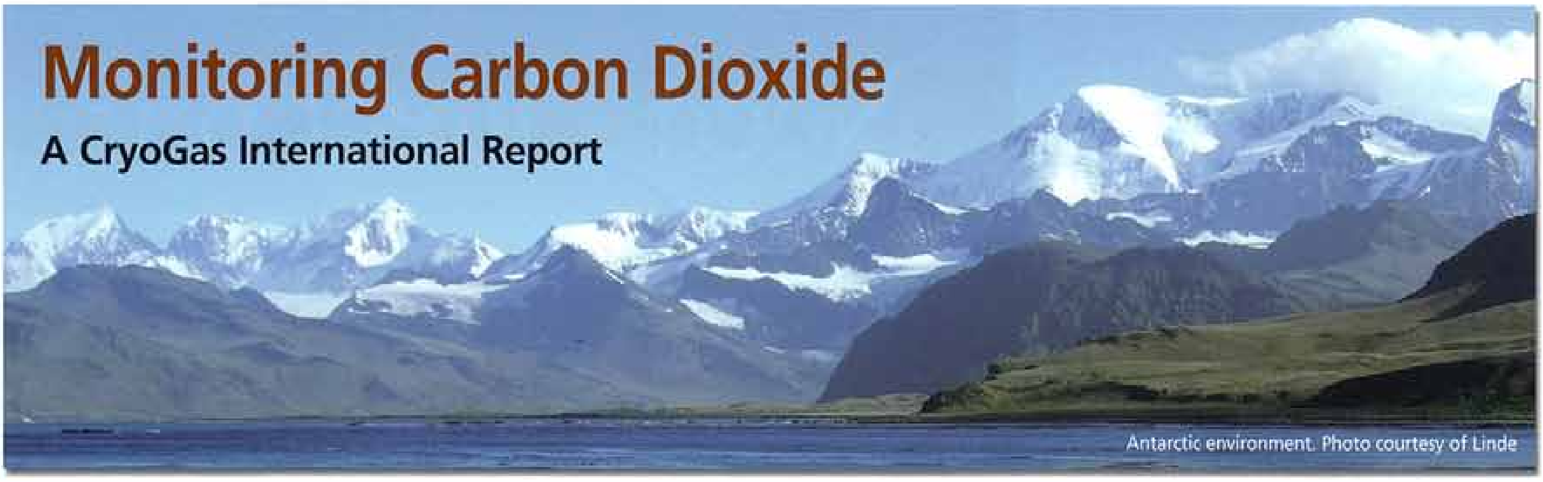
Monitoring Carbon Dioxide

A CryoGas International Report



Antarctic environment. Photo courtesy of Linde

In this section, we look at how industrial gas companies are working with scientists on projects that examine carbon dioxide levels in the Earth's atmosphere. Puzzling through the relationship between greenhouse gases and climate change relies on our ability to measure and monitor these gases, especially carbon dioxide. Today, CO_2 measurements are being derived by examining the ice in polar regions, which captures and stores greenhouse gases and their related markers, thus providing a historic record of emissions. CO_2 is also being monitored from space via satellites.

What Lies Beneath the Weddell Sea

Linde Gas (*www.lindegas.com*), a division of The Linde Group, has an agreement with the University of East Anglia (UEA) in the United Kingdom to support ANDREX (Antarctic Deep Water Rates of Export), a project that will research the role of the Southern Ocean in the global climate system. Linde Gas will help scientists look at CO_2 in the Antarctica region by supplying a technologically complex and rare reference gas required for the expedition. On the ship that is bringing the research team from the university's School of Environmental Sciences to the Weddell Sea in Antarctica, is a cylinder containing Linde's HiQ® calibration gas mixture with 30 parts per trillion (ppt) of sulphur hexafluoride (SF_6).

Since the Industrial Revolution, the world's oceans have absorbed approximately 30 percent of all anthropogenic — human created — carbon dioxide (CO_2) emitted into the atmosphere. Of all the anthropogenic CO_2 emissions to the atmosphere, approximately half stay there; the remainder are absorbed by the oceans and the land (through organic matter storage). The oceans and land act together to slow the accumulation of additional CO_2 in the atmosphere. While CO_2 is more soluble in freshwater than in seawater, freshwater represents only about three percent of the world's water and therefore is not as significant a collector of CO_2 as are the oceans.

Retrieval of the sampling bottle rosette onto the ship's deck. Photo courtesy of Linde

As global emissions have increased, oceanic uptake of CO_2 has also grown in magnitude, but concern exists as to the oceans' continued ability to absorb CO_2 at the pace at which it is being added to the atmosphere. Over timescales of thousands of years, it is estimated that the oceans are able to absorb approximately 80 percent of additional CO_2 added to the atmosphere. However, within shorter times frames (decades to centuries) the rate at which the oceans take up CO_2 will decrease.

A complex characteristic of the seawater carbon system, known as the Revelle factor, dictates that as the oceans take up CO_2, thermodynamic equilibriums change and these can hinder the absorption of more CO_2. The absorption of additional CO_2 by the oceans also makes the water more acidic and this threatens organisms that depend on the stability/level of ocean pH (potentiometric hydrogen ion concentration), like those that grow carbonate shells and corals. In addition, the warming of the surface area of the ocean, which has been linked to climate change, makes oceans less able to absorb additional CO_2. As the ocean's ecosystem is altered over time, it is believed that CO_2 from the atmosphere may be absorbed at a slower rate.

The Southern Ocean is a key region for the uptake and long-term storage of gases from the atmosphere. CO_2 storage processes are thought to be especially strong in the Weddell Sea, where wintertime heat loss and sea ice formation increase the density of the surface water. This density allows surface water to sink to the bottom taking with it gases —

such as CO_2 — that have been absorbed from the atmosphere, with a unique time signature imprint. This sinking process effectively removes the gases from the atmosphere, transporting them away from the surface on millennial timescales. In the interior ocean, the concentrations of these gases — or tracers — can be used as a record of the behavior of both the oceans and the atmosphere over the last 200 hundred years. These records can be analyzed to see how concentrations of gases have changed over time. Information regarding when a water mass was last at the surface is critical to understanding and assessing the role of the oceans in the global climate system, and their ongoing capacity to absorb human-derived constituents such as CO_2 from the atmosphere.

Human-derived carbon dioxide can not be directly measured in the oceans. Instead we measure other tracers that can be directly detected and have histories of atmospheric concentrations similar to anthropogenic CO_2. SF_6 is one such tracer that can be used to track anthropogenic carbon over the last 40 years. SF_6 is a very stable, conservative compound, meaning that it is not affected by the temperatures, chemistry, biology, or physics that it could experience in the ocean or atmosphere. Once in the ocean, its concentration will only be affected by the addition of further SF_6 from the atmosphere, or dilution through mixing with water that contains lower concentrations of SF_6 (or none).

As we have a historical record of the concentration of SF_6 in the atmosphere, and we know about its solubility in seawater, we can predict what its levels would have been at equilibrium with the atmosphere at any point in the last 40 years. By taking deep ocean measurements of SF_6, we can compare the value with the estimated surface equilibrium concentrations and estimate the time when the particular water mass sampled was last at the surface. Where there is no SF_6 detected, we know that this water mass was last at the surface before the 1970s. Where it is detected, we know that this would be younger water. Using these "ages" as a proxy for anthropogenic carbon, we can gauge the amount of anthropogenic CO_2 taken up by the water mass, and then assess the ocean's historical and future ability to absorb, transport, and store it on timescales important to humans (decades to centuries).

Previously, chlorofluorocarbons (CFCs) have been used as tracers of anthropogenic carbon dioxide. These were first released into the atmosphere in the 1930s and provide researchers with a specific time-scale marker. Like anthropogenic CO_2, CFCs had an almost exponential atmospheric growth rate. Since the mid-1990s, however, their atmospheric concentrations have been decreasing, thus diminishing their utility as ocean tracers. SF_6 however, is still increasing in the atmosphere and is a very useful tracer for the last 40 years, and especially for the last 20 years.

The ANDREX project will measure and analyze for SF_6 and compare the results to previous CFC measurements obtained during the 1990s, thereby providing valuable information on the absorption of human-derived CO_2 in this region.

Linde's HiQ 30 ppt gas mixture will be used as both a reference and calibration gas for determining SF_6 concentrations in seawater samples. The gas mixture is a unique blend, which at 30 ppt, involves extremely miniscule concentrations of SF_6 — as tiny as one second of time when compared to a period of 1,000 years, to draw an analogy.

"We are very proud to support the ANDREX project," says Stephen Harrison, Head of Specialty Gases and Specialty Equipment, Linde. "As the global community works towards reducing CO_2 emission, there is growing prioritization in monitoring and quantifying the impact it has on the environment. The accuracy and reliability in measurement has become critical. Our ability to develop and supply the project with such a technologically complex next generation gas standard is testament to our strengths as a world-leading gas technology supplier."

"It is critical to improve our understanding of the oceans' ability to absorb anthropogenic carbon dioxide from the atmosphere and store it over long timescales," said Dr. Peter Brown, of the British Antarctic Survey and the Laboratory for Global Marine and Atmospheric Chemistry at the University of East Anglia. "ANDREX will make a valuable contribution to this, and despite its many challenges, we are excited to have sourced such a technologically complex gas standard from a competent and supportive technology partner."

This section was written by Dr. Peter Brown, University of East Anglia and Stephen Harrison, Global Head of Specialty Gases & Specialty Equipment, Linde. For more information, contact Susan Brownlow, Linde UK Corporate Communications, at susan.brownlow@linde.com.