### Deep sea gradients in [DOC]





Figure 1 World map depicting locations sampled for the survey. Station locations are given in Table 1.



#### NMR and carbohydrate analyses of deep sea HMWDOC



monosaccharide distribution

#### NMR and carbohydrate analyses of deep sea HMWDOC

<sup>13</sup>C- and <sup>1</sup>HNMR of HMWDOC from deep samples in the Atlantic and Pacific Oceans appear to be very similar, suggesting similar composition throughout the deep ocean



### [DOC] can vary in space and time in the ocean due to changes in DOC production



### Production of DOC by phytoplankton in laboratory culture



Mague et al, 197X

#### Photosynthesis and excretion of photosyntheitc products during logarithmic growth of axenic algal cultures

#### Dunaliella tertiolecta

Hours	90	114	138	152
POM	9600	38600	103000	280000
DOM	373	1360	4140	11400
DOM(% total)	3.7	3.4	3.8	3.9

#### Skeletonema costatum

Hours	90	114	138	152
POM	9190	46400	116000	484000
DOM	457	1230	6700	28200
DOM (% total)	4.7	2.6	5.5	5.5

#### Monchrysis lutheri

Hours cells/ml	59 6530	71 11700	83 20200	108 57000	120 90500	163 576000
POM	3680	7070	12800	43200	68000	353000
DOM	86	134	320	1110	1710	10000
DOM (% total)	2.3	1.9	2.4	2.5	2.5	2.8

## Rate of CO<sub>2</sub> fixation and excretion of photosynthetic products

Incubation time	depth	Total CO <sub>2</sub> fixation (µg C/I day)	Excretion (µg C/I day)	%Excretion
6/9				
07:45-12:30	0	5.7	< 0.04	<1
	10	5.4	< 0.04	<1
	50	7.0	<0.04	<1
13:15-17:55	0	6.7	0.11	1.6
	10	6.1	0.13	2.1
	50	12.7	1.30	10
6/11				
15:00-19:45	0	3.3	0.55	17
	10	2.2	0.50	23
	50	2.3	0.37	16
6/12				
08:00-13:00	0	4.1	0.42	10
	10	3.1	0.09	3
	50	6.9	0.41	6
7/23				
08:15-15:15	0	3.1	0.25	8
	10	2.2	0.20	9
	50	3.4	0.22	7
14:10-19:10	0	1.7	0.04	2
	10	2.5	0.06	3
	50	3.5	0.14	4
7/24				
09:00-13:30	0	2.5	0.10	4
	10	3.0	0.36	12
	50	2.6	0.17	7
		4.3	0.26	7



# Production of DOC during grazing by macrozooplankton

Production of DOC in laboratory culture grazing experiments



<sup>14</sup>C activity with time for Calanus pacificus feeding on labeled Thalassiosira fluviatilis.

#### DOC dynamics in a simulated algal bloom



Most DOC accumulation occurs after nutrients are exhausted (bloom crashes)

During early log phase growth DOC is being respired by bacteria

Two pools of DOC, reactive and nonreactive (timescale of exp!). Are they being produced by two different classes of microbes?



## Production of reactive and non reactive DOC by phytoplankton and bacteria



#### DOC cycling and bacterial production in the ocean



DOC is the presumed substrate that supports bacterial metabolism in seawater.

There are three "types" of DOC that Occur in seawater:

Very reactive DOC- supports bacterial Production

Reactive DOC that is produced and Accumulates in surface seawater. Lost During convective mixing.

Non reactive DOC (most DOC)

#### Bacterial production and Bacterial Carbon demand

Bacteria are believed to be the principal sink for DOC in seawater. DOC fuels free-living bacterial production (BP) of biomass It is assumed that bacteria can out compete phytoplankton for nutrients, and that bacteria are substrate (C) limited.

Bacterial production is most often measured by changes in cell #s in a sample over time, or the uptake of <sup>3</sup>H-leucine to measure protein synthesis or <sup>3</sup>H-thymidine to measure nucleic acid synthesis.

Current estimates of global bacterial production have a wide range of values, but a mean of about 15% PP.

Bacterial production is the product of bacterial carbon demand (BCD) and efficiency. Estimates of bacterial efficiency also vary from About 10-50%. Therefore BCD may be 30-50% of PP.

#### Is there enough production of DOC to support BCD?



Carlson and Ducklow. DSR (1995)



\*Bermuda Atlantic Time Series, a JGOFs LTEM site

Region	New Production, Pg C yr'	ADOC:NP	Net DOC Production, Pg C yr <sup>4</sup>
	Igeyi		I g c yr
Tropical open ocean			
Upwelling	1.5 (21)	0.2	0.3 (21.6)
Turbulent Mixing	0.7 (9.5)	0.1	0.07 (5.7)
Southern Ocean	1.1 (15.5)	0.12	0.13 (10.8)
Subarctic gyres	0.3 (4)	0.15	0.04 (3.7)
Coastal upwelling	0.8 (11)	0.2	0.16 (13.1)
Monsoonal	0.4 (5.5)	0.2	0.08 (6.6)
Subtropical gyre	0.5 (7)	0.1	0.05 (4.1)
Continental margins			
Western boundary currents	0.7 (9.5)	0.2	0.14 (11.5)
Estuarine influenced shelves	1.2 (17)	0.2	0.24 (19.7)
Total	7.2		1.2

Table 2. Estimates of Net DOC Production Based on Regional Estimates of New Production for Component Regions of the World's Oceans.

The ratios of net DOC production to new production ( $\Delta$ DOC:NP) have been taken from the analyses presented in this paper, and from assumptions listed in the text. Values in parentheses represent percentages of the global estimate. See *Chavez and Toggweiler* [1995] for characterizations of regions and new production estimates.

#### Production of "semi"-reactive DOC by phytoplankton in culture

Is the composition of accumulating DOC similar to DOC in seawater?



#### Do phytoplankton produce semi-reactive DOC?

<sup>1</sup>HNMR of seawater



After filtration

In culture, phytoplankton release a large amount of DOC. The composition of this DOC does not look like DOC in seawater however (left). After bacterial degradation, labile DOC is removed leaving the semi-labile material behind.





#### Radiocarbon model of DOC cycling



## Changes in the semi-reactive DOC-14C value with residence time

As the difference between DOC(sr) and DIC residence time increases the difference in RC age will increase as well due to non-steady state conditions in upper ocean 14C.



year

### Radiocarbon analyses of HMWDOC carbohydrates

Sample	Hawaii	NPSG
DIC	72 <u>+</u> 7‰(n=4)	89 <u>+</u> 7‰
Glucose Galactose Mannose Xylose Arabinose Fucose	47, 58 67 65 52, 58 63 49, 52	79 103 99 94 ND 69
Rhamnose	40, 57	57
Average	56 <u>+</u> 6‰	89 <u>+</u> 13‰



Purification of a modern carbohydrate fraction from HMWDOC also isolates an older "humic" like fraction for chemical and isotopic analyses.

The "humic" fraction isolated from surface seawater.  $\Delta^{14}C = -416\%$ 

HMWDOC from the deep sea  $\Delta^{14}$ C = -380 to -440 ‰

#### How is nonreactive DOC removed from the ocean?



**Central North Pacific** 

#### Photo-oxidation of CDOM

Generally noted that DOC in surface waters is not colored

However, deep sea DOC is colored and has fluorescence

Does sunlight bleach DOC in surface water?

Is this the mechanism by which non-reactive DOC is removed from the ocean?

#### Ultrafiltration of 4000m NPSG water



## Production of LMW highly oxidized DOC with depth in the ocean

DOC + hv --->> LMW photo-oxidation products





Not produced in dark controls, but are produced in sterile controls

Highly oxidized LMW compounds are produced every Day in seawater by photo-oxidation. They serve as a substrate For bacteria and therefore a sink for non-reactive DOC



#### Removal of DOC by adsorption onto POC

Why does suspended POC age so much with depth?



### Summary

Isotopic evidence suggests that the large inventory of DOCi in seawater is synthesized in-situ by phytoplankton or bacteria

In culture, phytoplankton release about 10% of total PP as DOC. Most of this DOC is considered to be very reactive and is metabolized by bacteria in a few days, but some persists

Global estimates of bacterial carbon demand require a large Fraction of PP is funneled though DOC to bacteria (> 10%)

The reservoir of DOC that accumulates in the upper ocean is Not thought to fuel BP by some, but RC data suggests otherwise

Non reactive DOC is removed by photo-oxidation, and perhaps By adsorption onto sinking particles