ECO2, D3.2 Technical report on chemical sensors performance

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The report will present an overview of sensors that are useful for the study of seeps, and present a detailed comparison of commercial and prototype CO_2 and pH sensors.

CO_2 sensors: 1) Severinghaus CO_2 sensors (Microelectrodes ltd), 2) the HydroC-CO_2 logger sensor (CONTROS GmbH), 3) the "GasPro-pCO_2" (developed by the team coordinated by Prof. S. Lombardi; Sapienza - University of Rome-CERI), 4) the MuFo (Multifiber Optode logger, developed in this project in a collaboration between Prof. I. Klimant University Graz and the MPI-MM).

pH sensors: 1) glass electrodes (Microelectrodes ltd), 2) optodes (developed in this project in a collaboration between Prof. I. Klimant University Graz and the MPI-MM), 3) SeaFET (ion-selective field-effect transistor, Satlantic).

Introduction

We will report on the performance of chemical sensors that are useful for research and routine monitoring of CO_2 seeps.

Seeps are focused outlets in the seafloor through which gases and liquids are emitted from deep sediments into the watercolumn. The contents from natural seeps can be products of organic degradation, either biologically or thermally driven. Seeps are found in subduction zones, where oceanic or continental plates undergo metamorphic transformations. The products of this can be released to the biosphere via volcanism and hot seeps (e.g. black smokers). Alternatively, in seafloor formed by rapid sedimentation mud volcanoes are commonly formed by sediment compression and dewatering. Both types of seeps are strongly enriched by either thermally or biologically formed reduced substances. Finally, possibly human induced seepage is conceivable, not only by exploitation of oil and gas fields. The ECO2 project investigates the possibilities and consequences of CO_2 injection deep into the seafloor, as a countermeasure against global climate change due to use of fossil fuels. A concern is that the deep reservoirs may leak the CO_2 to the water column. This of course defeats the purpose of the exercise. Moreover, the concentrated CO_2 seepage may result in damage to the local ecosystem, especially in the deep sea, where the high pressure may lead to lethal CO_2 concentrations. As CO_2 is injected in depleted gas fields, also these seeps could be enriched in reduced substances.

Seepage fluids and gases thus are often enriched in CO_2, NH_4^+, Fe^{+2}, H^+, H_2S, H_2, a variety of carbon compounds (e.g. CH_4 and aliphatics), and the temperature can be enhanced. These form thus the chemical and physical parameters that are relevant for seepage studies. More specifically, for the detection of seepage we could make good use of sensors for these parameters. Direct sensing of the compounds, especially in situ, has enormous advantages over analyses of retrieved samples. Often the compounds are reactive, and their short half-life make quantitative in water samples difficult. Secondly, the gas concentrations in and near seeps in the deep sea can be very high. Thus upon retrieval of the samples, outgassing can change the sample content drastically. Direct sensing avoids

these problems. Moreover, the unlimited number of measurements that can be done with sensors allows long term monitoring and detailed distribution measurements. Sampling, storage, retrieval and analysis of water samples is a tedious and potentially expensive procedure, only recommended for those compounds that cannot be quantified by sensors.
A general problem for long term deployment of sensors is biofouling, the formation of biofilm on the sensing surface. They are layers of bacteria embedded in extra-cellular polymeric substances. Firstly, biofilms form a diffusional barrier, making the sensors slower. Secondly, the active biofilms may create their own microenvironment, typically lower in O_2 and pH. These growing biofilms lead to drifting and unreliable signals: instead of measuring in the water column, data on the base of a growing biofilm are collected. The time dynamics of drifting depends on the microbial growth rates, thus local nutrient and temperature conditions. Biofouling is a problem that can occur in weeks. It is not a problem for short term deployments of hours to days.
Several measures have been designed to fight biofouling, including mechanical wiping and chemical treatments. A simple method to avoid biofouling is to use microsensors, with such a small tip size that no biofilms adhere to it. Several of the compounds can be measured with microsensors with a tip of ~10 micron (O_2, H_2S, H_2, redox, H^+), that are so small that bacteria can not adhere to it. Only for long-term observations we have to consider fouling. Most applications involve deployments of hours to days.
In the introduction we will shortly review available sensors, and, as this project is on CO_2 further focus on CO_2 and pH sensing. We will not discuss the novel and promising lab-on-chip development, for measurement of nutrients.

Short overview
The compounds that can be measured with various types of sensors in the deep sea (>2000 m) are CO_2, O_2, pH, H_2, H_2S, redox, CH_4, several alkanes, and T.

1) **O_2** can be measured highly reliably with optical and electrochemical methods.
Optical methods rely on the fluorescence lifetime or fluorescence intensity of a fluorophore quenched by oxygen. Their advantage is low maintenance, low power requirements and long time stability. They become less sensitive at higher oxygen concentrations, and are typically used between 0-100% air saturation, with a detection limit of approximately 1 µM. The signal is highly sensitive to temperature, which must be measured in parallel to correct the calibration algorithm (the Stern-Volmer equation). There are no water-soluble interfering substances. The response time depends on the stirring speed, fluorophore layer/membrane thickness and tip size. Pencil sized sensors have a response time of about 10 seconds, in microsensors (<100 µm) this can be reduced to ca 1 second. A two point calibration is sufficient. The sensors measure partial pressure, thus a correction for the ambient salinity is needed in order to derive the dissolved oxygen.
Suppliers include Aanderaa (www.aadi.no), Presens (www.presens.de) and Pyroscience (www.pyro-science.com). Aanderaa sells units for deep sea use and can be mounted on CTDs and other moorings. Presens and Pyroscience so far supply units for laboratory use. Ongoing research continuously optimizes the chromophores (Borisov et al., 2010a; Borisov and Klimant, 2007; Borisov et al., 2008; Borisov et al., 2010b). The sensors from Pyroscience are accurately factory calibrated, and can be used as supplied, although regular checks on the calibrations must be recommended. Regular calibration is recommended for the Aanderaa optodes, by comparing the signal with Winkler titrations.
Electrochemical sensors for measuring O_2 in water are of the Clark type. The housing contains an electrolyte in which an anode and a cathode are placed. Oxygen enters the sensor via a gas

permeable membrane and is reduced at the cathode. The signal is proportional to the oxygen partial pressure, thus calibration under ambient salinity or a salinity correction is needed. The sensors consume oxygen and the macrosensors are stirring sensitive. However, they can be miniaturized with a tipsize of <5 µm, and then oxygen consumption and stirring sensitivity is insignificant. The life time of oxygen microsensors is approximately 1-2 years regular recalibration is recommended. Extremely high sulfide levels (>4 mM) interfere with the signal. A novel development is a Clark microsensor with an internal calibration, the STOX sensor(Revsbech et al., 2011). The sensor contains a second cathode that prevents entry of oxygen into the sensor. At regular intervals the second cathode is polarized to re-assess the zero current. The STOX sensor has a detection limit of <10 nM. This sensor seems very useful for long monitoring stability of OMZ waters. Very many suppliers for Clark type oxygen sensors can be found. Oxygen microsensors, including the STOX sensor can be purchased from Unisense (www.unisense.com).

2) **pH and CO_2** can be measured optically and electrochemically.
pH: *The electrochemical principle* measures the potential across a pH permeable membrane that separates a sample and a well-defined buffer. Thus, a reference electrode is needed. The potential follows the log-linear Nernst equation, a two point calibration is sufficient. The range of glass electrodes is from pH 1-11. The sensors drift, and regular, about weekly, recalibration is needed. There are too many suppliers of pH macrosensors available to list them all. Glass pH microsensors can be obtained from Unisense, with a tip size of ~10 µm. Minisensors, with a tipsize of 1 mm are available from Microelectrodes Inc. (www.microelectrodes.com), that however, is a size that may be sensitive to biofouling.
Another principle is the *ISFET.* An ISFET is an ion-selective field effect transistor used for measuring ion concentrations in solution. Here the current through the transistor will change when the ion concentration changes. An ISFET electrode sensitive to H^+ ion concentration can be used as a conventional glass electrode to measure the pH of a solution.
pH can also be measured *optically.* The principle is based on protonation/deprotonation of a dye or a PET (photoinduced electron transfer) group in the chemical structure of the dye, which changes its optical properties corresponding to the pH changes. Depending on the dye colorimetric (via absorption or reflection) or fluorimetric read-out is possible. When the dye shows a change in fluorescence the imaging of the analyte distribution is also possible.
CO_2: The Severinghaus type sensor is based on *electrochemistry*. The Severinghaus electrode consists of a pH-electrode in a chamber with weak buffer, mostly a $NaHCO_3$ solution. Carbon dioxide enters the chamber through a membrane and the pH change according to the equilibrium $CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^-$ is detected by the pH electrode in that chamber.
The Severinghaus electrodes (Severinghaus and Bradley, 1958) show linearity in a range between 1 and 11 kPa, but are not well applicable to measure low pCO_2 (e.g. the usual marine levels of about 0.04 kPa or 400 µatm or $1.36*10^{-2}$ mM). They can suffer from electromagnetic interferences.
Today optical CO_2 measuring techniques are prevailing. One method is to detect and quantify CO_2 molecules within an equilibrated gas stream by means of direct absorption in the infra red (IR) region of the electromagnetic spectrum (Fietzek et al., 2013). Another technique is an indirect measurement making use of the pH affecting property of CO_2 by applying spectrophotometry within an equilibrated pH-sensitive dye solution of known characteristics (DeGrandpre et al., 1995; Fietzek et al., 2013; Lefèvre et al., 1993). Both technologies have led to commercially available sensors. An overview of different CO_2 sensors is given in (Byrne et al., 2010).
Another *optical* principle, similar to the oxygen optodes, is under development. Highly sensitive sensors suitable for marine applications based on that principle are not yet commercially available;

less sensitive sensors can be obtained from PreSens (www.presens.de). A multiple fibre optics device - MuFO (Fischer and Koop-Jakobsen, 2012) for the CO_2 is in the prototype stage. The central component of the sensor chemistry is a pH-sensitive dye. It is embedded in an ethyl cellulose matrix together with a base, tetraoctylammonium hydroxide (TOA-OH). According to the equilibrium $CO_2 + H_2O + Ind^-TOA^+ \rightarrow Hind + HCO_3^-TOA^+$ the indicator dye (Ind) is protonated when CO_2 enters the sensing layer and changes its spectral properties. The emitted light is then guided to a camera via waveguiding fibres. Pictures are taken and divided in red, green and blue channel. Using this information pCO_2 can be analyzed.

3) **H_2** can be measured by many methods, such as MS, thermoelectric, electrochemical, resistance based, optical, and acoustic. For a review see (Hübert et al., 2011). Most of these methods are not easily applicable for marine studies. Amperometrical microsensors (Unisense) were used in marine studies on hot vents. The sensitivity to H_2S can be approximately 10% of that to H_2, and at very high sulfide levels the sensors become poisoned. Recently, a sensor was developed with a sulfide trap which solved the problem of sulfide interference (pers. comm. Prof. N.P. Revsbech). The sensors respond linearly to concentration, the detection limit of sensors with a tip size of 10 µm is approximately 0.5 µM.

4) **H_2S** can be measured by three electrochemical principles. Voltammetry (Luther III, 2002), potentiometrically (Revsbech and Jørgensen, 1986) and amperometrically (Jeroschewski et al., 1996). All have been used in marine research, potentiometry even for long time deployments (Le Bris et al., 2003). Potentiometry measures only S^{2-} ions and amperometry measures only H_2S. Total sulfide must then be calculated using these values and the local pH and the equilibrium constants (Millero, 1986). Therefore, parallel pH sensing is mandatory. Voltammetry measures total sulfide, no parallel pH measurements are needed. Which method is used may be a matter of personal preference, and what one is used to.
The detection limits are under normal marine conditions similar, about 1-10 µM. The potentiometric electrode is very simple in design: a silver wire coated with AgS. They can easily be miniaturized to 5 µm (Kühl et al., 1995). Especially at low sulfide concentrations the sensor has a long response time, in the order of minutes. A possible reason for concern is that the functioning is not really understood. According to the theory, the AgS membrane is in electrochemical equilibrium with the S^{2-} concentration. However, the S^{2-} concentrations are normally extremely low, as the pK is estimated to be between 10^{-15}-10^{-19}. An AgS microsensor immersed in a pH-neutral strongly sulfidic solution would encounter a few S^{-2} ions per minute, which defeats the statistical likelihood that a signal can develop. Yet these sensors respond reliably. A second concern is the large uncertainty of the pK values. Therefore, the sensors must be calibrated at several pH values in seawater. There is no interfering compound reported.
The amperometric sulfide sensors are always microsensors. Sulfide enters the sensor through a gas permeable membrane and is immediately oxidized to S0 by the Fe-cyanide in the electrolyte. The reduced Fe is then re-oxidised at an anode very close to the tip, and the resulting current is linearly proportional to the H_2S concentrations. The sensor can be used for 3-6 months. The dissolved Fe-catalyst is sensitive to light, and although the sensors are coated by black paint exposure to sunlight should be avoided. Disadvantage is that at high pH the sensitivity to total sulfide decreases, as the fraction of H_2S decreases. Studies are thus limited to pH values of 8.5 and lower.
Suppliers of instruments based on all 3 principles can be found.

5) The **redox** potential can be operationally defined as the potential between a Pt surface and a reference electrode. This is not the potential calculated from the sum of the redox species, as many species do not react with Pt or are out of equilibrium (Stumm, 1984). In marine environments the Pt sensor will respond to H_2, H_2S or HS^{-1} and Fe^{2+} by giving a more negative signal. It hardly responds to O_2, NO_3^- and SO_4^{2-}. Whereas no quantitative information is obtained on waterchemistry, redox sensors can nicely record the presence of seepage. E.g. one can trawl a logger across the seafloor and see the seeps as significant dips in the redox potential.

6) **CH_4 and alkanes** can be measured in situ by highly sophisticated equipment. There are several parallel developments of in situ analyzers based on Membrane Inlet Mass Spectrometry that can be operated to a depth of 4000m(Camilli and Duryea, 2007; McMutrtry et al., 2005). The instruments are very reliable, but expensive and require special expertise for the operation and data interpretation.
A second principle is the use of non-dispersive infrared spectrometry (NDIR). Several companies offer a methane logger that is easy to operate, can monitor for over 12 months and can be used to a depth of 4000 m or more. Companies are CONTROS GmbH (www.contros.eu) and Franatech GmbH (www.franatech.com). Initial stability problems are reported to be solved. Those sensors are especially suited for active searching for seeps as described above.

Detailed overview of pH and CO_2 sensing in the marine environment.

We will present a detailed description of the operational parameters of the sensors and sensor systems as listed before the introduction. Technical datasheets were obtained from the homepages of CONTROS GmbH (www.contros.eu) and Microelectrodes Inc. (www.microelectrodes.com). Additionally written requests via email were sent to CONTROS GmbH to Melanie Herrmann. Data and information about the GasPro-pCO_2 probes were received from S. Graziani (Sapienza University of Rome-CERI). Information about the SeaFET system was received from the homepage of Satlantic (www.satlantic.com) and via email from their customer service.
We will complement this information with experiences from users. In 2012 the HydroC, the MuFO, the dissolved CO_2 probe and a profiler with different electrodes were tested on a field trip at Panarea, Italy. Here the feedback of the diving team is summarized. In 2013 the MuFO device was used for a lab experiment at SAMS Institute in Oban, Scotland and the feedback of the users is also summarized.
The MuFO system and the GasPro-pCO2 probes are prototypes, and are still under development. The microelectrodes and the HydroC device are already commercially available.

Comparison of CO_2 sensors:
In the following the different CO_2 sensors are described in detail and a table (Table 1) showing an overview of the technical properties is also added in the end of this section. A difficulty in the comparison is that the companies and developing scientists often provide the measuring range in ppm, without specifying which ppm is meant: mg CO_2/liter or volume percent*10000 at 1 atmosphere. We recommend to use µatm. Concentrations of CO_2 can be calculated from the partial pressure, temperature and salinity. The accuracy of the CO_2 measurements does as consequence not

only depend on the CO_2 sensors, but also to the accuracy of the flanking parameters (T, salinity, pressure). When mentioned concentration ranges are given at 20°C and 3.5% salinity.

- **HydroC (CONTROS GmbH)**

Figure 1: HydroC device from CONTROS.

Principle: The HydroC CO_2 sensor is an underwater carbon dioxide sensor for in-situ and online measurements of dissolved CO_2, which is commercially available. Dissolved gas molecules diffuse through a thin-film composite membrane into the detector chamber, until equilibration is reached between the gas chamber and the waterphase. In the chamber the CO_2 concentration-dependent IR light transmission is recorded. To shorten the response time, water can be continuously pumped across the membrane with a rate of 100 ml/second. The logger is designed to measure in the water column. A specialized surface water version of the sensor is available. The HydroC is described in detail in (Byrne et al., 2010; Fietzek et al., 2013).
Stability/drift: The system is very stable and adaptive for long-term measurements due to i.a. its capability to carry out regular zero gas measurements during the deployment (so called *zeroings*). However, an annual recalibration is recommended by CONTROS.
Temperature range: Two versions are available. A normal version with a temperature range from +3 to +30°C and an arctic version with a temperature range from -2 to +15°C.
Response time: The response time (T_{63}) is typically smaller 1min, the t_{90} is about 2.5 minutes. The exact response time can be derived anytime during the deployment by analyzing the signal recovery after one of the regular zeroings. The actual temporal resolution can be higher than the response time if a time-lag-correction algorithm is applied on profiling and monitoring data (Fiedler et al., 2013).
Measuring range: The standard measuring range is from 200 to 1000 µatm ($6.8*10^{-3}$ to $3.4*10^{-2}$ mM). If required the device can be calibrated up to 6000 µatm ($2.0*10^{-1}$ mM).
Life time: During annual calibration which includes maintenance all wearing parts of the sensor are renewed if necessary; therefore there is theoretically no life time limitation.
Maintenance: The power consumption of the standard HydroC is approx. 300 mA for the sensor and additionally 600 mA for the water pump mentioned above. The power consumption can be customized by using the intergrated sleepmode and a smaller less consumable pump as well as by adapting the temperature control settings of the sensor. The HydroC can be either powered by cable or via an additional battery pack, which is available in different configurations of rechargeable or non-rechargeable batteries depending

on the deployment purpose. If a rechargeable solution is chosen the batteries can be charged via a cable, i.e. while inside the battery housing. Instead of cleaning a membrane by physical means, it should be exchanged after several months of continuous use or in the case of severe fouling. This change can be performed by the user himself. The HydroC device should be recalibrated once a year to maintain the stated accuracy of the sensor (recommendation of CONTROS).

Deployment: CONTROS offers the HydroC device as a "Plug and Play" system including the software, a sensor manual and an USB-serial adapter as well as a connection cable for configuration or laboratory purposes. The HydroC can be handled under water by one person. Besides stationary measurements on moorings, it can be used for transect measurements by trawling, scuba divers, on an AUV or a ROV. CONTROS offers a wide variety of power options, including various sizes and types of battery-packs and external power. The deployment time will thus depend on the measuring frequency, use of external pump and type of battery. The turnover time can be as short as 1 hour, which includes downloading data, a check of the data and exchange of battery pack.

Userfriendliness: CONTROS offers the HydroC device as a "Plug and Play" system including the software, a sensor manual and an USB adapter. The system shows a high accuracy (1%, or 5 µatm). it has an internal datalogger and can be connected to other devices (e.g. CTD). The software is understandable and easy to use. Data can be processed fast. The system is very adaptable and CONTROS offers assistance with designing the optimal configuration for the desired task.

Depth: The device can be used up to 6000m water depth.

Size: ø 90 x 376 mm, 4.7 kg (2.2 kg in water)

Costs: The HydroC device is commercially available for around 24000 € (Generation II with Sea-Bird pump SBE-5T, 2000 m depth rating, 200-1000 µatm, RS 232, +3 to +30°C, SubConn connector, internal datalogger) including an accessories kit (software detect 2.0 incl. manual, 3 spare membranes, USB 2.0 to RS 232 adapter, sensor manual and certification), cable equipment and offshore case. 5 membranes are available for 500 €. An annual recalibration costs 1750 €.

- **GasPro (Sapienza University of Rome)**

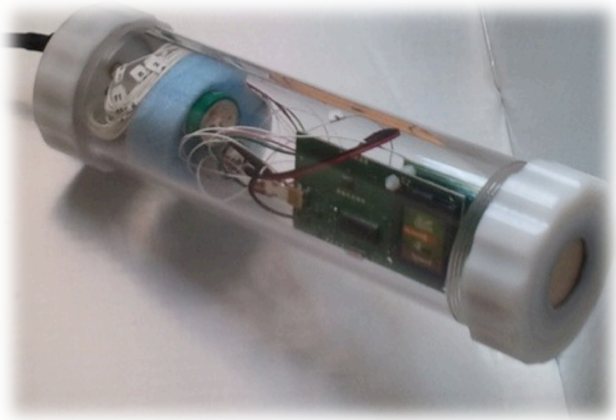

Figure 2: The Dissolved CO_2 probe in a Plexiglas housing.

Principle: The GasPro is a small, light-weight probe for long-term monitoring of CO_2. The probe can be deployed in different configurations, depending on the environment, site conditions, and study requirements. These include cabled probes linked to a central communication station or autonomous loggers with batteries and internal memory, with deployment in surface water, groundwater, the soil, and the atmosphere. Units deployed in water measure the partial pressure of the surrounding dissolved gas using NDIR (non-dispersive infrared) sensors located in a small-volume chamber behind a gas permeable membrane. The model reported here is the GasPro-pCO_2 for deployment in marine environments up to a depth of about 50m. The GasPro-pCO_2 was developed with low power consumption in mind to allow for long-term deployment, and thus pumps are not usually integrated in the system (although they can be added for short term deployments when faster response times are required).
Stability/drift: Although there is typically no artificial hydrodynamics that can assist in keeping the membrane free of biofilm growth, the type of membrane material is rather resistant to biofouling, as shown in both oligo to mesotrophic (Panarea) and eutrophic (Adriatic Sea) deployments over long periods (e.g. 2 months). That said occasional membrane cleaning may be necessary in highly eutrophic environments to minimize potential drift. The sensor does not offer auto-zeroing.
Temperature range: The probe operates at temperatures from 0 to 40°C.
Response time: While the sensor response time is rapid, the unit response time is dependent on gas diffusion rates across the membrane and equilibration between the sensor chamber gas volume and the surrounding water. As pumps are typically not used, response time will depend on current conditions and the concentration gradient, with a minimum time of about 2 minutes being required. T_{90} experiments have not yet been conducted under different hydrodynamic and gradient conditions.
Measuring range: The measuring range (zero resolution 1 µatm) is 0 to 5000 µatm (0 to $1.7*10^{-1}$ mM) with a full scale resolution of 15 ppm ($5.1*10^{-4}$ mM). If required, the device can be calibrated to a full scale of 5%.
Life time: The sensors and logger are highly robust. So far no instrument failure has been observed during deployment. No data on the total life time of the system is available.
Maintenance: The GasPro-pCO_2 can be mounted with either batteries that can be recharged via a cable mount outside the unit or with non-rechargeable batteries for long term deployments The loggers require 2 batteries. The integrated data logger and low power consumption (6-12 VDC; warm-up 2-30 min/40 mA) of the sensor make it suitable for long-term monitoring. Sampling frequency can be user set at the fixed rates of 1/min, 1/10min, 1/hour, 1/day, 1/week or 1/month. The data format is ASCII with real time clock information (date, hour, minute, second; resolution: 1 sec).
Deployment: Besides batteries no exchange of parts is needed between deployments. If the batteries need to be exchanged, the turnover time is about 1 hour, including downloading of data and removal of biofouling. As described above, the GasPro can be used as stand-alone (SD-card as removable memory) or connected to a modem or to control units for data transmission in real time.
The total deployment time for the stand-alone unit depends on the measurement interval. When measuring every 10 minutes, the batteries will have sufficient power for at least 4 weeks. When the interval is longer, the deployment time is proportionally longer. If probes are cabled to a central station, power can be provided by mains or by solar power for long-term deployments.

Userfriendliness: As it is a prototype no manuals exist. The software is simple, the interface may be improved. The servicing, calibration and redeployment of the unit can be done by 1 person. In this basic version no pump was added. Thus the battery life was very long, the devices could be shifted from location to location without changing batteries.
Depth: Under water it can be used at operation depths of 60 m (standard), 100 m or 200 m.
Size: ø 78 x 283 mm; 0.7 kg in air, slightly positively buoyant in seawater.
Costs: The material costs for the GasPro-pCO_2 are approximately 2500 €, hours of work not included. The 2 batteries for long deployments cost 27 € each. Depending on both the housing materials and the machining for the different prototypes the costs can vary widely.

- **Optodes/MuFO**

Figure 3: The MuFO system with 100 optodes positioned on a stick in bundles of 20 fibres each.

Principle: The MuFO is an optical multi fibre system of 100 CO_2 optodes with collective read out of all sensors simultaneously. The optodes can be positioned anywhere in the habitat, within the range of the optode length. It can thus provide the CO_2 dynamics in many sites within that habitat, including e.g. sediments, watercolumn, musselbeds, corals, etc. The measurement principle is based on optical chemosensing. The MuFO device consists of 3 main parts: The sensor that contains a pH-sensitive dye, the optical fibres that guide the excitation/emission light and the camera that takes pictures of the polished fibre ends.
Stability/drift: The photostability of the used dye is the limiting factor during long-term measurements. The sensing foils on the fibre tips should be exchanged periodically (time interval depends on the dye).
Temperature range: So far the optical sensors of the prototype were tested in a temperature range from +5 to +35°C. Their T-dependence is quite high. Therefore it is necessary to calibrate at the same temperature as the measurement.
Response time: The optical CO_2 sensors measure continuously. The response time (T_{90}; time needed for 90% of the signal change to occur) is 1 to 2 minutes.

Measuring range: The different dyes have different sensitivities. The measuring range of the optodes can be adjusted to the requirement of the user (starting from ca. 200 µatm ($6.8*10^{-3}$ mM) up to a few thousand µatm) by choosing the suitable dye for the desired concentration range.
Life time: This information is not yet available as the MuFO system is an ongoing development.
Maintenance: The batteries of the MuFO have to be charged via cable after appr. 24h of permanent use (duration of charging: ~10h). The accumulators of the camera have to be recharged or exchanged every 9h (duration of charging: ~2h) and are the limiting factor for the deployment length. Data are saved to the SD card of the camera. Both for charging the camera batteries and downloading the data the camera has to be removed from the MuFO housing, after which the camera has to be refocused. Thus the turnover time between deployments is approximately 10 hours.
Deployment: The MuFO prototype has an operating software and manuals for the sensor preparation, the calibration, the general handling and the software. Connected to a computer it can be controlled manually (e.g. for lab-applications) or programmed for an auto-start for a later measurement (e.g. for the diving team). The sensor tips are flexible, robust and well protected by metal sleeves. The contact surface is very small (ø ca. 1.5 mm). Therefore, the optodes can be used for profiling too, either in a fixed array of sensors, or by using a single optode that penetrates the sediments step wise. Measurements in the air are also possible.
Userfriendliness: After long-term measurements the amount of produced image data is huge. Therefore, the analysis can take quite a long time. The positioning of the sensors is complicated.
Depth: Up to now the optical sensors were tested in water depths down to 20 m.
Size: ø 280 x 400 mm; fibre length 5-6 m
Costs: Optodes are not very expensive (sensing foils cost up to a few € per sensor if selfmade). Price-calculation depends strongly on the material costs of the read-out-device. The material costs for the MuFO until now are around 3000 €, hours of work not included.

- **Severinghaus CO_2 sensors (Microelectrodes Inc., microelectrode MI 720)**

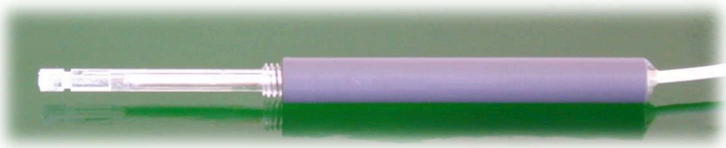

Figure 4: The Severinghaus CO_2 sensor microelectrode MI 720

Principle: The Severinghaus electrode is an electrochemical sensor for CO_2 measurements. It is a pH electrode in a chamber with buffer solution (usually a 1 mM $NaHCO_3$ solution with a pH of 8.2). Through a membrane the CO_2 concentration in this chamber can equilibrate with the sample. The pH in the chamber shifts proportionally to the sample CO_2 and this pH is measured.
Stability/drift: The sensors have a tendency to drift of approximately 1 mV/day. When measuring in the concentration range below 200 µM, this drift is 1-3 µM per day. Therefore,

they must be calibrated regularly. This limits their application for long term monitoring, although they can well be used to monitor dynamics. As the sensing surface is small, the sensitivity to biofouling is rather limited. The sensors behave log-linear from ca 3 µM-30 mM, i.c. below air saturation up to CO_2-saturated water.

Temperature range: This information was not available.

Response time: According to the specifications, the pCO_2 microelectrode has a response time of less than 1 min. However, stabilization times of several minutes are more typical. Therefore, measurements that are made frequently are best binned over 3 minutes.

Measuring range: The sensors behave log-linear from ca 3 µM-25 mM, i.c. below air saturation to CO_2 saturated water. The data sheet from the company indicates a range of 0.1-100 mM and 4.4-440 ppm, both must be a mistake. Upon request, the company elucidated that the sensors are tested at 0.1 and 30% CO_2 in a gas mixture.

Life time: The sensors can be used for several weeks to months, after which the membrane should be exchanged. The pH transducer has a life time of appr. 1 year. During measurements weak volatile acids can cause interferences.

Maintenance: The maintenance depends on the electronic loggers on which they are mounted. The company provides an amplifier (MV-ADPT Millivolt Adapter) with a battery life of 5 years. The loggers will need further battery power for data acquisition and storage. This will depend on the brand of logger. When the amplifier MV-ADPT Millivolt Adapter is used for the primary amplification, the battery charging or exchange depends further entirely on the logger system in which it is embedded. Also the downloading of the data depends on the logger system. The time needed for maintenance of the sensor between deployments is approximately 30 minutes. The chamber with membrane has to be regularly exchanged, which is a very simple operation. After this exchange the sensor must be recalibrated.

Deployment: The servicing, calibration and redeployment can be done by 1 person. When mounted on basic loggers, deployment can be done by scuba diving or snorkeling. The sensors can measure in the water column and inside sediments.

Userfriendliness: Electrodes are easy to handle, exchange of the membranes is very simple.

Depth: The electrode can be pressure compensated and can be used in water depths from at least 2000 m. High pressure will affect the sensor offset, thus an in situ calibration is needed. For this a water sample from the deployment depth must be taken and analysed for pH, DIC and alkalinity. From the appropriate equilibrium values the total carbonate system can be calculated, including the pCO_2 (Zeebe and Wolf-Gladrow, 2001).

Size: ø 6 x 86 mm

Costs: A pCO_2 microelectrode from Microelectrodes Inc. is commercially available for 490 USD (≈ 366 €). Additionally, the costs for a loggerhouse plus electronics need to be included. The preamplifier costs 199 USD (≈ 149 €).

Table 1: Overview of technical data of different CO_2 sensors (i.n.a.=information not available). Descriptions of the principles of the respective devices are mentioned above.

	HydroC	**Optodes/MuFO**	**Microelectrode MI 720**	**GasPro-pCO2**
Commercial availability	yes	no/prototype	yes	no/prototype
Response time	60 s (T_{63}), 150 s (T_{90})	60 to 120 sec	< 60 sec	Typically 5 min. It depends strongly on the water movement. A pump can be added to speed up the response.
Depth range	down to 6000 m	20 m (at least)	2000 m	60 m (standard), 100 m or 200 m
Costs	24000 € (standard version, including all accessories and in water calibration)	3000 € material costs (hours of work not included)	490 USD (366 €)	2500 € material costs (hours of work not included)
Costs for maintenance/ equipment	5 membranes for 500 €; Annual maintenance for 1750 €	i.n.a.	Preamplifier for 199 USD (~149 €)	2 batteries for loggers for 27 € each
T-range	3 to 30°C (standard) or -2 to +15°C (arctic version)	5 to 35°C	i.n.a.	0 to 40°C
Profiling inside sediment	No	Yes (5 to 10 cm depth)	Yes (5 cm depth)	No
Robustness	very robust	robust	i.n.a.	robust
Stability	very stable, but an annual recalibration is recommended	limiting factor = photostability of the chosen dye	i.n.a.	very stable, but daily cleaning because of biofouling can be needed
Dimensions	ø 90 x 376 mm 4.7 kg in air (2.2 kg in water)	ø 280 x 400 mm fibre length 5-6 m (slightly positively buoyant in seawater)	ø 6 x 86 mm	ø 78 x 283 mm 0.7 kg in air (slightly positively buoyant in seawater)
Measuring range	200 to 1000 µatm (standard) or 200 to 6000 µatm	6-200 µM (dye dependent) or: 200-5000 µatm	4.4 to 440 ppm Possibly incorrect. Experienced range: 3 µM-25mM	0 to 5000 µatm (others available)

			or 100-1000000 µatm	0 - 1.7*10^{-1} mM

Comparison of pH sensors:
In the following the different pH sensors are described in detail and a table (Table 2) showing an overview of the technical data is also added in the end of this section.

- **Glass sensors (Microelectrodes Inc., microelectrodes standard MI 405 and microelectrodes combination pH-electrodes MI 410)**

Figure 5: pH microelectrode standard MI 405 (above) and the microelectrode combination pH-electrodes MI 410 (below).

Principle: Here the potential across a pH permeable membrane that separates a sample and a well-defined buffer is measured. Thus, a reference electrode is needed. A two point calibration is sufficient. One can find a big assortment of pH electrodes. Here two types “microelectrode standard MI 405” and “microelectrodes combination pH-electrode MI 410” from Microelectrodes Inc. are described. The MI 410 sensors have an internal reference inside the protective needle. However, the use of an external reference is recommended, as the internal reference easily seals from the solution by grease or oil.
Stability/drift: Under ideal storage conditions these electrodes are long-term stable and can be used for appr. 1 to 2 years.
Temperature range: Both types can be used in a temperature range from -5 to +100°C. The signal has a T-dependence, thus calibration must be done at measuring temperature.
Response time: Both types show response times from 5 to 15 sec.
Measuring range: Their measuring range is between 0 and 14, but rather between 1 and 11 concerning the alkali/acid error. For marine applications with pH ~8.1 and pH ~5 at acidified sites this range is still well useable.
Life time: This information was not available.
Maintenance: As with all pH sensors, they must be stored wet, best in a buffer of pH 7. They can be cleaned in 0.1 M HNO_3 or a dilute bleach solution.
Deployment: Measurements in the sediment are possible with an immersion depth of 1.0 mm for type MI 405 and an immersion depth between 1.5 and 2.0 mm for microelectrode type MI 410. While they are steel enforced these glass electrodes do not easily break.
Userfriendliness: Electrodes are easy to handle.

Depth: This information was not available.
Size: ø 6 x 150 mm (MI 410); ø 2 x 146 mm (MI 405)
Costs: Microelectrodes for pH measurements are available for 200 to 500 USD (≈166 to 373 €), e.g. type MI 405 for 210 USD and type MI 410 for 325 USD.

- **Optodes/MuFO**
  Principle: The principle of the MuFO system was described before (see CO_2 sensors).
  Stability/drift: During long-term measurements the photostability of the used dyes is the limiting factor. Sensing foils on the optical fiber tips should be exchanged periodically (time interval depends on the dye).
  Temperature range: The pH sensors were tested in a temperature range between +5 and +35°C. They also suffer from T-dependence. Thus calibration should be carried out at the same temperature as the measurement using a thermostated waterbath for the calibration solution.
  Response time: Optodes in principle measure continuously. Exposed to a certain pH the response times can vary between sec and min. This depends on the chosen dye, the chosen matrix, the temperature and the layer thickness.
  Measuring range: Concerning the measuring range optodes are very flexible. Depending on the dye, that is used the measuring range can be tuned individually to the requirement of the user. In general a pH range from ±1 outgoing from the pKa-value of the dye can be measured. A combination of two or more dyes with different dynamic ranges can cover a much broader dynamic range, but the calibration of the sensor becomes more complicated.
  Life time: This information is not yet available as the MuFO system is a prototype in continuous development.
  Maintenance: The accumulators of the MuFO have to be charged via cable after appr. 24h of permanent use (duration of charging: ~10h). The accumulators of the camera have to be recharged or exchanged every 9h (duration of charging: ~2h) and are the limiting factor for measurements. Data are saved to the SD card of the camera. Both for charging the camera batteries and downloading the data the camera has to be removed from the MuFO housing. After this operation the camera has to be refocused.
  Deployment: The MuFO prototype has operation software, manuals for the sensor preparation, the calibration, general handling and for the software. Connected to a computer it can be controlled manually via the computer (e.g. for lab-applications) or programmed for an auto-start for a later measurement (e.g. for the diving team). The sensor tips are flexible, robust and well protected by metal sleeves. The contact surface is very small (ø ca. 1.5 mm). Therefore measurements in the sediment with an immersion depth down to a few cm are possible. Measurements in the air are also possible.
  Userfriendliness: After long-term measurements the amount of produced data is huge. Therefore, the analysis can take quite a long time.
  Depth: The optical pH sensors have not been tested at larger depths up to now.
  Size: ø 280 x 400 mm; fibre length 5-6 m
  Costs: Optodes in general are not expensive (sensing foils up to a few € material costs if selfmade). Price-calculation depends strongly on the material costs of the read-out-device. The material costs for the MuFO until now are around 3000 €, hours of work not included.

- **Isfets (ion-selective field-effect transistor, SeaFET from Satlantic)**

Figure 6: The SeaFET device for pH measurements from Satlantic.

Principle: SeaFET uses ISFET technology for pH monitoring. An ISFET is an ion-selective field effect transistor used for measuring ion concentrations in solution. Here the current through the transistor will change when the ion concentration changes. An ISFET electrode sensitive to H+ ion concentration can be used as a conventional glass electrode to measure the pH of a solution.
Stability/drift: SeaFET shows a typical change of 0.005 pH unit/month. In fact, after one year in use the deviation of the measured pH is approximately 0.06 pH unit. An annual maintenance is recommended.
Temperature range: Measurements can be carried out in a temperature range between 0 and 55°C. The calculated pH is temperature dependent. Therefore, a thermistor is attached very close to the ISFET where the measurement is taken.
Response time: The stabilization time if exposed to a different pH is up to 20 sec.
Measuring range: The device measures from pH 2 to pH 12 with an initial accuracy from 0.01 pH unit and a precision better than 0.001 pH unit (in a salinity range from 10 to 40 PSU).
Life time: Not known
Maintenance: The device has an internal memory of 2 GB, an internal battery set (10.5 V 19.8 Ah) and its power consumption is quite low with 20 mA while it is operating and 3.5 mA during the standby mode. If the external voltage is higher, an external supply supersedes the internal battery. It communicates via USB 2.0 and RS-232.
Deployment: It was slightly positive buoyant in water. Therefore, divers have to add some weight to use the device under water. The device can be operated with four different modes: a continuous mode (samples ~0.3Hz), a scheduled mode (operates on internally stored schedule), a polled mode (responds to data logger commands) and a sample averaging mode where it calculates the mean of 1 to 100 samples. The calibration is carried out via spectrophotometric determination of pH referenced to a certified TRIS (tris(hydroxymethyl)aminomethane) buffer.
Userfriendliness: The SeaFET technology can be used in many areas, e.g. industrial, clinical and environmental pH monitoring. The SeaFET itself measures pH accurately in both marine and freshwater environments.
Depth: SeaFET can be used in water depths down to 70 m.
Size: ø 114 (4.5") x 406 mm (16"); 4.1 kg in air
Costs: The SeaFET device itself is available for appr. 10000 USD (~7520 €). Accessories like a copper foul guard, a spare battery set, USB programming cable and other possible interconnect cables are available from Satlantic, too. An annual maintenance costs 1150 USD (~865 €). It includes the instrument cleaning, an inspection and a calibration.

Table 2: Overview of technical data of different pH sensors (i.n.a.=information not available). Descriptions of the principles of the respective devices are mentioned above.

	Glass electrodes (Microelectrodes types MI 405 and MI 410)	Optodes/MuFO	ISFETS
Commercial availability	yes	no/prototype	yes
Response time	5 to 15 sec	few sec to few min	20 sec
Depth range	i.n.a.	i.n.a.	70 m (max.)
Costs	MI 405 for 210 USD (156 €) MI 410 for 325 USD (243 €) Others: 200 to 500 USD (~150 to 373 €)	3000 € material costs (hours of work not included)	10000 USD (~7520 €)
Costs for maintenance/ equipment	i.n.a.	i.n.a.	annual maintenance for 1150 USD (~865 €)
T-range	-5 to +100°C	5 to 35°C	0 to 55°C
Profiling inside sediment	Yes (5 to 10 cm depth)	Yes (5 to 10 cm depth)	No
Robustness	robust (while steel enforced)	robust	robust
Stability	very stable, can be used for 1-2 years	limiting factor = photostability of the chosen dye	0.005 pH/month 0.06 pH/year an annual recalibration is recommended
Dimensions	ø 6 x 150 mm for MI 410 ø 2 x 146 mm for MI 405	ø 280 x 400 mm fibre length 5-6 m (slightly positively buoyant in seawater)	ø 114 x 406 mm 4.1 kg in air (slightly positively buoyant in seawater)
Measuring range	0 to 14 (effectively 1 to 11)	dye dependent => pKa ± 1	2 to 12

Experiences from users

In 2012 the compared devices CONTROS HydroC-CO_2, Optodes (MuFO), the GasPro-pCO_2 and a profiler equipped with different glass electrodes were tested all together at Panarea (southern Tyrrhenian Sea, Italy). In this submarine exhalative field located east of Panarea Island, the devices were tested at different sites, with different geochemical characteristics. Sites with and without CO_2 venting were studied. The diving teams operating with the devices were from the Hydra Institute (Elba, Italy) and GEOMAR/CONTROS (Kiel). The GasPro-pCO_2 was also used during a field trip to CO_2 seeps in a coral reef in New Guinee. The MuFO was additionally used in SAMS in a labexperiment. The divers and scientists gave the following feedback:

The HydroC device from CONTROS was small and very well manageable under water for the divers. On one occasion the battery was incorrectly connected and in consequence the device did not log data. In the meantime measures have been taken to avoid this problem. The very short response time allowed to measure the dynamics better than the GasPro-pCO_2. However, also on the GasPro-pCO_2 a pump can be mounted, resulting in similar response times.

The GasPro-pCO_2 probe was easy to handle, because of its small dimensions. Because of its low weight it floated and the divers had to put an additional weight on the device. Near seeps with strongly reducing fluid chemistry biofouling occurred on the membrane, that had to be removed every 3 days. It should be remarked that all sensors suffered from biofouling near these seeps. Use of an external pump would have reduced biofouling of the membrane. Biofouling is most easily removed with freshwater. On one occasion a logger had stopped after 10 measurements. A file with settings appeared empty, probably due to mishandling of the software. The file was replaced with one from another logger, after which the problem was solved. The problem did not reoccur.

The HydroC and GasPro-pCO_2 are comparable devices. The HydroC is more expensive, but this version with pump has a shorter response time, is supported by the services of a company, can be auto-zeroed to compensate for drift and can be used at much larger depths. The tested version of the GasPro-pCO_2 was a low cost solution with basic (and reliable) performance, therefore can be used in larger numbers, e.g. to monitor CO_2 dynamics in a heterogeneous habitat surrounding a seep. Also the GasPro-pCO_2 can be equipped with a pump to reduce response times. Obviously, the use of pumps will compromise the battery life and thereby user-friendliness. Both systems are versatile with respect to power solutions; different batteries or external power supplies can be used.

On land the MuFO system was difficult to handle, because of the 5-6m long optodes and the weight. Later the optical fibers were fixed to a frame, which made handling and deployment easier. The MuFO was slightly positive buoyant in water, so the divers had to add weight to position it on the seafloor. These weights made it extra heavy on land. *In 2013* the MuFO system was tested by Anna Lichtschlag and Peter Taylor at SAMS (Scottish Association for Marine Science) in a lab experiment. They gave the following feedback: In principle the system was good to handle. The battery change was complicated, because they had to put the camera out of the device every time. After changing the batteries of the camera it had to be focused again. The software was easy to understand and to handle, but the amount of data is huge and therefore it takes a long time to analyze the data.

The microsensor profiler with the Severinghaus pCO_2 sensor is big and heavy on land. The divers found it difficult to transport, and care had to taken to prevent breaking of the electrodes on the bottom. Under water it was easy to handle except in case of high current. The profiler is designed for deployments by winch from research vessels and can be mounted with 10 different sensors. However, it is not the most elegant solution for divers. It is possible to mount the electrodes on small loggers that can easily be handled by divers. The CO_2 electrode from Microelectrodes Inc. suffered from more drift than the CONTROS and GasPro devices. Advantage is that it can be used for profiling, and thus can obtain data from inside the sediments and can be coupled to benthic (micro)biology.

Another advantage is its price and ease of maintenance. Also, it can be easily mounted on a multisensor logger, thus the CO_2 signals can be compared with other parameters.

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