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### Deep aquifer sampling and the use of ball check-valves systems.

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#### Abstract

Accurate monitoring of deep aquifers is one of the challenges with  $CO_2$  Storage survey – but this challenge is not restricted to this thematic. Pumping deep waters is often not appropriate as it requires high amounts of water to be purged. Therefore deep sampling is often performed. Several devices exist; the simplest ones are based on the lowering of bottles with opened valves that are closed at the targeted depth. Improvement comes with bottles that are only opened at desired depth, or with bottles having an initial volume equal to zero that is enlarged through the functioning of a moving part that creates space and allows water to flows in.

The problem with such bottles is that the volume is limited (from hundreds of mL to several litres) and that the bottle has to be risen up at the surface when filled. This may take much time. This sampling is also problematic if proper characterisation of dissolved gas species has to be done: an appropriate transfer system is required at surface. Sample handling may also modify physico-chemical characteristics of the fluid that may become lesser representative of in-situ conditions – even if it is established that sample retrieval will affect, whatever we do, some parameters (*e.g.* temperature).

To overcome some of these problems, other systems have been developed such as the Westbay system (May and Waldmann, 2014, Greenhouse Gas Sci Technol. 4, 176–190) that allows having multiple sampling points in the same borehole. This system allows the collection of samples at formation pressure in containers recovered at the surface, but of relatively low volume (300 mL in the case of CO2FieldLab experiment; Denchik et *al.*, 2014, IJGGC 28, 275-282). Another limitation is that the completion is borehole specific. Other systems are based on ball check-valves and high pressure gas drive. One of the most known is the U-tube system (Freifeld *et al.*, 2005, JGR 110, B10203) that has been deployed at depths greater than 2 km. It operates by collecting water using N<sub>2</sub> supply in the drive leg after the tubes were filled by water up to hydrostatic level. The water is collected at the surface from the sampling leg thanks to the gas pressure. The surface installation is quite complex (Freifeld, 2010, doi:10.2204/iodp.sd.8.07).

The GazOGaz<sup>©</sup> (GOG) sampling system (Gal *et al.*, 2014, EAGE Workshop, Stavanger, 22-24 April) is equally based on valves and inert gas pressure ( $N_2$  or He) but is designed to be more

flexible. It can be deployed and retrieved on a short time scale, quickly adapted to perform kind of "logging by sampling" along the water column, or installed permanently in boreholes for long term monitoring. Such monitoring is performed since more than 10 years in the Eastern Paris basin (France). To date, investigations have been performed down to 1030 m depth but investigation depth is virtually unlimited. Here we present intercomparaison with bottle sampling methods, to ask one of the most frequent wonderings about deep sampling, sample representativeness.

Thorough characterisation of physico-chemical parameters along the water column (*e.g.* temperature, conductivity, pH...) is the first task to perform in order to adequately select the levels to be sampled. In this study, the borehole is located in the Paris basin (Albian aquifer). Water table level is close to -130 m below surface and screens are from -295 to -330 m depth. Casing is made of low grade steel but screens are of stainless steel. As a consequence, data may differ from regional knowledge on Albian chemistry.

Comparison of GOG and bottle samplers has been done for dissolved elements and dissolved gases. Two conventional samplers were used: the first (referred to as SP) relying on filling after valve opening thanks to electrical impulsion (bottle of 0.5 L flushed with  $N_2$ ) and the second (referred to as GS) relying on filling thanks to piston displacement after a fixed time period (bottle of 0.9 L flushed with Ar). Samplers had similar diameters (GS: 48 mm; GOG: 50 mm; SP: 60 mm) but different lengths (2.5 m, 0.6 m and 3 m respectively).

Physico-chemical parameters were recorded at surface at the opening of the bottle (SP and GS) or in the flow (GOG). Apart from temperature that was no more representative of in-situ conditions (time for device retrieval or for water rise in tubes), pH and electrical conductivity were in good agreement between methods (8.15-8.3 and 198-230  $\mu$ S.cm<sup>-1</sup> respectively). Best preservation of dissolved oxygen values was found for SP device (0% sat.), the maximum aeration being found for GS device (52% sat.). Redox potentials varied accordingly. No significant changes were found for cations and anions except some deviations in the Fe(II) content that may linked to unappropriated site conditioning of the GS sample (no filtration, no acidification of the sample).

If the sampling procedure does not drastically affect the water chemistry, it has more influence onto the dissolved gas concentrations. Additional bias may have occurred during sample transfer on site. The GS sampler appears to be sensitive to atmospheric contamination:  $N_2/O_2$  ratio is close to that of atmosphere (3.7) with residual Ar contamination. SP and GOG samplers have different ratios (9.4 and 6.5 respectively) suggesting that the protocol is better constrained. These 2 samplers give similar dissolved  $O_2$  concentrations ( $1.7 \times 10^{-3}$  mol/L) whereas Ar and  $N_2$  concentrations were lower for GOG than for SP ( $1.1 \times 10^{-4}$  mol/L –  $1.1 \times 10^{-2}$  mol/L and  $4.6 \times 10^{-4}$  mol/L –  $1.6 \times 10^{-2}$  mol/L respectively). Slight air contamination during transfer for SP sample may exist. The GOG sampler may be thus advantageously used for either water or dissolved gas sampling. Work is in progress to enhance the reliability of this sampler and to perform gas characterisation directly on site.

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