

# The syringe sampler: An inexpensive alternative borehole sampling technique for CO<sub>2</sub>-rich fluids during mineral carbon storage

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## Abstract

Mineral carbon storage involves the dissolution of injected gaseous or supercritical CO<sub>2</sub> followed by interaction of the carbonated solution with the host rock at depth resulting in the precipitation of carbonate minerals. Monitoring of elemental chemistry and tracers is required to evaluate the evolution of the fluid geochemistry and degree of CO<sub>2</sub> mineralization during its injection into the subsurface. To avoid degassing during sampling, which is a common feature of commercial groundwater samplers, especially vacuum samplers, a syringe-like sampler was designed, constructed and tested in the lab and field. This system was successfully deployed during the injection of 175 tons of pure gaseous CO<sub>2</sub> at the CarbFix injection site in Hellisheidi, SW-Iceland. This study presents in detail this sampling tool and its application to the monitoring of the CO<sub>2</sub>-rich fluid evolution during subsurface carbonation. The syringe sampler was developed as flexible and mobile unit of low investment and operating costs making it an attractive option for deployment at small scale carbon storage demonstration sites that do not command the budgets to deploy commercial alternatives, e.g. from the oil and gas industry.

## 1. Introduction

University of Iceland, Reykjavik Energy, CNRS in Toulouse, and Columbia University initiated CarbFix ([www.carbfix.com](http://www.carbfix.com)) to develop the technology for mineralogical CO<sub>2</sub> storage in basalts in SW-Iceland. The overall aim of the project is to mineralize CO<sub>2</sub> as carbonates by interaction of CO<sub>2</sub> charged water with basaltic rocks.<sup>1-4</sup> The injection borehole is approximately 2000 m deep and cased down to 400 m. Research plans call for the injection of gaseous CO<sub>2</sub> and H<sub>2</sub>S together with groundwater provided from an adjacent deep groundwater well into the borehole where it has been demonstrated that CO<sub>2</sub> will be fully carbonated before entering the aquifer at ~540 m depth.<sup>5</sup> To evaluate the hydro-geochemical patterns and proportions of CO<sub>2</sub> mineralization in the aquifer, a full-scale monitoring program of the water geochemistry and its temporal evolution is required. In the case of CarbFix, geochemical monitoring includes conservative and isotope tracers injected with the waters. This approach requires high quality sampling at depth and sample recovery at elevated pressure. Generally, gas bubbles are observed when using common groundwater sampling gear, such as the snap sampler<sup>6</sup>, which are undesirable during collection of CO<sub>2</sub>-rich fluids. To quantitatively describe the CO<sub>2</sub>-H<sub>2</sub>O system at injection conditions, two out of the six crucial parameters pH, *f*CO<sub>2</sub>, alkalinity, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, and dissolved inorganic carbon (DIC) have to be accurately determined. Our efforts focused on measuring the pH and DIC downhole during field CO<sub>2</sub> injection. Any pressure loss and concomitant gas bubble formation during sampling and subsequently on the surface has to be suppressed which requires maintaining the in-situ reservoir pressure of the sample prior to analysis. It is not desirable to evacuate the sampler prior to sampling as this would lead to vigorous phase segregation, which could cause carbonate precipitation and clogging of the valve orifices.<sup>7</sup> Hence, commercial vacuum samplers cannot be deployed either. Inspired by the mechanism of a syringe and standard positive displacement bottom hole samplers from the oil and gas industry, a new groundwater sampler was designed, constructed and successfully tested in the lab and field before and during CO<sub>2</sub> injection. Special emphasis was placed on developing a mobile, economically highly attractive, robust, and reliable device without the need either for a nitrogen or gas booster routinely employed in the oil and gas industry to ensure

one-phase fluid sampling or electric wiring (for instance to enable surface actuation of the shutting valves) as these options would render preparation and performance of the sampler more cumbersome, expensive and prone to malfunctions. Likewise, any further cost-intensive requirements, such as tubing from the reservoir to the top-side facility as well as large amounts of purging nitrogen required for the U-tube, were omitted. This study presents and evaluates this eclectic, purely mechanical, wireline sampling tool.

## **2. Sampler**

### ***2.1 Description***

In the literature many descriptive adjectives can be found preceding the word ‘sampler’, such as ‘borehole’, ‘bottomhole’, ‘downhole’, ‘groundwater’, ‘slickline’ (or slick wireline), ‘subsurface’, or simply ‘well’. In this study, the terms ‘syringe sampler’ and ‘PDS’ (for ‘positive displacement sampler’) are used interchangeably to describe this type of wireline deep well sampler. A recent review article<sup>7</sup> describes and explains in detail the fundamental differences of available downhole sampling techniques, which is beyond the scope of this article. Suffice it here to say that our sampler works similar to a combination of a positive displacement sampler and a syringe. A pressure differential between outer reservoir and inner sampling chamber pressure drives the fluid into the sampler, moving a piston/plunger along the sampling chamber from the upstream towards the downstream end and thus controlling the inflow. This process is called positive displacement. The sampler is then hauled to the surface and by attaching a high-pressure pump to the downstream end the flow is reversed, exerting a high hydraulic pressure which pushes the plunger back towards the upstream end and dissolves any potential gas bubbles. This latter action describes the syringe-like character of the sampler.

The syringe sampler constructed for this study consists of two metal cylinders that are connected via a series of valves and a piece of small ID tubing (Fig. 1a). Prior to sampling, the lower cylinder (the proper sampling chamber) is filled with de-ionized (DI) water and acts like a resistance to fluid

flow. The upper cylinder ('collector' in Figure 1a) is evacuated so that it can accommodate the DI water that is being displaced from the PDS during sampling.

The sampling chamber is a 160 cm long, 40 mm x 30 mm (ODxID) stainless steel tube with a sampling volume of ~1 L. Removable, threaded caps are located on both ends (Fig. 1, boxes 2, 5) to open the syringe sampler and remove/replace the plunger and clean the barrel, if necessary. It withstands pressures of  $\leq 100$  bar at temperatures  $\leq 50$  °C, more than sufficient given the injection conditions in Iceland (540 m, ~35 °C reservoir temperature). Note, the PT rating is a function of the selected cylinder material and thickness and can be adjusted to the specifics of the project. The caps have an oblique sampling-hole, placed in the middle of the inner side but diverted towards the rim on the outer side of the cap to lodge the ball valve (Fig.1, boxes 2, 5). Ball and check valves (L1 and L2) are connected to the bottom cap, controlling the inlet flow of the PDS (Fig. 1A, lower part). This asymmetric set-up prevents the valve handle from extending beyond the outer diameter of the PDS. Consequently, the OD of 40mm is not surpassed by the presence of the valves, an important pre-requisite given the usual restrictions on the nominal ID of the cased wellbore.

One key component of the PDS is a movable internal stainless steel plunger of 10 cm length (see Fig. 1, box 3 for the following description). The plunger uses two replaceable metal O-rings (white circles) that secure four replaceable thermoplastic polyurethane (TPU) O-rings. These O-rings provide for leak-tight movement of the plunger. Not shown is a strong internal magnet in the centre of the plunger, which enables the easy determination of its position at any time before/after sampling. This contraption works as a gas and watertight syringe plunger and facilitates the application of an external hydraulic pressure on the sampled fluid in the barrel. Thus, bubbles that may potentially have formed during the sampling process or that were present in the formation can be forced back into the fluid. Note that the cap on the upstream side has a cone-shaped inner side to concentrate these potential bubbles (Fig. 1B, box 5). The plunger is also used to drain out the sample for further treatment and analysis.

Additionally, a second check valve (U2), with adjustable cracking pressure, is set at a high cracking pressure, according to the sampling depth within the borehole. Its function is to pressurize the PDS with DI water prior to sampling and to avoid inflow of injection/aquifer fluid before reaching the desired sampling depth. It follows a 15  $\mu\text{m}$  stainless steel filter to prevent clogging of the subsequent 1/16" PEEK tubing of very small ID that works as a flow restrictor and controls the sampling time (Fig. 1A). The outlet of this restrictor is connected to an evacuated cylinder (collector), made of the same material as the sampling chamber and holding the same volume. On top of both end caps, protection caps are installed to avoid damage during downhole sampling (Fig. 1, box 4).

## ***2.2. Sampling***

Sampling is initiated by positive displacement, that is, the pressure differential between the reservoir at depth and the sampling chamber of the PDS. The higher outer pressure exerts a force on the piston such that the well fluid enters through the upstream valves (L1 and L2) and displaces the compressed liquid present in the sampling chamber (water in our case). The first step in assembling the PDS is to fill the compartment between inlet ball valve (L1) and the piston (<5 mL) with bubble-free and degassed deionised (DI) water. Then, the PDS is entirely filled with DI water, sealed with the outlet cap and pressurized to 32 bar. The cracking pressure of the outlet check valve (U2) is crucial for successful sampling and is adjusted slightly higher (34 bar) to avoid any DI water escaping the PDS into the collector and the concomitant loss of pressure. The cracking pressure depends on the prevailing well pressure at sampling depth and on the internal PDS backpressure. At the Icelandic injection site, at 540 m depth, a hydrostatic pressure of 44 bar is observed because the depth to the water table is 100 m. Some excess pressure is required to overcome friction between the O-rings of the plunger (Fig.1, box 3) and the inner stainless steel wall of the barrel. This excess pressure was found to be ~10 bar during repeated laboratory tests, determined by replacing the outlet check valve (U2) with a backpressure regulator and, by varying pressure, measuring the pressure differential between applied outer hydraulic pressure and regulator backpressure at which

flow *out* of the PDS started. In all, the interplay between outer pressure, piston friction, and cracking pressure permits a pressure drop of 12 bar when the CO<sub>2</sub>-charged fluid enters the PDS. It is crucial to keep the pressure drop to a minimum as it restricts the outgassing of CO<sub>2</sub> during sampling and, more importantly, suppresses carbonate precipitate formation in the sampling line.

The cracking pressure of the inlet check valve (L2) is <1 bar (10 psi) to allow aquifer fluid into the PDS at depth and to avoid any sample loss when hauling the PDS back to the surface. The collector at the end of the set-up is a vital piece of the sampler because it receives the DI water volume displaced from the PDS by incoming sampling fluid. Therefore, the volume from the outlet ball valve (U1) to the end of the pipe is evacuated to 10<sup>-3</sup> bar. This evacuation is carried out using a portable vacuum pump in the field right before lowering the sampler into the borehole. In a previous publication an alternative way of collecting the 1L DI water draining from the PDS was described.<sup>8</sup> Instead of a collector, continuous tubing from the surface to the submersed PDS at depth was installed and tested but this set-up proved too costly, awkward, and prone to failure to be of long-term usability.

When the sampler reaches 540 m depth, the outer pressure overcomes the sum of internal plunger pressure and downstream check valve (U2) cracking pressure and the PDS is sampled bottom-up (Fig. 2). The flow restrictor behind the outlet check valve (U2) controls the flow rate of sampling. The goal is to find a compromise between a relatively smooth inflow of downhole fluid into the PDS to minimize any CO<sub>2</sub> degassing while keeping the sampling time to a minimum. Laboratory tests indicate two hours was ideal for this purpose.

In summary, the syringe sampler fulfils three functions; a) it enables the sampling of a pressurized fluid at depth while minimizing phase separation, b) it drives gas back into the liquid and thus creates a one-phase system through recombination at the surface, and c) it allows for adjustment of the sampling time.

### **2.3. Data acquisition**

After sampling, the PDS is hauled to the surface and disconnected from the waterlogged collector. The outlet ball valve (U1) of the PDS is then connected to a high pressure liquid pump (HPLC) creating a hydraulic overpressure on the plunger of 30 to 40 bar higher than during sampling while rotating the PDS vertically several times to force any gas back into the fluid (Fig. 3). Afterwards, the PDS is connected to a series of evacuated glass bottles to collect gases and gas tracers, and subsequently hooked to a specially designed sampling line that has been previously pressurized hydraulically (Fig. 4). The fluid sample passes through a sampling loop of known size and exits via a backpressure regulator. In-situ measurements of pH and redox state are performed by high P/T electrodes (Corr Instruments, TX) placed in-line (Fig. 4a). The sampling loop yields a known volume for DIC determination. The CO<sub>2</sub> is degassed out of the loop into a syringe containing 0.5 M of KOH to collect all CO<sub>2</sub> for subsequent titration analysis. For dissolved elements, fluid is simply collected after depressurisation (Fig. 4b) and analyzed off-site.

Previous laboratory studies were not consistently successful in avoiding all gas bubbles but this was because the PDS's set-up was slightly different, causing greater volumes of degassed CO<sub>2</sub> during sampling and because the PDS was not rotated sufficiently.<sup>8</sup> During these lab tests, a high pressure 5L titanium batch reactor containing CO<sub>2</sub> saturated water equilibrated at 40 bar pressure was used. The PDS was filled completely with the carbonated water from the vessel, which took approx. 2 hours. Afterwards, the PDS sampling valve was connected to a thick glass tube to monitor the volume of remaining gas.<sup>8</sup> Any potential gas bubbles in the system were immediately spotted and their combined volume determined by the time it took for the gas to pass the known inner volume of the glass tube. Subsequent laboratory experiments confirmed that no gas bubbles remained when applying a hydraulic pressure of 80 bar, rotating the PDS every minute for 15 min total and re-pressurising the PDS after 5 and 10 min, respectively. Re-pressurisation is crucial because the void left by dissolving bubbles causes the plunger to move forward lowering considerably the applied hydraulic pressure. Note that all of the tests were carried out with a fully CO<sub>2</sub> saturated solution

(~1.4 molar) whereas the field injection was conducted at slight undersaturation with respect to CO<sub>2</sub> to avoid any degassing during possible pressure drops in the injection system.

### ***3. Discussion***

Monitoring the CO<sub>2</sub> plume after injection is integral part of any geologic carbon storage project. Wireline logging and/or surface-based geophysical monitoring tools are frequently deployed to follow the supercritical portion of CO<sub>2</sub><sup>9</sup> but for dissolved CO<sub>2</sub> and its migration and effect on the mobility of other elements in the reservoir in-situ fluid sampling is required. These pressurised downhole samples are routinely degassed, either at the wellhead during production or after transporting the sample to the surface and the in-situ pH, alkalinity, and mineral saturation indices are consistently recalculated with geochemical modelling software.<sup>10-13</sup> This is a legitimate approach as long as carbonate precipitation during CO<sub>2</sub> degassing can be compellingly ruled out; the pH/pCO<sub>2</sub> conditions under which carbonate formation is likely during sampling into a vacuum sampler have been discussed in detail elsewhere.<sup>7</sup> Those carbon storage projects, such as CarbFix, targeting (ultra)mafic terrains and/or the use of a carbonated solution as injection fluid are more prone to potential carbonate precipitation upon degassing and rely more than any other carbon storage initiative on accurate data of the aqueous geochemistry and its temporal evolution in the reservoir. Thus, a slickline sampler was developed that would avoid the crucial limitations imposed by the presence of bubbles due to degassing and the potential of carbonate precipitation during sampling. Another important goal was to design an affordable, cost-conscious alternative to already available well-based subsurface monitoring tools and commercial wireline samplers. Based on the recent review<sup>7</sup> on available downhole sampling techniques for groundwater in different deep settings, our syringe sampler is a very economic sampling solution. Besides extensive lab and field tests, the PDS was successfully deployed during a small scale CO<sub>2</sub> injection test in spring of 2012. During six weeks, 175 tons of pure gaseous CO<sub>2</sub> were injected into basaltic rocks at the CarbFix injection site in Hellisheidi, SW-Iceland. Among the main objectives of this test injection phase was the validation of the monitoring equipment. The PDS was tested during the whole injection period,



with the objective to measure the *in situ* pH and dissolved inorganic carbon (DIC) of the carbonated water within the injection well, at the targeted injection depth. These parameters are crucial for confirming the CO<sub>2</sub> dissolution process which was designed to take place within the borehole, before entering the aquifer. In total 13 fluids samples were obtained from a depth of 540 m of the injection well during the test injection performed in 2012 (Fig.5). Each of the acquired fluid samples was processed in a provisional mobile container 20m next to the injection site and analyzed for DIC; the in-situ pH of six of the 13 samples was also measured. Figure 5 illustrates the very good match between measured DIC concentrations and those calculated from the flow rates of CO<sub>2</sub> and water, respectively at the injector.<sup>5</sup> The DIC was calculated from the flow rates, assuming that all the CO<sub>2</sub> gas was fully dissolved within the injection well. The pH of the carbonated water was modelled with the computer code PHREEQC<sup>14</sup>, by equilibrating the injection water with the known amount of CO<sub>2</sub> gas<sup>4</sup>. The average calculated DIC was 0.87 mol/L with a standard deviation of 0.02 whereas the DIC titrations from the sampler yielded an average of 0.86 mol/L with a standard deviation of 0.05. It means that within statistical errors, the syringe sampler accurately reproduced the average amount of DIC entering the aquifer over the entire injection period, except for the very first sample. This sample was the first one to be taken under real injection conditions and taking the associated issues of developing a flawless sampling routine under these circumstances into account, the deviation is not too surprising. A similar close correspondence applies to the geochemically modelled pH versus the measured pH derived from the sampling set-up depicted in Figure 4a. Except for one data point all in-situ pH measurements fall within 0.1 pH units of the expected values. Given an uncertainty of the pH measurements of 0.1 log units, they agree well with the geochemically modelled pH. These findings altogether clearly support the operational capability of the PDS and sampling line for the specifics of the CarbFix injection site.

There are a number of sampling alternatives to the syringe sampler<sup>7</sup>, one of which is the so-called U-tube which has been deployed for geochemical monitoring during carbon sequestration activities, at the Frio site in Texas<sup>15</sup>, the Australian Otway Project<sup>12</sup>, and the Cranfield site in Mississippi<sup>13</sup>,

among others. It is worth highlighting the fundamental differences of the syringe sampler of this study to the U-tube as both have proven successful in acquiring borehole chemical data during CO<sub>2</sub> injections. A key difference of the PDS to the U-tube –and any other commercial positive displacement sampler of its kind– is the investment costs. Production costs for the CarbFix sampler were less than USD 3,000, already lower than the costs for the steel material alone required for the total tubing of the sample and drive leg of the U-tube. Material operating costs include periodic replacement of the O-rings around the plunger, which are trivial compared to the 200+ L of N<sub>2</sub> that each sample from the U-tube consumes (at 250 bar and 1400 m depth).<sup>16</sup> Because it requires no electric or electronic (controlling) equipment, the slick wireline syringe sampler is robust and reliable. Furthermore, not being stationary was another necessity for the CarbFix project to avoid any iron or metal contamination from the stainless steel that, under the corrosive injection conditions, could potentially alter the geochemistry in the reservoir. The primary limitations of the syringe sampler are the labour time and associated costs as each sampling and sample collection requires the full-time dedication of personnel and the time lag from sampling to analysis (the labour time strongly depends on the sampling depth because the sampler has to be lowered and hauled with an electric winch of finite motor capacity). While the U-tube delivers gas and solute compositional data in real-time on-site, this is not the case for the syringe sampler; samples are collected and processed on-site but analysis takes place in the lab. This entails an information gap on geochemical subsurface developments of at least a day that may be important if immediate response is required. Furthermore, the volume of sampled injection/reservoir fluid is orders of magnitude different. For a wireline sampler there is a maximum to its sampling volume because of the limitations from the wellbore design and diameter. A volume between 0.6 to 1.0 L is quite common. Using a U-tube can yield volumes one to two orders of magnitude larger. Other differences between these sampling techniques, and formation and fluid properties, may influence selection of the most convenient sampling option<sup>7</sup>. For example, injection of scCO<sub>2</sub> into a deep saline aquifer may not be associated with dissolution/precipitation phenomena anticipated in a basaltic reservoir and which have to be

monitored closely and accurately without forming secondary phases during the sampling process. Besides, the CarbFix sampler was tested up to 100 bar in the lab but the use of a check valve (U2) with an adjustable cracking pressure close to the reservoir pressure puts limitations to the maximum operational depth in terms of acquiring such a check valve or manufacturing the right spring for it.

#### **4. Conclusions**

Laboratory tests and field immersions before and during CO<sub>2</sub> injection indicate that the Icelandic syringe sampler is capable of sampling pressurized carbonated fluids in injection and monitoring wells, respectively. Furthermore, a specially designed sampling line enables the in-situ measurements of the vital parameters DIC, pH, and the redox state. The lower part of the sampler represents a syringe whose hydraulically stimulated plunger facilitates the recombination of potentially degassed CO<sub>2</sub> and other soluble gases with the fluid whereas a flow restrictor controls the smooth flow of DI water from the sampling chamber into a collector. Degassing cannot be totally averted during sampling but the set-up keeps the pressure drop during sampling low. Note, that neither the sampler's overall set-up, consisting basically of an empty compartment (collector) behind a compartment filled with displacement fluid (sampling chamber) and a piston, nor its constituent parts are *per se* novel. However, the fact that these parts were assembled for a fraction of the price of commercial alternatives and tested successfully during a CO<sub>2</sub> field injection constitutes an innovative step. Furthermore, this contribution facilitates in detail the sampler's blueprint and workings to disseminate its use. This low cost sampler yields quality samples for major and trace elemental analyses, including isotope ratios and soluble conservative tracers (such as a dye or <sup>14</sup>C) injected with the carbonated fluid. While developed for a mineral sequestration initiative its overall concept should equally well be applicable to other geologic carbon sequestration efforts involving scCO<sub>2</sub> and higher pressures. The principal requirements are initial laboratory tests to find the right interplay between adjustable cracking pressure of the downstream check valve (U2), the internal PDS backpressure caused by the plunger and the well pressure at injection depth. Over pressurisation of the PDS after sampling to force back any bubbles is not even

needed when dealing with scCO<sub>2</sub>. The tenet for this procedure is the assumption that all carbon dioxide in the aquifer is dissolved and needs to be quantified in order to gauge the degree of carbonatization. For scCO<sub>2</sub> applications, the CO<sub>2</sub> molar fraction corresponding to carbon dioxide solubility under injection conditions (i.e., at reservoir temperature, pressure, and salinity) is of interest and therefore a hydraulic pressure on the plunger corresponding to the sampling depth suffices to potentially recombine that portion.

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### Figure captions

Figure 1. a) The downhole sampler set-up. Ball (U1, L1) and check valves (U2, L2) are connected to the upper and lower caps. A flow restrictor controls the sampling flow and is connected to an evacuated collector, placed above the sampling chamber. b) Basic lay-out of the PDS. Depicted are illustrations of the dimensions of the chamber and collector (box 1), the upper and lower caps (boxes 2, 5), and the plunger (box 3). Stainless steel protection caps are placed on both ends (box 4).

Figure 2. Different phases of downhole sampling in the CO<sub>2</sub> injection well. a) When the PDS reaches 540 m depth, the higher outer pressure is conveyed via the piston and compressed DI water to the adjustable outlet check valve (U2) which opens and the CO<sub>2</sub> charged water starts to flow into the sampling chamber via the valves L1 and L2. This action moves the plunger upwards (b) and squeezes the DI-water out through the flow restrictor into the evacuated collector until all water has been displaced (c).

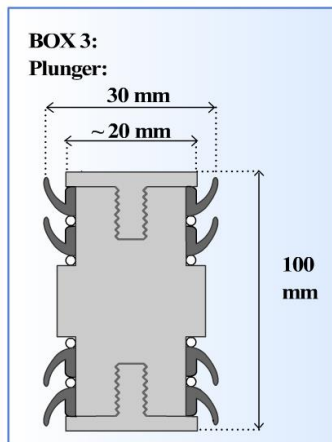
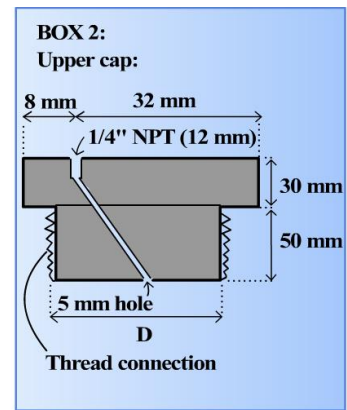
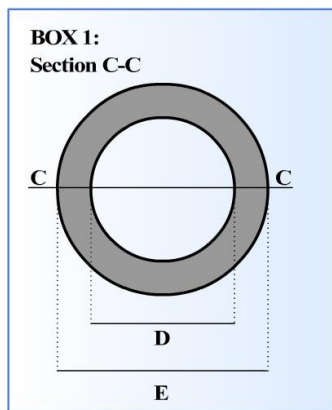
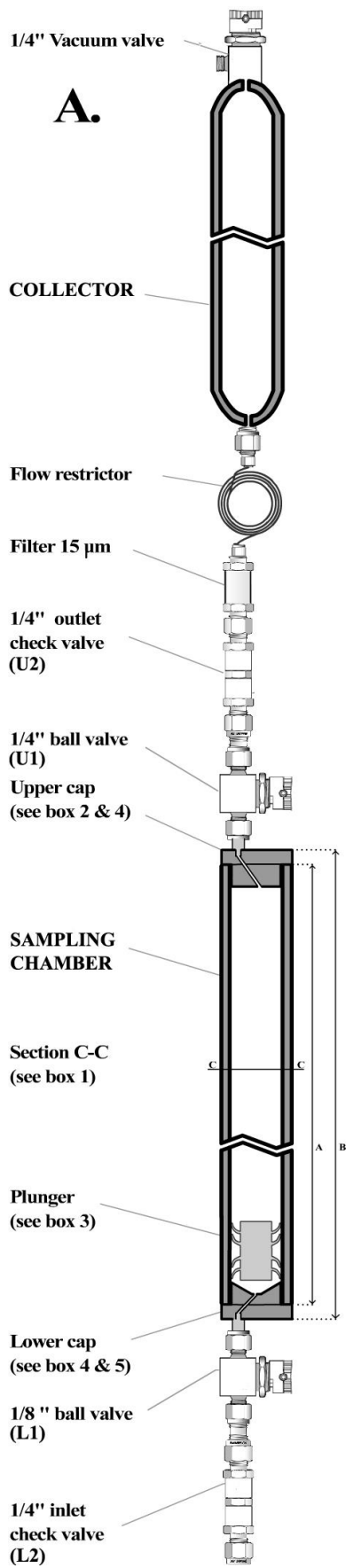
Figure 3. Using a high-pressure liquid pump, hydrostatic overpressure of DI water is applied to the downstream side of the PDS where the plunger has moved during sampling. Continuous vertical rotation of the PDS together with repeated re-pressurization leads to a gas free aqueous sample that can be collected.

Figure 4. Design for on-site sample treatment. A high-pressure liquid pump was added to the downstream side of the PDS (on the right, where the plunger moved during sampling), equipped with a pressure gauge (P). The sampling line consists of a ¼" needle valve, a 6-port 2-way valve with a known volume sample loop, a gas-tight syringe for CO<sub>2</sub> sampling, in-line P/T electrodes for pH and Eh measurements, followed by a backpressure regulator (BPR). a) Loading of the sample

loop and simultaneous pH/Eh determination. b) Gas expansion from the loop into a syringe, containing 0.5M KOH for CO<sub>2</sub> collection and analysis. Dissolved elements were sampled from the BPR outlet.

Figure 5. Similarity of dissolved inorganic carbon (DIC) calculated from the injection system (DIC-calc) with the measured DIC from the sampler (DIC-meas) plotted over the entire injection period from late January to early March 2012. The modelled pH (pH-calc) on the right-hand y-axis is plotted with the measured pH (pH-meas) from the sampling set-up (cf. Fig.4a).





Legend	Size
Pipe length = A	160 cm
Total length = B	166 cm
ID = D	30 mm
OD = E	40 mm

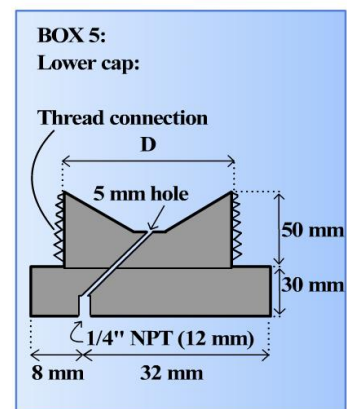
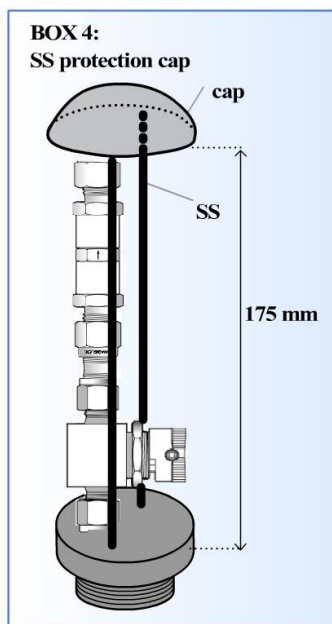
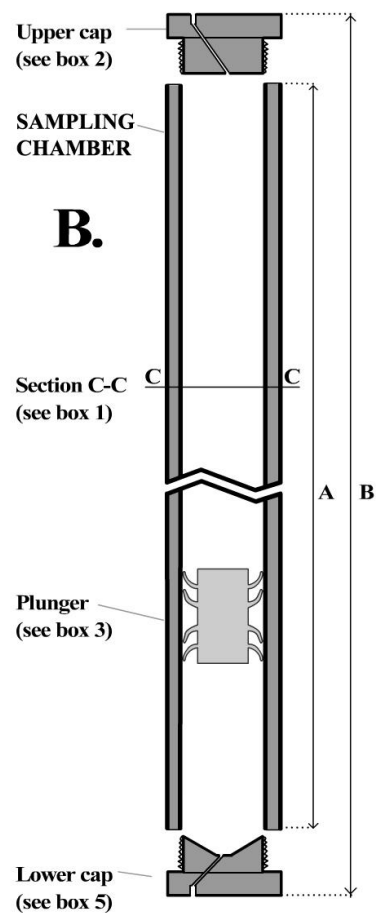


Figure 1

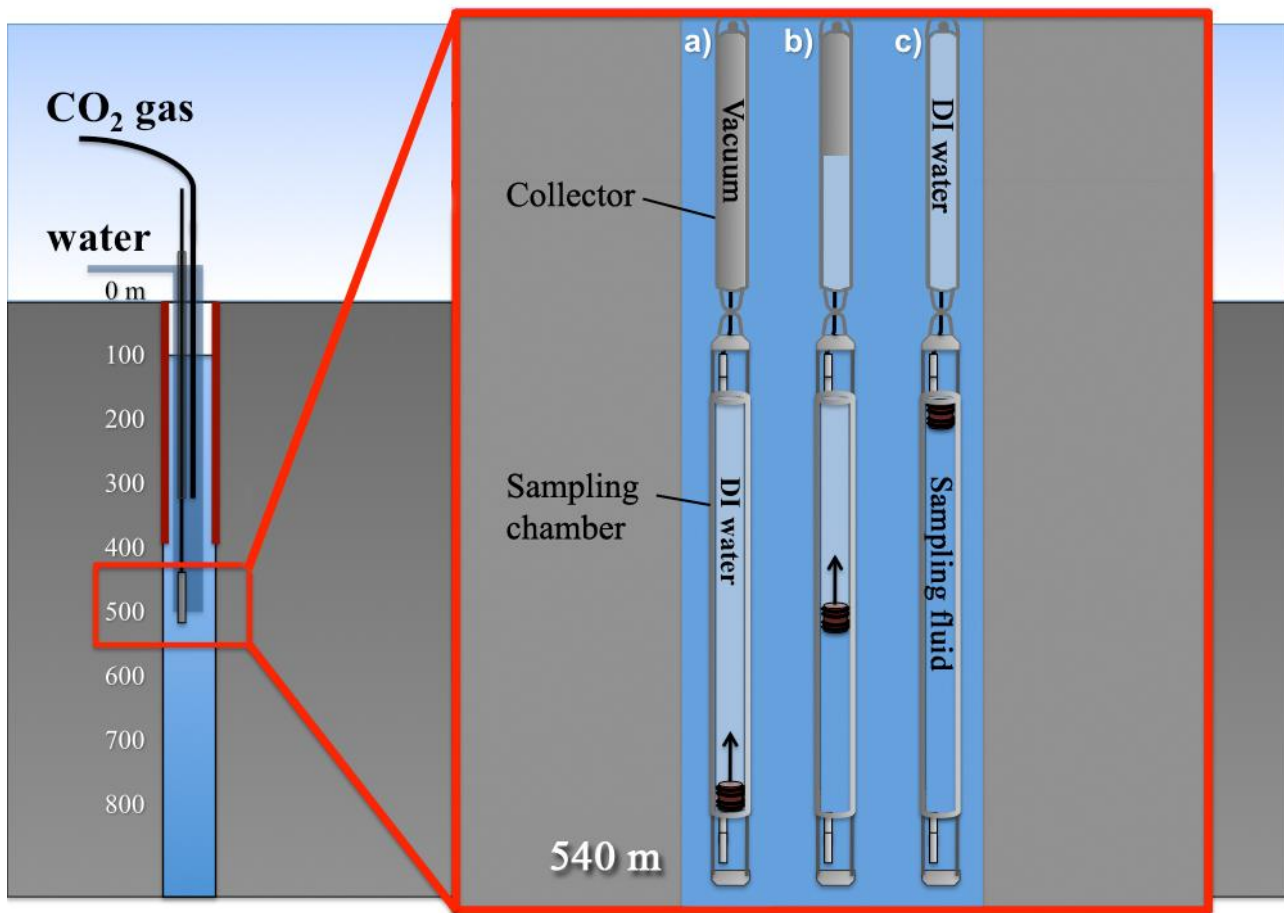


Figure 2

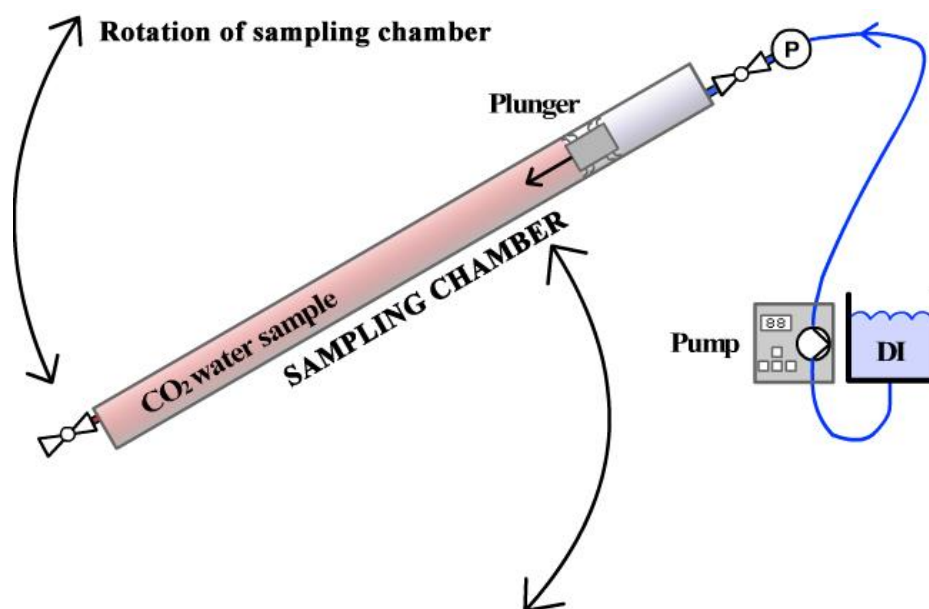
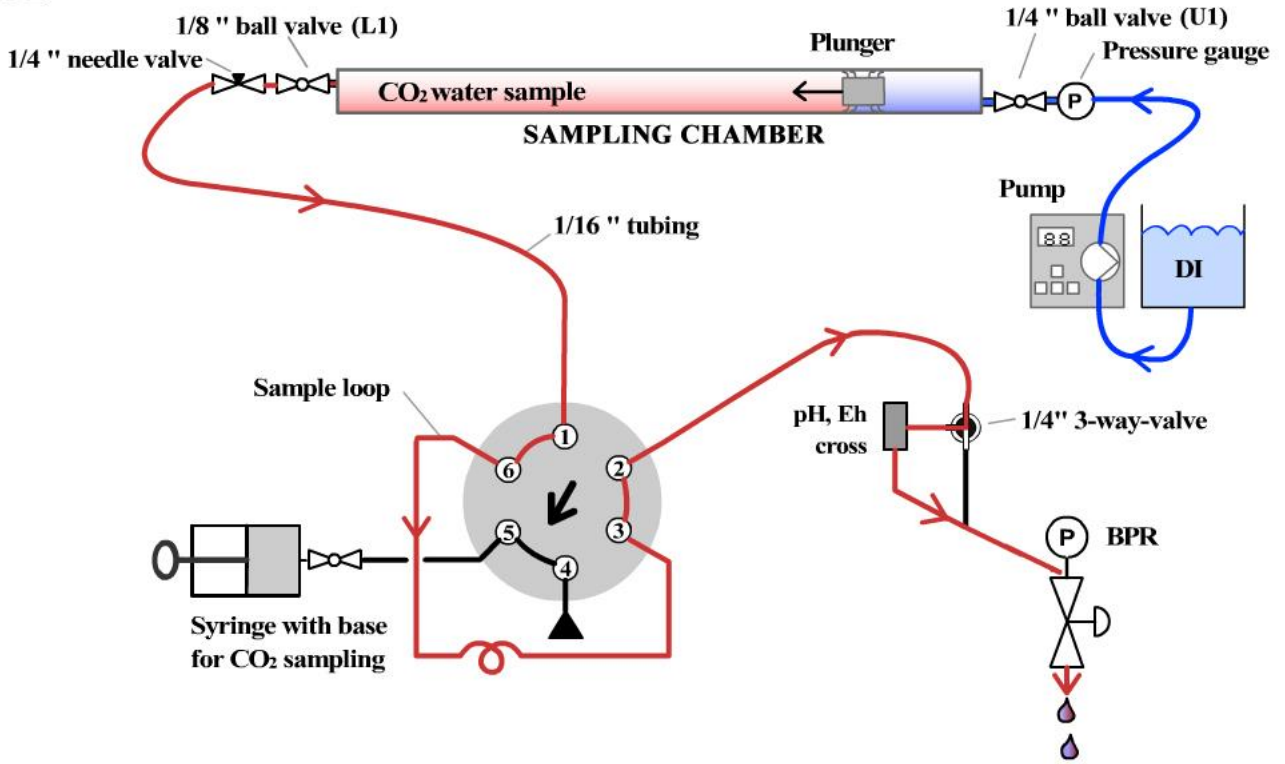


Figure 3

**A.**



**B.**

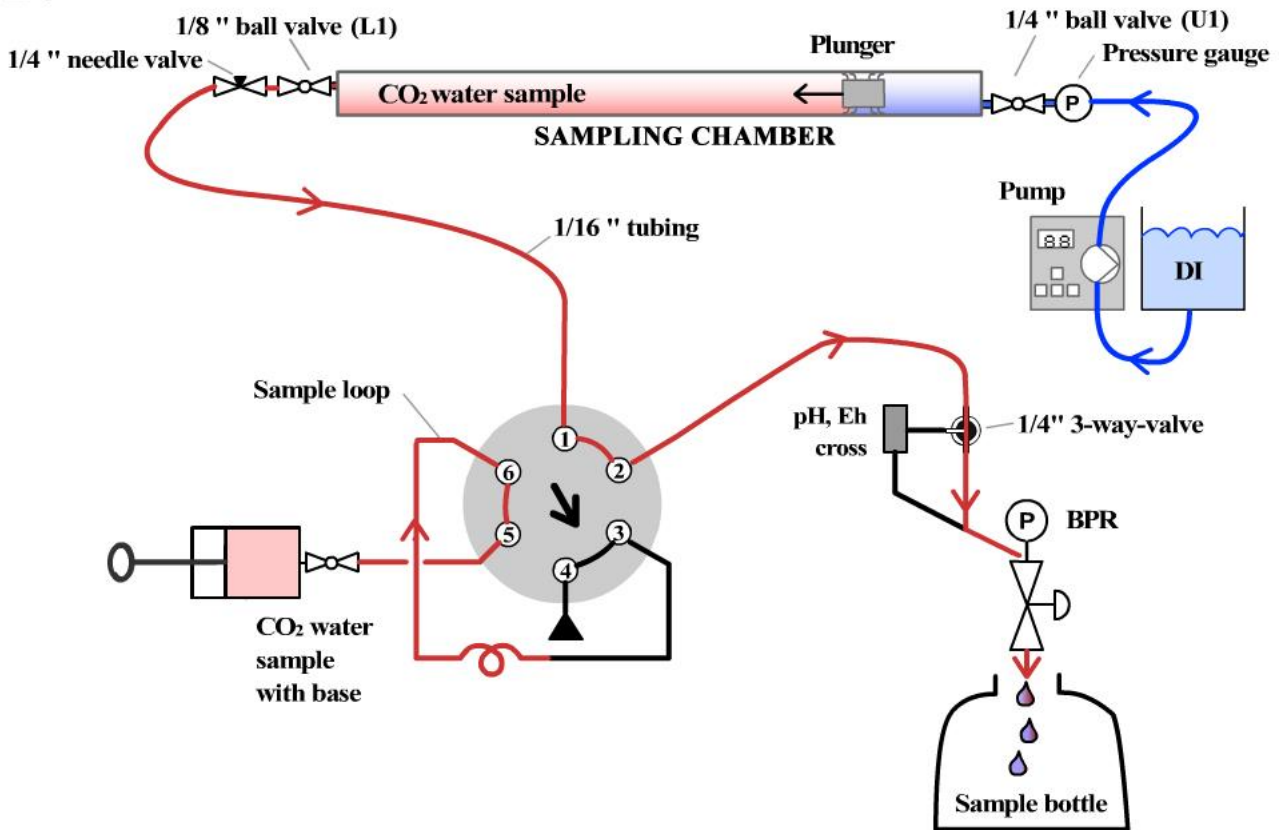


Figure 4

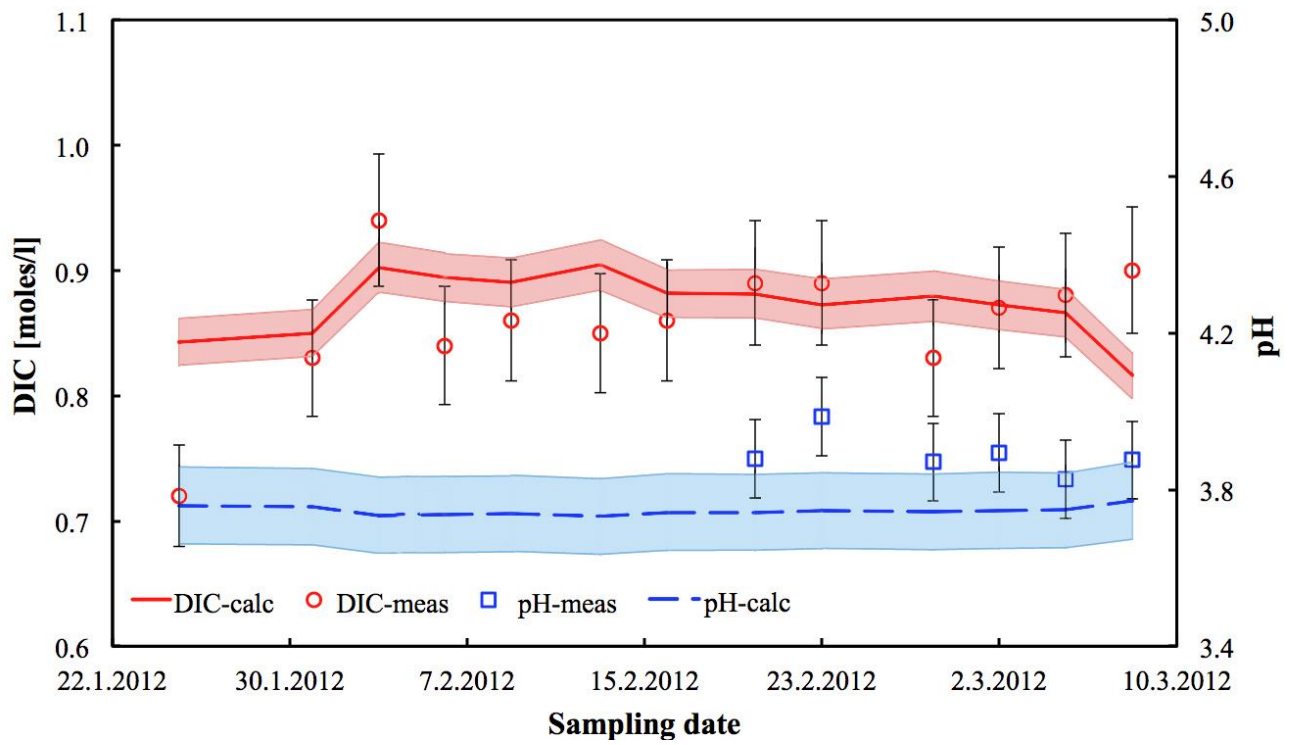


Figure 5