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Effect of sampling conditions on colloids and ground water chemistry

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Keywords: Ground water, colloidal material, sampling, chemical analysis, Eh, marl

ABSTRACT

Accurate colloids and ground water data are required to model contaminant migration in subsurface systems. The effect of different sampling techniques was consequently investigated on colloid population and chemistry of a deep marl ground water. The study was performed during borehole drilling and after drilling: downhole and at the wellhead, from open hole and from the interval between packers. Ground water colloids and chemistry are affected by sampling conditions, such as tubing type (steel or PVC) and whether sampling is downhole or at the wellhead. Colloid concentrations varied over at least 3 orders of magnitude because the steel pipe affected the colloid chemistry or because downhole probe induced resuspension of colloids during sampling. Colloid data obtained by sampling at the wellhead with double-packer and PVC tubing presented minimal artefacts. In the deep ground water (Na-HCO₃ type, pH 8.5, Eh -310 mV), the chemistry of metal ions was affected by the presence of HS⁻ (10⁻⁴ M) limiting their solubility. Ground water colloid concentrations were of the order of 100 µg·l⁻¹ for sizes in the range of 100 to 1000 nm (a particle number concentration of 6·10⁹ l⁻¹ for sizes larger than 100 nm). These colloids were mainly chlorite and smectite/illite. Aluminium concentration in the unfiltered water may be used as an indicator for clay colloids.

RESUME

La modélisation du transport des contaminants dans les systèmes souterrains nécessite l'utilisation de données exactes sur l'eau souterraine et ses colloïdes. L'effet des différentes techniques d'échantillonnage de l'eau est étudié sur sa chimie et la population des colloïdes. La présente étude a été réalisée durant le forage et après son exécution: dans le puits de forage, à sa tête, depuis le forage ouvert ou depuis un interval entre obturateurs. Les colloïdes et la chimie de l'eau sont affectés par les conditions d'échantillonnage tels que: le type de tuyau (acier ou PVC) ou le niveau de l'échantillonnage: dans le trou de forage ou à sa tête. La concentration des colloïdes varie selon 3 ordres de grandeur parce que le tuyau d'acier affecte la chimie des colloïdes ou parce que l'échantillonnage en trou de forage induit la resuspension de colloïdes durant son exécution. Les données des colloïdes échantillonnées à la surface et avec le tuyau en PVC présentent le minimum d'artefacts. Dans l'eau souterraine (de type Na-HCO₃, pH 8.5, Eh -310 mV), la chimie des ions métalliques est affectée par la présence de HS⁻ (10⁻⁴ M) limitant leur solubilité. La concentration en colloïdes est de l'ordre de 100 µg·l⁻¹ pour des tailles allant de 100 à 1000 nm (soit une concentration en terme de nombre de colloïde de 6·10⁹ l⁻¹ pour des tailles plus grandes que 100 nm). Ces colloïdes sont principalement composés de particules de chlorite, et de smectite/illite. La concentration en aluminium de l'eau non-filtrée peut être utilisée comme un indicateur de ces colloïdes d'argile.

1. Introduction

Accurate chemical data are required to model the geochemical behaviour of ground water and contaminant transport. Of particular interest are pH and Eh data, as well as the concentrations of major, minor and trace elements. Careful sampling is required prior to water analysis, especially for trace elements (McCarthy & Degueudre, 1993; Puls et al., 1992; Barcelona, 1990; Barcelona et al., 1985).

Trace element behaviour in water may be affected by the presence of colloids i.e. particles with sizes between 1 and 1000 nm (Stumm, 1992; Degueudre et al., 1989). To evaluate the in-

fluence of colloids on contaminant transport, information on colloid concentrations, size distribution and chemical nature is needed. Effective studies of ground water colloids require very careful sampling (McCarthy & Degueudre, 1993; Backhus et al., 1993) and chemical analysis of the water as well as accurate colloid analysis. Factors influencing colloid concentrations and properties, including acidity and redox conditions (pH and Eh), are best monitored both at the wellhead and downhole.

The site chosen to examine the effect of sampling conditions on chemistry and colloids is located in the Wellenberg

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2.2 Water sampling and analytical technique

Water sampling was performed by pumping during well construction or by collection from the artesian flow after well construction. Samplings at the wellhead were simply carried out from a stainless steel capillary installed on the stopper of the well tubing. Bottles and containers were maintained at 15 °C in an isotherm box, and transported to the laboratory (PSI) within 2 hours after collection prior to injection into a colloid counting unit. The wellhead stopper was removed when using the down hole sonde (from Geocom GmbH). This sampling system consisted of a stainless steel reservoir (2.17 m long, external diameter 3.6 cm, capacity 600 ml, initially filled with nitrogen). Its opening at the sampling level was led by an electromagnetic valve. The steel electro-cable used was connected to the sonde and positioning in the well was possible with a precision of one centimetre.

During sampling (all wellhead), the water was routinely analysed. The dissolved tracers were determined by fluorescence spectroscopy for uranine and by High Pressure Liquid Chromatography (HPLC) for m-TFMBA. For dissolved and suspended solid contents, ion chromatography was used for assaying major anions, and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) was used for major elements. On selected samples Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) was used for trace element analysis. For ICP analysis, water samples were collected in polyethylene bottles cleaned with 1 weight % nitric acid, and the samples were spiked with ultra-pure nitric acid (Merck) on site to 1 weight % nitric acid. For the other analyses, glass bottles or stainless steel containers (5 l Amicon) were used throughout. Flow-through-cells were used when necessary for on-line processes.

Specific analyses, as well as separations and characterisations of colloids were occasionally performed on-site. The analytical systems used on site included pH and Pt electrodes and a filtration unit in a plastic glove-bag under N₂ atmosphere. Outside the glove-bag, an on-line analyser (Dohrmann) for Total Organic Carbon (TOC) and Inorganic Carbon (IC), and a single particle counter (Horiba unit) were used. The pH was measured with a precision of ± 0.05 units after careful standardisation with buffers (4, 7 and 9). However, measurements were recorded on-line to ± 0.1 units because of the strong CH₄ degassing which can affect the pH-measurement. Monitoring of the redox potential was carried out for up to 3 months with a Pt electrode (flat disk) vs. a 3 M KCl Ag/AgCl reference electrode.

Similar measurements and separations were also carried out in the laboratory. Tests were performed with a filtration cell (Amicon minicell), a TOC unit (Dohrmann) and a single particle counter (Horiba) as well as by ICP-AES and ion-chromatograph. The experimental procedures are discussed in detail by McCarthy & Degueldre (1993). TOC was analysed using the wet oxidation technique with UV-irradiation under

acidic conditions (Dohrmann analyser). On-line measurements avoid contamination problems for both TOC and inorganic carbon measurements (Degueldre et al., 1996a).

Occasionally, particle counting was carried out in the field, on-line but more often counting was done in the laboratory with a Horiba PLC311 particle counter (Degueldre et al., 1996a) after in-line dilution of the ground water sample in a stream of ultra-pure water (Milli-Q from Millipore). To our knowledge, this was the first time that a single particle counting unit was used in the field. In addition, an UV-VIS-NIR spectrometer was used occasionally on site to study the dissolved species by spectroscopy. The unit was a Guided Wave Model 260 equipped with two light sources (a D-lamp for UV and a W-Lamp for VIS and NIR). Spectroscopic analysis was carried out on-line utilising a micro-cell with optical fibre cables connecting the cell to the light sources and the spectrometer.

Colloid separation was performed with the filtration unit using Nuclepore membranes of 10, 1, 0.1, 0.05, 0.03 μm pore size, with filtered volumes ranging from 50 to 800 ml (Degueldre et al., 1989; Degueldre et al., 1996a). The filtration unit was a Amicon minicell and the gas used to pressurise the fluid was 99% N₂ – 1% CO₂ (as required by the geochemical modelling, see Section 4). Scanning electron microscopy (SEM/EDX) analysis was performed after filtration with Amicon XM50 membranes of 3 nm (filtered volume 0.5 to 50 ml). The SEM unit utilised was a Zeiss DSM962 unit with a Noran Instrument as EDX Voyager system. The colloid samples collected on a membrane were coated with a Pt-Pd film of 20 nm thickness prior to investigation with the SEM unit. In addition, XRD analyses of the colloids on membranes with selected cut-off (0.10 μm after a 1 μm pre-filtration) were performed using a Rigaku unit and a Geigerflex diffractometer. The Cu K α line was used with a copper anode under 40 kV.

3. Results

3.1 Sampling during drilling

During drilling, ground water inflow was detected from an open vein at a depth of about 305 m. The interval from 298 to 317 m (the borehole bottom at the time) was isolated with a single-packer and a constant rate withdrawal test was started. The water was pumped at a rate of 1 l·min⁻¹ and sampled after 5 days. The drilling fluid tracer contents of these samples were 1–3% of the nominal concentration in the drilling fluid. Table 1 presents the results of the chemical analysis. The water is of a Na-HCO₃ type (Jächli, 1970). Ground water colloids were not analysed at this stage because the water appeared muddy due to residual bentonite drilling fluid. After collection of this sample, drilling continued, and other water bearing zones were intercepted in the marl formation.

Table 1: Comparison of the ground water data

	During drilling	Steel (wellhead)	Steel (downhole)	PVC (wellhead)	PVC (downhole)
Sample Nr.	1	2	3	4	5
date sampled	Nov-22-91	Aug-12-92	Feb-10-93	Aug-19-93	Sep-27-93
number of day	-	71	253	52	91
pH	9.0*	9.15	8.5	8.6	8.5
Eh/mV	105*	-420	(-310)	-310	(-310)
Li ⁺	1.30 10 ^{-5*}	1.73 10 ⁻⁵	-	1.73 10 ⁻⁵	1.44 10 ⁻⁵
Na ⁺	1.79 10 ^{-2*}	2.09 10 ⁻²	2.25 10 ⁻²	2.20 10 ⁻²	2.15 10 ⁻²
K ⁺	3.33 10 ^{-5*}	2.58 10 ⁻⁶	4.63 10 ⁻⁵	1.89 10 ⁻⁵	2.48 10 ⁻⁵
Rb ⁺	<5.86 10 ^{-6*}	<5.86 10 ^{-6*}	-	<1.17 10 ^{-6*}	<1.17 10 ^{-6*}
Cs ⁺	<3.77 10 ^{-6*}	<1.51 10 ^{-6*}	-	<7.54 10 ^{-7*}	<7.54 10 ^{-7*}
NH ₄ ⁺	1.50 10 ^{-5*}	2.22 10 ^{-5*}	-	3.33 10 ^{-5*}	3.50 10 ^{-5*}
Mg ²⁺	3.92 10 ^{-5*}	4.24 10 ⁻⁵	6.91 10 ⁻⁵	3.49 10 ⁻⁵	3.84 10 ⁻⁵
Ca ²⁺	5.50 10 ^{-5*}	3.94 10 ⁻⁵	3.94 10 ⁻⁴	4.29 10 ⁻⁵	5.34 10 ⁻⁵
Sr ²⁺	<5.72 10 ^{-6*}	4.43 10 ⁻⁶	6.89 10 ⁻⁶	5.98 10 ⁻⁶	5.79 10 ⁻⁶
Ba ²⁺	4.36 10 ^{-7*}	9.40 10 ⁻⁸	1.13 10 ⁻⁶	3.68 10 ⁻⁷	1.20 10 ⁻⁶
Mn ²⁺	3.10 10 ^{-7*}	1.19 10 ⁻⁶	4.32 10 ⁻⁶	3.28 10 ⁻⁸	3.77 10 ⁻⁷
Cr	-	-	-	<1.93 10 ^{-8*}	-
Fe	2.51 10 ^{-5*}	3.61 10 ⁻⁵	3.97 10 ⁻⁴	1.61 10 ⁻⁷	7.84 10 ⁻⁶
Ni	<1.71 10 ^{-7*}	<8.53 10 ^{-8*}	-	<8.53 10 ^{-8*}	8.53 10 ^{-8*}
Cu	1.73 10 ^{-7*}	<7.88 10 ^{-8*}	-	<3.15 10 ^{-8*}	1.10 10 ^{-7*}
Zn	<7.66 10 ^{-7*}	<3.06 10 ^{-7*}	4.37 10 ⁶	<3.06 10 ^{-7*}	6.13 10 ^{-7*}
Pb	<2.42 10 ^{-8*}	1.45 10 ^{-8*}	-	9.67 10 ^{-9*}	4.83 10 ^{-9*}
Al	5.20 10 ^{-5*}	8.15 10 ⁻⁷	6.41 10 ⁻⁶	1.11 10 ⁻⁷	2.04 10 ⁻⁵
F ⁻	8.96 10 ^{-4*}	1.29 10 ⁻³	1.18 10 ⁻³	1.21 10 ⁻³	1.29 10 ⁻³
Cl ⁻	2.74 10 ^{-4*}	7.01 10 ⁻⁴	6.59 10 ⁻⁴	7.66 10 ⁻⁴	7.38 10 ⁻⁴
Br ⁻	2.51 10 ^{-6*}	8.76 10 ⁻⁶	-	1.25 10 ⁻⁵	1.08 10 ⁻⁵
I ⁻	9.47 10 ^{-6*}	2.05 10 ^{-5*}	-	2.21 10 ^{-5*}	2.21 10 ^{-5*}
SO ₄ ²⁻	9.91 10 ^{-5*}	6.76 10 ⁻⁶	(< 10 ⁻⁷)	4.00 10 ⁻⁶	(< 10 ⁻⁷)
P	7.11 10 ^{-6*}	1.62 10 ^{-6*}	-	1.29 10 ^{-6*}	1.62 10 ^{-6*}
NO ₂ ⁻	<1.10 10 ^{-6*}	2.83 10 ^{-7*}	-	2.61 10 ^{-6*}	2.18 10 ^{-7*}
NO ₃ ⁻	<1.62 10 ^{-6*}	<1.62 10 ^{-6*}	-	<1.62 10 ^{-6*}	<1.62 10 ^{-6*}
As	<1.34 10 ^{-8*}	<6.69 10 ^{-9*}	-	<1.34 10 ^{-8*}	<1.34 10 ^{-8*}
Se	<7.89 10 ^{-9*}	<3.95 10 ^{-9*}	-	<7.89 10 ^{-9*}	<7.89 10 ^{-9*}
HCO ₃ ⁻	1.43 10 ^{-2*}	1.91 10 ⁻²	-	1.89 10 ⁻²	1.97 10 ⁻²
CO ₃ ²⁻	1.16 10 ^{-3*}	9.99 10 ^{-4*}	-	7.21 10 ^{-4*}	5.50 10 ^{-4*}
H ₂ S, HS ⁻ , S ²⁻	-	< 10 ⁻⁶	1.40 10 ⁻⁴	9.99 10 ⁻⁵	1.15 10 ⁻⁴
H ₂ SiO ₃	1.28 10 ^{-4*}	8.75 10 ⁻⁵	1.71 10 ⁻⁴	1.65 10 ⁻⁴	1.86 10 ⁻⁴
H ₃ BO ₃	1.07 10 ^{-4*}	9.23 10 ⁻⁵	-	9.07 10 ⁻⁵	9.23 10 ⁻⁵
DOC	1.25 10 ^{-3*}	9.17 10 ⁻⁵	-	5.84 10 ⁻⁵	2.09 10 ⁻⁴

Conditions: during drilling, at wellhead, downhole, with steel or PVC line. All concentration in Molality, precision about 2 %.

- non measured, (x) evaluated values (see text);

* value from Mineralwasser Labor, Zurich (sample 2 on Aug. 28, sample 4 on Aug. 19, sample 5 on Sep. 24) as reported in (BLASER 1993).

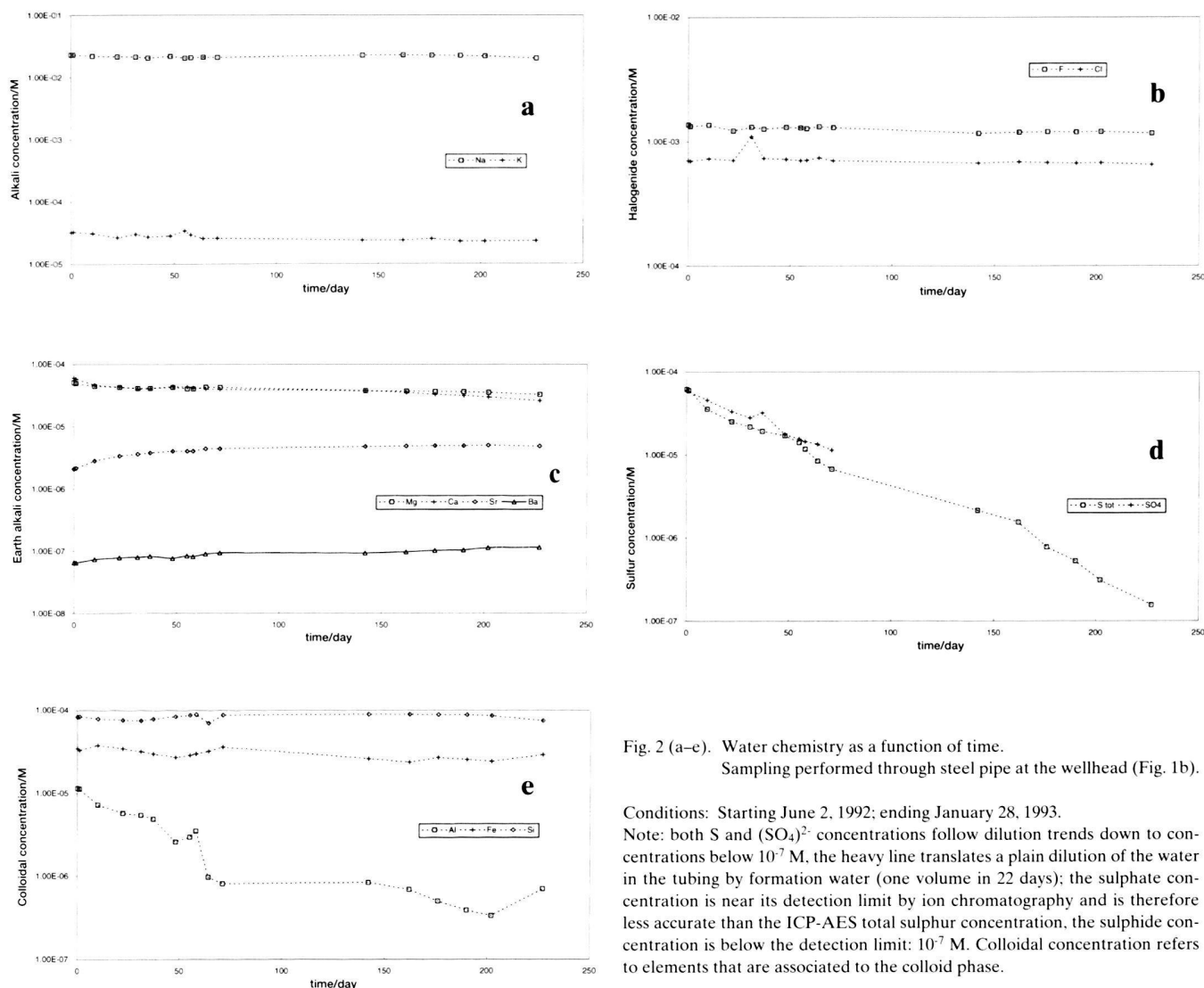


Fig. 2 (a-e). Water chemistry as a function of time.
Sampling performed through steel pipe at the wellhead (Fig. 1b).

Conditions: Starting June 2, 1992; ending January 28, 1993.
Note: both S and $(\text{SO}_4)^{2-}$ concentrations follow dilution trends down to concentrations below 10^{-7} M. the heavy line translates a plain dilution of the water in the tubing by formation water (one volume in 22 days); the sulphate concentration is near its detection limit by ion chromatography and is therefore less accurate than the ICP-AES total sulphur concentration, the sulphide concentration is below the detection limit: 10^{-7} M. Colloidal concentration refers to elements that are associated to the colloid phase.

3.2 Sampling with the steel casing

After borehole completion (430 m), colloids were sampled after steel pipe installation and borehole flushing and closing (see Fig. 1b). The colloid work started on June 2nd 1992 with a preliminary study of the ground water chemistry and long term chemical monitoring. This first campaign ended on January 28, 1993 with collection of a downhole sample. The first water sample was taken with a flow rate ranging from about 300 to 200 ml·min⁻¹. At an average flow rate of 200 ml·min⁻¹ and an internal steel tubing diameter of 15.5 cm, the time required for the ground water to flow from a depth of 400 m to the surface was about 25 days. The tracer concentration was always smaller than 1% of the nominal concentration in the drilling fluid.

Sampling at the wellhead

Sampling and monitoring at the wellhead began on June 2nd 1992 (day 0). The water was of the Na-HCO₃ type and had relatively constant concentrations of major elements (Fig. 2a, b, c, d). However, the sulphate concentration decreased steadily with time (Fig. 2d). After 8 months of flushing, the total sulphur concentration was down to 10^{-7} M, because the sulphate present in the water of the borehole when sampling began was diluted by fresh ground water flowing from the formation. Changes in the concentrations of alkaline-earth elements were also noted (Fig. 2c). The pH of the water was 9.15 and did not change significantly during sampling. Chemical compositions are given in Table 1. Changes in the chemistry of major elements associated with the colloid phase are given in Fig. 2e.

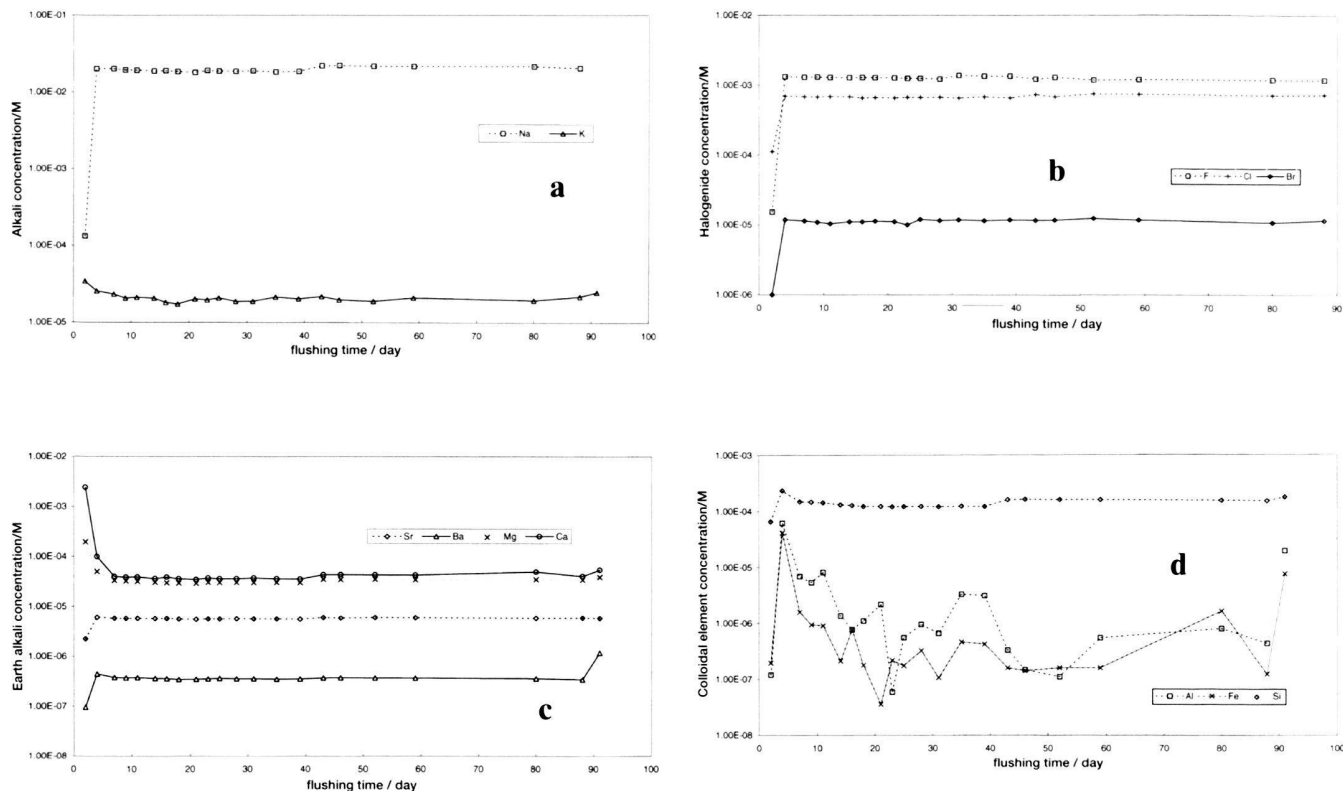


Fig. 3 (a-d): Water chemistry as a function of time. Sampling performed through PVC pipe at the wellhead (Fig. 1b). Conditions: starting on June 30, 1993 (day 0).

Four periods:

- 1.: Shallow Ca-HCO_3 water used for installation of packer.
 - 2.: Water contaminated from the tubing and packer installation.
 - 3.: Marl ground water.
 - 4.: With the downhole sonde.
- Colloidal elements Al, Si, Fe may be associated to the colloid phase.

Colloid gravimetry results, see (McCarthy & Degueldre, 1993), indicated the presence of suspended particles larger than $1\ \mu\text{m}$ but no particle larger than $5\ \mu\text{m}$. The colloidal cakes produced by filtration were initially black and turned red after contact with the 500 ppm O_2 atmosphere in the glove-bag for about 24 h. This could be due to Fe(II) oxidation by minute amounts of oxygen trapped within the membrane pores. In order to eliminate this interference, membranes were purged under N_2 (1 bar over-pressure) prior to the filtration. The colloid cakes produced using this procedure were initially black but also turned red, although more slowly. The colloidal particle concentration ($2\ \text{mg}\cdot\text{l}^{-1}$) was determined by gravimetry. Chemical analysis of both ground water and filtrate showed that the colloids were composed of iron rich particles but aluminium and silicon were also occasionally detected. Particle counting measurements were performed on site and concentration results were comparable to those obtained in the laboratory after water transfert. In this case, the ground water was

collected in a 5 l Amicon stainless steel container after 4 h flushing and transported to PSI within 2 hours after collection, prior to measurement with the Horiba monitor (see results in Table 2). Results were the same on site and in the laboratory.

Sampling downhole

On February 9, 1993 (day 253), downhole water sampling was carried out in duplicate at a depth of 358 m with a stainless steel sonde. The chemistry of the waters sampled are shown in Table 1. Water analysis after sequential filtration ($2\ \mu\text{m}$ followed by $0.2\ \mu\text{m}$) showed that most of the colloidal particles were composed of iron and calcium. The residual dissolved iron concentration ($4\cdot 10^{-7}\ \text{M}$) was consistent with the values measured on samples from the wellhead with the PVC line, as discussed below.

Large concentrations of iron rich colloids were found in the ground water from this interval ($2\ \text{mg}\cdot\text{l}^{-1}$ at the surface and

Table 2: Ground water colloid number concentrations

size/nm	[coll] _a /l ⁻¹	[coll] _m /l ⁻¹	[coll] _M /l ⁻¹
steel casing			
>100	1.2 10 ¹¹	7 10 ¹⁰	2 10 ¹¹
>200	1.3 10 ¹⁰	8 10 ⁹	2 10 ¹⁰
>500	3.8 10 ⁹	2 10 ⁹	6 10 ⁹
PVC tubing			
>100	6.0 10 ⁹	4 10 ⁹	3 10 ¹⁰
>200	1.0 10 ⁸	5 10 ⁸	5 10 ⁹
>500	6.9 10 ⁸	1 10 ⁸	2 10 ⁹

Conditions: situation: steel and PVC sampling at wellhead (see Fig. 1b)
 90 days after free outflowing of artesian ground water,
 in-flow of ultrapure water, single particle counting
 using a HORIBA particle counting monitor.
 [coll]_a: average concentration
 [coll]_m: minimum concentration
 [coll]_M: maximum concentration

50–100 mg·l⁻¹ downhole). However, most of these were found to be artefacts induced by corrosion of the steel well casing. Corrosion also affected the water chemistry in the borehole (Hewitt, 1992). To eliminate the effect of the steel well casing, a PVC pipe and a double-packer system were installed.

3.3 Sampling with the PVC line

Sampling at the wellhead

Both water chemistry and colloid monitoring started again at the wellhead on June 30, 1993 (day 0). With the PVC tubing the water residence time was only two days in the interval between the two packers, followed by a two day transit time from the interval to the surface, when the interval was flowing freely at 0.30 l·min⁻¹.

Water from the tubing flowed through the on-line analytical system without exposure to the atmosphere. Water chemistry and colloid (> 100 nm) concentrations are shown in Figs. 3 and 4 respectively. Flow began with Ca-HCO₃ water of the type used for packer and tubing system installation, containing calcium carbonate particles at a concentration of about 100 µg·l⁻¹. The water changed to one containing iron- and clay-rich colloids at a concentration level of some 1000 µg·l⁻¹, which likely represents the flushing of artefacts due to packer installation and the presence of residual corrosion products. Finally, marl water appeared to contain colloids from the marl. The water chemistry results and colloid concentrations are reported in Table 1 and 2, respectively. The colloid concentration in the marl water was of the order of 100 µg·l⁻¹. X-ray diffraction analysis of colloids from 0.10–1.00 µm collected on membrane

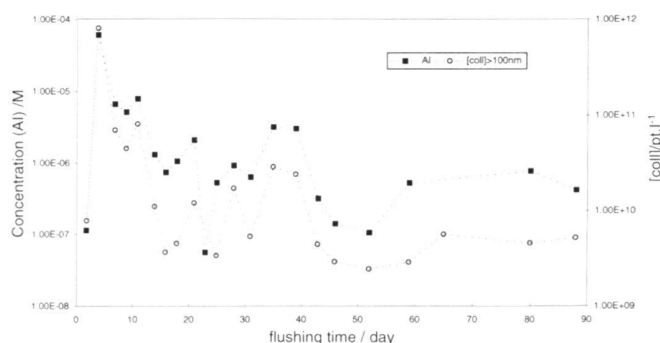
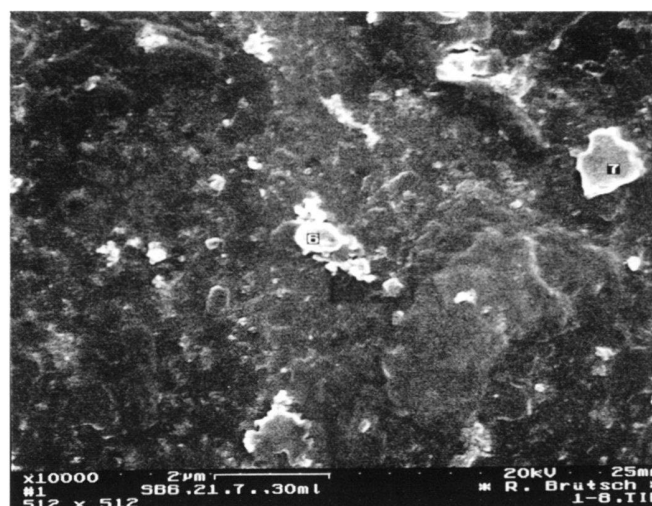


Fig. 4: a Typical SEM micrograph of marl water colloids.
 b Colloid and aluminium concentrations as a function of time
 Sampled from PVC pipe at the wellhead.
 conditions: starting on June 30, 1993 (day 0).

Periods:

- 1.: Shallow Ca-HCO₃ water used for installation of packer.
- 2.: Water contaminated from the tubing and packer installation.
- 3.: Marl ground water.

Note: aluminium from the unfiltered water is tested as colloid element signature.

Colloid for size > 100 nm, marl ground water colloids composed mostly of clays (on SEM micrograph: elements detected by EDS: Si, Al, Mg, Fe, S).

filters showed that they were composed of chlorite and illitised smectite with the same proportions as for the marl.

The TOC of this water was not significantly high (0.7 mg·l⁻¹) and the UV-VIS-NIR spectrum of the marl water does not present any signature of strongly complexing organic ligands such as humic or fulvic compounds. HS⁻, which was not found in the water collected through the steel casing because of FeS precipitation on the steel, was detectable in the marl water. The total sulphur concentrations obtained by ICP-AES do not include HS⁻ because during sample preparation the spike of nitric acid induced H₂S formation. HS⁻ was measured in later samples with an ion specific electrode. The concentration of

the sulphate in water was extremely low (see Fig. 2). The presence of sulphide delayed the attainment of a stable redox signal. The Eh recorded on-line after 10 days was -310 ± 30 mV Vs NHE. This preliminary value was confirmed later with repetitive measurements.

Sampling downhole

The downhole sonde was also used to sample water at a depth of 358 m (early October 1993). This sample had a colloid concentration of some $1000 \mu\text{g}\cdot\text{l}^{-1}$, which is higher than that of the water collected at the wellhead. This is attributed to the fact that sampling downhole induces a shock when the sonde is opened, which is presumed to detach colloids sticking on the tubing. This high colloid concentration cannot be a sedimentation effect, because the downhole sonde aperture was above the water input opening of the PVC tubing in the interval. This higher concentration of colloids affected the concentrations of minor elements associated with the colloid phase (Table 1). The TOC was also higher than at the wellhead, but HS^- had a similar concentration.

4. Discussion

4.1 Comparison of the effects of different sampling conditions

A comparison of the analytical results for ground water collected under the different conditions shows that water sampled during drilling was strongly affected by drilling artefacts, and that water sampled through steel casing was contaminated by corrosion products. In contrast, water sampled at the surface through the PVC line at the surface was not affected by drilling and corrosion artefacts. Whether sampling was done at wellhead or downhole had an influence on pH, as well as on element and colloid concentrations. Each sampling method drew samples from different locations in the formation (during drilling 298–317 m, steel casing 332–430 m, steel sonde 358 m, PVC tubing 356–365 m and PVC sonde 358 m). However, the marl waters were comparable for sodium, fluoride, chloride, bicarbonate and even borate contents. A consistent picture is emerging.

The flushing time of **samples taken while drilling** was not large enough to properly flush the interval and allow either accurate colloid or trace element analysis. Because of possible mixing with drilling fluid and other contaminants in the ground water, the pH measurements only roughly reflected the “in-situ” conditions, and element concentrations were restricted to those that can be evaluated after correction of the drilling fluid content.

Ground water **samples taken through the steel casing** were rich in soluble and colloidal iron. At the wellhead, the redox potential ($\text{Eh} = -420$ mV) was very low and the water was rather alkaline (pH 9.15). Gas analysis from the effervescent water revealed around 1% (vol) hydrogen in the presence of methane (Blaser, 1993) which together with the high iron (II) content affects the Eh measurement.

The corrosion rate of the borehole pipe was estimated to evaluate its contribution to the iron and hydrogen content of the water. Corrosion data from Kreis (1991) are available for a chemically similar ground water ($\text{Na-HCO}_3\text{-SO}_4$ type water, with comparable ionic strength). For a pH around 8, a corrosion rate in the order of $10 \text{ mmol}\cdot\text{m}^{-2}\cdot\text{y}^{-1}$ of iron may be used as a lower limit. For the 300 m long casing which contains 6 m^3 water, the metal surface in contact with the ground water is of the order in 300 m^2 . During the 500 hours of contact between the water and the pipe, the Fe(II) concentration could rise to about $17 \mu\text{M}$ or $1 \text{ mg}\cdot\text{l}^{-1}$ which is similar to the iron concentration in the unfiltered water shown in Fig. 2e.

The presence of iron-rich colloids and to a lesser extent clay was confirmed by energy dispersive analysis for iron, silicon and aluminium on particles collected by filtration at the surface. For the pH and Eh of the ground water, FeCO_3 (siderite) and to a lesser extent Fe_3O_4 (magnetite) were expected to be oversaturated (Mulder et al., 1975; Brookins, 1988).

Both, sulphate and total sulphur concentrations (Fig. 2d) of the water decreased as a function of outflow time. It appeared that the sulphate produced by sulphide oxidation during drilling activities was diluted by the flow of marl water. In the well, the sulphides reacted with soluble iron(II) from the steel tubing, yielding iron sulphide and quantitatively eliminating sulphide from the water. Full calculation with a dilution model may be made using:

$$\ln [S]_t = \ln [S]_0 - Q \cdot V_s^{-1} \cdot t$$

with $[S]_t$ the concentration of S at time t , Q the water flow rate and V_s the volume of the system. This model assumes no internal cross flow including input and output features in the open hole, and mixing in the large tubing. For an average flow rate of 0.35 m^3 per day, V_s calculated from the data from Fig. 2d was 13 m^3 . This value was larger than the borehole volume (8 m^3), indicating that the oxidation of pyrite in the marl as well as of sulphide in the water may have occurred. The apparent larger volume could also have been an artefact of the mixing model chosen to fit the straight line in Fig. 2d. The sulphate concentration in the original marl water was estimated to be less than 10^{-7} M .

With the steel casing, downhole sampling induced more colloids, because the opening of the sonde created a shock which caused detachment of colloids previously attached to the borehole walls.

This detachment behaviour was also verified during the **sampling with the PVC tubing**. It is known, that colloid attachment in sodium rich (and calcium poor) ground water is reversible, and that detachment is relatively easy (Degueldre et al., 1996b; Hahn et al., 1995). Using a downhole probe for sampling induced water acceleration and consequently colloid resuspension. This was recently pointed out as a key factor affecting the colloid concentration. Colloid concentrations were observed to change by several orders of magnitude during

Table 3: Calculated (EQ3) saturation indice for ground water sampled at the wellhead with steel and PVC pipes.

Pipe	steel	PVC
Selected measured parameters		
pH	9.15	8.6
Eh / mV	-410	-310
[SO ₄ ²⁻]	6.8·10 ⁻⁶	4.0·10 ⁻⁶
[HS ⁻]	< 10 ⁻⁶	1.0·10 ⁻⁴
Calculated parameters		
Eh / mV (SO ₄ ²⁻ /HS ⁻)	-360**	-330
log P _{CO2}	-3.1	-2.6
Saturation indices		
Calcite (CaCO ₃)	0.4	0.1
Dolomite (Ca,MgCO ₃)	0.6	-0.2
Siderite (FeCO ₃)	1.2	-1.2
Fe(OH) ₃	-3.7	-6.9
Goethite (FeOOH)	1.4	-1.7
Magnetite (Fe ₃ O ₄)	5.3	-4.0
Chalcedony (SiO ₂)	-0.5	-0.1
Gypsum (CaSO ₄)	-6.0*	-6.0*
Pyrite (FeS ₂)	<4.5	6.2
Troilite (FeS)	<0.6	0.2

Conditions: concentration in M (mol·l⁻¹), other data from Table 1

Note * should be smaller because measured SO₄²⁻ is due to oxidation and sulphate concentration in the formation ground water must be lower than the concentration reported in this Table, ** fixed value.

water flow rate variations while sampling at a wellhead (e.g. Degueldre, 1997; Laaksoharju et al., 1994; Vilks et al., 1993). As a consequence, the water chemistry measured on unfiltered samples changed from one sampling procedure to another. While the major elements (e.g. sodium) were not significantly affected by the sampling conditions, trace elements such as barium, iron and aluminum changed by orders of magnitude because they are associated with the colloid phase. The results from the wellhead sampling with the PVC line were most representative of the ground water, because of the rapid flush out of the installation artefacts (see Fig. 3, periods 1 and 2). The concentration changes with time followed a plug flow system. After out flow of a ground water volume of at least 10 bore-hole volumes, the ground water may be considered artefact free (see Fig. 4, period 3).

A ground water colloid number concentration of about 6 10⁹ l⁻¹ for sizes larger than 0.10 µm (see Tab. 2), or of about 100 µg·l⁻¹ for a colloid density of 2 g·cm⁻³ and for size ranging

from 0.10 to 1.00 µm, was found. Based on SEM micrographs (e.g. Fig. 4), the colloid morphology indicated a composition of mostly clay particles (aluminium, silicon detected by EDS) and silica. Iron was also found occasionally. The colloids as determined by X-ray diffraction spectroscopy were chlorite and illitized smectite. These particles are expected from the rock mineralogy described in Section 2.1. The aluminium concentration in the unfiltered water may be used as a colloid indicator (an element associated with the colloid phase) and correlation between colloid and aluminium concentrations (Alaux-Negrel et al., 1993; Degueldre et al., 1996a) has been useful to evaluate the presence of colloids (see Fig. 4).

The deep water was of Na-HCO₃ type, with an Eh of -310 ± 30 mV and a pH of 8.5. The concentration of bivalent cations (Ca(II), Mg(II), Fe(II)) able to enhance the colloid attachment was low. The TOC of the marl water has an average concentration of 0.7–0.6 mg·l⁻¹ and may have contributed slightly to colloid stability. Careful water sampling in a chromatography loop followed by direct ion chromatography analysis demonstrated the predominance of sulphide as sulphur species. The sulphide concentration was 10⁻⁴ M while 4 10⁻⁶ M sulphate was detected. This result was affected by the irreversible oxidation of sulphide. The sulphate concentration is expected to be less than 10⁻⁷ M.

4.2 Geochemical modelling

Conventional geochemical modelling was performed only on the water samples taken at the surface. The mineral saturation indices from such modelling can provide information on the internal consistency of the analysis, and hence on changes during sampling. The modelling was carried out with the EQ3 program (Wolery, 1992) using the chemical data from Table 1. Selected results are given in Table 3.

For the water taken with the **steel tubing**, with a measured Eh of -420 mV, the program calculates the reduction of bicarbonate to methane. This is unrealistic with the 500 h residence time of the water in the well tubing. Since the bicarbonate is not reduced to methane in spite of the low Eh induced by steel corrosion in the tubing, the Eh was arbitrarily fixed at -360 mV so that bicarbonate reduction was not modelled. Under these conditions, at pH 9.15 the calculated P_(CO2) was 10^{-3.1} atm. Because the pH was increased by iron corrosion, calcite and dolomite were oversaturated. Fe(OH)₃ is undersaturated because of the low Eh. Siderite, goethite and magnetite are oversaturated. This is a direct consequence of the corrosion of the tube yielding the high iron concentration. Siderite and magnetite were the two main phases produced as corrosion artefacts during contact with the steel line, however for the Eh at which calculations were carried out, magnetite predominated. Chalcedony was slightly undersaturated, which may be due to the increase of pH consequent of the corrosion. The sulphate concentration of the water was very low, so gypsum was undersaturated. This phase is not found in the marl. Pyrite and troilite saturation indices had limiting values based on the de-

tection limit of the sulphide using an ion specific electrode at-line.

For the water taken with the **PVC tubing**, the pH was 8.6 and the calculated $P_{(CO_2)}$ was $10^{-2.6}$ Atm. Calcite and dolomite, the dominant carbonate mineral phases in the marl, were all-most in equilibrium with the water. Siderite, $Fe(OH)_3$, goethite and magnetite were undersaturated because iron was then present at a low concentration. Chalcedony was saturated indicating temperature equilibrium between the water reservoir and the sampling point. The water had a low sulphate content and sulphate phases such as gypsum were undersaturated. At the measured Eh, sulphur was mainly present as sulphide (HS^- : 10^{-4} M), which limits the solubility of several elements in the ground water. Although pyrite is oversaturated, troilite a phase that forms before pyrite from water is nearly saturated. This behaviour is known, as studied by Bågander & Carman (1994). For the samples taken through PVC tubing, the Eh calculated from the sulphur species concentrations was in good agreement with the measured value.

5. Conclusion

Progress has been made in understanding and optimising the sampling of marl water and its colloids. For a typical artesian water from an aquifer, as well as for a pumped ground water, selection of well construction characteristics (e.g. material, line size) is crucial. Geometry and material of packers and tubing are important parameters. Artefact free samples were obtained with tubing materials such as PVC. The marl ground water was of a $Na-HCO_3$ type, with pH 8.5 and Eh -310 mV. The concentration of elements such as transition metals was affected by the presence of sulfide (HS^- : 10^{-4} M). The ground water colloid concentration was of the order of $100 \mu g \cdot l^{-1}$ for sizes 100 to 1000 nm which corresponds to a particle number concentration of $6 \cdot 10^9 l^{-1}$ for sizes larger than 100 nm. These colloids were mainly chlorite and smectite/illite with the same proportions as in the marl. Aluminium concentrations in the non-filtered water may be used as a clay colloid signature.

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