins for carbon and nitrogen analysis for ground-truthing multi-beam acoustic data.

Year 3 - Data Synthesis and Scaling Up of Data to ACCZ

- Year-long data on river outflow characteristics (Years 1 and 2) linked to process measurements (Year 2).
- Scaling-up of data on carbon export to ACCZ using established carbon export (neural network-based) models.
- Scaling up of carbon deposition to ACCZ using established empirical models.