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

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Abstract

Investigations using deep water sampling systems are reported for the Albian aquifer, Paris Basin. Two wireline samplers and one ball-check valve sampler were used to determine fluid physico-chemical parameters, concentrations in major and trace elements and dissolved gases concentrations.
Some physico-chemical parameters (*e.g.* temperature) of the fluid are affected by the use of a deep sampling system whatever the sampler used. Fluid chemistry can be characterized with a good confidence level. Dissolved gas concentrations are more difficult to accurately evaluate but it can be demonstrated that ball-check valves systems may help to improve to such measurements.
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Keywords: deep sampling; wireline tool; ball-check valve sampler; aquifer monitoring; physico-chemical parameters; major and trace elements; dissolved gases

1. Introduction

Reliable and accurate monitoring of fluids in deep aquifers is one of the key geochemical monitoring that has to be performed in several applications such as deep geological storages, shale gas exploitations or geothermal applications. Among deep storages, those consisting in storing CO_2 in deep geological formations – and especially in deep aquifers – are of particular interest [*e.g.* 1]. They not only include the storage formation itself but also

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shallower formations that can contain water resources either unexploited or used for water supply. The latter is of great concern and numerous works are reported worldwide with special emphasis on trace elements remobilization [*e.g.* 2, 3, 4, 5, 6].

Although deep aquifer monitoring is of great concern, there are relatively few works reporting in details the way the fluids are recovered at surface [7]. Nevertheless, the confidence scientists and site operators may have in the characterization of the fluids is of great importance. Measuring fluids parameters as close as possible to *in situ* ones is relevant to characterize the fluid and for further modelling steps. If there is a high uncertainty during the field step then the following stages will become even more poorly constrained. The way the fluid is characterized and collected at surface is then a key step and particular caution has to be taken especially regarding the gas phase as highlighted by Conaway *et al.* [8] in their recent paper.

In that perspective, deep sampling systems are one of the best ways to get reasonable estimations of the fluid chemistry [8]. At the opposite, the use of electric submersible pumps – and worse the use of gas-lift methods – can induce disturbances of the physical and/or chemical properties of samples [7] thus leading to biased characterizations of the fluids. Deep sampling systems may be wireline tools: a sampling bottle (either under vacuum or at reservoir pressure) is lowered down to the targeted depth of sampling and the fluid is collected at surface using specific transfer system after the sampler has been recovered at the surface. Deep sampling systems may also be systems allowing fluid recovery directly at the surface. This last category is largely represented by the U-tube system [9] that uses stainless steel tubing and ball-check valves operated using compressed nitrogen supply. This system is mainly operated in US projects and suffers from a drawback as it is fixed in the borehole and thus only allows the collection of water at a fixed depth.

Here we present some investigations using a system also relying on the use of ball-check valves (GazOGaz – GOG – system) but allowing performing sampling at any depth in a borehole [10]. Investigations are compared with two wireline tools. The goal is to gain confidence in results obtained with deep sampling systems and to demonstrate operability of the GOG sampling system as well as to validate its use.

2. Settings

2.1. The sampling systems

Two wireline sampling systems were used. The first (referred to as SP system) is a titanium bottle of 0.5 L volume that is flushed with N_2 and lowered to the sampling horizon. Valve opening is operated from the surface thanks to electrical impulsion. SP system can operate at pressure up to 150 bars (*c.a.* 1500 m depth). The second system (referred to as GS system) is a stainless steel bottle of 0.9 L of volume that is flushed with Ar prior to use. The bottle is filled automatically by piston displacement after a fixed time period that is determined beforehand at surface prior to lowering the sampler. GS system can operate up to 100 bars of hydrostatic pressure (*c.a.* 1000 m depth). These two systems may operate in narrow boreholes (respective diameters: 60 mm for SP system and 48 mm for GS system) but have lengths of 3 m and 2.5 m respectively. The GS system has been found to suffer from malfunctioning probably linked to the automatic opening of the system after a certain period of time has elapsed and/or because of fine particles clogging. Fluids were only recovered at the second trial at each depth, first trial failing to get any fluid – it may be a consequence of bad evaluation of the time needed to lower the sampler at the desired depth or a malfunctioning of the timer that did not trigger the opening of the valve.

The GOG sampling system is a ball-check valve system using flexible tubes (polyamide) for inert gas supply. Gas is N_2 for routine use but tests have been done using He for evaluating the cross-contamination of the gas phase by the pressuring gas phase [10]. The system has been developed since the early 2000's and has been patented in 2014. By building the system allows the collection of 1.2 L of fluid per 100 m of tube (4 mm internal diameter) – by comparison, U-tube can collect 2.8 to 6.4 L of water per 100 m (6 mm to 9 mm internal tube diameter). The system can sample fluids at any depth in the water column thanks to the use of tube that are non-attached to the walls of the borehole. The upper sampling limit is under 10 m of water column at minimum – the ball-check valves need at least a difference of pressure of 1 bar relative to operate – and the lower sampling limit is virtually unlimited – to date samples have been retrieved at 1030 m depth. The GOG requires lower N_2 amounts to work than U-tube system as

only one leg is lowered down to the desired sampling depth and ball check-valves are not lowered deeper than 250 m depth. As such, a kind of “logging by sampling” can be done in boreholes only requiring quick adaptations of the geometry of the system as function of the depths to be sampled. At the opposite, the system can also be installed permanently in boreholes for long term monitoring as performed since more than 10 years in the Eastern Paris basin (France).

2.2. Study site

The study site is emplaced in the Parisian Basin and reaches the Albian aquifer – an aquifer level that is used for water supply and that is located well above deeper saline aquifers that may be used for CO_2 storage in the future. As such the monitoring of this aquifer is quite strategic even if the depth it reaches at Bussy-en-Othe (Burgundy) is only around 300 m. Some characteristics of the Bussy-en-Othe borehole are reported in Figure 1. The main feature is the water table level that is quite deep (lesser than -127 m by reference to the top of the casing): many pumping devices cannot reach such depths so that the use of deep sampling may be of interest even if the depth is not as high as frequently observed for the monitoring of deep storages. Although this borehole was drilled in 2010, and not developed after completion, another point to mention is that the casing is made of low-grade steel tube – only the screened section is in stainless steel. Corrosion processes are then present from -130 m to -280 m in the water column and some samples can be affected by this bias. Last, it has to be mentioned that the GOG system was used without any centering tool: during some sampling sessions it has not been possible to go inside the screened section as the annulus between the two casings is neither cemented nor protected by an appropriated metal part.

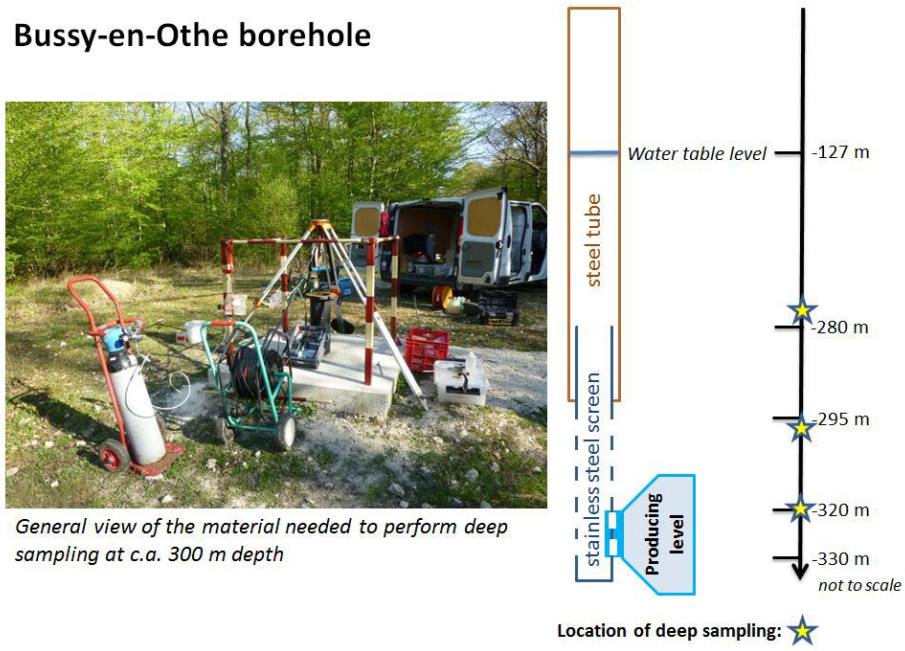


Fig. 1. (left) Bussy-en-Othe borehole wellhead and material required for deep sampling; (right) technical section of the borehole and location of sampled levels.

2.3. Field operations

The use of deep sampling systems or systems like U-tube or GOG ones is based on the assumption that the physico-chemical characteristics of the water column are known. This is the condition to perform the sampling at the depths were some interesting information will be gathered otherwise the sampling is done under a blind mode. Such investigations were done by borehole logging prior to any sampling in the borehole as shown in Figure 2. From the measured parameters (temperature, pH, electrical conductivity, dissolved oxygen and redox potential), the following features appear:

- The thermal gradient is close to +3.7°C per 100 m of water column and is coherent with values known at regional scale. There is a slight deviation from this equilibrium gradient at the bottom of the borehole ; this corresponds to the producing part of the aquifer (permeability has been evaluated as a low one: 3.3 $x10^{-5}$ m/s);
- The water column is oxygen free excepted the firsts tens of meters that may be influenced by reactions between the casing and the water;
- As a consequence the redox potential (ORP) has a more pronounced reducing character at greater depth;
- pH and electrical conductivity (EC) values are – as the other parameters – only representative of those of the aquifer quality in the screened section and especially its lower part. The Albian aquifer is characterized by low mineralized waters (EC close to 200 $\mu S.cm^{-1}$) with some heterogeneity inside the screened section. pH values are around 8.3 to 8.4, a value that is in the upper range of the values known for this aquifer in similar settings [11].

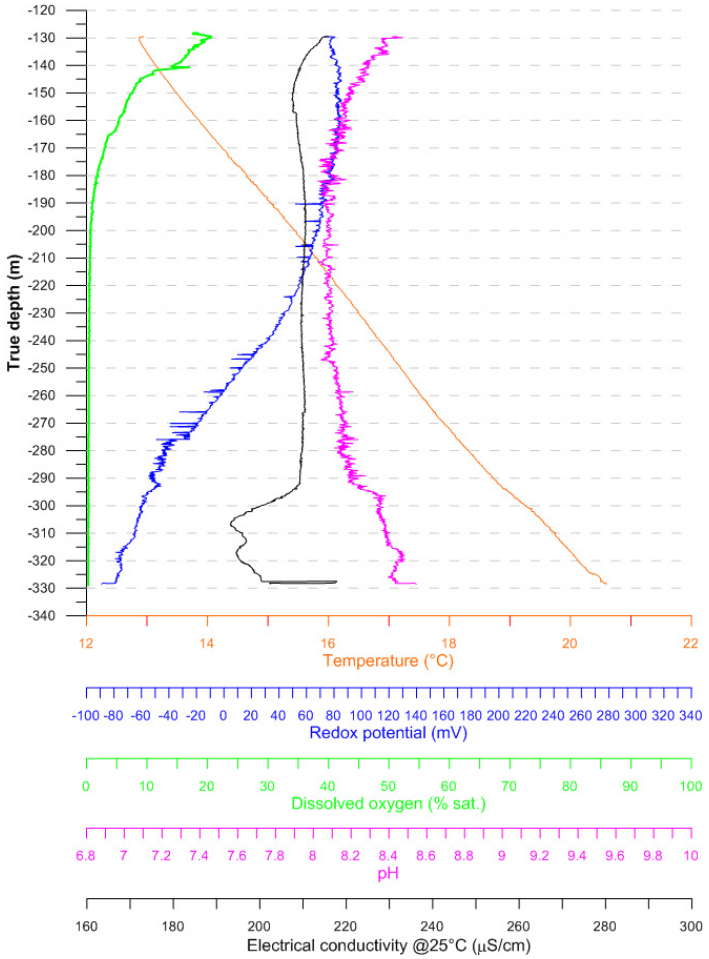


Fig. 2. Physico-chemical parameters as directly measured in the water column of Bussy-en-Othe borehole – the screened section extends from -295 m to -330 m. Example of the April 2014 run.

3. Results

Four sampling sessions have been done at Bussy-en-Othe from September 2013 to April 2014. Not all the sessions have been dedicated to the comparison of deep sampler capabilities but each session has offered the possibility to get fluids using the GOG sampler. When performed, comparisons of samplers are based on physico-chemical characterization, major and trace elements concentrations determinations and dissolved gas concentrations measurements.

3.1. Physico-chemical parameters

Physico-chemical parameters are reported in Table 1. Comparison with data reported in Figure 2 highlights the following points:

- The water temperature measured at the surface is largely influenced by atmospheric conditions. When the air temperature is clement, then the water temperature is found to be close to the one at depth. When the sampling is performed during winter times, then the temperature is significantly lower. This is one of the drawbacks when using deep sampling systems. Wireline tools need time to be recovered at surface so that the water – the volume of water is quite restricted – has time to cool down. At the surface, as the transfer for physico-chemical measurements was performed by direct flowing from the sampler to the measurement cell, additional interaction with atmosphere, especially during the time needed for sensor equilibration, may have occurred. A similar phenomenon is found with the GOG sampler, this is again a known drawback of the ball-check valves samplers as a result of fluid transport in narrow tubes and consecutive cooling [8].
- As the pH of the water is – among other parameters – a function of water temperature, there is an influence of this temperature onto the results: the pH shall be higher when the temperature is lower. This is generally true in the present case, but two additional variables have to be taken into account: first the measurements were not performed in the meantime and second the depths of sampling may change (pH varies along the water column). Nevertheless, apart from one measurement (29 Jan. 2014 (a)) that may not be representative due to contamination from previous experiments, all the other measurements fall within a narrow range (8.2 to 8.5 pH units) that is well in agreement with the knowledge we have from pH of the Albian aquifer. Another parameter that may have had an influence onto pH measurements: the borehole has not been well purged after its drilling so that residual waters may also be influenced by drilling mud and/or by cementing fluid that are still present bottomhole.
- Electrical conductivity measurements are expressed at reference temperature (25°C) so that any influence of temperature is damped. There is a good agreement between EC measurements from deep samplers and in-situ measurements (except for the 28 Jan. 2014 measurement that was not performed in the screened section so that physico-chemical parameters may be affected by interaction with steel tubing or residues from the drilling process).
- Measurements of the ORP and the dissolved oxygen concentration are the most affected by the contact of the fluid with the atmosphere and may be therefore not representative. If the measurement is done directly in the sampling bottle (data from the 12 Sept. 2013) without handling of the fluid, the evaluation of ORP and dissolved oxygen concentration is satisfying. Better transfer from the sampler to a specific measurement cell at the surface may have enhanced the representativeness of these measurements especially considering that dissolved oxygen concentrations are also sensitive to temperature changes (ORP measurements account for the temperature as they are expressed at 25°C by reference to the potential of the hydrogen electrode).

From these statements, it appears that deep sampling may suffer from intrinsic drawbacks that may not allow proper characterization of all the fluid characteristics – *in-situ* measurement remain the best way to get reliable data. Nevertheless, if the transfer of the fluid at the surface is well operated, quantification of some parameters can be planned with sufficient level of confidence.

Table 1. Physico-chemical parameters as measured at surface after pouring in measurement cell without the use of transfer bench.

Date of sampling	Depth (m/wellhead)	Water temperature (°C)	pH	EC@25°C ($\mu S.cm^{-1}$)	ORP norm. H_2 electrode (mV)	Dissolved oxygen (% sat.)	Sampler
12 Sept. 2013	320	21.2	8.30	230	-100	0%	SP
14 Nov. 2013	320	7.5	8.23	239	+240	27%	GOG
28 Jan. 2014	270	9.4	8.27	292	+320	19%	GOG
28 Jan. 2014	300	10	8.49	218	+310	23%	GOG
29 Jan. 2014 (a)	330	9.4	7.74	198	+210	26%	GS
29 Jan. 2014 (b)	330	9.7	8.15	198	+290	52%	GS
16 Apr. 2014	260	20.9	8.40	199	+250	66%	GOG
16 Apr. 2014	320	24.6	8.20	202	+220	36%	GOG
16 Apr. 2014	325	12.5	8.50	187	+300	33%	GOG

3.2. Fluid chemistry: major and trace elements

The evolution of fluid chemistry during the sampling sessions has been mainly evaluated using major elements concentrations (Figure 3) and trace elements concentrations for the samples collected using the GOG system (Figure 4).

The Ca-HCO_3 character of the Albian water is well described by all the samples albeit there is an intrinsic variability of the concentrations considered specie by specie (Figure 3). This may be a consequence of two processes, on one side the sampling at different levels in the screened section and on the other side the influence of drilling residues existing in the borehole. This last phenomenon is particularly visible for the sample gathered at 270 m on the 28 January 2014 with high content in Na and Cl (concentrations are 3 times higher than measured in other samples). As a consequence, the Cl/Na ratio for this sample (1.3) differs from those of the other samples (1 to 1.1). A similar statement can be made for the sample obtained at 300 m depth on the 29 January 2014 using GS sampler: the Cl/Na ratio is 1.5 thus suggesting this sample has to be discarded as a consequence of sampling bias probably resulting from defective cleaning prior to its use (see previous section).

As the borehole progressively cleans itself (the September 2013 pumping session has not allowed a complete recovery of equilibrium parameters), the more recent the data are, and probably the more representative they are. This is suggested by the good agreement between the 3 samples collected at 3 different depths on the 16 April 2014.

Trace elements concentrations were only evaluated using the GOG sampler so that comparison with other technologies is not possible. Nevertheless, the changes in concentrations are relatively limited for trace elements (Figure 4). As the only metal parts are the ball-check valves (stainless steel), contaminations in trace elements are not likely to occur. Polyamide tube – like all tubes – may be subject to precipitation processes over time but the investigations presented here are done for a water with low mineralization and such process is again not likely to occur (the polyamide tube used at Bussy-en-Othe has not been changed during the field acquisitions period). If deviations are stated during long-term monitoring of a well, changing the polyamide tube is not a tremendous operation compared to changing hundreds of meters of stainless steel tube.

From the above mentioned results, it appears therefore possible to get reliable estimates of the fluid chemistry using deep sampling systems even in low permeability aquifers – as far the well has been developed after its completion and its screened section is not plugged by drilling residues or by bacterial films.

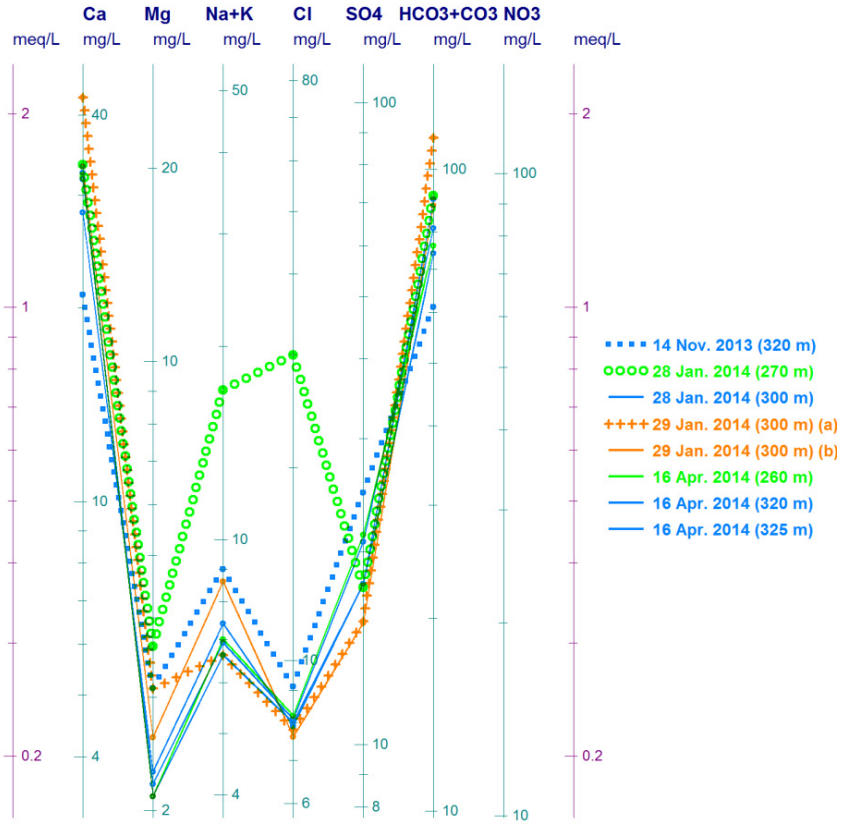


Fig. 3. Schöller-Berkaloff diagram: evolution of major elements concentrations during deep sampling sessions; data in green and blue are acquired using GOG sampler, data in orange using GS sampler.

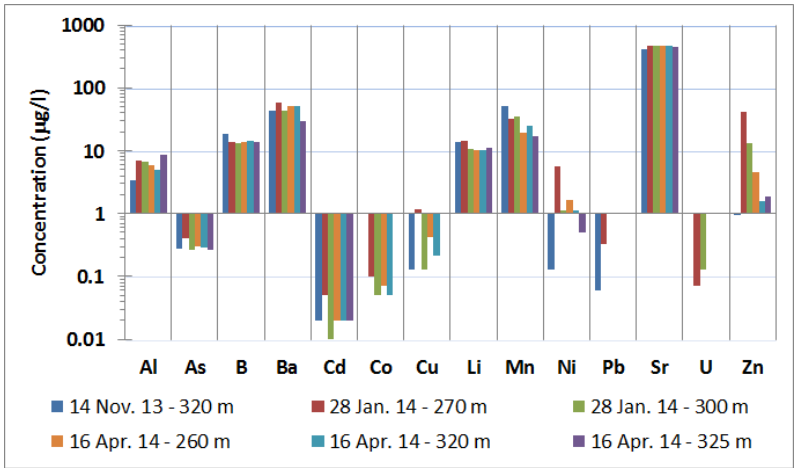


Fig. 4. Trace elements concentrations; all the samples were collected using GOG sampler.

3.3. Fluid chemistry: dissolved gases

The evaluation (is a specific gas phase present?) and the quantification (what is the quantity of this phase?) of gas phases are probably one of the main challenges deep sampling systems have to face. Recent literature [8] well establishes this challenge for deep CO_2 storage by stating that, in case of little gas in the samples, the gas composition results are strongly influenced by the sampling methods. Conaway *et al.* [8] found that wireline samplers (vacuum samplers according to their terminology) and U-tube system are the system that performs "most favorably" this evaluation of the dissolved gas content.

In the present study, we had to deal with even lower gas contents as no gas phase is naturally expressed at the surface unless the water sample is exposed to vacuum. This points out the great importance of well controlling the transfer of the sample from the bottle (in case of wireline sampler) or the sampling system (GOG system) to the final tank. Tanks used for storing the dissolved gas samples are glass bulbs with two stop cocks that are conditioned under vacuum. Once sampled, the glass bulbs are sent to laboratory for gas chromatography analyses; the gas phases are determined in % volume of the gas phase and dissolved concentrations are calculated using Henry's law parameters.

The results of gas chromatography analyses are given in Table 2 and relationships between gas species are presented in Figure 5.

Table 2. Dissolved gas concentrations.

Date of sampling	Depth (m/wellhead)	N_2 (mol/L)	O_2 (mol/L)	Ar (mol/L)	CO_2 (mol/L)	CH_4 (mol/L)	Sampler
12 Sept. 2013	320	1.60×10^{-2}	1.70×10^{-3}	4.60×10^{-4}	1.70×10^{-5}	1.80×10^{-6}	SP
14 Nov. 2013	320	2.90×10^{-2}	6.50×10^{-3}	3.90×10^{-4}	7.10×10^{-5}	4.1×10^{-6}	GOG
28 Jan. 2014	270	1.50×10^{-2}	3.60×10^{-4}	2.10×10^{-5}	2.90×10^{-5}	6.40×10^{-8}	GOG
28 Jan. 2014	300	4.10×10^{-3}	8.40×10^{-4}	5.80×10^{-5}	1.60×10^{-5}	4.00×10^{-6}	GOG
29 Jan. 2014 (a) – sample 1	330	8.10×10^{-2}	2.10×10^{-2}	4.60×10^{-3}	1.80×10^{-5}	7.50×10^{-6}	GS
29 Jan. 2014 (a) – sample 2	330	6.70×10^{-2}	1.80×10^{-2}	9.80×10^{-4}	2.30×10^{-5}	9.50×10^{-5}	GS
29 Jan. 2014 (b) – sample 1	330	6.50×10^{-2}	1.80×10^{-2}	3.50×10^{-3}	5.30×10^{-5}	3.40×10^{-6}	GS
29 Jan. 2014 (b) – sample 2	330	7.20×10^{-2}	1.90×10^{-2}	9.40×10^{-4}	3.30×10^{-5}	3.00×10^{-6}	GS
16 Apr. 2014	260	3.20×10^{-3}	2.40×10^{-4}	2.10×10^{-5}	6.40×10^{-5}	1.30×10^{-7}	GOG
16 Apr. 2014	320	1.10×10^{-2}	1.70×10^{-3}	1.10×10^{-4}	8.50×10^{-5}	1.90×10^{-7}	GOG
16 Apr. 2014 – voluntary air contamination	320	5.90×10^{-2}	1.10×10^{-2}	5.50×10^{-4}	1.40×10^{-4}	1.20×10^{-6}	GOG

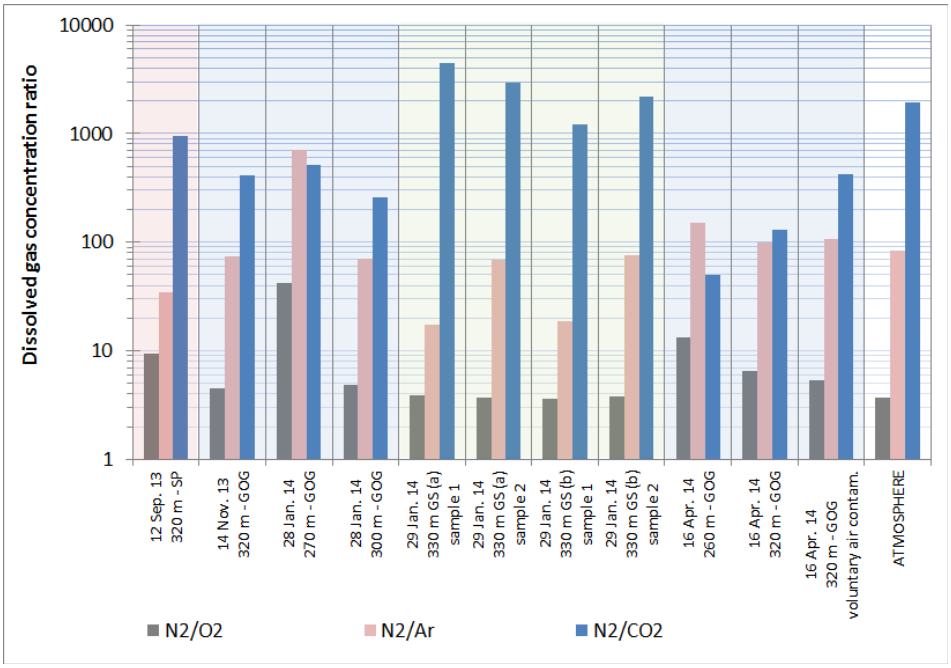


Fig. 5. N_2/O_2, N_2/Ar and N_2/CO_2 ratios of the dissolved gas phases and comparison to the ratios of the atmosphere.

The following statements can be made:

- As expected, the concentrations in dissolved gas species are low. The Albian aquifer is not known to interact, in the area it was sampled, with horizons enriched in gas phases (e.g. organic-rich horizons – there are some deeper seated formations where oil is exploited in the Paris Basin) or with brines (the Dogger aquifer, used for geothermal purposes, can be enriched in H_2S and other gas phases) ;
- The N_2/O_2 ratio suggests that samples collected from the GS sampler are strongly disturbed by atmospheric contamination. Two samples were taken each time the sampling bottle was retrieved at surface but none of them gave a N_2/O_2 ratio different from that of the atmosphere. The sample obtained by the SP sampler has a clearly different ratio, suggesting that N_2 is more abundant. A comparison with Table 2 shows that this is not a consequence of high contamination by air as the abundance of N_2 is far from that stated when a sample is exposed to the atmosphere. This is rather the consequence of low O_2 concentrations (no dissolved O_2 was found during physico-chemical well logging). Nevertheless, some O_2 was found in the sample so that a slight atmospheric contamination during transfer of the sample from the sampling bottle to the glass bulb cannot be discarded. Last, samples obtained using GOG sampler are less affected by atmospheric contamination (the residual O_2 concentration is lower) but for few samples (28 Jan. 2014 – 270 m) enrichment in N_2 can be stated; this is probably a consequence of bad evaluation of the time of sampling. The presence of N_2 is reported by Conaway *et al.* [8] as an artifact of the U-tube sampling system. The GOG sampling system, as it uses polyamide tube that are transparent, allows to visually evaluate if a gas phase is present – or not – inside the tube. It's known that the firsts arrivals of water at surface have strongly interacted with the N_2 used for pressuring the system. As the water flows, the residual contamination decreases and there is a time window during which the fluid (water + dissolved gases) has very low contact with N_2. Samples have to be collected during this time window. At the end of this window, the velocity of the fluid increases inside the tube: this comes before pure N_2 reaches the surface when the sampling leg of the system becomes empty;

- The N_2/Ar ratio is also informative: the two samples, collected each time the GS system was used, clearly show that the first sample is affected by Ar contamination. This system uses Ar as a flushing gas prior to use and it was not possible to vacuum the connection between the system and the glass bulb at the time the sampling was done. As a consequence, there was residual Ar present in the system, and the first sample is contaminated. The N_2/Ar ratio strongly differs for the second sample as the system was cleaned during the collection of the first sample. For the other samplers, this phenomenon does not exist and evaluation of the concentrations can be considered as more realistic. It shall be noted that the very high N_2 excesses found during the use of U-tube sampler, with N_2/Ar ratio from 500 to 700 [8], are absolutely not found when using the GOG sampler; as explained in the previous paragraph, the GOG sampler allows a better control of the N_2 contamination.
- A third ratio is used, the N_2/CO_2 one, albeit the CO_2 concentrations are very low (Table 1). The GS sampler data suggest that all the samples have a ratio greater than the one of the atmosphere; this may be a consequence of N_2 enrichment – but the origin of this enrichment is not obvious – or a consequence of water degassing and loss of CO_2 either during the sampling itself or during the transfer at surface. The other sampling systems have N_2/CO_2 ratios lower than the ratio of the atmosphere thus suggesting the water is slightly enriched in CO_2 compared to equilibrium with the atmosphere. As the Albian aquifer is a carbonated one, finding dissolved CO_2 in water is not surprising. The evaluation of the precise CO_2 amount dissolved in water is nonetheless quite difficult to reach but systems like the GOG may allow, when long term monitoring is performed, to highlight deviations from baseline values or from natural yearly trends existing in water bodies.

The use of a sampling system (GOG) that directly drives the fluid up to the surface, inducing unavoidable fluid depressurization, does not appear as a drawback when dissolved gas concentrations are compared with deep samplers. Evaluation of gas species even appears better using the ball-check valves system as the transfer of the fluid and the fluid collection can be more easily constrained at the surface than with deep samplers. For specific site monitoring or for long term monitoring, it can be envisaged to connect the ball-check valves system with other systems (e.g. gas chromatography) in order to repeat the measurements and to get an evaluation of the uncertainty such a system induces on dissolved gas concentrations measurements. Such an opportunity appears less obvious with deep samplers that have to be lowered each time a sample is needed and that offer only relatively small volumes to be sampled.

4. Conclusions

Investigations using deep sampling systems are reported for the Albian aquifer, Parisian Basin. Two wireline samplers and one ball-check valve sampler were used to investigate fluid physico-chemical parameters, concentrations in major and trace elements and dissolved gases concentrations. In parallel, geochemical logging of the water column was done prior to each use of a deep sampler.

All the sampling systems failed to give good estimates of the temperature at the sampling point as a consequence of time delay between the sampling itself and the collection of fluid at surface. Dissolved oxygen and redox potential measurements may also be influenced by the contact of the fluid with the atmosphere if no transfer bench is available in the field. At the opposite, good estimates of the electrical conductivity can be obtained as well as pH values as far as the bottom temperature can be evaluated in order to correct the pH value.

The chemistry of the fluid can be characterized with a good confidence level using the different deployed systems. The borehole used for this study being subject to some changes during times (*e.g.* pH decrease), it is not obvious to separate the variations that are monitored in between the sampling sessions from the sampling process or external causes. The GOG sampling system has been found not to be a source of contamination in trace elements as stainless steel parts are restricted to connectors and ball-check valves. Deep sampling then appears to be a valuable tool to get water even in low permeability environments where pumping can induce severe drawdowns of the water table level.

The evaluation of concentrations in dissolved gases appears to be most difficult when using deep samplers. The need to transfer the fluid into appropriate containers in the surface is the most problematic step. Ball-check valves systems, that induce depressurization when the fluid rises up in the sampling leg, are not suffering from this bias.

The GOG system offers the possibility to get repeatable evaluations of the gas concentrations at least for the main species but no strong bias can be highlighted when considering gases present at trace levels such as CO_2. The deep sampler using Ar as a flushing phase appears to be sensitive to various contaminations.

As ball-check valves systems offer the opportunity to collect virtually unlimited fluid quantity, their use can be advantageously envisaged for deep aquifer monitoring. Flexible systems such as the GOG one additionally offer the opportunity to perform investigations at several depths in the water column in case the aquifer is not homogeneous. This avoids the use of complicated systems relying on packers and pumps and, for greater depths, the use of several dedicated sampling systems operating each at a specific level.

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