Aboard the French research vessel the *Marion Dufresne*, the researchers investigated the gas emissions of phytoplankton in the southern Atlantic – usually in stormy seas and sometimes with a view of icebergs.
Searching for Traces in Heavy Seas

Precisely which gases escape from the sea into the atmosphere is important for climate change, but it is an issue that remains largely unexplored as yet. Jonathan Williams and his colleagues at the Max Planck Institute for Chemistry in Mainz embarked on board a research vessel to investigate the emissions.

Althought most of our planet is covered by water, it is called Earth. This could be because we know so little about the oceans and have only recently been able to investigate them. Isaac Newton’s comment, “What we know is a drop, what we don’t know is an ocean,” hits the nail on the head. One of the fields where there are large gaps in our knowledge is the exchange of gases between the ocean and the atmosphere – especially if one considers how much is known about comparable processes on land. This knowledge is sorely lacking, because the fact that seawater can absorb or release gases plays a major role in global atmospheric chemistry. It is precisely to enable us to take these processes and their effects on climate change better into consideration that we must investigate them in greater detail.

We have particularly little knowledge about the group of organic – that is, carbon-containing – compounds that are volatile, meaning they evaporate quickly. Experts call these volatile organic compounds, or VOCs. They are chiefly released into the air by trees and plants, and the plants in the ocean are called phytoplankton. These substances can have an important effect on key compounds in the atmosphere, such as ozone. For many of the VOCs, very little research has been done as yet on what role the oceans play.

WHAT SUBSTANCES DO MARINE PLANTS RELEASE?

On a global annual basis, plants on land convert about 56 billion tons of carbon, present in the atmosphere as carbon dioxide, into biomass. This plant matter weighs roughly 100 times more than the total world population. Although the mass of the plants in the oceans measures just one hundredth of that of the plants on land – because there are no trees, for example – they absorb about the same amount of carbon: 49 billion tons. For the most part, researchers can only guess what other substances are exchanged and in what quantities. There is thus an urgent need to investigate the interface between the ocean and the atmosphere in order to understand the global atmospheric chemistry of the past, present and future.

To enable the unanswered questions concerning the atmosphere-ocean interface to be addressed, the European Union provided a budget of two million euros for the period 2005 through 2008 for a research project called OOMPH – “Organics over the Ocean Modifying Particles in both Hemispheres.” The OOMPH project brought together an international consortium of nine research groups from Germany, France, Greece, the United Kingdom, Italy, Belgium and Hungary, and was conceived and coordinated by my group at the Max Planck Institute for Chemistry in Mainz.

Our project investigated organic compounds – from their production by phytoplankton in seawater to the transfer into the gas and aerosol phases and onward to regions of the upper atmosphere. An essential part of the work involved a bit of an adventure: a journey through the Roaring Forties aboard the French research vessel the Marion Dufresne. This part of the southern Atlantic, between 40 and 50 degrees south latitude, owes its name to the roaring winds that often sweep across it at hurricane force. The voyage was to take us...
top  Sea in green: The green streaks of the algal bloom are clearly visible on an aerial photograph.

bottom  Sea in blue: Outside of the plankton bloom, only the sky determines the color of the ocean – plenty of opportunity for the scientists to measure clean air as a reference.

Photos: Okapia (top)/iStockphoto (bottom)
from South Africa to Tierra del Fuego in Chile and lead us through a particularly lush bloom of phytoplankton.

**PLANKTON GASES IN A LAB TEST**

But before we installed our measuring instruments on board the ship, the OOMPH team worked in the lab to determine which particular organic emissions actually originate from phytoplankton and how they depend on light and temperature. We wanted to determine in advance which organic components we were likely to encounter during the ship-based measurement campaign.

The team thus selected several types of phytoplankton that are plentiful all over the world and grew them as monocultures in incubation chambers. Clean air was streamed through the culture chambers under different day/night light cycles and this flushed all of the gases emitted by the phytoplankton out of the chamber and toward the detectors. Interestingly, all of the phytoplankton cultures we measured emitted carbon monoxide, albeit in varying quantities. The plants clearly changed their carbon monoxide emissions as a function of the incident light. We thus knew that phytoplankton release carbon monoxide from the ocean into the atmosphere during the daylight phases.

Even after the lab tests were completed, it was still not time to put to sea. We first wanted to draw up a forecast as to which volatile organic compound emissions we could expect to record during our measurement campaign on the ocean. To this end, our team combined the VOC emission data of different phytoplankton species with new satellite images of the global phytoplankton distribution.

By combining the emission rates and the emission distribution in a global model, we were able to estimate the global emission of selected compounds from seawater. In this way, we proved that the annual quantity of isoprene that escapes from the ocean is between 0.31 and 1.9 million tons, and thus well below the 500 million tons that the plants on land emit.

These results made a valuable contribution to the heated debate over a 2006 publication on satellite measurements. That study championed the view that marine isoprene from a phytoplankton bloom in the southern Atlantic had influenced the properties of the clouds above it. The OOMPH team’s findings lead us to take the view that too little isoprene rises from the sea to influence cloud formation. It is our opinion that a different explanation will have to be found for the changes observed.

**TRIAL RUN OFF THE WEST COAST OF AFRICA**

We were now finally able to start the preparations for our ship-based measurement campaign, which was intended to show whether our results from the laboratory and from our model could be confirmed in nature. But before the actual measurement campaign in the southern Atlantic, we set out on a trial run to test how the newly developed instruments worked. The journey took us through the calm waters of the tropical Atlantic off the west coast of Africa.

The analysis of the tests showed that the ideal region for the efficient measurement of sea emissions had to fulfill the following three criteria: it should be free of terrestrial influences from its environment, and it should have high wind speeds and a high phytoplankton occurrence that must be easy to locate. The Roaring Forties in the southern summer thus offer the ideal conditions.
Our measurement campaign aboard the *Marion Dufresne* took place between January and March 2007 and took us from Cape Town, South Africa to Puntas Arenas, Chile and back to Durban, South Africa. At this time of year, a large region of phytoplankton bloom that looks like a huge flower when viewed from satellites forms in the southern Atlantic.

**RESEARCHING ON SHAKY GROUND**

There is hardly a better region on Earth to look for absolutely clean air than the southern Atlantic Ocean – far removed from dry land and human activities. The strong winds are also welcome, because they promote the exchange of trace gases between ocean and atmosphere. However, these winds often develop into hurricane-force storms, which provided all of us with a range of new work experiences. It wasn’t only the fact that we had to carefully tie down all of our instruments. Every movement on the rolling ship becomes a balancing act. And, at least in the beginning, some of us were very pale around the gills as we monitored our measurements. It wasn’t the results that caused us to blanch, but the seasickness, which affected almost every one of us for a couple of days during the voyage.

Every now and again huge waves towered up in front of us, and our ship rocked so much that one or another of us was sometimes thrown off their chair. Under such conditions, the captain naturally forbade us to venture out on deck, or even to the mast in the bow where we had installed the inlets for our analytical instruments.

Whether we were eating, walking across the deck or playing basketball in the ship’s hold, when the ups and downs of the ship often made us feel as if we were flying or falling into an abyss – our daily routine became very shaky. Despite the difficult working conditions and one or two technical difficulties that we simply had to improvise our way through, we busily collected data.

Before we came to the region of the algal bloom, the measurements proved how clean the air above this part of the ocean is. The team detected extremely low terrestrial emissions, such as nitrogen monoxide and nitrogen dioxide, during the voyage. The measurements of the unpolluted air provided the background for the research on the plankton bloom. As we reached this region, we could see from the deck that the water suddenly turned green. At the same time, the measured levels of many components suddenly showed extreme peaks.

As expected from the lab tests, increased carbon monoxide values could also be measured in the seawater in the bloom region. As we reached this region, we could see from the deck that the water suddenly turned green. At the same time, the measured levels of many components suddenly showed extreme peaks.

**ENCOUNTER WITH A FISHING FLEET**

Interestingly, the composition of the VOCs changed as the ship crossed the bloom. The same was true of aerosols. Electron microscope images of aerosols from this region showed gelatinous fibrous lumps on sea salt particles with significantly more organic matter than is found outside the bloom. In the aerosols, we detected methane sulfonic acid, a product of DMS oxidation. The changes to the gas and aerosol composition correlate with the varying phytoplankton distribution we observed on our voyage.

Although we planned our route through one of the most remote and inhospitable regions of the world, we did not escape the effect of human activity – this seems to be almost impossible on the Earth of the 21st century. Just as we were crossing a high-chlorophyll region on February 2, 2007, the *Marion Dufresne* completely unexpectedly encountered a large fishing fleet consisting of around 150 to 200 ships at about 45 degrees south and 59.3 degrees west. The fleet caught squid, mainly at night, and used a huge number of very powerful lights to lure them to the boats. This illuminated fleet is so bright that it can easily be seen on
The light requires around 200 megawatts of power – as much as a small power station – which the fleet produces with its diesel engines. In a region that is characterized by the natural emissions of phytoplankton bloom, the ships thus represented a powerful source of anthropogenic gases, especially nitrogen monoxide and nitrogen dioxide.

**OZONE FROM SHIP EMISSIONS AND PLANKTON GASES**

Although the objective of the OOMPH ship-based campaign was to investigate natural emissions, this chance meeting provided us with a further interesting finding: with an atmospheric chemistry model adapted to ocean measurements, we demonstrated that a large amount of ozone is produced where the emissions from ships and the natural emissions of phytoplankton bloom coincide. This is a problem that should not be underestimated, because fishing normally takes place in regions that are rich in phytoplankton, where fish find a plentiful supply of food. Our future atmospheric chemistry models must thus take into account how the emissions from the phytoplankton and the ships interact.

At the end of six or so weeks of taking measurements aboard the Marion Dufresne – a little less than three weeks for the outward voyage and somewhat longer for the return – we had collected a great deal of valuable data. Together with the tests done in the lab, the modeling and the satellite measurements, they reveal much about the volatile organic substances that escape from the sea. The pioneering work done in the OOMPH project has thus successfully characterized many processes that affect organic compounds. This more than compensates for the often inhospitable conditions on board, as do the encounters with whales and icebergs that gave this research expedition its very special appeal.

The research team on board the Marion Dufresne: Jonathan Williams, Project Manager at the Max Planck Institute in Mainz, kneeling in the second row wearing sunglasses.

**GLOSSARY**

**Phytoplankton**
Encompasses the types of plankton that carry out photosynthesis. It is the first link in the aquatic food chain.

**VOC**
Volatile Organic Compound; the volatile organic compounds include methane from marshes, rice cultivation and cattle farming, as well as traces of solvents and combustion residues from engines, plus isoprene and terpenes released by plants.

**Aerosols**
Droplets or solid particles that are suspended in the air and play an important role in chemical processes in the atmosphere, as well as in cloud formation.