> To this point, no studies have directly examined the potential importance of Sargassum as a source of polyphenolic CDOM in open ocean waters

The role of Sargassum in the production of oceanic dissolved organic matter

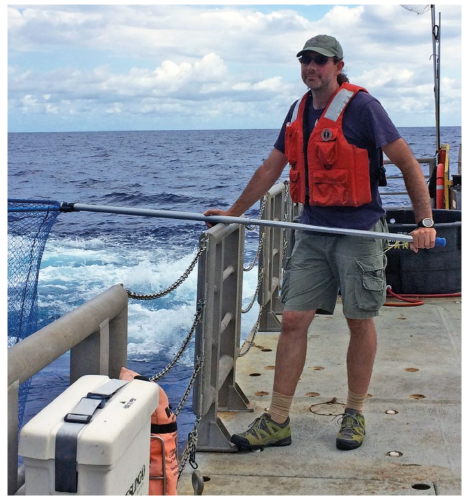
Dissolved organic matter plays an essential role in influencing underwater light fields and facilitating biogeochemical reactions in the ocean but to date, scientists know very little about the structure and diversity of these compounds. **Professor Michael Gonsior**, of the University of Maryland Center for Environmental Science, and **Rossana Del Vecchio** and **Neil Blough** of the Department of Chemistry and Biochemistry at the University of Maryland, have been working on a National Science Foundation-funded study researching the role of Sargassum seaweed as a source of dissolved organic matter in the open ocean.

Dissolved light absorbing compounds, collectively known as chromophoric or coloured dissolved organic matter (CDOM), play an essential role in marine and freshwater ecosystems. Its primary role is to absorb sunlight and generate photochemical reactions in the sea. These compounds are therefore known to play an important role in carbon cycling, mixing of surface water masses and basin-scale biogeochemical processes such as the production and degradation of reactive oxygen species and the cycling of biologically important trace elements. However, to date, we do not have a good understanding of these compounds. In coastal systems, we know the major source of CDOM is run off from terrestrial sources, but in the open ocean, sources of marine CDOM remain debatable and a comprehensive understanding of its origins, distribution and fate have been difficult. Professor Michael Gonsior and his team from the Chesapeake Biological Laboratory are looking at the potential sources of CDOM, specifically, the role of the brown macroalga, Sargassum, in the process.

WHERE DOES CDOM ORIGINATE?

Despite its importance in oceanic habitats, the structure and diversity of CDOM has been largely unknown. It is widely accepted that in estuaries and nearshore waters, CDOM mostly comes from rivers that drain the land, and is most notably comprised of the degradation products of lignins. Lignin is a substance unique to vascular plant cell walls and is a class of complex organic polymers that form important structural support. Sea grasses and mangrove leaf litter also have an important role in CDOM generation in sub-tropical or tropical coastal waters. On a global scale, organic export from tropical mangrove expanses comprises >10% of the terrestrial organic matter pool in oceanic waters. In the open ocean, however, the sources of these compounds are not widely understood.

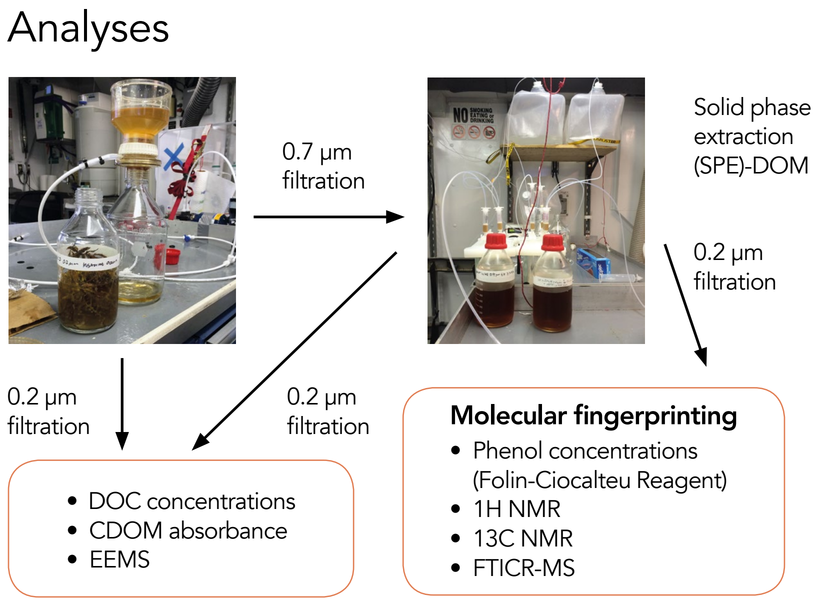
It has been suggested that oceanic CDOM is derived during the microbial transformation of particulate or dissolved marine source



Above: Michael patiently waits for *Sargassum* sightings.

Left: Niskin bottles to sample ocean water at any desired depth.

Right: Chemical Analyses of *Sargassum*-derived DOM.
Below: Freshly collected *Sargassum* from the Gulf Stream.



materials originating from phytoplankton, or that has a basis in zooplankton, cyanobacteria or as a result of microbial action. Some studies refute this based on the optical properties of the source materials and suggest that it is a remnant of terrestrial material which has been diluted and modified during transit to the oceans. It is however understood that the widely distributed brown algae, Phaeophyceae, contains a specific group of polyphenols known as phlorotannins. These compounds are known to absorb sunlight and protect the plants from harmful UV rays, extending into longer wavelengths in the visible creating an absorption spectrum similar to that of CDOM from terrestrial sources. As with lignins, phlorotannins also provide structural support to the plant and have antioxidant and antimicrobial properties. In addition,

> ***Sargassum* exudates high levels of coloured antioxidants known as phlorotannins**

it is thought that the algae exude these phlorotannins as protection from grazers and herbivorous fish and, as growth inhibitors for epiphytes.

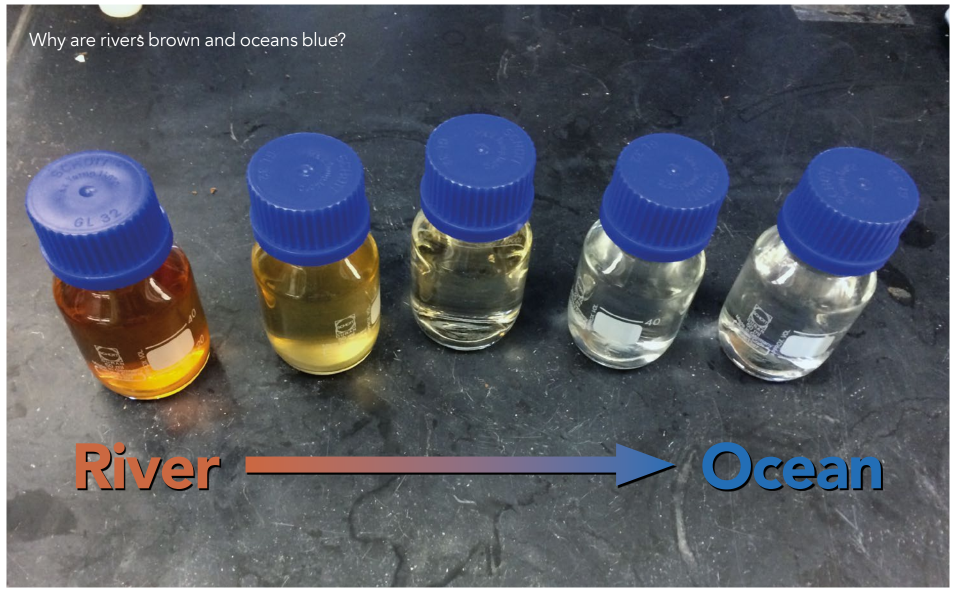
DOES SARGASSUM HAVE A ROLE IN OCEANIC CDOM?
One such brown alga is Sargassum. Professor Gonsior's study hopes to elucidate the role of these continually produced phlorotannins from these plants and their importance in the production of oceanic CDOM.

The team selected Sargassum natans and Saragssum fluitans as study organisms as these are macroalgal species known to be truly holopelagic, that it floats throughout its lifespan and can, therefore, be found in offshore environments. These species live in the surface waters of the Gulf of Mexico, the Western Atlantic and the Sargasso Sea where they form extensive mats large enough to be observed by satellites and contribute a significant biomass to the local ecosystem in summer months.

Plants were collected from the study area and treated in the lab. Preliminary data from the studies confirmed that DOM (dissolved organic matter) exuded by Sargassum has polyphenol-like structures and could, therefore, provide a significant source of CDOM in this region.

Earlier work on Sargassum exudation (Shank et al 2010) supports this finding and highlights environmental variations on exudation rates due to the length of incubation, light and temperature variations. For instance, higher water temperature has a positive correlation with CDOM production. This is also reinforced by a Norwegian study (Abdullah and Frederiksen 2004) which showed that 26% of carbon fixed by kelp was exuded as DOC.

These results challenge the long-held belief about the terrestrial origin of oceanic CDOM and suggests that Sargassum may be a significant contributor to the marine DOC pool



Q&A

Based on the findings from Sargassum and the Norwegian study on kelp, can you suggest the percentage of nearshore/estuarine CDOM from coastal algal sources?
CDOM is not a thing, it is an optical property and you cannot determine its concentration, or how much there is. However, Krause-Jensen and Duarte (2016, Nature Geoscience) estimated that macroalgae export 0.36 Pg C per year as DOC.

Do the different algal groups release different concentrations of phlorotannins? For instance, brown vs red algae which is most susceptible to light damage.
Only brown algae release phlorotannins. However, algae all contain different classes of polyphenols. Even though these compounds have been extracted from algae, there is not much information on how much phenolics algae actively release.

Do you think there are additional alternative sources of CDOM in areas where free-floating macroalgae does not exist?
Yes, possibly from picocyanobacteria. See publication: (Zhao Z, et al. (2017) Picocyanobacteria and deep-ocean fluorescent dissolved organic matter share similar optical properties. (Nature Communications 8:15284.)

In large lakes such as the Great Lakes in Northern US, does all the CDOM come from riverine sources? Are the riverine inputs significant enough to support the extensive water volume?
I think CDOM mostly comes from the land that drains into the lake but there are likely *in situ* sources as well.

You mention CDOM moving through the water column – what is the significance of this and can it be recycled through biological activity?
If photochemical degradation is the primary sink for CDOM, any CDOM that makes it below the mixed layer could potentially be sequestered for 500 – 1000 years if it's biologically recalcitrant. Biology is likely responsible for degrading some fraction of CDOM, but it also can produce CDOM, which is another reason why marine CDOM sources are so poorly understood.

in the Gulf of Mexico, and the Western North Atlantic, where it grows abundantly.

In addition to the surface release described in these studies, Sargassum could also be an important source of phlorotannins throughout the water column. As the plants sink due to damaged air bladders, the chemical is released as the plant dies, by microbial degradation.

APPLICATIONS
Information on the primary sources and global distribution of CDOM in open oceanic waters has only recently emerged. As CDOM plays an important role in the optical properties of surface waters, satellite ocean colour measurements have also been employed to examine its distribution and dynamics over broad temporal and spatial scales, thus providing important data for these large-scale processes. A deeper understanding of these processes is also essential to understand the potential damage to light-sensitive organisms. CDOM interferes with remote sensing of ocean chlorophyll and can control UV-induced damage to organisms such as corals so developing our understanding of CDOM dynamics will support predictions on longer-term reef vitality in these tropical and sub-tropical regions.

Professor Gonsior's study confirms that Sargassum has a role to play in the generation of CDOM. Further work will continue to characterise the optical properties and molecular composition of Sargassum-derived CDOM including its aerobic oxidation and photochemical behaviour, as well as to quantify Sargassum-derived CDOM to better estimate its possible contribution to the CDOM pool in the Sargasso Sea and Gulf of Mexico.

Detail

RESEARCH OBJECTIVES
Professor Gonsior and his colleagues are researching the role of Sargassum seaweed as a source of dissolved organic matter in the open ocean. This NSF project investigates the molecular complexity and reactivity of DOM released from brown algae with the aim to understand how these are related to general CDOM photochemistry.

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COLLABORATORS
University of Maryland:
- Rossana Del Vecchio (rossdv@umd.edu)
- Neil Blough (neilb@umd.edu)

BIO
Professor Michael Gonsior is a researcher and lecturer at Chesapeake Biological Laboratory within the University of Maryland Center for Environmental Science. He received his Chemistry PhD at Otago University Dunedin, New Zealand. His area of expertise is the molecular diversity of complex dissolved organic matter.

CONTACT
(Prof) Michael Gonsior, PhD
Assistant Professor
University of Maryland Center for Environmental Science (UMCES)
Chesapeake Biological Laboratory
146 Williams Street
Solomons, MD 20688
USA

E: gonsior@umces.edu
T: +1 410 326 7245
W: www.umces.edu/michael-gonsior
W: www.mdsg.umd.edu/reu/mentors/michael-gonsior-phd