Automation of the acidification parameters for the Oceans as a result of climate change

Ocean acidification affects marine life. Oceans absorb about 30% of the carbon dioxide that humans emit. Seawater is acidified by a chemical reaction of CO_2 with water, releasing hydrogen ions. The acidification has consequences for marine life because less lime is available for animals to form their skeletons. (See literature reference)

By more accurate determination of the acidification parameters such as **DIC** (Dissolved Inorganic Carbon), **TA** (Total Alkalinity) and **pH** (Acidity) and possibly the **DOC** (Dissolved Organic Carbon), and acidity, a good picture can be formed of the condition of this seawater.

Skalar Analytical has started a collaboration with the RBINS in Belgium to automate and optimize analysis of these acidification parameters for a fast and accurate measurement on a SAN^{++} analyzer.

The Operational Directorate Natural Environment (OD Nature) is one of the Operational Directorates of the RBINS and is a "knowledge center in fundamental and applied research into biodiversity and ecosystems and this in support of the protection and sustainable management of the natural environment".

The approximately 100 employees of our OD Nature have diverse expertise and work spread over 2 locations in Brussels and Ostend.

This Operational Directorate has 4 missions;

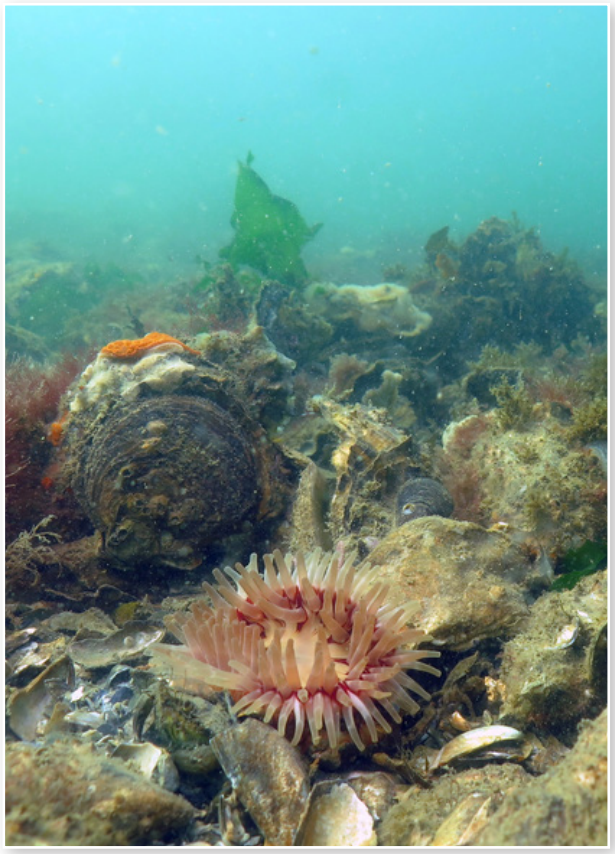
- The study of the biotic and abiotic components of the natural environment and of the interactions between the systems.
- Applying scientific expertise such as a monitoring program for the North Sea and capacity building for biodiversity in developing countries.
- The management and improvement of databases and major scientific instruments such as the research vessel RV Belgica.
- Representing the federal State of Belgium in international policy bodies.

The group ECOCHEM (Ecosystems Physico-Chemistry), ISO 17025 certified, scope 279-Test.pdf (fgov.be), aims to improve the knowledge of the marine, freshwater and terrestrial environment through analytical-chemical, physical and biochemical analyses, through these further developing analyzes and by validating the results.

ECOCHEM's field of activity is broader than just performing and developing salt analyses. Based on this expertise, ECOCHEM advises both within and on behalf of OD NATURE. To this end, ECOCHEM participates in (inter)national working meetings (such as ICES, OSPAR, Quasimeme, etc.). As a result, ECOCHEM contributes to making measurement methods comparable and influences the development in the field of standardization of environmental measurements, both in a National, European, and International marine context.

They also have the additional task of creating intercalibration samples for the analysis of Nutrients, Total Nitrogen, Total Phosphorus, Dissolved Organic Carbon (DOC), Salinity, Dissolved Inorganic Carbon (DIC) and Total Alkalinity for Quasimeme. (WEPAL)

The monitoring program for the North Sea and analysis of samples from the North Atlantic will map the acidification and for this the samples will be taken and delivered by the Belgian Oceanographic research vessel: Research Vessel Belgica. (RV BELGICA, (naturalsciences.be))



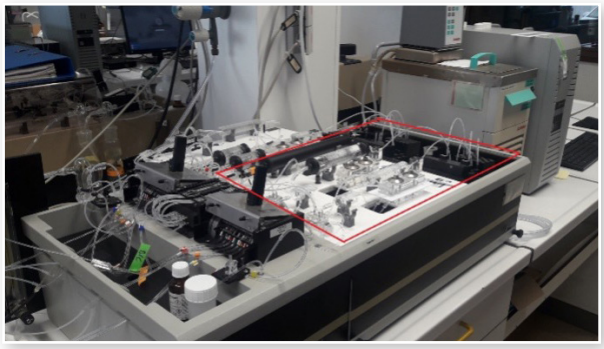
RV Belgica

The ship will be made available to Belgian scientists to carry out marine scientific research.

Approximately 200 seawater samples are delivered per monthly campaign, stored at 4°C and measured as quickly as possible for the parameters DIC, TA and pH.

40 ml vials with septum are used which are filled on board as advised by Andrew Dickson, kept cool after sampling and then placed in the sampler for the analyses.

Analytical modules have been built on the Skalar SAN^{++} analyzer that allow the different parameters to be determined simultaneously from a single sample recording.



Skalar SAN^{++} analyzer showing the acidification parameter modules DOC, DIC, TA and pH

Sampler with 120 positions for 40ml VOA vials with septum

The method for DIC involves acidifying the samples on a dialyzer with a gas dialysis membrane where the CO_2 formation gives a pH shift of the phenolphthalein indicator: the decrease in color is determined spectrophotometrically at a wavelength of 550 nm.

Total Alkalinity is measured using a Bromophenol blue indicator, the absorbance is measured using a spectrophotometer and an interference filter at a wavelength of 600 nm.

The pH module operates with an m-Cresol purple as indicator, is thermostated at 25°C and measured with a matrix spectrophotometer at the wavelengths 580 and 650 nm.

The method for analysis of DOC is carried out after acidifying the samples to remove inorganic carbon, then the sample is irradiated with UV light in the presence of persulfate to convert the organically bound carbon to CO_2, a dialyzer with a gas dialysis membrane wherein the formed CO_2 gives a pH shift on the phenolphthalein indicator: the decrease in color is determined spectrophotometrically at a wavelength of 550 nm.

Because the accuracy of the analyzes is of great importance, some performance characteristics are included below to get a good picture of the analysis data obtained.

Performance characteristics:

	pH	**Total Alkalinity**	**DIC**	**DOC**
Measuring range	7.65 – 8.35	40 – 300 mg $CaCO_3$/l	4.8 – 36 mg C/l	0.09 – 4 mg C/l
Detection Limit	> 7.65	2.5 mg $CaCO_3$/l	0.5 mg C/l	0.09 mg C/l
Repeatability	0.046%	0.70%	1.00%	3%
Reproducibility	0.043%	1.04%	1.60%	9%
Accuracy/Bias	Accuracy 0.003 pH	Bias 0.30%	Bias 1.20%	Bias 4%
Measurement uncertainty	0.1277%	2.0%	3.0%	14%

Why choose Skalar analyzer?

Given the experiences RBINS has with Skalar, and the good relationship in the field of method development in potentially interesting research domains for Skalar, Skalar was prepared to integrate these modules for acidification parameter on one of the three SAN^{++} analyzers available.

By starting this project together and supporting it with years of expertise in the field of automation from Skalar Headquarters in Breda-NL, this project has become a success.

The methods that are now being developed for analysis in the lab will be translated into an online monitoring system (ferry box) at a later stage.

Future?

Publishing is an important task for every researcher. Only in this way can the new knowledge be disseminated to colleagues and to the wider public. Moreover, the research output is one of the criteria for funding, both for the individual researcher and for his research group and knowledge institute.

literature references,

1) Buis, A. (2019, October 9). The Atmosphere: Getting a Handle on Carbon Dioxide. Retrieved on December 26, 2020, from NASA: https://climate.nasa.gov/news/2915/the-atmosphere-getting-a-handle-on-carbon-dioxide/

2) Littschwager, D. (2018, Apr). Ocean Acidification. Retrieved from Smithsonian Ocean: https://ocean.si.edu/ocean-life/invertebrates/ocean-acidification

General info

The Federal Science Policy Office is the proud owner of the Belgian oceanographic research vessel: RV Belgica. The ship will be made available to Belgian and foreign scientists to carry out marine scientific research. The OD Nature of the RBINS is responsible for the budgetary management of the ship, the scientific instrumentation, and the planning of the scientific campaigns. The French Genavir provides the crew, the 3 captains come from the Belgian Navy, which provides a berth in the naval base Zeebrugge.

The RV Belgica is at sea for up to two hundred days a year. In periods from Monday to Friday, but also during weekends and consecutive periods of 6 to 8 weeks, the ship departs from Zeebrugge and sails to all corners of the Belgian part of the North Sea, but also far beyond into Moroccan, Portuguese, Spanish, French, British and Irish waters. The research vessel was already operational in the Mediterranean and has ambitions for research in the Arctic.