Monitoring marine methane

Dr Valérie Chavagnac sheds light on the importance of improving data on the origin and amount of methane in marine environments and details the headway her project is making.

Can you begin by discussing your career, including the influences that sparked your interest in ocean geophysics?

I studied geology and geochemistry during my undergraduate and Master’s studies. I then did my PhD on the old continental crust looking at the behaviour of the isotopic system. My aim was to assess the reliability of ages obtained on metamorphic rocks to better constrain crustal growth and/or tectonic events. My interest in the ocean started in 2000 when I moved to the National Oceanography Centre in Southampton, UK. Here, I changed my research theme radically to focus on marine hydrothermalism.

What role does methane play in both ocean biogeochemistry and climate change?

The present perturbation of the atmospheric radiative balance on Earth, and hence the global climate, is mainly due to anthropogenic emissions of carbon dioxide and methane – both important contributors to the greenhouse effect. Although methane is a trace gas, it contributes to up to 20 per cent of the greenhouse effect due to its high global warming potential, which has resulted in a doubling of the atmospheric methane concentration within the last 300 years.

Coastal environments account for 75 per cent of oceanic emissions to the atmosphere, which contribute to about 2 per cent of the global atmospheric emission.

Why is it important to improve knowledge about the sources and amount of methane in our oceans?

The world climate is undergoing an evolution and this will have significant effects on global temperature, hydrology of land surfaces and sea level. Consequently, it will be critical to quantify the global warming effects of methane emissions from wetlands and oceans.

How would you describe the current state of available data on marine methane?

Despite the high concentrations of methane present in fluids and sediments, oceans remain under-saturated with respect to the atmosphere due to the effective consumption of methane from microbial oxidation.

However, significant uncertainties about the amount of methane emitted and absorbed by the oceans still exist, due to the high variability of methane emissions, as well as the unknown distribution of marine sources and sinks. The current evaluation of the methane produced by the oceans – and more generally by aquatic ecosystems – could be underestimated due to the hitherto lack of high-resolution measurements.

Is the field of ocean biogeochemistry responding to this concern?

Environmental observation strategies are currently shifting from the acquisition of discrete samples towards the use of fixed or mobile platforms instrumented for acquiring data at remote locations. This is true for both continental and oceanic environments. At sea, different mobile strategies, as well as a combination of observational strategies, offer the ability to cover a wide range of spatial scales, while fixed platforms such as moorings or bottom landers allow long-term temporal observations.

Can you explain how your work on PROMETHEUS fits into this context?

Technological advances made in supramolecular chemistry and photonic devices were combined in a recent study to detect and measure methane concentration in oceanic environments. Their strategy, which we have built upon in PROMETHEUS, was based on the deposition of a selective and sensitive polymeric film that changes its refractive index (RI) by adsorption of methane and alters the RI measurements by surface plasmon resonance (SPR). The sensitive thin film is composed of cryptophane-A molecules mixed within an optically transparent polymer coating. The fibre sensor under development in our project employs a polymeric film containing cryptophane molecular traps sensitised to methane.

Testing of the prototype in a laboratory environment indicates a detection limit of 0.2 nM of methane, a response time of 1.8 minutes, a sensitivity of 3.2-5.1 x 10⁻⁹ RIU/nM of methane, and a good reproducibility of the sensor within the range of 180-300 nM. The technical features of this prototype suggest that the sensor could be used in the marine environment.
Oceans of change

A diverse group of researchers led by the Geosciences Environnement Toulouse is developing and testing a novel in situ aqueous gas sensor that will improve monitoring of greenhouse gas emissions.

Throughout History, the Earth’s climate has undergone a number of natural changes as a result of small variations in the planet’s orbit. Presently, however, Earth is experiencing a warming trend that is proceeding at an unprecedented rate. Scientists have found evidence that the change is human induced, with the increasing amount of greenhouse gases being emitted into the atmosphere causing our planet to warm in response. These warming conditions have numerous serious effects on the planet, such as rising sea levels, warmer oceans, glacial retreat and more extreme weather events.

Warmer temperatures also cause the melting of permafrost – soil that is at or below the freezing point of water for two or more years. This releases large amounts of methane into the atmosphere. Although it is not one of the most abundant gases, methane is a greenhouse gas that has a global warming potential 25 times more influential than carbon dioxide over a 100-year timescale. Higher ocean temperatures and variations in the sea level also lead to the destabilisation of gas hydrates in the oceans. Therefore, in light of these changes and the major effect of methane on global conditions, there is an urgent need to understand the location and amount of methane in Earth’s marine environments to paint a picture of their likely contributions to worldwide methane volumes.

Dr Valérie Chavagnac of the Geosciences Environnement Toulouse is working on a project that is co-funded by the French National Research Agency (ANR) and German Research Foundation (DFG) that will profile methane emissions in the seas by developing novel molecular receptors for methane recognition. The project, entitled ‘PROfiling METHane Emission in the Baltic Sea: Cryptophane as in-situ chemical Sensor’ (PROMETHEUS), brings together a transdisciplinary team of chemists, marine geochemists, optical technologies specialists and engineers. Their aim is to significantly improve the current methods and tools employed by ocean geochemists to perform marine measurements of methane.

Shifting Sampling Techniques

Traditionally, researchers collect samples during research vessel cruises or field programmes that are later analysed in a laboratory setting. As Chavagnac points out, however, there are some shortcomings to this process that can affect the final data output. “There are several inherent disadvantages in using sampling approaches: sampling is time consuming, expensive and significant errors may arise due to the volatile nature of hydrocarbons,” she outlines. “In general, laboratory-based analyses are performed under temperature and pressure conditions that are significantly different from those of the natural sampling site.”

There have been efforts made to address these limitations by conducting on-ship analyses with dedicated laboratory equipment that is designed to measure key oceanographic conditions such as temperature, depth, conductivity, oxygen concentration and turbidity. While this has marked an improvement, there is still a need for monitoring tools that can deliver real-time, in situ measurements of chemical parameters, such as dissolved methane.

Innovating with Sensors

In response to the need for new receptors for methane recognition, Chavagnac and her team of scientists have developed new optical sensors to identify dissolved methane. The first makes use of surface plasmon resonance, as Chavagnac details: “A polymeric thin film is deposited at the outer interface. The interaction of light waves with the free electrons in the metal leads to the creation of an evanescent field that can be used as a platform and sensitised for interaction with the targeted chemical species.”

Based on the initial results obtained during the previously completed MAISOE project, funded by Thematic Networks for Advanced Research (RTRA) – Science and Technology for Aeronautics and Space (STAE), France, the sensor is under further development in PROMETHEUS and utilises an innovative technique exploiting a polymeric film containing cryptophane molecular traps that are sensitive to methane and form a sensing layer that is interrogated optically. Cryptophanes are a class of organic supramolecular compounds, and in recent years, research with cryptophane hosts
INTELLIGENCE

PROMETHEUS: PROFILING METHANE EMISSION IN THE BALTIC SEA: CRYPTOPHANE AS IN SITU CHEMICAL SENSOR

OBJECTIVE
To create and validate the findings of a new sensor for in situ, real-time methane measurements in aqueous environments based on the refractive index modulation of a sensitive film composed of a polydimethylsiloxane layer incorporating molecules of cryptophane-A.

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DR VALÉRIE CHAVAGNAC
was educated as a geologist-geochemist at Paris XI during her undergraduate studies. She then attended University of Joseph Fourier and University Rennes 1 for her Master’s studies. She earned her PhD while jointly working between the University of Rennes 1, France, and the University of Bern, Switzerland, by looking at the behaviour of isotopic systems on the old continental crust.

has shown that they are particularly well suited for recognising various gaseous compounds like noble gases. “To render the fibre sensor more robust to environmental perturbations such as temperature and vibration, the sensor is mounted in a differential set-up and exploits a synchronous detection system, which further improves its sensitivity to methane,” Chavagnac adds.

LOCATION IS KEY
The PROMETHEUS team needed to find the right environment for testing the effectiveness of its new sensor. Chavagnac explains the ideal conditions for this work: “Testing this sensor in the natural and marine environment required access to an oceanic region presenting strong dissolved methane gradients through the water column, while most of the other chemical features would be already assessed and understood.”

Taking into consideration these criteria, the researchers are focusing their effort on the Baltic Sea, which is home to a succession of basins surrounded by submarine sills, each of which exhibits different hydrological conditions. “The central basins show the strongest enrichments in dissolved methane close to the seafloor – up to 1,000 nM in the Landsort Deep and 500 nM in the Gotland Deep,” Chavagnac elaborates. “However, concentrations decrease rapidly toward the redoxcline, as low as 4–5 nM in theoxic surface waters, corresponding to 120–200 per cent saturation with respect to atmospheric equilibrium.” Moreover, the GODESS station in the Baltic Sea registers a number of parameters with high temporal and vertical resolutions. Adding a dissolved methane sensor on the profiling platform, which is already hosting a sensor suite, enables the PROMETHEUS team to better understand methane biogeochemical cycle.

VALIDATING RESULTS
With a suitable location identified, the researchers were ready to begin testing their sensor for the first time in August 2012. Sampling and measurements using the dissolved methane sensor were conducted at 10 stations in the Baltic Sea. An in situ water pumping system with methane detection on board the research vessel allowed for continuous water sampling down to 400 m depth.

After collecting the data, the researchers wanted to ensure the information they collected was accurate. Therefore, they compared it to data that had been previously collected on methane concentrations using other reliable techniques. The datasets were similar, proving that in situ sensing technology to detect and measure methane concentrations in the water column is possible. However, the team notes that it is too early in the project to shed new light on methane emissions in the Baltic, or the processes by which oceanic methane is released into the atmosphere in general.

Nevertheless, the future looks positive for the new techniques and the researchers intend to extend them to detect other gases such as carbon dioxide and H₂. The advance will be greatly welcomed in the field where sensor development has taken a long time to come to fruition. “Although many sensors are currently available for underwater use, there remains a lack of new biogeochemical sensors, especially for long-term deployment in a deep-sea environment,” Chavagnac highlights. She believes that future advances in this area will be aided by her close network of experts working on sensors in the aqueous environment. Although a niche area of research, the work of the small team will have global benefits, as monitoring of greenhouse gas emissions is a worldwide concern.