### Phytoplankton community structure and trace gas studies

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### Why are we interested

- Primary production by plants and algae forms the base of all marine ecosystem processes.
- Phytoplankton are fundamental to climate change studies.
- A wide range of micro and macroalgae are known to produce halogenated trace gases through their metabolic processes.



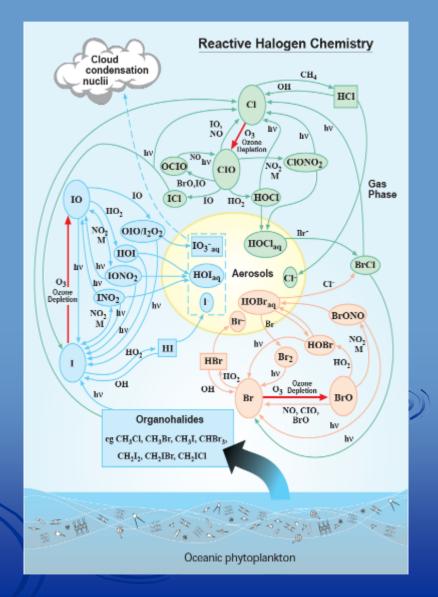
## Halogen Chemistry

Once in the atmosphere, these gases provide mechanisms by which chlorine, bromine and iodine species reach the stratosphere and are involved in the catalytic destruction of ozone.

Many of these gases also contribute to Global Warming.

Others are known to instigate the production of cloud condensation nuclei and might help mitigate it.





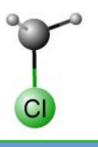
#### Oceanic source

**Ocean source is patchy** both spatially and temporally.

MeBr

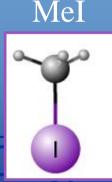


MeCl



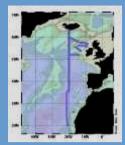
Major ocean source. Related to diatoms and prymnesiophytes. Also chemical interactions

Source or sink unclear Related to diatoms in open ocean and culture.

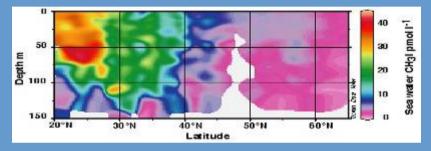


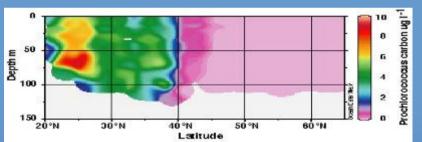
Coastal source related to macroalgae. Open-ocean source related to photochemistry and cyanobacteria

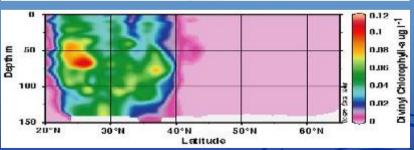




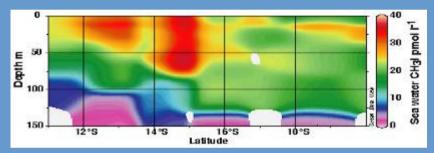
## Methyl Iodide and Prochlorococcus

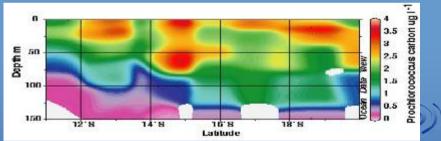






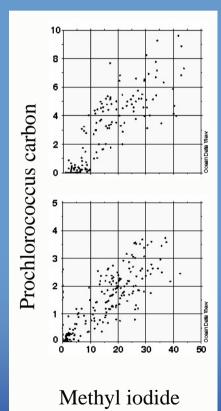
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Smythe-Wright et al., 2006

### Biological relationship





National Oceanography Centre, Southampton Studies have shown that biological gas release is not solely related to one species or taxa.

It is more likely to be controlled by community structure and/or environmental conditions.

To further our knowledge of trace gas release it is vital to monitor changes in phytoplankton community structure seasonally, inter-annually and on decadal timescales.

In turn, this will help us better understand how phytoplankton released gases might force or mitigate climate change.

#### Automated Equipment

Working alongside a standard Ferrybox system (which logs temperature, salinity, fluorescence and oxygen).

The ferry operates two return journeys per week throughout the year and crosses a number of oceanic and biological provenances, thereby providing data over a variety of temporal and spatial conditions.







#### P&O Pride of Bilbao ferry route

Project started April 2002 Online "Web sensors" @ 1Hz Conductivity Temperature Chlorophyll-fluorescence @ 30secs  $O_2$  (start 2005) pCO<sub>2</sub> (mid 2005-7)

#### Monthly water samples

From Feb 2003 **NO<sub>3</sub>**, **Si**, **PO<sub>4</sub>**, **Chl a**, Salinity, O<sub>2</sub> (2004 -), **Alkalinity**, **TCO<sub>2</sub> (2005-)**, **pH (2007-)** 



National Oceanography Centre, Southampton



### Trace gas equipment

Consists of an autonomous membrane-inlet purge and trap system, taking samples from the ship's seawater intake, coupled to a GC-MS which is installed within a specially designed laboratory area aboard the MV Pride of Bilbao.

Co-axial stainless steel/silicone tubes act as a membrane for the gas transfer from sea water and the gas is trapped and pre-concentrated using a carboxen trap.

All coupled to an Agilent 6890GC/5973 MSD, fitted with a 30 m CB Sil-5, 0.32 mm id column.

The system, including data collection, is PC controlled and the carrier gas is helium throughout.





#### Robotic sampler

The robotic arm collects three types of sample.

An injection system fills racks of amber glass bottles and cryovials (containing appropriate preservatives) for taxanomic identification by microscopy and flow cytometry

A filter head which filters seawater samples through a series of filter holders for plant pigment analysis.

Where appropriate the robotic arm moves the samples to -20 °C and -80°C freezers.



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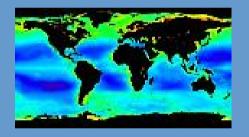




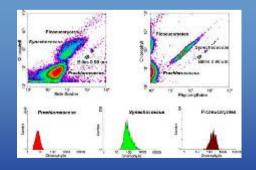
### Limitations



Microscope counts -Time consuming Limited coverage



Ocean colour -Near surface only Large temporal and spatial variability Uncertainties in algorithms





National Oceanography Centre, Southampton UNIVERSITY OF SOUTHAMPTON AND NATURAL ENVIRONMENT RESEARCH COUNCIL Cytometer counts -Primarily small organisms Bulk composition Little information on species

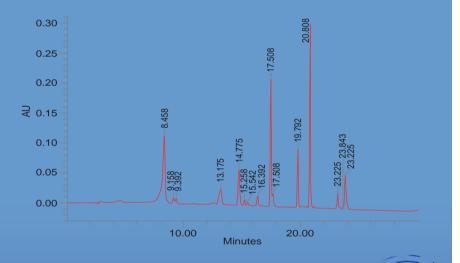
#### Advantages of Pigments

Large number of natural pigments.

Can get definitive identification and quantification using HPLC techniques.

Large sample throughput.

Good geographical coverage throughout water column.



Different taxa and species have different pigment compositions.



#### Pigment Signatures

#### **PIGMENT**

Chlorophylls Chlorophyll a Chlorophyll b Divinyl chlorophyll a

#### Carotenoids

Peridinin Zeaxanthin Fucoxanthin Diadinoxanthin 19 Hexanoyloxyfucoxanthin 19 butanoyloxyfucoxanthin

#### Degradation products Phaeophorbides + many others



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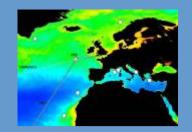
#### **TAXONOMIC SIGNIFICANCE**

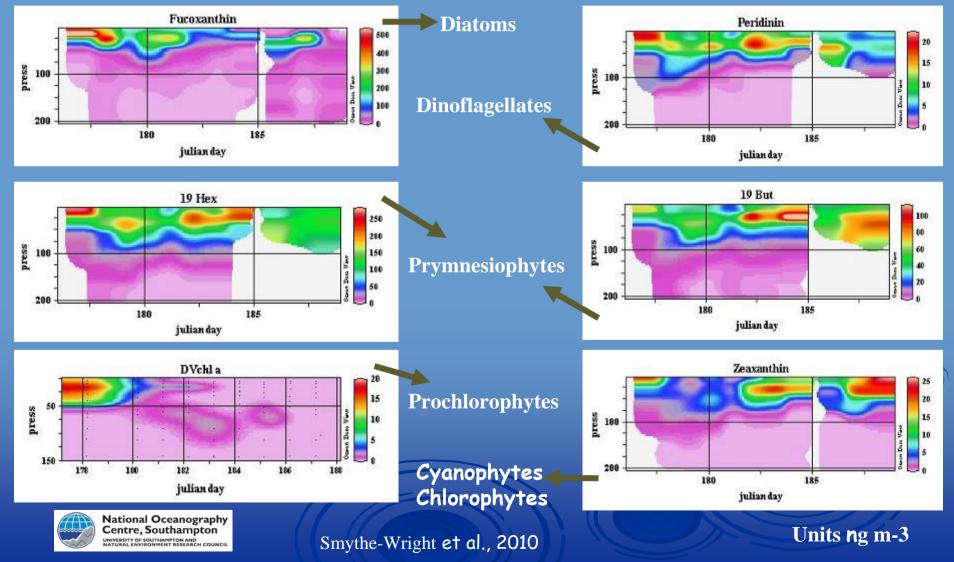
Phytoplankton biomass Green algae (Chlorophytes/Euglenophytes) Prochlorophytes

Photosynthetic dinoflagellates Cyanophytes/Prochlorophytes/Chlorophytes Diatoms Diatoms and prymnesiophytes Prymnesiophytes some prymnesiophytes

Zooplankton grazing/cell senescence

### Pigments



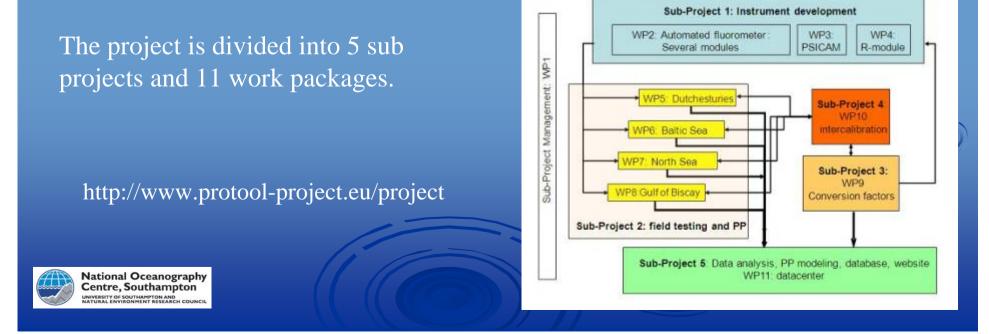


# EU PROTOOL Project



PROTOOL stands for PROductivity TOOLs: Automated Tools to Measure Primary Productivity in European Seas.

Three year (2009-2012) project to develop and adapt technology to measure primary production of phytoplankton with automated optical techniques, so that they can be placed on ships of opportunity (SOOP, ferries, container ships).



#### Conclusions

We have developed an automated trace gas system and a robotic biological samplers for use on the Pride of Bilbao ferry.

They will be used in assessing how trace gas release and phytoplankton production will impact on and in turn be altered by climate change.

Robotic sampler and pigment analysis part of the PROTOOL EU programme.

We are looking for other routes - particularly across the Atlantic and into the Arctic.



# Thank you

