Ammonia concentrations and processes in Oligotrophic Oceanic Waters

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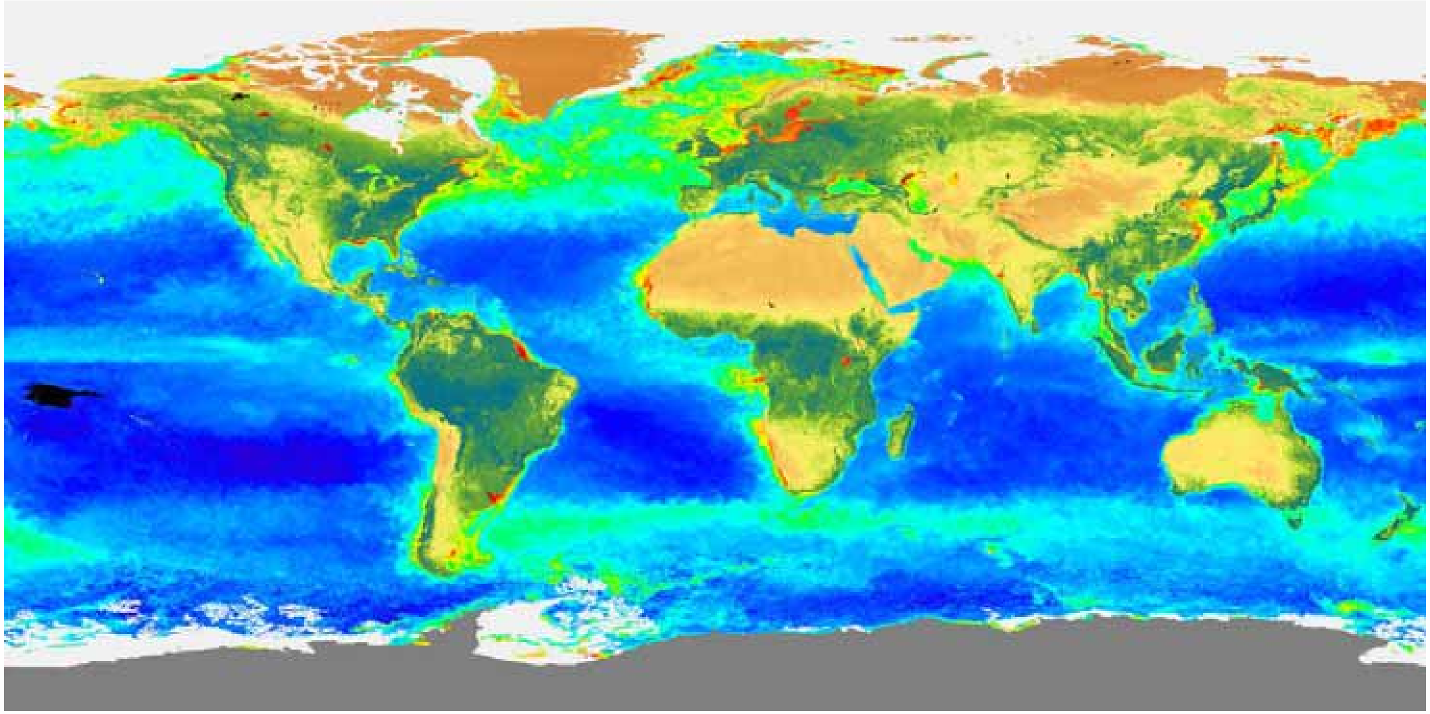
Presentation outline:

- Background, N cycle
- Nutrient analytical techniques and developments
- Oceanic sampling areas and the AMT
- Sampling systems, and limitations
- Ammonium concentrations from oligotrophic waters
- Water column concentration gradients
- Ammonium photoproduction in offshore waters
- Near surface ammonium gradients
- Nutrient uptake, 15N

Why study the Oceans ?:

About 70% of the Earth's surface consists of water.
The oceans are key for the existence of life on Earth.
The atmosphere we breathe, and which controls the weather and climate, is intimately connected to the oceans - half of the oxygen produced by plants is produced in the ocean, and the oceans are also responsible for absorbing about 50% of the carbon dioxide humans have released into the atmosphere by burning fossil fuels for energy.
But, our understanding of the oceans and the processes involved is poor to say the least !



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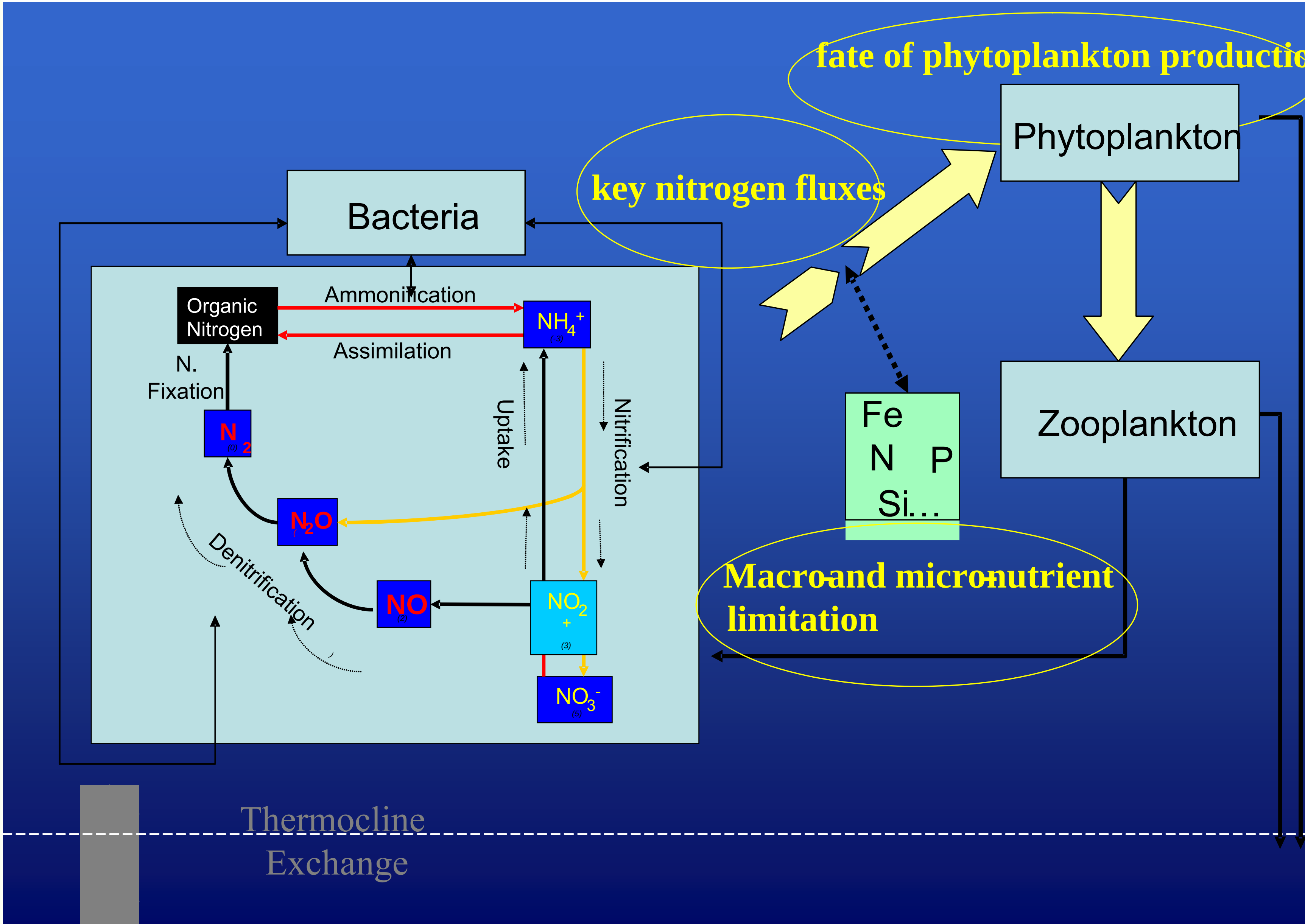
Background

- In wide areas of the world's oceans phytoplankton productivity is limited by the availability of nitrogen. The surface waters and the surface mixed layers of many temperate oceans, eg the Atlantic, typically are greatly depleted of dissolved inorganic nitrogen species (ammonia, nitrate and nitrite), with concentrations often below 5 nmol L-1 during the months of summer stratification, and the permanent thermocline.
- Studies of oligotrophic waters have for many years reported undectectable concentrations of the major nutrients. Therefore, quantification of biogeochemical processes would not be practicable for these waters when there are no reliable data.
- Results from water column samples in the upper 200m will be presented from a research transect cruise from the UK, through both the Atlantic gyres, down to South Africa; also results for cruises to the Tasman Sea and the eastern Mediterranean.
- Reliable ambient concentrations of ammonia, often less than 5 nanomoles l^{-1} are seen in the water column. This often showing a biologically derived maximum found at the top of the deep chlorophyll/nitrite maximum zone, and this is a characteristic of nutrient deplete oceanic waters.
- Results from detailed surface sampling in the upper 10 metres of a surface mixed layer oceanic water column, and from experiments investigating ammonium photo-production in open ocean waters.

Nutrient Cycling in surface mixed layer



Method developments:

- This has been and still is a major challenge in marine nutrient chemistry to develop robust and reliable sea-going analytical techniques for often extreme oceanic environments.

- A fluorescence detection system following gas diffusion across a Goretex teflon membrane has given us the required sensitivity for ammonia, 2-3 nanomoles/litre.

- Most methods measure the sum of NH_4^+ + NH_3. These exist in equilibrium within the water column with ammonium being the dominant form.

- The fluorescence technique here is based on the conversion of the NH_4^+ to NH_3 by pH and the subsequent diffusion across a membrane.

- Developments in the technology of long path-length Liquid Waveguide Capillary Cells (LWCC), up to 2 metres in length, and used in conjunction with sensitive segmented-flow colorimetric analysis systems, allow us now to achieve these nanomolar detection limits also for nitrate, nitrite and phosphate.

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Analytical Methods:

Manual analysis techniques, slow, not suited to ships.
Micromolar Techniques: Segmented flow autoanalyser

NO_3^-: > 25 nmol l^{-1}
NO_2^-: > 20 nmol l^{-1} Woodward (1994)

NH_4^+: >80 nmol l^{-1} Mantoura and Woodward (1983)

PO_4^{3-}: > 20 nmol l^{-1} Segmented flow colorimeter Kirkwood (1989)

Woodward, E.M.S. 1994. Plymouth Marine Laboratory

Woodward, E.M.S., Rees, A.P. 2001. Deep-Sea Research II 48(4/5), 775-793.

Nanomolar Techniques:

NO_3^-: > 1 nmol l^{-1}
PO_4^{3-}:
NO_2^-:
Liquid Waveguide Capillary Cells, following segmented flow analytical techniques.

Woodward, E.M.S, Kitidis, V (2003). In prep.

NH_4^+: > 2-3 nmol l^{-1} Gas Diffusion and Fluorescence detection from Jones (1991)

Woodward, E.M.S, Rees, A.P (2001). Deep Sea Research II, 48, Nos. 4-5, 775 – 794.

Other techniques for Ammonia: , FIA, selective electrodes, cathodic stripping voltametry, Chromatography, solvent extraction.

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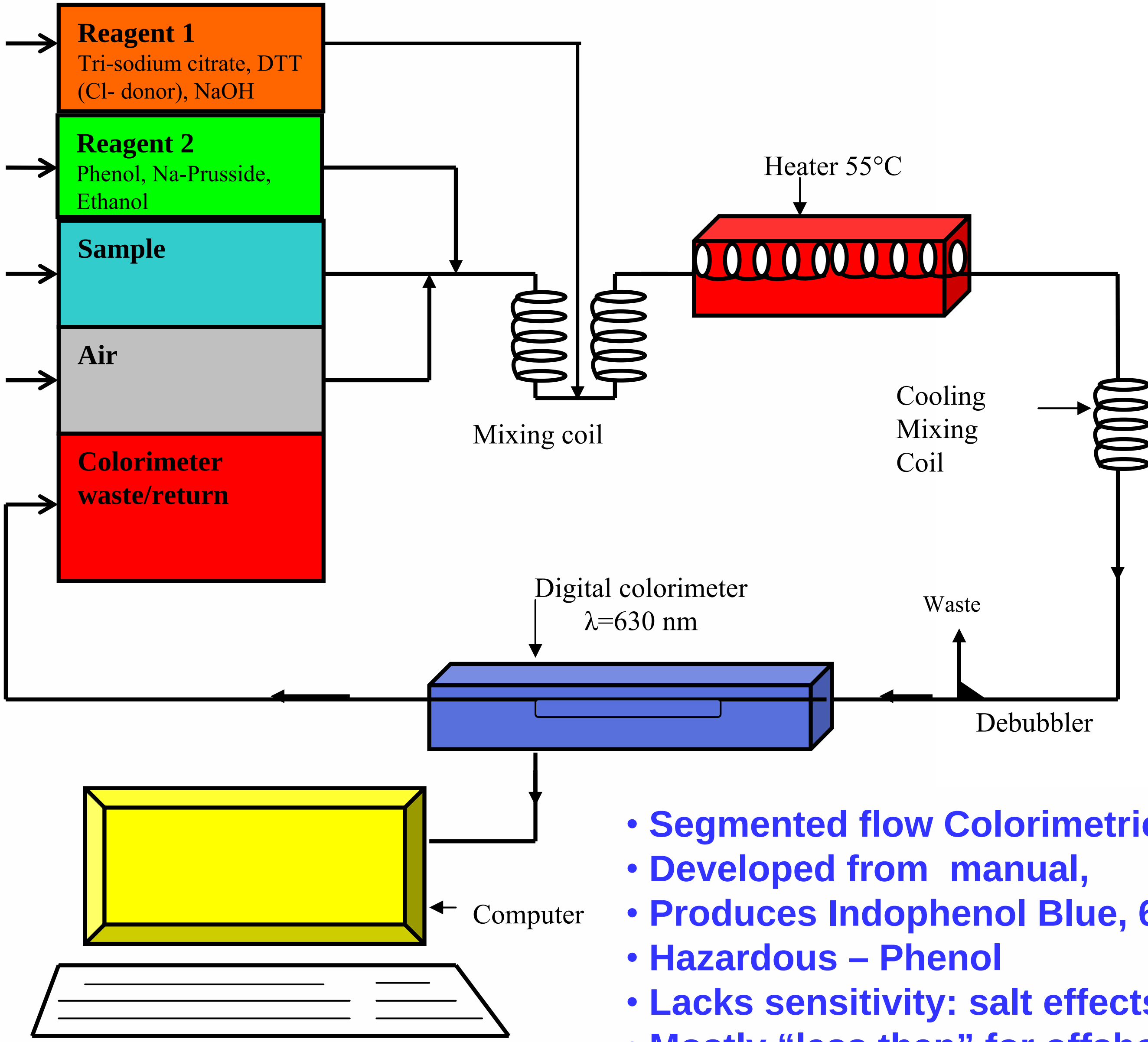
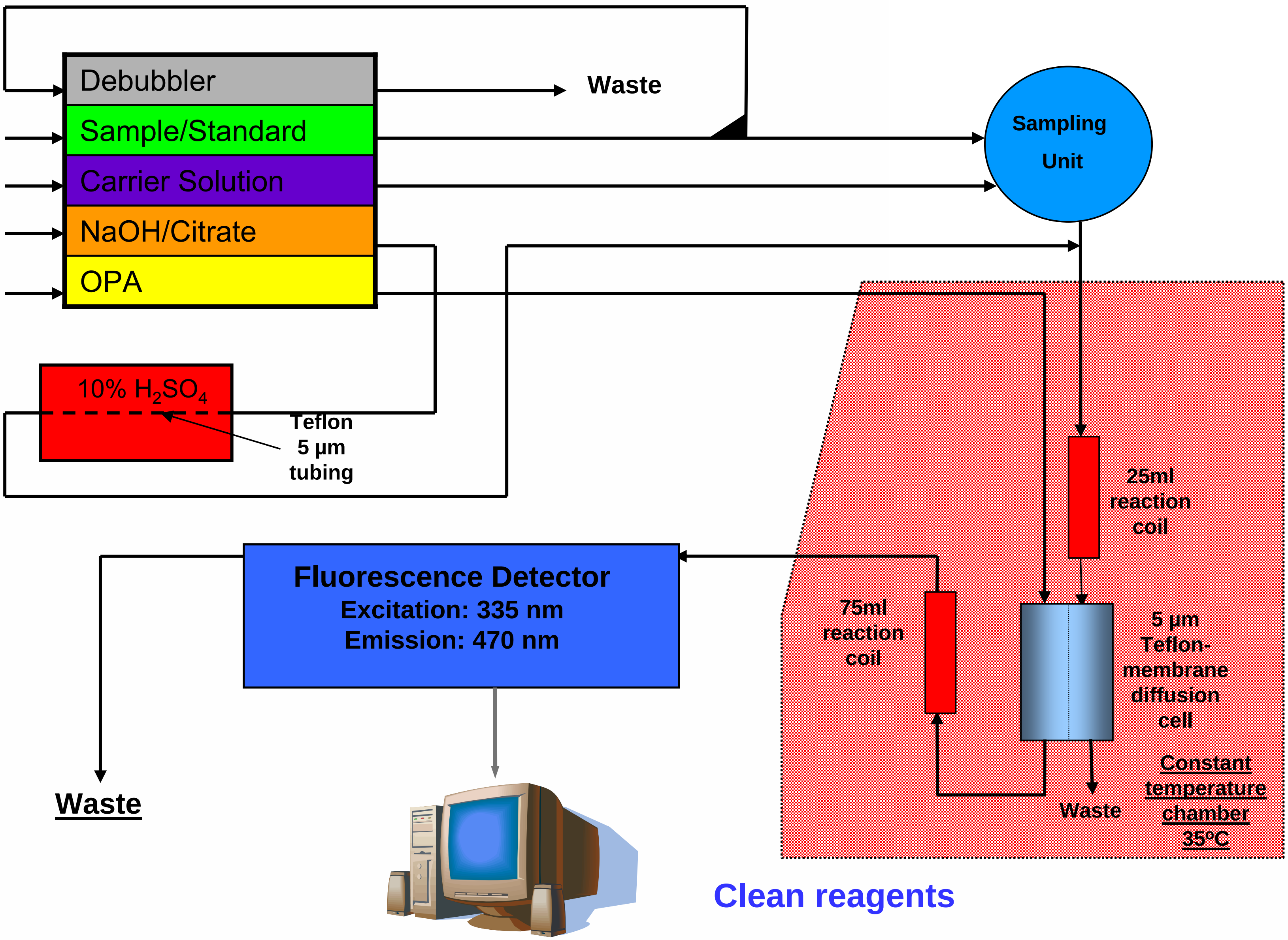
Ammonia Chemistry: Colorimetric



- Segmented flow Colorimetric analysis
- Developed from manual,
- Produces Indophenol Blue, 630nm
- Hazardous – Phenol
- Lacks sensitivity: salt effects, precipitation
- Mostly “less than” for offshore

Nanomolar Ammonia Chemistry Manifold



Clean reagents

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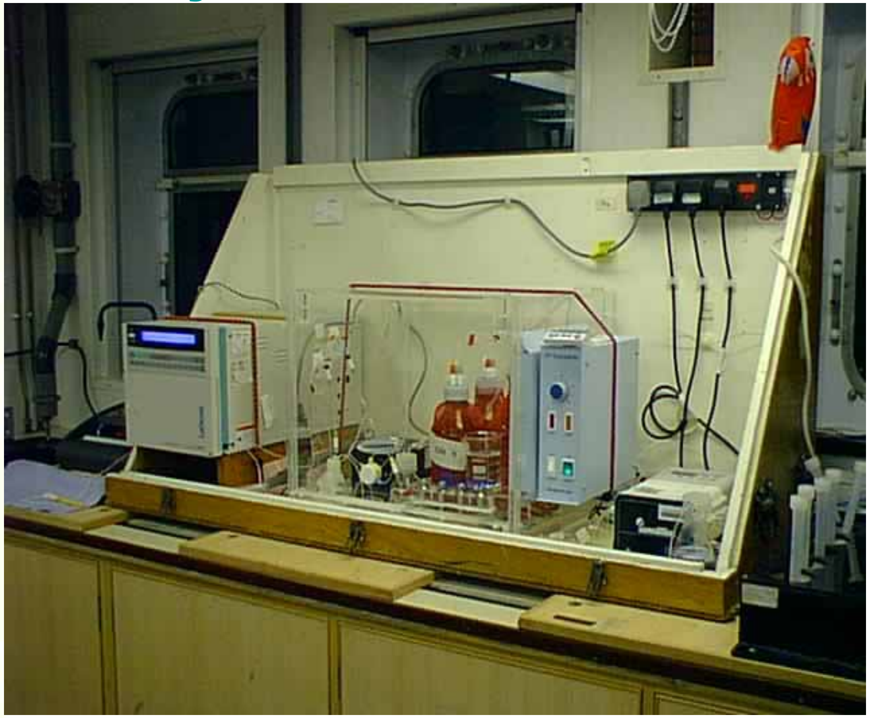
Analysis at sea:



Needs to be robust and reliable,
and tied down securely.

So does the operator !

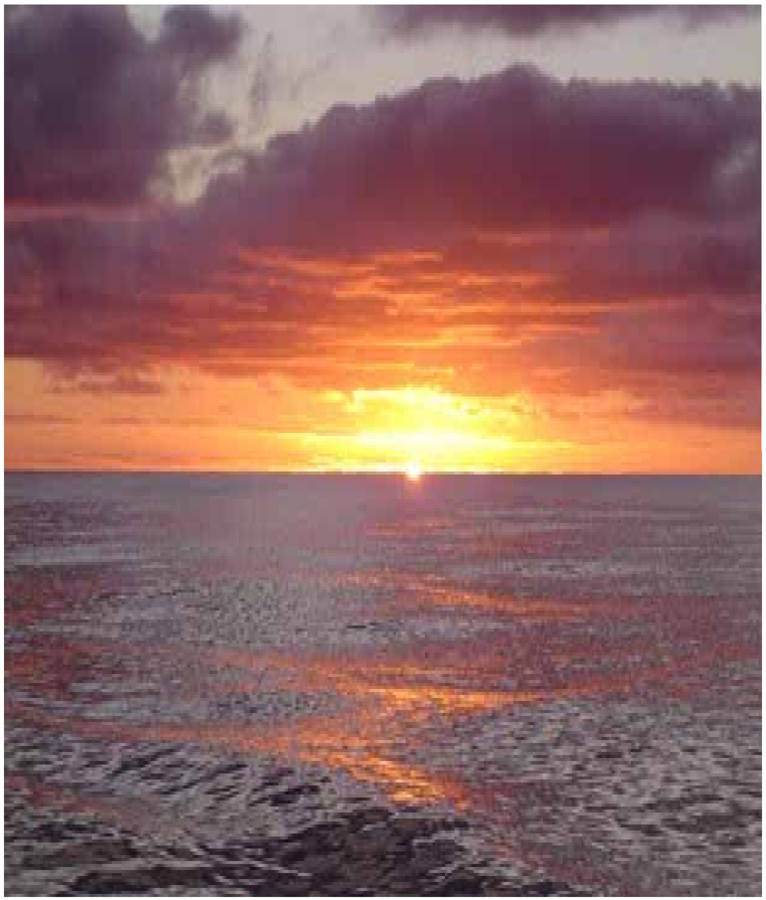
Analysis at sea:

CTD-Rosette System
24 x 20 litre bottles
Target the depths

<u>Clean Sampling and analysis</u>

- Gloves
- Clean ‘aged’ sampling bottles
- Position in sampling system as early as possible
- Analyse asap within 2 hours
- Store cool and in dark
- No filtering
- Definitely no freezing or poisoning the samples

The Perceived View



Calm Seas
Beautiful sunsets
G and T’s on the foredeck…………………. dream !

Often the Reality

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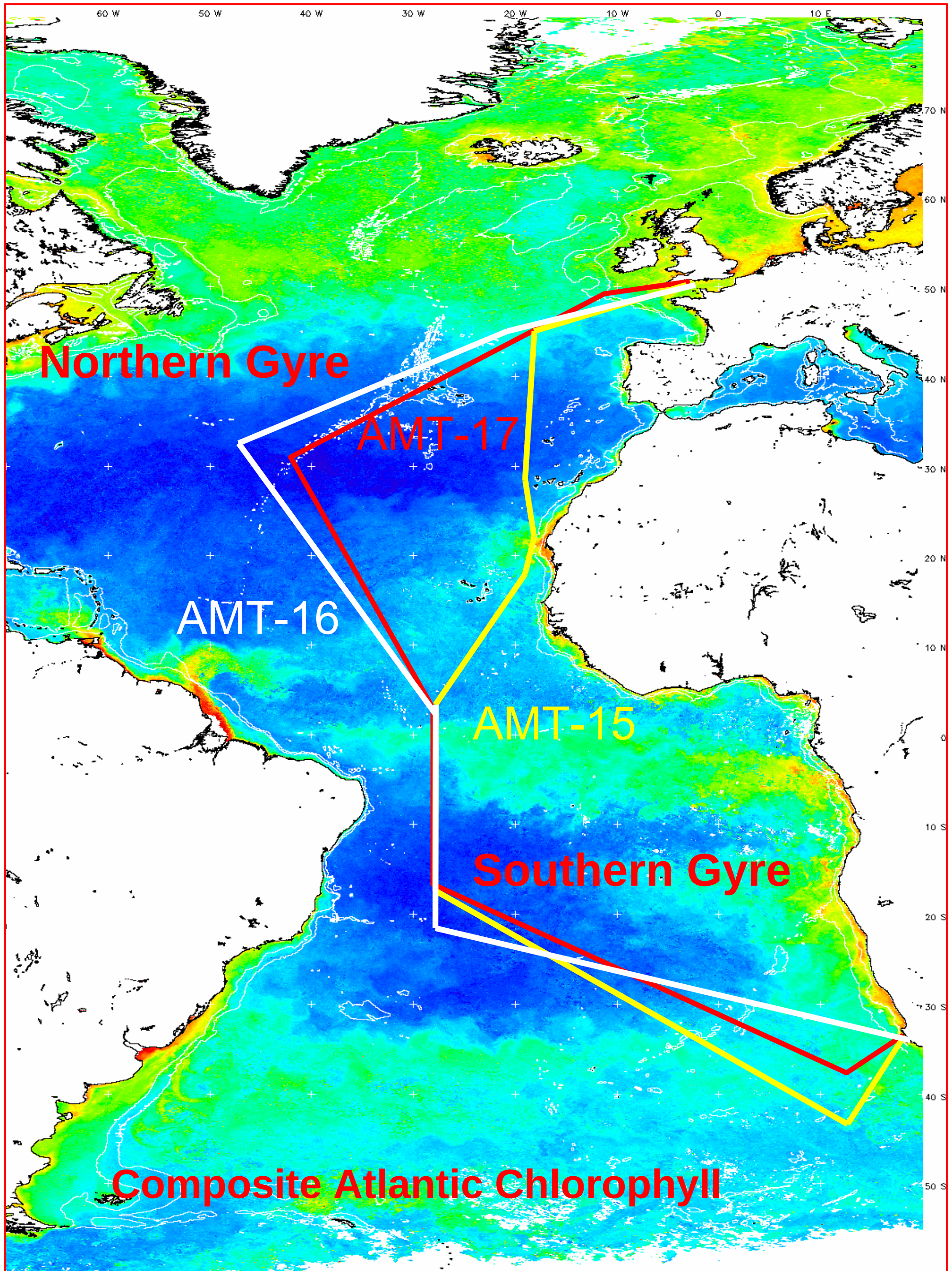
The Atlantic Meridional Transect Programme - AMT



17 Atlantic cruises, 1995-2005

First NERC Consortium project

Website at
www.amt-uk.org

A multidisciplinary programme to determine:.

1. -how the structure, functional properties and trophic status of the major planktonic ecosystems vary in space and time.
2. - the role of physical processes in controlling the rates of nutrient supply, including DOM, to the planktonic ecosystem
3. - the role of atmosphere-ocean exchange and photo-degradation in the formation and fate of organic matter.

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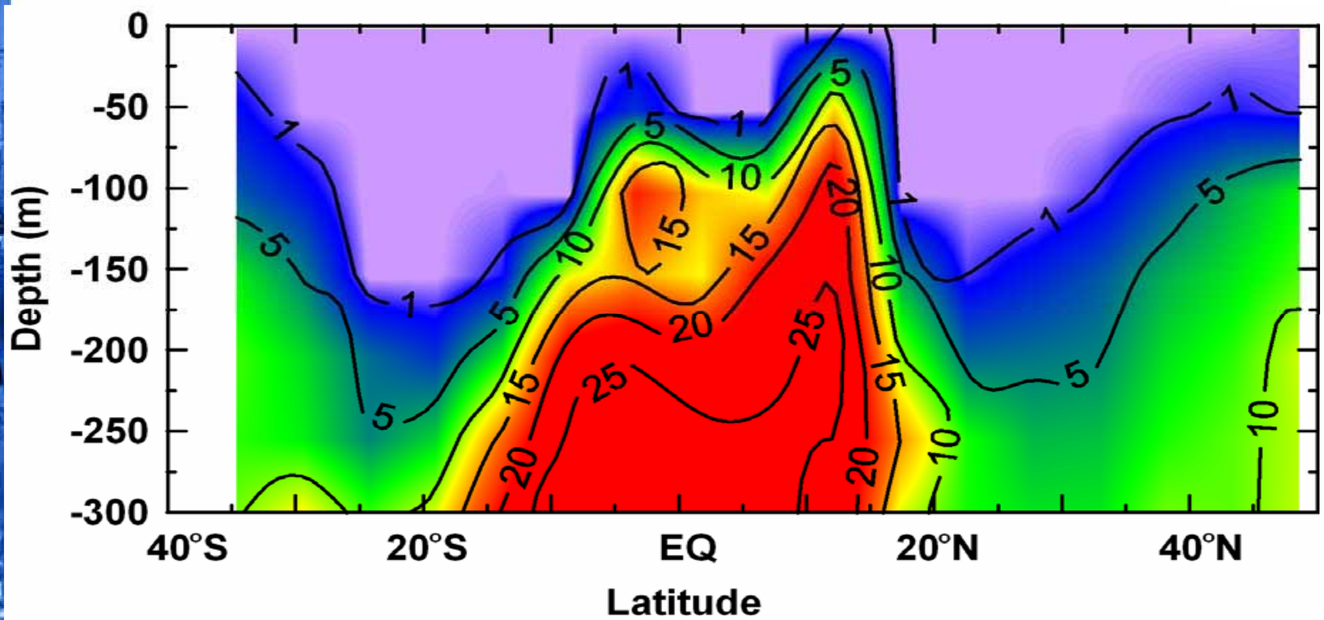
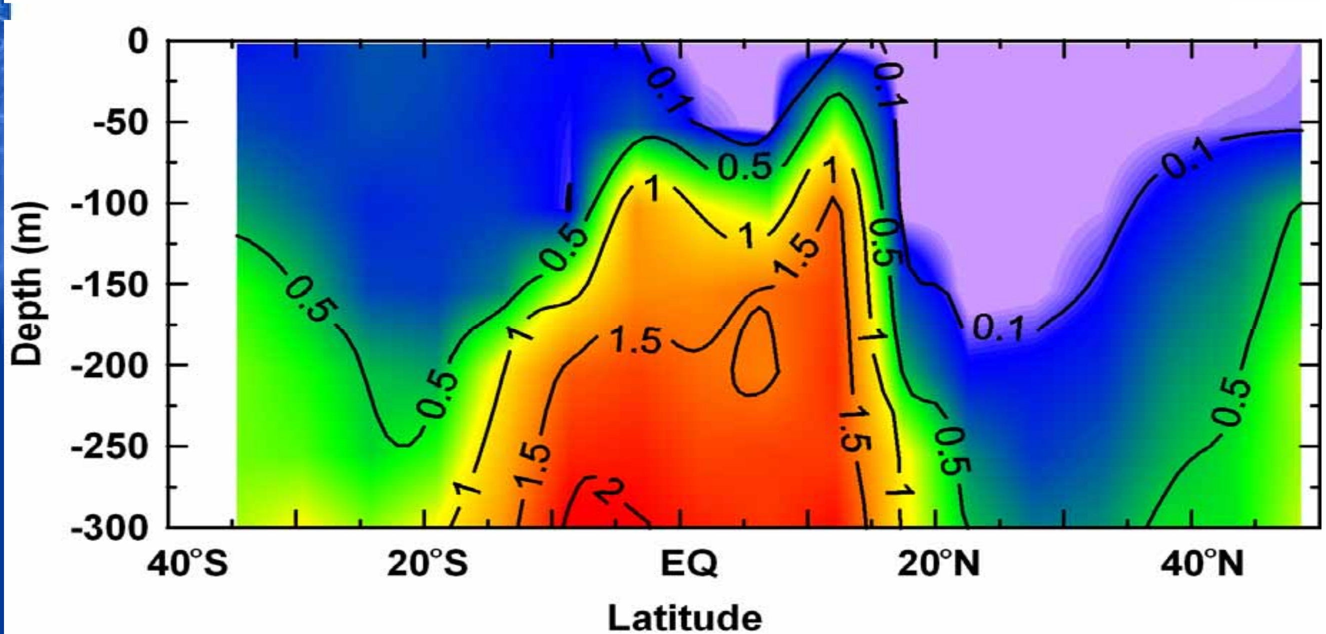
Atlantic Ocean Macro-Nutrient Structure

Twice Daily CTD profile
7 weeks at sea

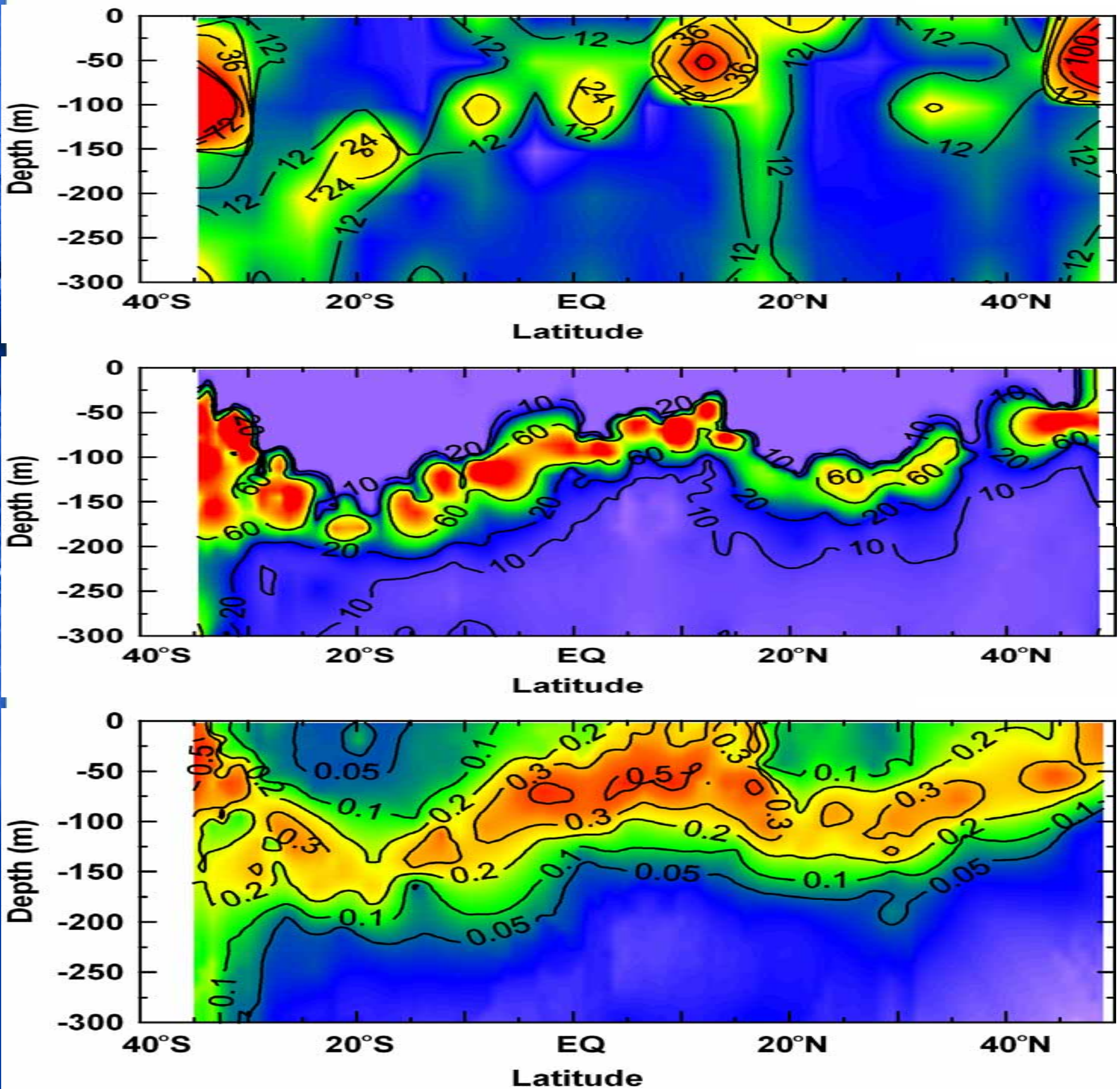


Nitrate (uM)



Phosphate (uM)

AMT-17, Nov, 2005



Nanomolar Ammonium

Nanomolar Nitrite

Chlorophyll-a (mg m-3)

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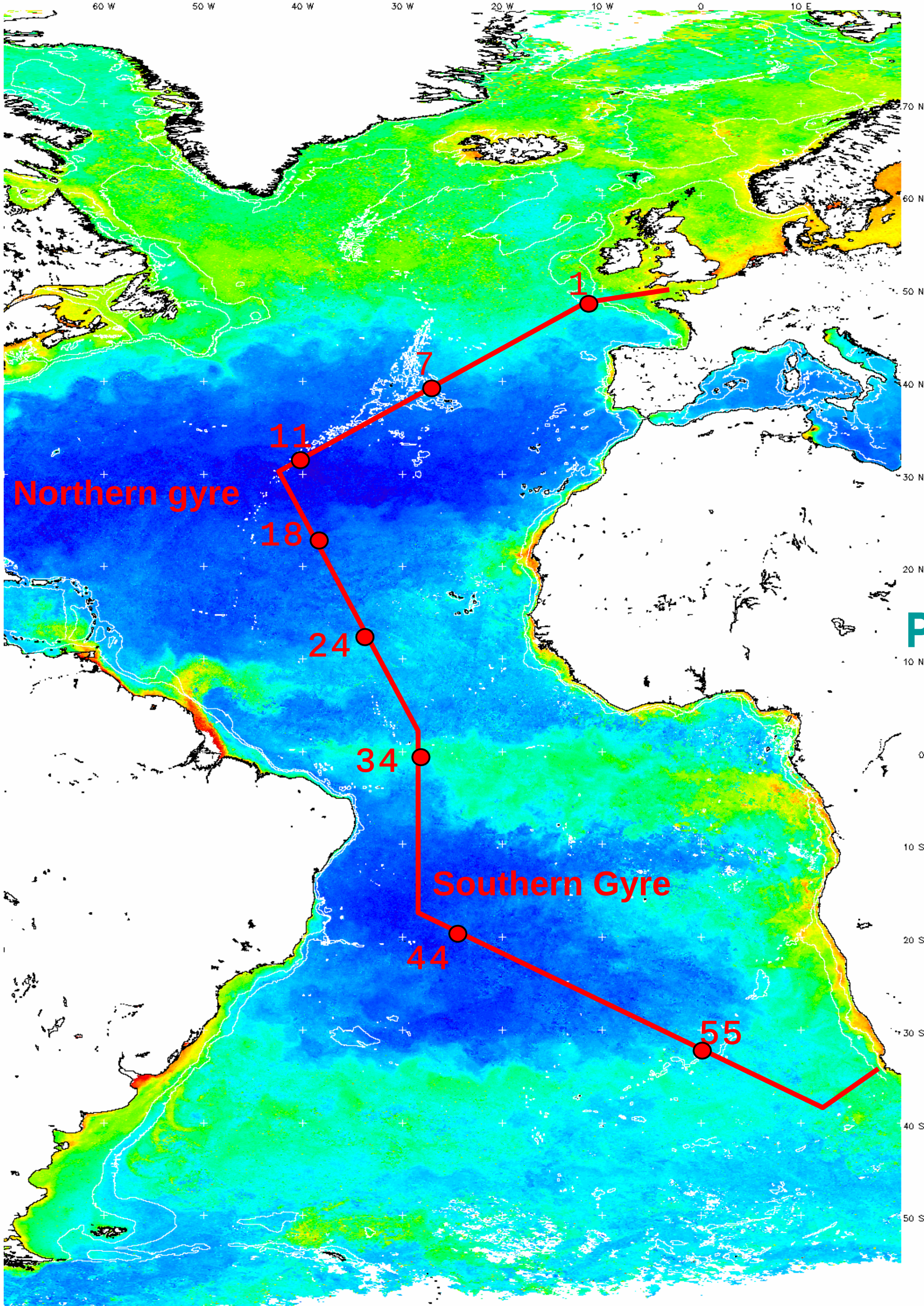
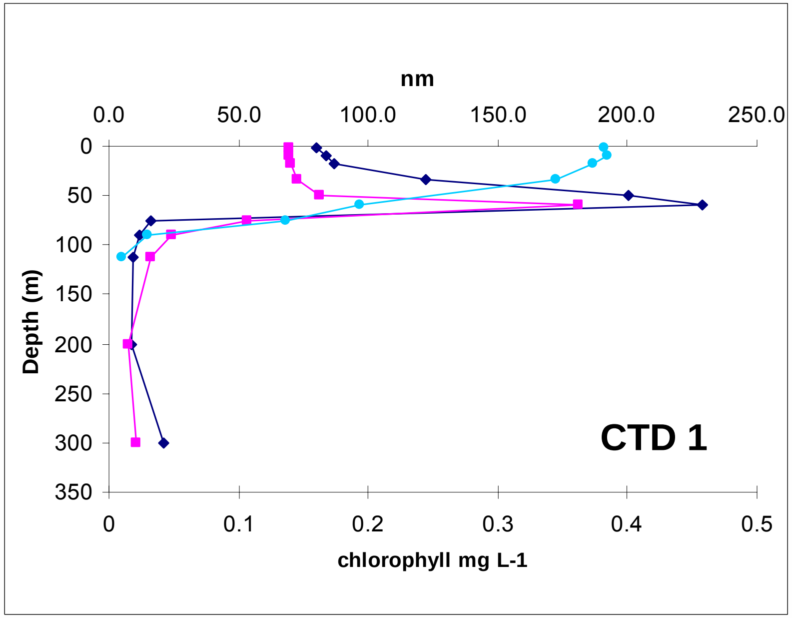
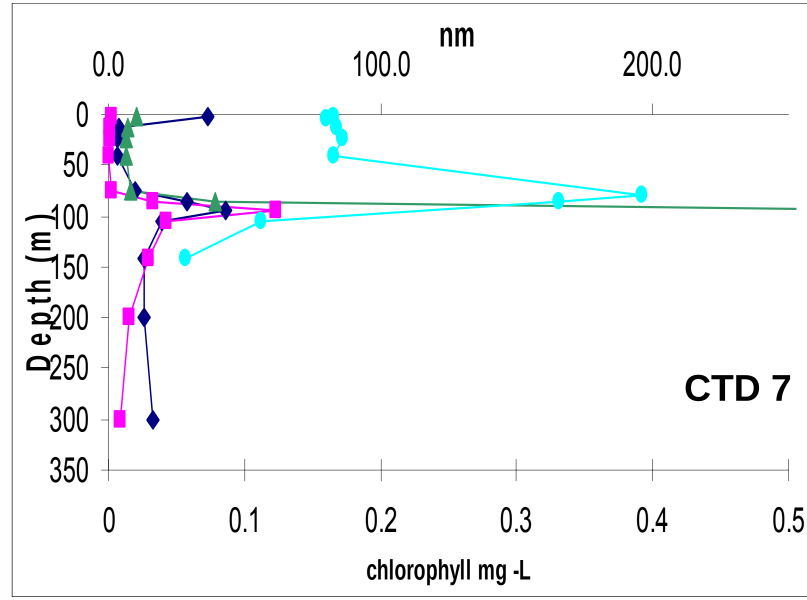
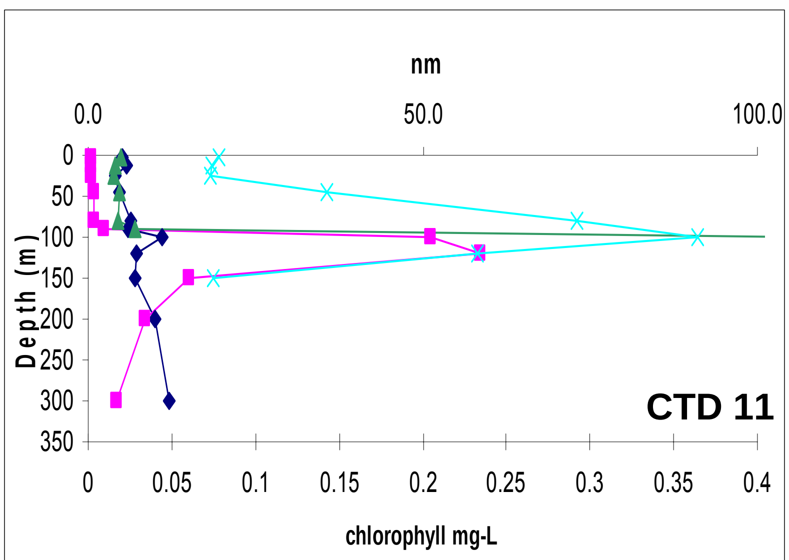
Cruise Track, AMT-17, Positions of CTD Sections

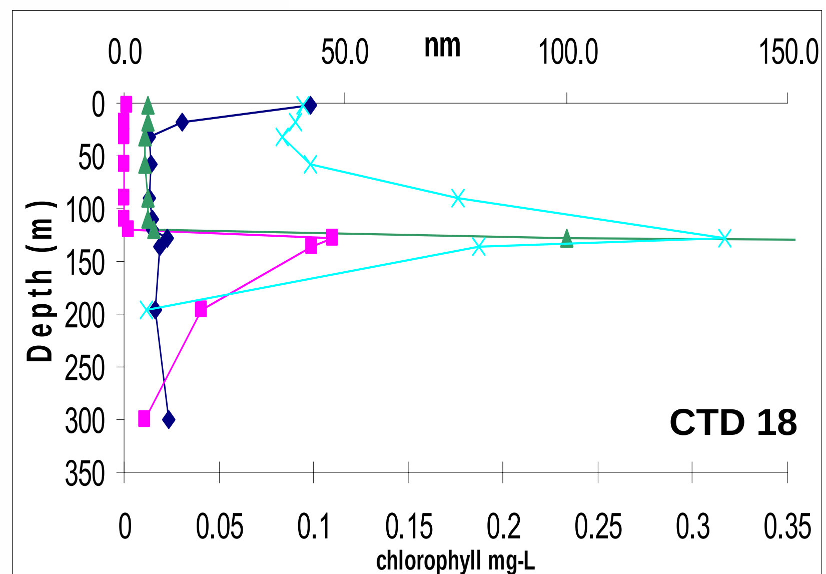


CTD Profiles: Off Shelf, Intermediate and Northern Gyre









DB=NH4 ; Gr=No3; Mau=NO2; LG=Chl

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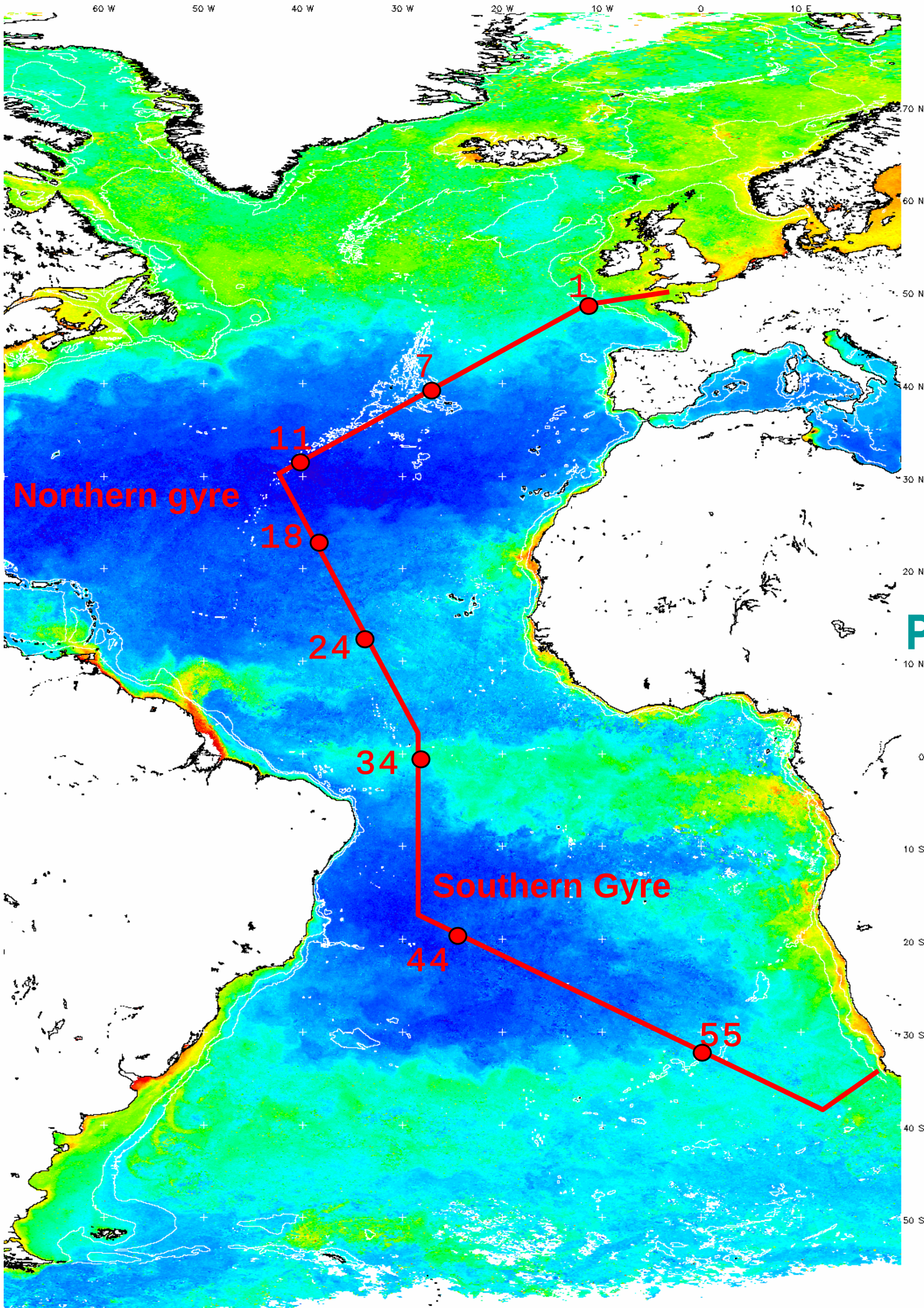
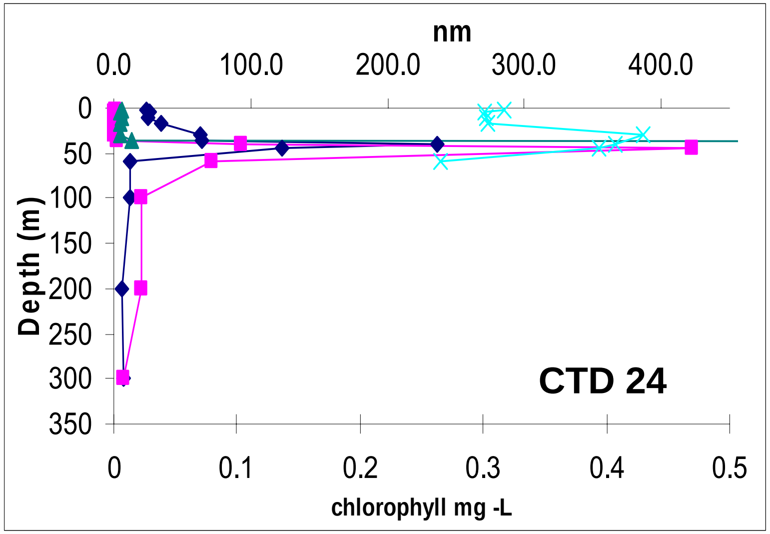
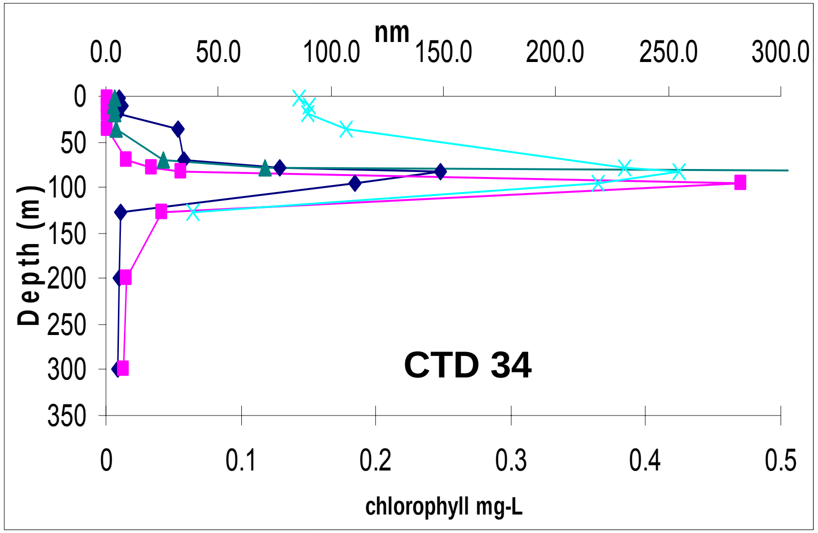
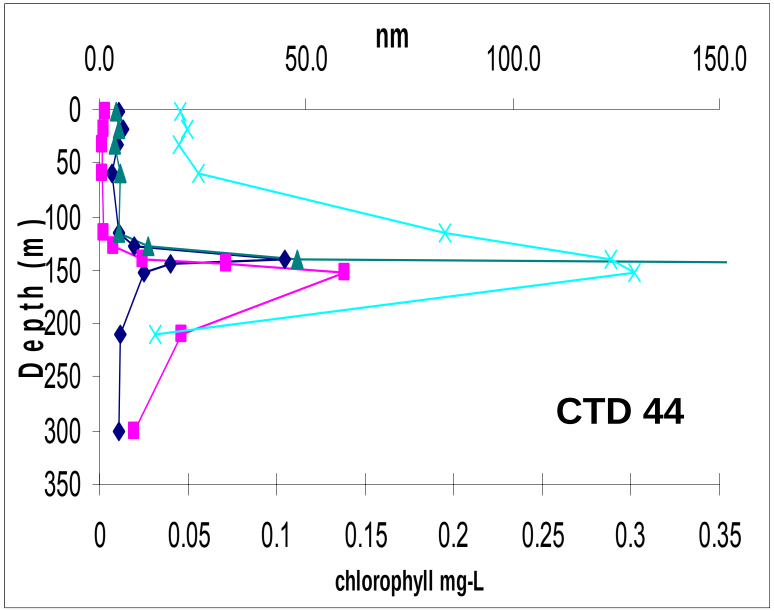


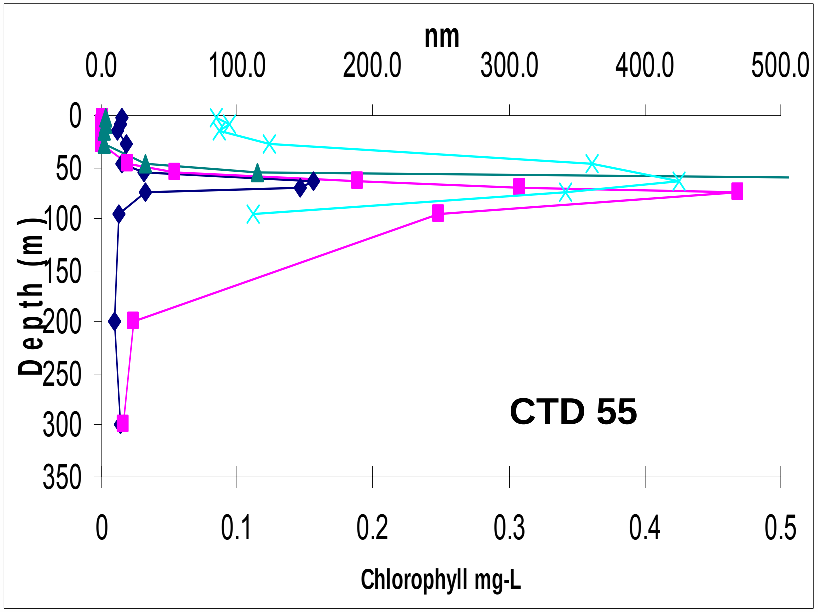
Cruise Track, AMT-17, Positions of CTD Sections

CTD Profiles: Equatorial Upwelling, Southern Gyre and Gyre Edge









DB=NH4 : Gr=NO_3; Mau=NO_2; LG=Chl

Water column maxima:

- Ammonia Concentrations exhibit a sub-surface maximum at a depth consistently near to the observed deep nitrite maximum.
- The nitrite maximum was present along with the Ammonia maximum in the region of maximum vertical temperature change, effectively at the thermocline, and it was also associated with the chlorophyll maximum region, where there is increased biological activity.
- Nitrite and ammonia maximum have been observed elsewhere in oligotrophic oceans
- The ammonia maximum may be as a result of the heterotrophic bacterial decomposition in the water column, or may be as a result of phytoplankton excretion.
- Generally it is produced by biological processes that are associated with zooplankton grazing and the bacterial decomposition of PON.
- The nitrite maximum has 2 suggested maintenance mechanisms:
  a) Bacterial nitrification and b) phytoplankton nitrite excretion during algal reduction of nitrate.
- However these two maxima are both linked as being at the region of the chlorophyll maximum and further detailed studies of all the possible processes need to be carried out simultaneously to confirm these processes.

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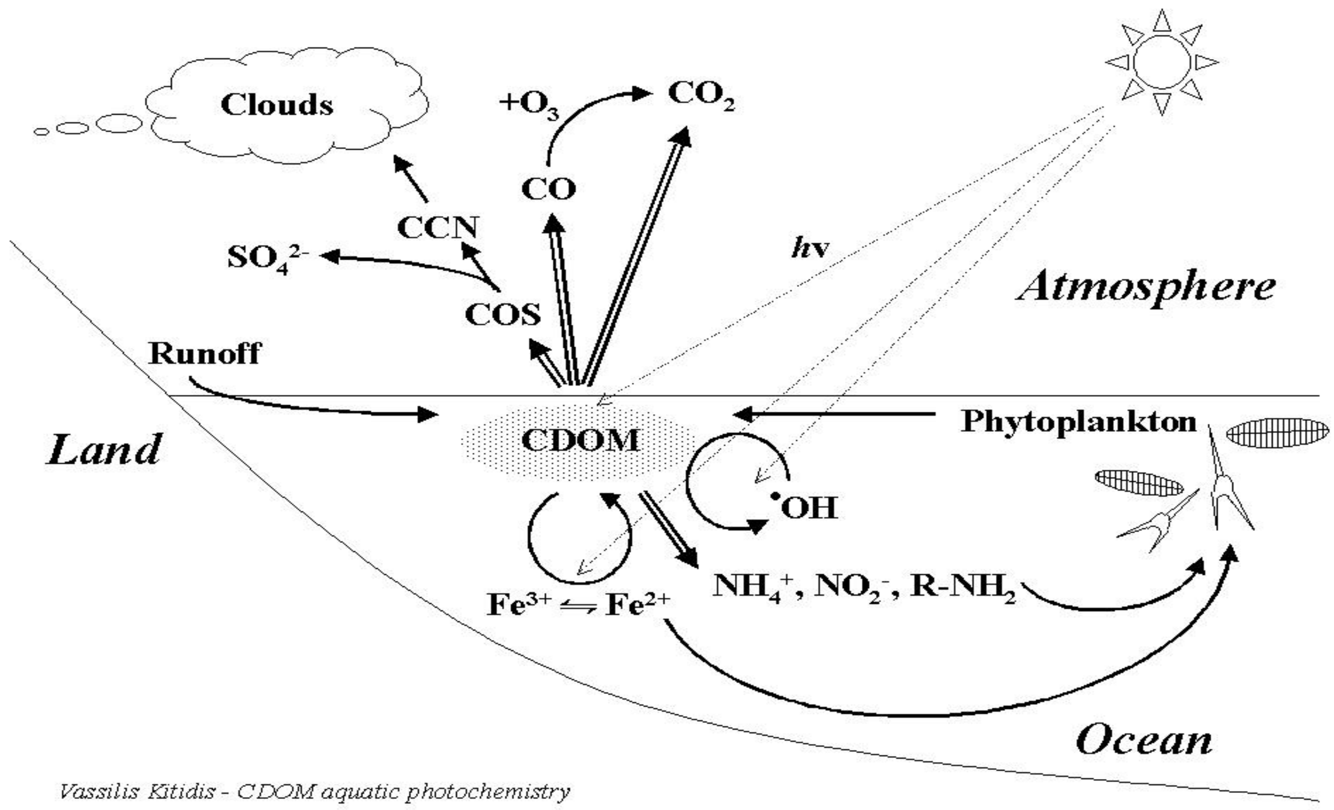
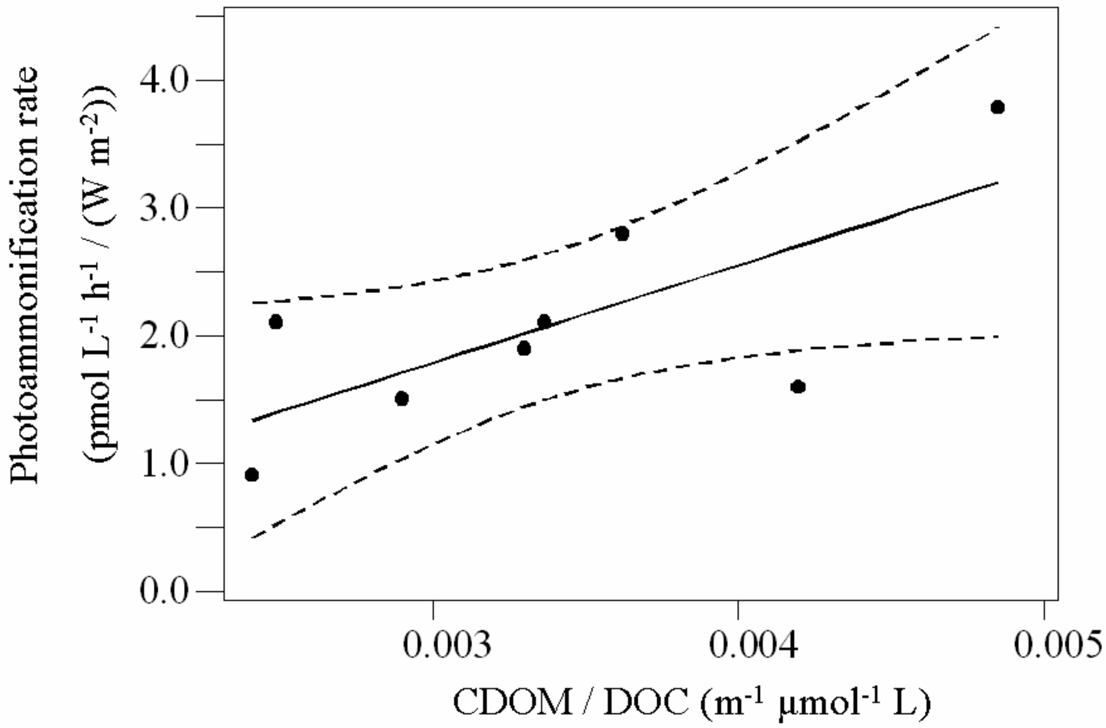
CDOM experiments (Coloured dissolved organic matter)



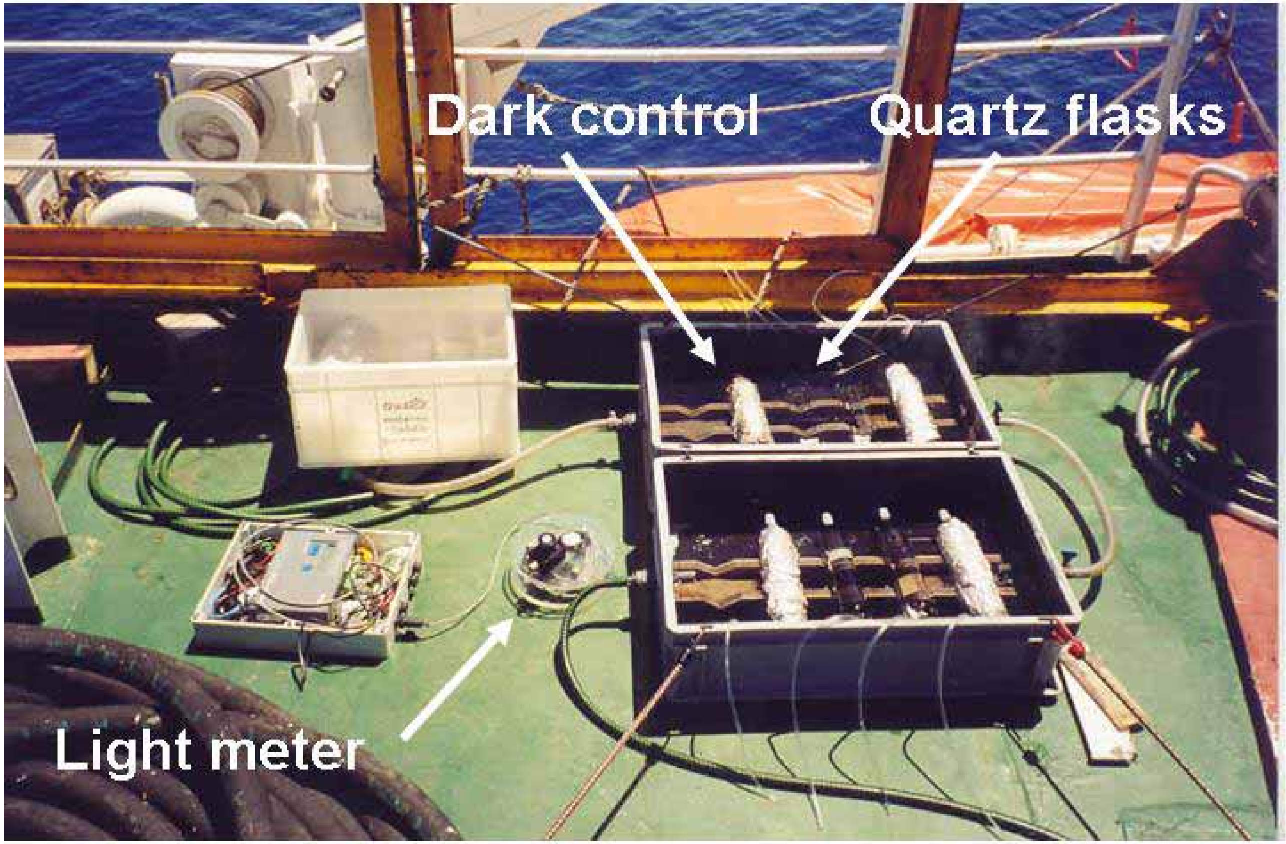
Ammonium production within the water column in oligotrophic waters:
observed when studying the photo-production processes involved when exposing CDOM to UV radiation.
Also nitrite and urea produced by irradiance.

Ammonia production rate



Photoammonification rates (photo-production of ammonium) were significantly correlated with Chromophoric Dissolved Organic Matter (CDOM) absorbance at 300 nm normalised to Dissolved Organic Carbon (DOC). i.e. the more coloured DOM is, the more NH4+ is likely to be photo-produced.

CDOM/Photochemistry technique



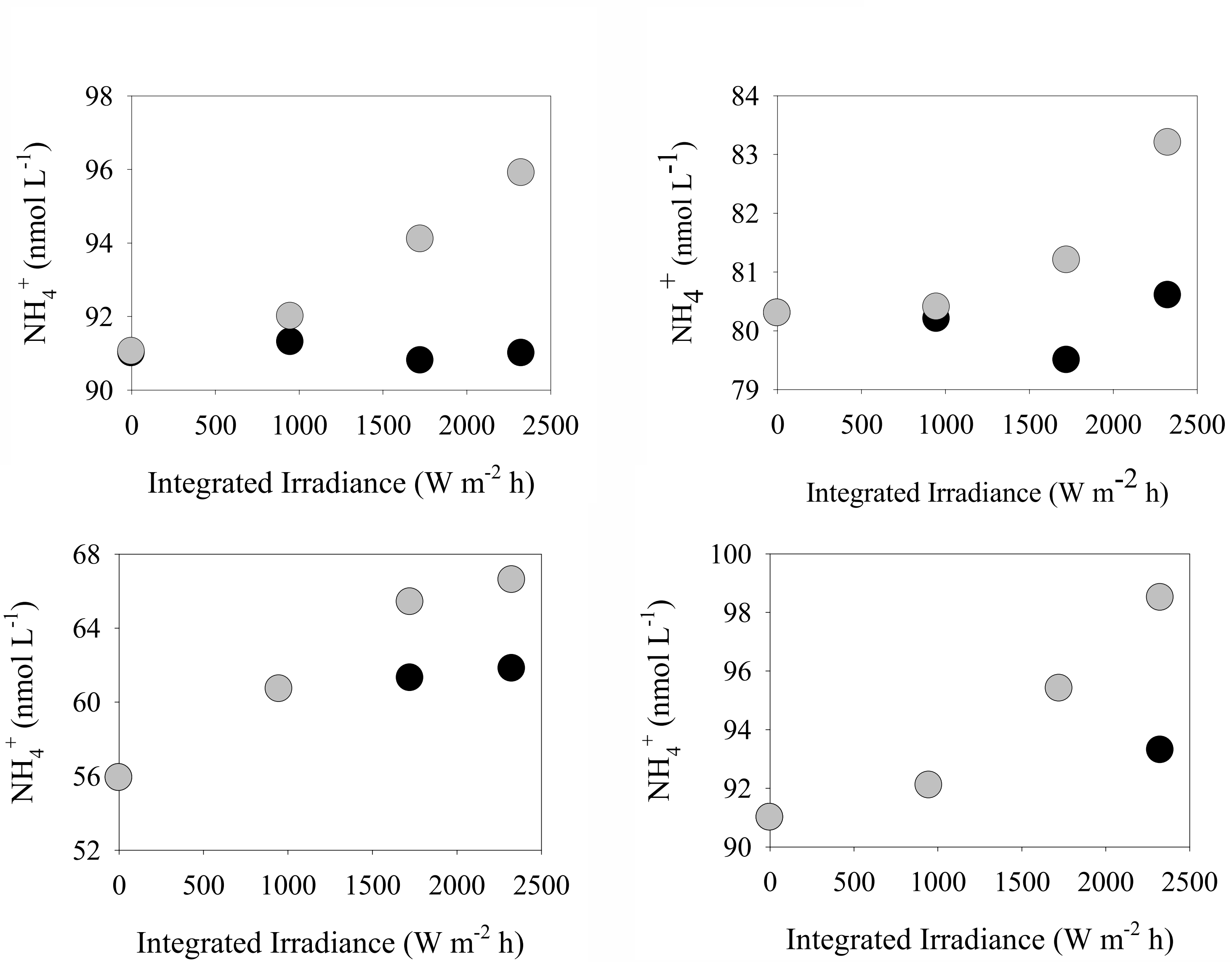
•Samples were 0.1 μm filtered

•Removal of >99.5 % of bacteria and picoplankton

•9 irradiation experiments

•Measure NH_4^+, NO_3^-, NO_2^-, CDOM (a_{300})

Irradiation results, ammonia production.



Ammonia produced over time, exposure over solar noon
Low but significant increases

Ammonium Production in the water column

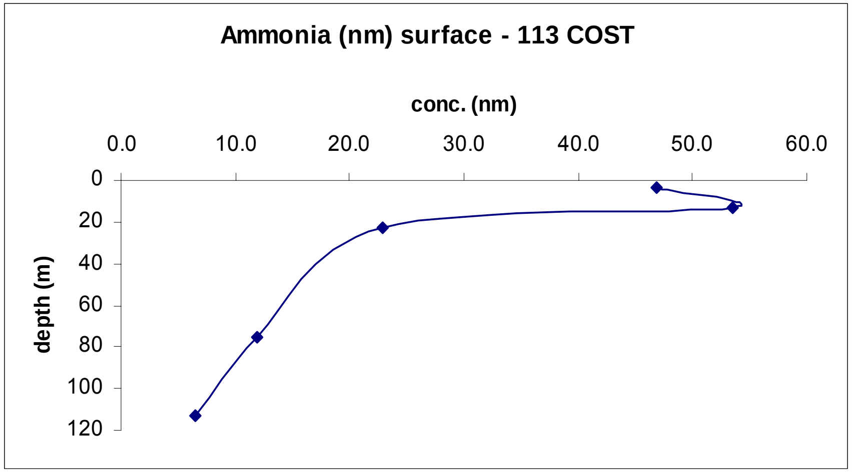
Ammonia is photo-produced in oligotrophic waters

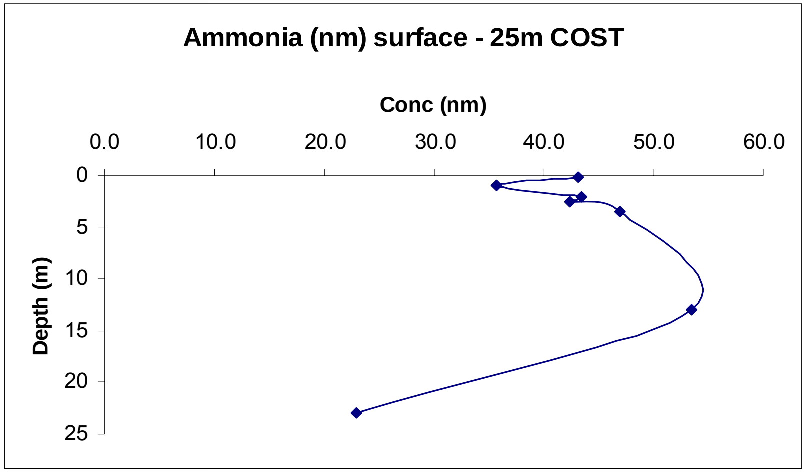
Photoproduction of ammonium via the photodegradation of CDOM can significantly modify the inorganic nutrient budgets of aquatic ecosystems (Bushaw et al., 1996). He also estimated photoammonification on the Southeastern US continental shelf to contribute an additional 20% to riverine inorganic nitrogen export. Similarly, Morell and Corredor (2001) estimated the contribution of NH4+ photoproduction to the phytoplankton nitrogen (N) demand of the eastern Caribbean Sea at about 50 %.
These were results for coastal and near shore waters.

No studies have previously looked at oligotrophic waters – analytical capability !

Combining our experimental data with estimates of annual solar irradiance and water column light attenuation yields we calculated an annual photoammonification rate for the Cyprus Gyre of 40 ± 17 mmol m-2 a-1, equivalent to ~12 ± 5 % of the previously estimated annual nitrogen requirement of new production and in the same order of magnitude as atmospheric N deposition in this region.

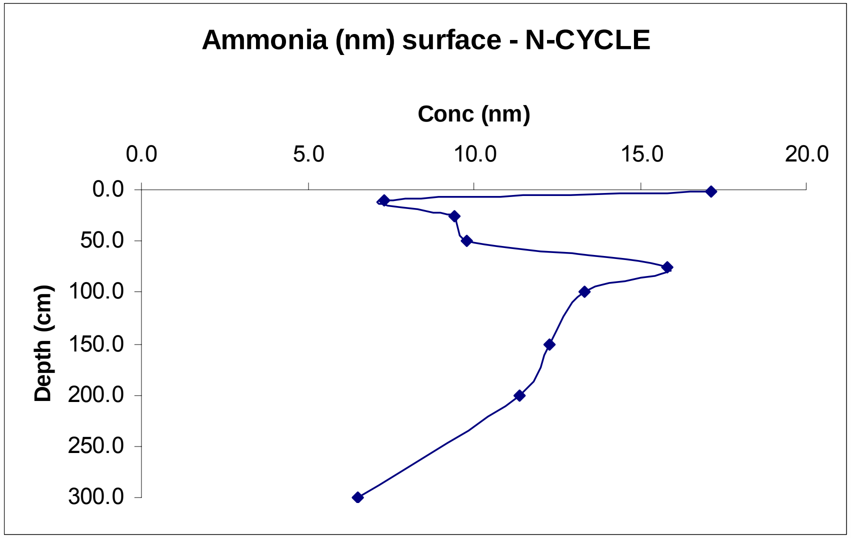
Near surface studies of ammonia



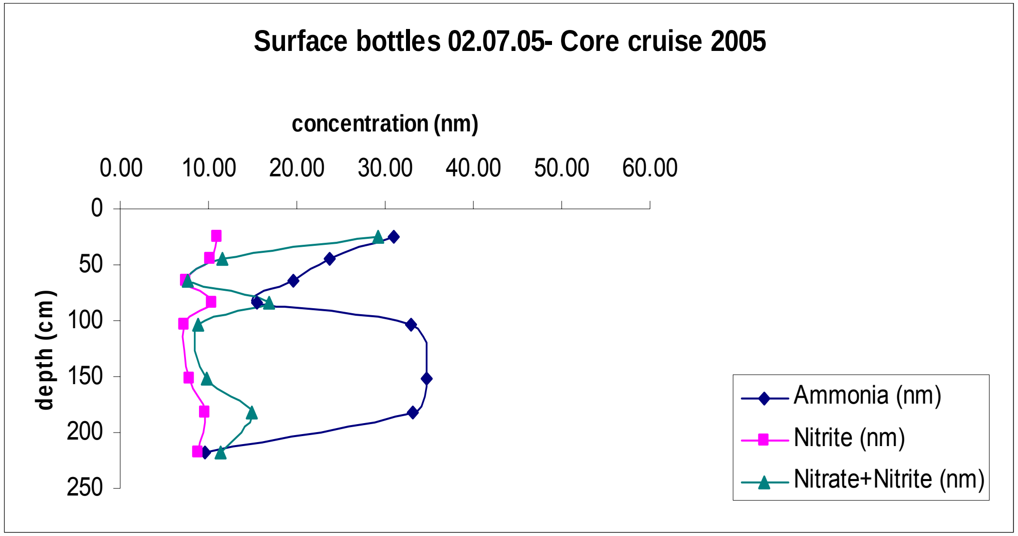


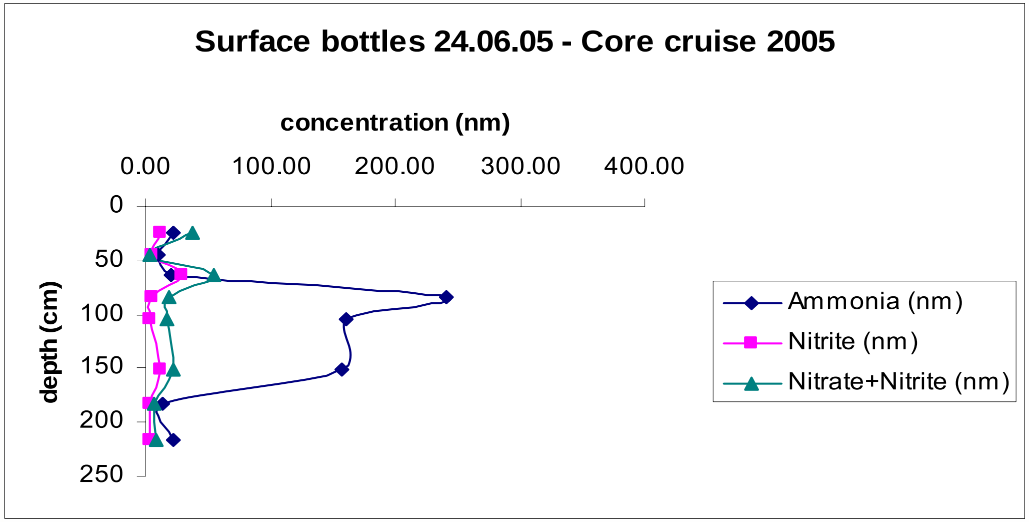
Oligotrophic Tasman Sea
CTD Bottles – 1 metre !

Clean sampling system, teflon tubes and syringes
Indications of surface maxima and also at sub-surface region



Near Surface ammonia profiles





Implications for a source (photoproduction) and sink (atmospheric losses) imbalence.

Indications:
Ammonia is photoproduced at 100-150 cms area
Nearer the surface there is then gas exchange so consumption to atmophere exceeds production
Right at the surface few cms photoprod becomes dominant and NH3 increases again.

Other aspect is the contribution of phytoplankton – unknown. Known that they take up the ammonia deeper in the water column.

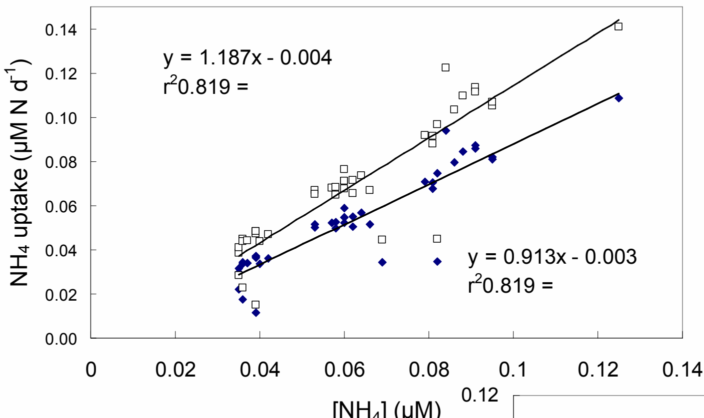
Nutrient Uptake studies

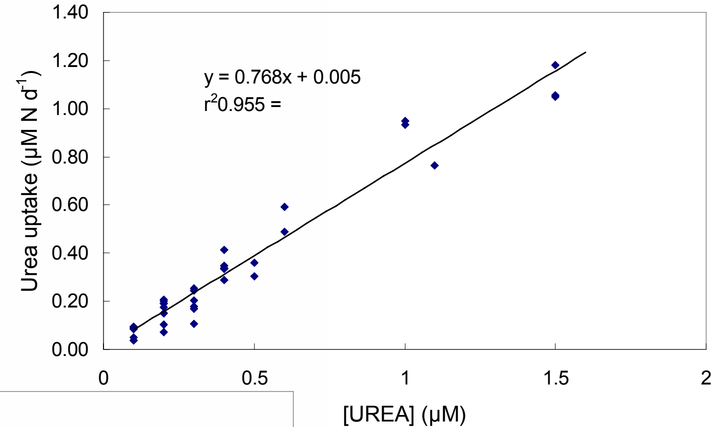
3 main sources of nitrogen for the phytoplankton – Ammonia, Urea and Nitrate

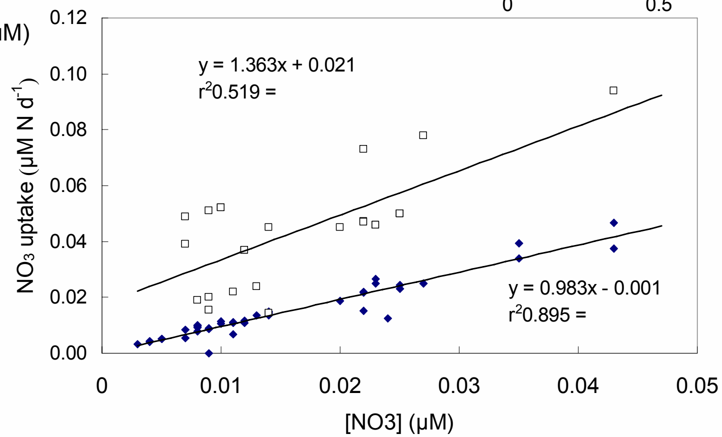
Studies have shown that ammonium supports up to 95% of the phytoplankton demand for nitrogen in oligotrophic seas.

Kinetic analysis has showed that ammonium is preferentially utilised over Nitrate over the full concentration spectrum, nano – micromolar.

Compared to nitrate, phytoplankton generally prefer ammonium because of the additional energy that is required for them to reduce nitrate to ammonium.







Uptake proportional to concentration

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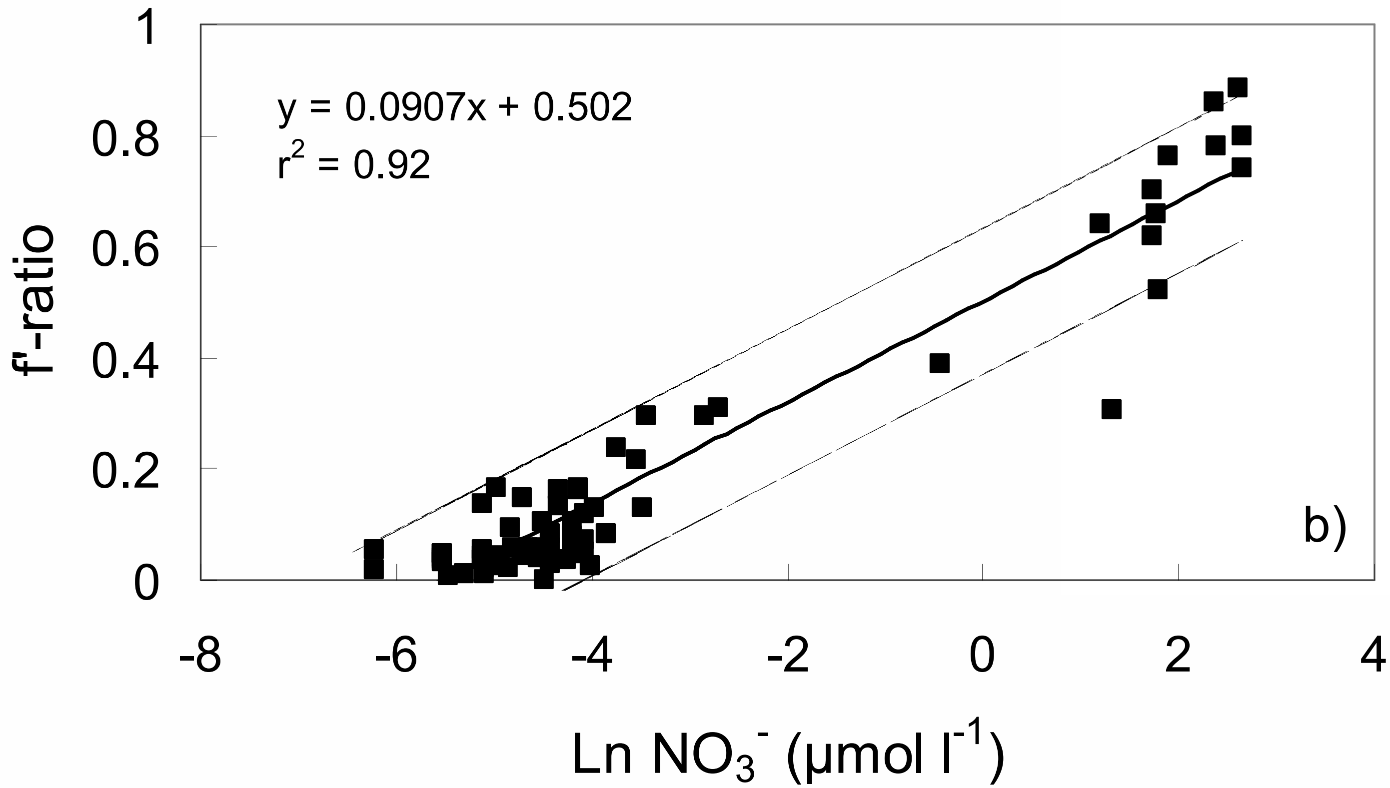
f ratio

By combining these uptake ratios we can produce the f ratio to indicate what nitrogen species is dominating phytoplankton production.
Less than 0.5 indicates that NH4 is dominating the production
In the Atlantic gyres and other oligotrophic oceans ammonium is supporting the primary production.



Conccs: 0=1uM NO3
-2=14nM NO3

Conclusions

Ammonium concentrations less than 10nM in the surface oceanic waters

But more studies need to be done to increase the database for the oceans

The results could have wider implications for global nutrient budget calculations, also nutrient limitation studies

Ammonium increases due to photoproduction over solar noon, again important in budget calculations

Maxima observed sub surface (100-150cms) in fine scale studies

Also surface maxima observed

Links between air-sea exchange and the fluxes need to be studies

Ammonium is the preferred species for phytoplankton and for driving the primary production in the nutrient deplete oceanic waters.

Most important is need for many more oceanic measurements !

Thanks to my colleagues at PML:
Vas Kitidis and Katie Chamberlain

THANK YOU for Listening

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