Primary production by plants and algae forms the base of all ecosystem processes, and it is likely that phytoplankton community structure will change over the next century due to climate change. The effect of this on the ocean uptake of carbon dioxide, biodiversity, and hence at a higher level on fisheries is unknown. In addition, the oceans and their margins are home to a wide range of micro- and macroalgae that are known to produce halogenated trace gases through their metabolic processes. Once in the atmosphere, these gases provide mechanisms by which chlorine, bromine, and iodine compounds reach the stratosphere and are involved in the catalytic destruction of ozone. Many of these gases also have the ability to contribute to global warming, while some appear to instigate the production of cloud condensation nuclei that may help mitigate it.

Fig 1 shows the distribution of two important trace gases, methyl bromide and methyl iodide in the North Atlantic and how they respectively follow the distribution of Dinoflagellates and Prochlorococcus (and its marker pigment divinyl chlorophyll-a) and are able to escape to the atmosphere [1]. In general ocean trace gas production and release is patchy both temporally and geographically and this makes assessment of the global ocean air-sea flux difficult to assess.[2]

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. Therefore, to further our knowledge of trace gas release and to understand how marine ecosystems might change in the future 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. To this end, we have developed automated systems for the collection of biological samples and the analysis of halogenated trace gases for deployment on ships of opportunity such as the Pride of Bilbao ferry.

The biological sampler (see Fig 2a) is a robotic arm that collects three types of samples using an injection system. Racks of amber glass bottles and cryovials (containing appropriate preservatives) are filled for taxonomic identification by microscopy and flow cytometry and up to 3 litres of seawater is filtered 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, from where they are collected for processing back in the National Oceanographic Centre, Southampton.

The trace gas instrument is an autonomous membrane-inlet purge and trap system, taking samples from the ship's seawater intake, coupled to a GC-MS (see Fig 2b). It comprises co-axial stainless steel/silicone tubes that act as a membrane for the gas transfer from sea water and a carboxen trap, all coupled to an Agilent 6890/5973 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.

The two systems are installed within the engine room of the MV Pride of Bilbao and attached to the ship's seawater intake. They work alongside a standard ‘Ferrybox system’ which logs temperature, salinity fluorescence and oxygen and sometimes includes a CO₂ measuring system.

The MV Pride of Bilbao ferry form Portsmouth, UK to Bilbao, Spain covers two return journeys per week throughout the year. The route crosses eutrophic inlets, stratified and well mixed coastal seas, the shelf break and an oligotrophic deep-sea section of the Bay of Biscay. This enables us to study the dynamic processes that control trace gas production and loss and the consequential air-sea gradient of these environmentally important compounds over a range of temporal and spatial scales and relate them to oceanic, meteorological and biological conditions. Not only does the work give insight into air-sea gas exchange, but also assists in our understanding of phytoplankton community structure, its natural variation and that which is responding to global change, including ocean acidification. The information is being used to better characterise phytoplankton communities from ocean colour, plant pigment and species analysis and ultimately to better estimate the
The extent of oceanic trace gas production on a global scale, thereby reducing the uncertainty in halogenated trace gas fluxes globally.

The novelty of the work is the integrated long time-series, simultaneous, high density measurements of a range of halogenated trace gases in seawater and air together with associated biological and other measurements. The community structure work forms part of the new EU programme PROTOOL and the concept will be taken forward within the SCOR/IAPSO (Scientific Committee on Ocean Research/International Association for the Physical Sciences of the Ocean) working group Ocean Scope.

REFERENCES


Figure 1 Gases and phytoplankton in the Atlantic Ocean

(a) (b)

Figure 2: The automated biological and trace gas samplers