Evidence for TiO2 nanoparticle transfer in a hard-rock aquifer

Lise Cary, Hélène Pauwels, Patrick Ollivier, Géraldine Picot-Colbeaux, Philippe Leroy, Bruno Mougin, Gilles Braibant, Jérôme Labille

To cite this version:

HAL Id: hal-01169974
https://brgm.hal.science/hal-01169974
Submitted on 30 Jun 2015

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Evidence for TiO$_2$ nanoparticle transfer in a hard-rock aquifer

*Lise Cary$^{1,*}$, Hélène Pauwels$^1$, Patrick Ollivier$^1$, Géraldine Picot$^1$, Philippe Leroy$^1$, Bruno Mougin$^2$, Gilles Braibant$^1$, Jérôme Labille$^3$

$^1$BRGM, 3 avenue C. Guillemin, BP 6009, 45060 Orléans, France
$^2$BRGM Service Géologique Régional Bretagne, 2 rue de Jouanet, 35700 Rennes, France
$^3$Aix-Marseille Université, CNRS, IRD, CEREGE UM 34, Aix-en-Provence 13545, France

*Corresponding author: Phone number: 00 33 2 38 64 32 60; e-mail: l.cary@brgm.fr

Intended for publication in Journal of Contaminant Hydrology

Abstract

Water flow and TiO$_2$ nanoparticle (NP) transfer in a fractured hard-rock aquifer were studied in a tracer test experiment at a pilot site in Brittany, France. Results from the Br tracer test show that the schist aquifer can be represented by a two-layer medium comprising i) fractures with low longitudinal dispersivity in which water and solute transport is relatively fast, and ii) a network of small fissures with high longitudinal dispersivity in which transport is slower. Although a large amount of NPs was retained within the aquifer, a significant TiO$_2$ concentration was measured in a well 15m downstream of the NP injection well, clearly confirming the potential for TiO$_2$ NPs to be transported in groundwater. The Ti concentration profile in the downstream well was modelled using a two-layer medium approach. The delay used for the TiO$_2$ NPs simulation compared to the Br concentration profiles in the downstream well indicate that the aggregated TiO$_2$ NPs interacted with the rock. Unlike Br, NPs do not penetrate the entire pore network during transfer because of electrostatic interactions between NP aggregates and the rock and also to the aggregate size and the...
hydrodynamic conditions, especially where the porosity is very low; NPs with a weak negative charge can be attached onto the rock surface, and more particularly onto the positively charged iron oxyhydroxides coating the main pathways due to natural denitrification. Nevertheless, TiO$_2$ NPs are mobile and transfer within fracture and fissure media. Any modification of the aquifer’s chemical conditions is likely to impact the groundwater pH and, the nitrate content and the denitrification process, and thus affect NP aggregation and attachment.

Highlights
A study of TiO$_2$ NP transfer at a pilot site in a hard-rock aquifer.
The TiO$_2$ NPs were mobile in the schist aquifer and transferred in aggregate form.
Unlike Br, NPs do not penetrate the entire pore network during transfer.
A large amount of NPs was deposited on the aquifer walls in the flow pathways.
Any modification of the aquifer’s chemical condition will impact NP aggregation and sorption.

Keywords: TiO$_2$ nanoparticles, groundwater, hard-rock aquifer, transfer, zeta potential, pH$_{PZC}$, field tracer test
1. Introduction

Not only are TiO\textsubscript{2} nanoparticles (NPs) nowadays one of the most widely produced NPs by weight with, for example, 4 million metric tons of TiO\textsubscript{2} NPs being manufactured worldwide in 2006 (Robichaud et al., 2009), but the range of their application has expanded very rapidly over the past decade. Due to their photocatalytic activity (Gaya and Abdullaha, 2008), high refractive index, high specific surface area and sorption capacity for ionic and non-ionic species, TiO\textsubscript{2} NPs are currently used for industrial and household purposes such as photovoltaics, ultraviolet blocking sunscreens, self-cleaning surfaces (such as glass), and antimicrobial, antibiotic and antifungal agents. They are also used as a scavenger of inorganic and organic contaminants in water treatment plants and for the remediation of polluted subsurface environments (Pena et al., 2006).

The increasing use of TiO\textsubscript{2} NPs is inevitably leading to its introduction into different environmental compartments, including soil, surface water and groundwater (Ben-Moshe et al., 2010; Chen et al., 2011; Fang et al., 2013; Holbrook et al., 2013; Johnson et al., 2011; Lin et al., 2010; Lowry et al., 2010; Reijnders, 2009). Anticipated groundwater contamination by NPs and their related by-products is expected to occur in different ways, including accidental events, inappropriate storage of nano-waste, normal aging during regular use, soil leaching and infiltration after spreading sludge from wastewater treatment, during groundwater/surface water exchanges and even by direct injection as for remediation purposes (Bennett et al., 2010; Elliott and Zhang, 2001; Gondikas et al., 2014; Holbrook et al., 2013; Su et al., 2013). The spread of makeup and sunscreens into surface waters and swimming pools has been observed to be responsible for the presence of significant concentrations of manufactured TiO\textsubscript{2} NPs in the water (typically >1 \( \mu \)g NP per litre of water [Kaegi et al., 2008]). TiO\textsubscript{2} NPs, however, have been classified as potentially cancerous for humans by the International Agency for Research on Cancer (IARC, 2006), so where groundwater is widely used for drinking water, any contamination could have an adverse impact on human health. The adverse impact of these NPs has already been shown on
bacteria (Santaella et al., 2014), crustaceans (Fouqueray et al., 2013), mice (Liu et al., 2009; Ma et al., 2009), plants and human lymphocytes (Ghosh et al., 2010). Consequently, the potential exposure of TiO$_2$ NPs through groundwater contamination needs to be studied and assessed.

NPs are characterized by a high surface charge density and a very high surface area to volume ratio (Leroy et al., 2011; Petosa et al., 2010; Wiesner et al., 2006), with the result that electrostatic interactions between NPs themselves and between NPs and the surrounding geogenic material control the complex processes that regulate NP transport and deposition in natural water (Moore, 2006; Wiesner et al., 2006). Their environmental fate, however, is highly dependent on their volume fraction in water, on their intrinsic properties such as solubility, surface properties, zero point charge pH ($\text{pH}_{zpc}$), surface area, crystallinity, shape and size, as well as on the groundwater’s overall physical and chemical properties (Auffan et al., 2009; Brant et al., 2005; Chen et al., 2012; French et al., 2009; Godinez and Darnault, 2011; Guzman et al., 2006; Keller et al., 2010; Petosa et al., 2012; Shih et al., 2012; Zhang et al., 2009). Since NPs are rarely in a perfectly dispersed state in natural water (Keller et al., 2010), their transport behaviour is also dependent on the formation and eventual break-up of NP aggregates, which are influenced by the flow velocity and interaction energies between particles (Brant et al., 2005; Fang et al., 2013; Godinez and Darnault, 2011).

In porous media, NP mobility is controlled by the reactive transport properties that affect NP-rock interactions (Petosa et al., 2010; Solovitch et al., 2010; Tufenkji and Elimelech, 2004); depending on the rock’s surface charge and the flow rate, dispersed nanoparticles can be adsorbed or repulsed in the vicinity of mineral grains. In addition, the rock’s permeability, plus the pore size and organization, will also affect aggregate transport and deposition. TiO$_2$ NPs aggregates are clearly shown to remain mobile in artificial porous media despite their aggregation under a wide range of physical and chemical conditions (Guzman et al., 2006), but few studies (French et al., 2009; Keller et al., 2010) have been
dedicated to TiO$_2$ NP transfer in groundwater along with the wide range of natural physical and chemical conditions.

Hard-rock aquifers contain major water resources and their vulnerability to pollution is a crucial issue (Ayraud et al., 2008; Jaunat et al., 2012; Guihéneuf et al., 2014; Pauwels et al., 2015, among others). The purpose of our study is to investigate the potential transfer of TiO$_2$ NPs in a hard-rock aquifer whose fracture connectivity determines the main pathways for groundwater flow and whose low ionic strength is expected to influence the NPs transport. The groundwater's low organic content at the study site is expected to limit NP aggregation, with the precipitation of Fe oxyhydroxides in the main pathways after natural denitrification being the main process affecting NP transport. To the best of our knowledge, there has so far been no attempt to quantify the mobility of TiO$_2$ NPs in a hard-rock schist aquifer through an experimental tracer test at a pilot site. Here, we studied the transfer of TiO$_2$ NPs through a schist aquifer, monitoring the NPs within both the injection and pumping wells.

2. Site description

The pilot site, located in the small Naizin catchment 85 km west of Rennes in Brittany (France), is underlain by a Precambrian (Brioverian, 530 Ma) schist aquifer (Pellerin and Van Vliet-Lanoe, 1994). The basin's hydrogeological system is influenced by the presence of two aquifer compartments, resulting in a variable hydraulic conductivity and porosity (Fig. 1): (1) the saprolite, or weathered layer from the surface to 15 m depth and overlain by surficial formations (soil and alluvial deposits), is a clay-rich facies with a mostly interstitial porosity ensuring the storage function of the aquifer compartment, and (2) the underlying weathered-fissured zone, showing a lesser degree of weathering and with a dense horizontal fissuring, grading down into the deep fresh and fractured rock ensuring the transmissive function of the aquifer. The main permeability in this medium, which can be represented as a dual porosity system, is related to tectonic fractures (Martelat and Lachassagne, 1995).
regionally inherited from Hercynian and Alpine orogeneses, and it is the fracture connectivity that mainly controls groundwater flow (Dewandel et al., 2006; Maréchal et al., 2004).

Groundwater abstraction in the catchment consists of rare agricultural pumping and can be considered negligible compared to the annual recharge (319 mm per year of effective rainfall). The global groundwater flow direction is from the plateau to the river (from DNS1 to F1) and is completed by a vertical component from the depth to the surface, and to the river. In periods of low water levels such as the period of the test, water flows downward (Pauwels et al., 2000).

The groundwater’s chemical composition at the site has been extensively described. It shows a strong variability from the surface to 15 m depth due to intensive agricultural activity (Pauwels et al., 2000), whilst in the underlying fissured schist it results from a mixing between old water and recent denitrified groundwater from the overlying weathered layer (Ayraud et al., 2008). The groundwater in the underlying fissured schist shows a weak mineralization (ionic strength of $3 \cdot 10^{-3}$ mol.L$^{-1}$), near neutral pH conditions (6.5 to 7.0) and reductive conditions with a low oxygen content; its slow organic content originates from reaction with oxygen during its passage through the upper soil and weathered layer. The groundwater in the schist compartment also appears to be totally denitrified through microbial autotrophic denitrification between nitrate and pyrite, leading to the production of Fe (II) and subsequent precipitation of Fe (III) hydroxides or oxides (Boisson et al., 2013; Pauwels et al., 1998; Tarits et al., 2006) that can strongly interact with NPs (Dzombak and Morel, 1990).

3. Material and methods

3.1 Aquifer characterization

The schist, in decreasing relative mass proportions, consists mainly of quartz, muscovite, chlorite and, to a lesser extent, K-feldspar and plagioclase. Pyrite is the main accessory
mineral below 7 m depth and varies between 0.3‰ and 5.0‰ of the dry rock weight. Secondary phases include illite, smectite, kaolinite and various Fe-oxyhydroxides (e.g. hematite and goethite) and sulphate phases such as jarosite (Pauwels et al., 1998).

The apparent zeta potential (Bouhaik et al., 2013; Crespy et al., 2007; Leroy et al., 2011) of the schist was measured in the laboratory using streaming potential measurements (ZetaCad, CAD Instruments, France) at a pH and ionic strength (IS) close to the natural conditions of the study site’s groundwater (i.e. pH6 and 7, and IS = 1.5·10^{-3} M), and using HCl or NaOH for pH adjustment. The NaCl and CaCl₂ concentrations were respectively 0.70 and 0.28 mM. The measured apparent zeta potential was slightly negative (-6.3 mV at pH6 and -6.1 mV at pH7). Although the schist’s mineral composition is heterogeneous, its surface charge is controlled by the quartz and phyllosilicates. Note that the magnitude of the schist’s apparent zeta potential is low, probably because of the presence of ionized Ca at twice the positive charge of the ionized Na.

### 3.2 TiO₂ Nanoparticle characterization

The TiO₂ NPs used in this study (stock number 39953, anatase, Alfa Aesar, 32 nm; see Solovitch et al., 2010) consisted of balls with diameters ranging from 10 to 50 nm, but capable of forming aggregates around 100 nm in size as observed by TEM (Hitachi S4500, SEB) on dry powdered TiO₂. XRD analysis (automatized Siemens D5000 diffractometer) showed anatase, a TiO₂ mineral, with trace quantities of rutile. The specific surface area of the TiO₂ NPs determined by BET analysis (Tristar 3000, Micromeritics) was 47.6 m².g⁻¹, consistent with the 52 m².g⁻¹ value given by the supplier.

Aggregation tests were conducted in the laboratory to better foresee the NPs aggregation rate according to their concentration in contact with MilliQ water and the schist’s groundwater previously collected and kept in natural conditions (atmosphere-free) and with ultrasonification or not. The pH corresponding to a TiO₂ electrophoretic mobility of zero, pH_{IEP} (isoelectric point pH), was 5.5 ± 0.1 (Solovitch et al., 2010). On site, the TiO₂ NPs (200 g)
were added to 30 L of groundwater. To prevent the NPs’ time-dependent aggregation phenomenon, the NP suspension was injected into Well F1 very shortly (~1h) after its preparation. The size and zeta potential of the TiO$_2$ NPs were measured on site immediately after mixing with the groundwater sample prior to injection, and also throughout the experiment; the apparent zeta potential was determined by electrophoretic mobility measurements using a zetasizerNanoZS (Malvern Instruments). The uncertainty was +/- 3 mV on 3 measures. The average hydrodynamic aggregate diameter was also measured on site using a zetasizerNanoZS with the Dynamic Light Scattering (DLS) method. The polydispersity index (PdI) was used as an indicator of the distribution width. The derived count rate indicating the intensity of light scattered by the particles was used to follow the relative evolution of particle concentration in the sampled water.

3.3 Transfer test design

The test consisted in first injecting a conservative tracer solution (NaBr) and then the TiO$_2$ NP suspension directly into the groundwater in order to compare their respective transfers. The pilot test experiment, outlined in Fig. 1, was conducted using stabilized and continuous pumping between the injection well, F1, and the downstream pumping well, DNS1, where the flow rate was stabilized at 2.46·10$^{-4}$ m$^3$.s$^{-1}$ (except during two short electricity cuts caused by thunderstorms). The upstream injection well F1 is 82 m deep and is screened between 32 and 82 m depth, which represents the fissured and unweathered part of the aquifer with a more permeable fracture zone at 70 m depth. The pumping well DNS1, located 15 m downstream from F1, is 97 m deep and screened between 1 and 97 m. The groundwater level in DNS1 was first stabilized by pumping for four days at 2.44·10$^{-4}$ m$^3$.s$^{-1}$, after which the groundwater came mainly from fracture flow with a partial contribution through leaching from the surficial horizons (Pauwels et al., 2000). The natural Na and Br concentrations measured in Well F1 before the injection of the NaBr solution were 0.7 and 3.0 µmol.L$^{-1}$, respectively; the conservative NaBr tracer and the TiO$_2$ NPs were then diluted with water collected.
from well F1 –3kg of NaBr in 50 L and 200 g of TiO₂ NPs in 30 L. To avoid any TiO₂ aggregation due to the increased ionic strength induced by the presence of high Na⁺ and Br⁻ concentrations resulting from the NaBr injection, a six-day delay was applied between the NaBr injection and the TiO₂ NP injection to ensure a Br concentration low enough not to influence the groundwater’s ionic strength. Continuous mixing of the water within the injection well F1 throughout the test period was ensured by recirculation (pumping at 1.4·10⁻³ m³.s⁻¹ and re-injection) between 6 and 70 m depth so as to avoid sedimentation at the bottom of the piezometer. According to the volume of water recirculating (0.63 m³) in the well between 6 and 70 m depth, and assuming that the mixing along the water column due to the pumping and re-injection was instantaneous, the concentrations of Br and Ti just after their injection were calculated to be 45 mmol.L⁻¹ (3.6 g.L⁻¹) and 3.8 mmol.L⁻¹ (182 mg.L⁻¹), respectively. These concentrations correspond to a point-source pollution context (industrial accident during production, accident during transportation...).

3.4 Water sampling and analysis

The groundwater chemistry was analysed in the injection and downstream wells before the experiment for cations, anions and dissolved and total organic carbon (DOC and TOC), and during the experiment for Br and Ti. The groundwater in the injection well was sampled 16 h after the NP injection, whilst the physical and chemical parameters and the zeta potential and electrophoretic mobility were monitored throughout the experiment to check the evolution of the NP suspension. After each injection, the groundwater was sampled from the pumping well DNS1; during the day this was done manually every hour for the first 4 hours of the experiment, and then manually every 4 hours for the next 7 days, and at night by automatic sampler every 4 hours for the following 7 nights. A total of 74 samples was analysed for Br. Sampling for the TiO₂ NPs was undertaken every 12 h from day 6 to day 15 and then every 24 h from day 16 to day 30; a total of 40 samples was selected for Ti analysis. Measurements of the physical and chemical parameters (temperature, electrical conductivity [EC], pH,
oxidation-reduction potential, and dissolved oxygen) were made in situ in the field, using probes throughout the experiment just after sampling.

For further chemical analysis, the groundwater samples were filtered in the field through 0.45 µm cellulose acetate filters. Those for cation analysis were then acidified by HNO₃ at pH 2, whilst those for anion analysis were stored without acidification. The analyses for Ca²⁺, Mg²⁺, Na⁺ and K⁺ were carried out by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Ultima-2 model, JobinYvon), and those for Cl⁻, SO₄²⁻ and NO₃⁻ by ion chromatography (model DX120, Dionex). The accuracy of both techniques was greater than 5 %, depending upon the concentration. The alkalinity was measured on site by titration with HCl, and the equivalent point was determined by the Gran method. Aliquots (50 mL) for Br measurement were filtered through 0.2 µm filters, with the Br⁻ concentration being determined firstly on site with a Br-electrode, and later in the laboratory by ionic chromatography (Dionex) with a 5 % uncertainty; the quantification limit (QL) was 1·10⁻³ mmol.L⁻¹. Aliquots (50 mL) for Ti measurement were acidified to pH 2 with suprapur HNO₃, the Ti concentration being determined by ICP-MS at a detection limit of 0.004 µM. TiO₂ NP standards were prepared using TiO₂ anatase NPs diluted with natural water from the aquifer. The correlation line between the NP-defined standards and the measured Ti concentrations was good (r² = 0.90). For total organic carbon (TOC) and dissolved organic carbon (DOC) analyses, respectively, unfiltered and filtered water was collected in brown glass bottles and acidified with H₂SO₄; the TOC and DOC were analysed by oxidation with sodium persulphate.

Despite anaerobic conditions having been characterized in both wells, the pumping in Well DNS1 induced mixing with oxygenated water from the surficial weathered layer, thus enhancing the natural partial contribution by leakage of the surficial horizons due to the downward flow. It thus favored local transient aerobic conditions. Nevertheless, TiO₂ NPs are not affected by groundwater oxido-reductive conditions. Before the experiment, the groundwater pH was sub-neutral (6.94 in Well F1 and 6.54 in Well DNS1) and its
electrical conductivity was low (225 µS/cm in F1 and 210 µS/cm in DNS1, Table 1). The dominant cations for wells F1 and DNS1, respectively, were Na⁺ (0.70 and 0.75 mmol.L⁻¹) followed by Mg²⁺ (0.40 and 0.38 mmol.L⁻¹) and Ca²⁺ (0.31 and 0.24 mmol.L⁻¹). With Cl⁻ (0.72 and 0.76 mmol.L⁻¹) and SO₄²⁻ (0.25 and 0.28 mmol.L⁻¹) being the dominant anions; alkalinity was low (0.7 to 1.0 meq.L⁻¹). The NO₃⁻ content was very low (respectively below the quantification limit [QL] and 0.034 mmol.L⁻¹) due to denitrification (Pauwels et al., 2000). The Br⁻ content was respectively 3.7 and 3.0 µmol.L⁻¹ for Well F1 and Well DNS1 (Table 1), with a geochemical background value at 3.2 µmol.L⁻¹. The ionic strength was 3·10⁻³ M, indicating a low mineralization of water as previously shown by Pauwels et al. (2000). The Ti concentrations before the experiment were equal to the QL (0.002 µmol.L⁻¹) in both wells. TOC and DOC were generally low, although slightly higher in Well F1 (respectively 0.20 and 0.14 mmol C.L⁻¹) than in Well DNS1 (<QL).

3.5 Modelling tool

Modelling the Br and TiO₂ recovery was done using CATTI (Computer Aided Tracer Test Interpretation) software (Sauty, 1989) and assuming radial convergent flow between the upstream and downstream wells along with instantaneous tracer injection and recirculation. The flow and solute transports were modelled assuming that the aquifer was homogeneous and horizontally infinite. In addition we considered that the tracer, under the predominant influence of the hydraulic gradient imposed by pumping in Well DNS1, propagated through two different media of contrasted porosities and dispersivities and that the flow rate was constant. The two media will be hereafter referred to as the fissured medium with slow transport and the fractured medium with fast transport.
The transport parameters, i.e. the effective porosity and the longitudinal dispersivity of each medium, were estimated by fitting the calculated conservative solute breakthrough curve to the Br experimental breakthrough curve (BTC) using the CATTI’s automatic identification tool based on non-linear least squares estimation methods. Different initial values of parameters were tested to find the best fitted parameters. The selected ones were the best we could find corresponding to the highest mass recovery. But because, in the case of a radial converging flow and transport, no analytical solution exists to exactly calculate the solute concentration in the downstream well at a given time after injection (Sauty, 1989), an approximate solution can be used to estimate the solute concentration with time as long as the Peclet number (Pe) is high enough (>2).

Here, \( Pe = \frac{r}{\alpha} \) which gives Pe ≈ 9.4 for the fractured medium (F) and Pe ≈ 6 for the fissured medium (f) (Sauty et al., 1992). The approximate solution, where the second and third terms correspond to the concentration in the fractured and fissured media respectively, is:

\[
C(r, t) = C_i + \frac{\Delta M_f r}{2Q_f \sqrt{\pi D_L f} t^{3/2}} \exp\left(-\frac{(r-u_f t)^2}{4D_L f t}\right) \exp(-\lambda t) + \frac{\Delta M_f r}{2Q_f \sqrt{\pi D_L f} t^{3/2}} \exp\left(-\frac{(r-u_f t)^2}{4D_L f t}\right) \exp(-\lambda t)
\]

where \( C \) is the solute concentration, \( C_i \) the solute geochemical background concentration [kg.m\(^3\)], \( r \) the radial distance between the injection and pumping wells [m], \( t \) the time [s], \( \Delta M \) the injected mass in each layer[kg], \( Q \) the pumping rate of the downstream well passing through each layer (\( Q_F \) and \( Q_f \) for the fractured and fissured media respectively) [m\(^3\).s\(^{-1}\)], \( \lambda \) the decay rate [s\(^{-1}\)] characterised as an exponential decrease function of the shape \( e^{-\lambda t} \),

\( D_L \) the longitudinal dispersion coefficient [m\(^2\).s\(^{-1}\)] where \( D_L = \alpha_L u \), with \( \alpha_L \) the longitudinal dispersivity [m] (\( \alpha_{LF} \) and \( \alpha_{Lf} \) for the fractured and fissured media respectively) and \( u \) the pore velocity [m.s\(^{-1}\)] expressed by \( u = \frac{Q}{2n \pi rh} \), where \( n \) is the effective porosity (\( n_F \) and \( n_f \) for the
fractured and fissured media respectively)[-], and h the aquifer thickness [m] (hF and hF respectively).

A recovery factor (RF) is used to take into account the unexplained mass losses, where $\Delta M = \Delta M_{\text{inj}} \times RF$ with $\Delta M_{\text{inj}}$ the injected mass in the injection well.

The fate and transport of the TiO$_2$ NPs were then estimated using the previously calculated aquifer transport parameters (effective porosity, longitudinal dispersivity; Pauwels et al., 1998) and the experimental results of the NP breakthrough curve. Two specific parameters, i.e. a recovery factor and a delay term relative to Br behaviour, were used to characterize the TiO$_2$ NP transfer through the schist aquifer and compared to the Br behavior. The concentration is equal to 0 kg.m$^{-3}$ when $t = t_r - D < 0$, with $t_r$ for the real time. Then the concentration is calculated by the equation.

4. Results and discussion

4.1 Hydrological characterization of the aquifer

Hard-rock aquifers are very complex systems in which the role of fracture connectivity, which affects both time transfer and chemical processes, is important for groundwater flow and contaminant transport. In the present experiment, the test with Br aimed at a better characterization of the aquifer medium for evaluating the NP transfer.

After the NaBr injection, the flow rate in Well DNS1 was globally $2.46 \cdot 10^{-4}$ m$^3$.s$^{-1}$. The recorded evolution of the Br concentration with time within the injection well is shown in Fig. 2. Given that renewal of the entire water volume in the well takes 8 minutes with a recirculation pumping rate of $1.4 \cdot 10^{-3}$ m$^3$.s$^{-1}$, mixing is instantaneous and the Br concentrations rapidly became homogeneous in samples collected 65 m above the injection point at 70 depth (Br = 6 mmol.L$^{-1}$ one hour after Br injection). That this value remained
below the expected concentration, assuming instantaneous mixing (45 mmol.L$^{-1}$), was most probably because the Br transfer towards Well DNS1 started very rapidly in the vicinity of the fracture at 70 m depth where the concentrated Br solution was injected. The Br concentration decreased with time, confirming the continuous transfer of the injected solutes within the aquifer (Fig. 2). Two days after injection, the dilution factor ([Br]$_{\text{injected}}$ / [Br]$_{\text{at } t+2}$) reached 18. Fig. 2 also shows that the measured Br concentration and the EC of the water are well correlated during the first week after Br injection. This confirms that the Br$^-$ concentration in water overrides the natural geochemical background and that EC can be used to probe its fate during this period (Revil and Glover, 1997). After 6 days, the Br concentration (1 mmol/L) was still higher than the background level.

The measured Br (mmol.L$^{-1}$) breakthrough curve in Well DNS1 is shown in Fig. 3; the time axis at day 0 represents the injection. About 31.3% of the conservative Br tracer was recovered at Well DNS1 over the total duration of the measurement, meaning that 68.7% of the tracer was not captured by the applied pumping flow. A temporal flow change due to the pumping stops and rainstorms is supposed to be at the origin of the small second Br peak. However, part of the missing Br could have arrived after the end of the experiment as a result of diffusion through the non-active porosity, as indicated by the EC value which still remained higher than the initial measurement after 30 days of test (270 > 225 µS.cm$^{-1}$). Moreover, although the surface charge of the schist is slightly negative, the Br$^-$ ions can interact with the positive surface charges present in minor quantity such as iron oxides and oxyhydroxide. A Br early breakthrough is therefore not expected. Ultimately, part of the missing Br must also have been transported in pathways that do not converge towards Well DNS1.

The simulated BTC corresponds to the superposition of the transport rates through the lesser and the more conductive zones, respectively. We took into account the distance between Well F1 and Well DNS1 (15.20 m) and the entire aquifer thickness (50 m), which includes two media of equal thickness (25 m) as defined by Pauwels et al. (1998); one for a network of small fissures in which solute transport would be slower and the other for the
large fissures (fractures) in which solute transport would be relatively fast, as represented by the major fracture at 70 m depth in Well F1. No solute exchange between the two media was taken into account. The parameters were calibrated manually and the parameters giving the best shape of the BTC and the best mass recovery are presented here. The final BTC is thus the sum of each medium's BTC. The superposition of the measured Br-BTC on the two breakthrough curves appears to be an adequate approximation of the general behavior confirming that the two different pathways converge towards the downstream well DNS1, which is in agreement with previous studies (Pauwels et al., 1998). The transport parameters (effective porosity and dispersivity of each medium) were then fitted to the Br breakthrough curves using a recovery factor of 31.3% as previously described. The other parameters described in Table 2 are taken from the simulation of Pauwels et al. (1998) and defined by the experiment (i.e. layer thickness, injected mass, flow rate, background concentration).

In the Br-BTC, the estimated effective porosities in the simulated Br-BTC are low (<1%). The calculated porosity of the slow transport medium (0.73%) is three times higher than that of the fast transport medium (0.24%), in agreement with representative data for schist (de Marsilly, 1981). The longitudinal dispersivity calculated by the model for the slow transport medium is also higher than for the fast transport medium, and this by a factor of 1.5 (i.e. 2.5 vs. 1.6 m). The result can be explained by the textural heterogeneity of the schist which is characterized by a set of more or less conductive fracture and fissure zones (Dewandel et al., 2011; Maréchal et al., 2004) inducing a high heterogeneity of transport paths between the two wells; in effect, water connectivity is dependent on the geometrical properties of the fracture network. The hydraulic conductivity of the fissures in the weathered-fissured facies is lower than that of the fissures in the fresh rock facies due to possible closure and filling with clay materials or iron oxides. When the transport occurs through the connected fractures or larger fissures, it is relatively rapid and the dispersivity displayed by the tracer is low.
Conversely, transport within the small, poorly connected and less conductive fissures is very slow and dispersivity is high. This implies a long-term restitution of the Br within the pumping well at very low concentrations that could remain in the range of the natural background concentration (3 µmol.L⁻¹).

4.2 Evolution of the TiO2 NP suspension in the injection well water (F1)

During laboratory tests, TiO₂ NPs (0.035 mg.L⁻¹) were diluted in MilliQ water and in groundwater from well F1. A quick aggregation was pointed out after mixing with the natural groundwater, i.e. an average size of 2780 to 4170 nm at pH 7, with a polydispersity index of 0.5-0.6. Similarly, the hydrodynamic size of the TiO₂ NPs increased dramatically when diluted in the water (50 L) just collected from Well F1 (Fig. 4) as opposed to MilliQ water, with values between 1700 and 3500 nm (approximate mean of 3070 nm) and a weakly negative zeta potential at -13.2 mV (electrophoretic mobility [EM] = -0.93 µm s⁻¹·V⁻¹·cm; Table 3). Because of the low Na concentration in the Well F1 groundwater, which is significantly lower than the critical coagulation concentration of 1-4·10⁻² M for pH 8 (Solovitch et al., 2010), the rapid aggregation was probably related to the presence of significant concentrations of divalent counter-ions, in particular Ca²⁺ (0.31 mmol.L⁻¹), and to the groundwater pH of 6.5-6.9, which is close to the 5.5 pHₐₑₚ of TiO₂ NPs (Belen Romanello and Fidalgo de Cortalezzi, 2013; Liu et al., 2011; Praetorius et al., 2014).

The average scattered intensity (derived count rate) recovered with each DLS size measurement in the water decreased with time, suggesting a decreasing NP concentration and thus the settling out of TiO₂ NPs from the suspension (Table 3). The intensity at 1.5 h following the NP injection was 138650 kcps (as against the natural groundwater background of 6645 to 9700 kcps); it decreased to 75900 kcps after 16 h and returned to the natural background level of 6650 kcps after 72 h. The size distribution measured in these samples revealed a polydisperse system with the presence of aggregates larger than 1 µm.
average size decreased slightly from 3.0 to 1.3 μm during the first 30 minutes, suggesting that the largest particles were progressively and preferentially removed from the water. Several hypotheses can be suggested to explain this trend: settling, filtering, and passage through the pumps or breakage through shearing due to the water recirculation in the well and to the vertical flow in the well (Riley et al., 2011) or the lateral flow in the fracture. But according to Stokes’ law in the absence of agitation (Lamb, 1994), 6 μm-diameter particles would drop by only 10 m depth within 56 hours, assuming a mass density of 4 g.cm$^{-3}$ for the TiO$_2$ and a dynamic viscosity of 1.13·10$^{-3}$ Pa s at 14°C for the water. Thus settling of the largest aggregates under the test conditions is unlikely because the continuous circulation within the well would have enabled the large aggregates to reach shallow levels of the water column. In contrast, the shear rate induced by the fluid flow through Well F1 might have played a significant role. Considering a well of 11.2 cm diameter and a flow rate of 1.4·10$^{-3}$ m$^3$.s$^{-1}$, the resulting shear rate would be 10 s$^{-1}$. The related dissipation energy is likely to cause fragmentation and/or erosion of the largest NP aggregates that had formed (Zahnow et al., 2011) and thus to lead to the lower measured average size (Bouyer et al., 2005). Finally, the NPs were injected at the depth of a large fracture which size is unknown (Fig. 1) to limit the consequences of possible spreading in the well.

It is unlikely that natural organic matter (NOM) played a role here on the NP dispersion by creating additional steric and repulsive electrostatic forces between the NPs (Belen Romanello and Fidalgo de Cortalezzi, 2013; Chen and Elimelech, 2007; Labille and Brant, 2010; Labille et al., 2012; Praetorius et al., 2014). The apparent zeta potential of the NPs did not, in fact, evolve during the experiment (-16 mV after 1 h of mixing, -14.9 mV after 72 h). Moreover, the DOC and TOC concentrations were very low compared to usual observed effects (Keller et al., 2010) and their slight decrease after the NP injection was more likely due to natural variations (e.g. 9 months before the test the DOC and TOC were <QL). Finally, a grey deposition observed on the well casing and piping at the end of the experiment can be attributed to TiO$_2$ NPs attachment onto the plastic surfaces during
passage through the pumps (recirculation and abstraction) and mixing in the well. Although this loss remains difficult to quantify, the chemical monitoring of water within the injection well proves the persistence of TiO$_2$ NPs in the water available for transfer towards the pumping well.

4.3 TiO$_2$ NP transport in the schist aquifer

The measured Ti (µmol.L$^{-1}$) breakthrough curve is plotted as concentrations versus time (day) in Fig. 5. Even though the NP injection occurred six days after the Br injection, the figure provides a comparison between the Br transport and that of the TiO$_2$ NPs in the hard-rock aquifer. A low, but measurable, fraction of Ti ranging from <QL to 0.033 µmol.L$^{-1}$ was recovered 2.5 days after the NP injection in Well DNS1. The TiO$_2$ NP breakthrough curve indicates the presence of two peaks during the first 12 days after the NP injection and the appearance of a small bulge at around 16 days after injection (Fig. 5). The latter is mostly attributed to the entry of rainwater after rainfalls. Furthermore, a delay is observed between the increases in the Br and Ti concentrations in the water of Well DNS1. The chemical and physical processes responsible for NP transport in porous media are known to be very complex due to NP-NP, NP-rock and NP-indigenous particles interactions, which themselves depend on the various surface charges, the pore network structure and connectivity, the size and shape of the NP aggregates, the solid NP and rock compositions, the groundwater’s chemical composition and the hydrodynamic conditions (Bouhaik et al., 2013; Dewandel et al., 2011; Petosa et al., 2010; Tufenkji and Elimelech, 2004; Yang et al., 2013).

The behavior of the TiO$_2$ NP in the aquifer was identified using the CATTI software. Features that retard the NP motion, such as weak and reversible interactions of TiO$_2$ NPs with the rock and structural factors (dispersivity, porosity for each medium), are taken into account by a delay term, whilst irreversible NP deposition (attachment, pore clogging, sedimentation) is taken into account in the mass-recovery factor. The effective porosities and the longitudinal
dispersivities for the simulated Ti-BTC were fixed from the Br-BTC modelling for each medium. The final BTC for such a heterogeneous medium is a superposition of the two BTCs corresponding to the two main circulation zones that were simulated by the Br and TiO$_2$ BTCs. The fitted curve (Fig. 5) was obtained by applying a recovery factor of 0.1 (see Section 4.4) with a delay term of 0.58 day. This small delay term representing the mass losses of Ti can be attributed to a part remaining unexplained as for Br and to the physical-chemical reactivity of the NPs likely to interact with the surrounding schist. The optimized parameters (Ti-mass recovery factor, delay) confirm that, in a given fracture/fissure, the TiO$_2$ NPs were reactive and not necessarily transferred along the same pathways; unlike the conservative Br tracer, they do not penetrate the entire pore network during transfer, especially where the porosity is very low, due to electrostatic interactions between the NP aggregates and the rock and also to the aggregate size and the hydrodynamic conditions (Solovitch et al., 2010; Huber et al., 2012). The transport behaviour of TiO$_2$ NPs can be considered as hydrodynamic-dependent, especially when forming aggregates around μm in size. One could expect that not only would the aggregated NPs be more liable to mechanical deposition in pore spaces than the dispersed NPs, but also that they would migrate more rapidly through preferential pathways toward the farther end points as the capacity of large aggregates to penetrate the pore network is less than that of a single NP due to their size. The motion of suspended particles where hydrodynamic streamlines are concerned depends on their aggregation state and fractal dimensions. Porous aggregates exhibit a low drag coefficient, favouring their deposition onto surfaces, whereas individual NPs would preferentially follow streamlines through the pore network (Solovitch et al., 2010; Veerapaneni and Wiesner, 1996). If this was the case in the present study, we should expect the mobile NPs to have followed preferential pathways and breakthrough more rapidly than the Br, and at the same time be subject to reversible NP-rock attachment that may be reversible. These assumptions are consistent with the observed NP restitution peak, which is delayed and narrower compared to the Br one.
4.4 TiO$_2$ NP loss in the schist aquifer

The Ti mass (0.065 %) was calculated from the sum of the Ti recovered masses over the total amount of injected Ti (120 g). It is in the same order of magnitude as the recovery factor (0.1%) in the TiO$_2$ breakthrough curve simulation. By comparison, the conservative tracer was characterized by a Br mass recovery factor of 31.3%. As already indicated, a loss of TiO$_2$ NPs at the injection well probably contributed to the restitution difference between the Br and the TiO$_2$ NPs.

Different phenomena are likely to contribute to the high deposition rate of TiO$_2$ NPs along the largest and well-connected fissures. Firstly, the measured aggregation of the NPs certainly favours mechanical filtering through fissures and fractures of the schist media, implying decreasing deposition with distance from injection (Solovitch et al., 2010; Tufenkji and Elimelech, 2004; Tufenkji and Elimelech, 2005). Secondly, the charge heterogeneity of the schist due to its mineral composition is a key factor controlling the deposition of NPs on mineral surfaces (Torkzaban et al., 2010; Tufenkji and Elimelech, 2005). TiO$_2$ NPs are weakly negatively charged under the groundwater’s pH conditions and the apparent zeta potential value of the schist is also weakly negative, although this results from a mixing of positively and negatively charged mineral surfaces. In effect, the point of zero charge of the schist’s major primary and secondary minerals is low, implying negatively charged surfaces within the aquifer under the groundwater pH conditions (6.5-6.9). Both the fresh and the weathered-fissured schist are made up of quartz ($\text{pH}_{\text{PZC}} = 2.3$ [Leroy et al., 2013]), K-feldspar ($\text{pH}_{\text{PZC}} = 2.0$ to 2.4), kaolinite ($\text{pH}_{\text{PZC}} = 2.4$ [Leroy and Revil, 2004; Tombacz and Szekeres, 2006]) and chlorite ($\text{pH}_{\text{PZC}} = 3$ [Yin et al., 2013]), as well as other minerals, such as iron oxides and oxyhydroxides, characterized by a basic $\text{pH}_{\text{PZC}}$ close to 8 (Dzombak and Morel, 1990). These latter minerals are positively charged at a pH of around 7 and are likely to favour electrostatic attraction between the NPs and the Fe-oxide surfaces with a resultant deposition of the negatively charged NPs. The iron oxyhydroxide phases are known to have
an important adsorption potential due to their high specific surface area (Dzombak and Morel, 1990) and so we can assume that a certain amount of TiO$_2$ NPs could also be attached by electrostatic attraction onto the Fe oxyhydroxides. The local geochemical conditions of the schist aquifer, favouring denitrification and subsequent iron oxyhydroxide precipitation or presence as colloids in the main water pathways due to pyrite and Fe$^{2+}$ oxidation by nitrates (Pauwels et al., 2000), are likely to enhance attenuation mechanisms by reducing contamination levels during the NPs migration through the aquifer.

TiO$_2$ NPs can also be favourably attached in the weathered parts of the aquifer; in the present case the weathered saprolite facies of the schist has a porosity that is solicited by pumping in Well DNS1. The weathering products of the saprolite are likely to give different reactions; for example, attachment of the NPs will be enhanced by the presence of iron oxyhydroxides, whereas electrostatic repulsion of the NPs will be favoured by clay minerals that are mostly negatively charged at a pH of around 7 (Fig. 1). Although the role played by the weathered part of the aquifer was not studied due to the NPs being injected at a depth of 70 m in the aquifer, the unsaturated weathered facies and its thickness will nevertheless play a significant role as regards the aquifer’s vulnerability by reducing the downward migration speed of water and contaminants through the medium (Brouyère et al., 2004). Finally, a more detailed study is underway to explore the role of the different minerals with respect to the attachment process, with experiments of TiO$_2$ NP circulation through fresh schist cores from the same aquifer (Ollivier et al., in prep).

5. Conclusions

The physical and chemical processes responsible for NP transport in porous media are very complex due to NP-NP and NP-rock interactions, which themselves depend on the various surface charges, the pore network structure and connectivity, the groundwater’s chemical composition and the hydrodynamic conditions.
Our small-scale tracer experiment conducted in a schist aquifer is an attempt to understand the physical and chemical processes occurring should TiO$_2$ NPs happen to penetrate a hard-rock aquifer. One of the major results is that the TiO$_2$ NPs were found to be mobile, transferring in an aggregate form through the conductive zones of a heterogeneous schist. During the transfer, a large amount of the NPs was also deposited onto the rock surface through sedimentation, clogging and attachment. The natural denitrification process occurring in the aquifer is responsible for the presence of precipitated and positively charged iron oxyhydroxides in the main flow path that are capable of adsorbing a large amount of negatively charged TiO$_2$ NPs. It is worth noting that NP attachment can be reversible due to the possible evolution of the surface charge of the different minerals constituting the schist rock according to the environmental conditions. For instance, any modification of the aquifer’s chemical conditions may impact the pH and the denitrification process, as well as the heterogeneity of the schist. Regional changes in agricultural practices that lead to a lower nitrate input could typically play a role in TiO$_2$ NP transfer.

As a first approach, our work confirms both the potential for TiO$_2$ NPs to be transported in natural groundwater and the vulnerability of the hard-rock aquifer. Further investigations, currently in preparation, are required for a better understanding of the processes occurring during NP transfer, including the role of the different minerals with respect to sorption processes. Other questions to be addressed concern the evolution of NP aggregates during transport due to dilution and interaction with organic matter or to shearing energy. Longer experiments aiming at studying the release of NPs deposited within the aquifer are also required. The increased knowledge from such field experiments is also dependent on the evolution of analytical techniques both for NP measurements, particularly at very low NP concentrations, and on-site measurements.

Acknowledgments
This work was supported by the French National Agency for Research (ANR; grant number PNANO ANR-07-NANO-035) and the BRGM through the AquaNano project. C. Crouzet of the BRGM laboratories is thanked for providing experimental and monitoring facilities, and T. Laurioux is thanked for the ICP-MS measurements. We also kindly thank Dr. Natacha Solovitch for her help with streaming potential measurements, as well as the three anonymous reviewers for their thorough revisions of the manuscript. We are grateful to Patrick Skipwith for revising and editing the English text.

References


Maréchal, J.C., Dewandel, B. and Subrahmanyam, K., 2004. Use of hydraulic tests at
different scales to characterize fractures. Water Resources Research 40(40): 17.
Morbihan), hydrologie : détermination des caractéristiques hydrodynamiques du
système aquifère au lieu-dit le Stimoës. Unpublished BRGM report, n°
R38474DR/HYT95, 54 p.
Moore, M.N., 2006. Do nanoparticles present ecotoxicological risks for the health of the
test for denitrification in a pyrite-bearing schist aquifer. Applied Geochemistry, 13(6):
767-778.
aquifer: influence on water chemistry and isotopes. Chemical Geology, 168(3-4): 307-
324.
Hydrochemical borehole logs characterizing fluoride contamination in a crystalline
et du Haut Evel (Morbihan): Rapport sur les travaux de cartographie et de
stratigraphie. Unpublished report, University of Brest.
on nanocrystalline titanium dioxide. Environmental Science & Technology, 40(4):
1257-1262.
and Deposition of Engineered Nanomaterials in Aquatic Environments: Role of
Physicochemical Interactions. Environmental Science & Technology, 44(17): 6532-
6549.
nanoparticles in saturated granular porous media: Role of water chemistry and
Heteroaggregation of Titanium Dioxide Nanoparticles with Model Natural Colloids
under Environmentally Relevant Conditions. Environmental Science & Technology,
48(18): 10690-10698.
Riley MS, Tellam JH, Greswell RB, Durand V, Aller MF. Convergent tracer tests in
multilayered aquifers: The importance of vertical flow in the injection borehole. Water
Resources Research 2011; 47: n/a-n/a.
of Upper Bounds and Trends in Nano-TiO2 Production As a Basis for Exposure
Santaella, C., Allainmat, B., Simonet, F., Chanéac, C., Labille, J., Auffan, M., Rose, J. and
Achouak, W., 2014. Aged TiO2-Based Nanocomposite Used in Sunscreens Produces
Singlet Oxygen under Long-Wave UV and Sensitizes Escherichia coli to Cadmium.
Environmental Science & Technology, 48(9): 5245-5253.
assistée par ordinateur. Mode d'emploi de CATTI. Version 2.0. Logiciel distribue par
IGWMC (International Groundwater Modeling Center).
Interpretation Program Documentation. BRGM - Gesamthochschule Kassel
Universität: 64 p.


Figure caption

Fig.1: Cross section illustrating the injection well F1 and the downstream pumping well DNS1 during the tracer test experiment (adapted from Pauwels et al., 1998). The diagram highlights the presence of a deep major fracture at 70 m depth in Well F1 (thick black line) and the main expected Br and NP pathways.

Fig.2: Measured Br concentration (mmol.L\(^{-1}\)) in Well F1 groundwater versus time during the Br-tracer test. “EC” stands for electrical conductivity. The Br geochemical background value corresponding is 3 \(\cdot\) 10\(^{-3}\) mmol.L\(^{-1}\).

Fig.3: Experimental data and modelling of Br concentrations versus time in the downstream pumping well, DNS1. The Br geochemical background value is 3 \(\cdot\) 10\(^{-3}\) mmol.L\(^{-1}\) (in grey).

Fig.4: Size distribution of the TiO\(_2\) NPs in MilliQ water, in the injection solution, and in Well F1 groundwater after injection.

Fig.5: Experimental data and modelling of Ti concentrations versus time in the downstream Well DNS1. The Ti geochemical background value is 0.002 \(\mu\)mol.L\(^{-1}\) (indicated in grey) and the quantification limit is 0.002 Ti \(\mu\)mol.L\(^{-1}\).

Table list
Table 1: Apparent physical and chemical composition of the groundwater in wells F1 (injection) and DNS1 (pumping). TiO$_2$ NP injection was made 6.1 days after Br injection.

<table>
<thead>
<tr>
<th>Well</th>
<th>EC (25 °C) µS·cm$^{-1}$</th>
<th>pH</th>
<th>T °C</th>
<th>Dissolved O$_2$ mg·L$^{-1}$</th>
<th>Alkal. meq·L$^{-1}$</th>
<th>Na mmol·L$^{-1}$</th>
<th>K mmol·L$^{-1}$</th>
<th>Ca mmol·L$^{-1}$</th>
<th>Mg mmol·L$^{-1}$</th>
<th>Cl mmol·L$^{-1}$</th>
<th>NO$_3$ mmol·L$^{-1}$</th>
<th>SO$_4$ mmol·L$^{-1}$</th>
<th>Ti µmol·L$^{-1}$</th>
<th>Br µmol·L$^{-1}$</th>
<th>TOC mmol·L$^{-1}$</th>
<th>DOC Mmol·L$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1 24 h before Br injection</td>
<td>225</td>
<td>6.94</td>
<td>12.4</td>
<td>0.7</td>
<td>1.08</td>
<td>0.70</td>
<td>0.03</td>
<td>0.31</td>
<td>0.40</td>
<td>0.72</td>
<td>&lt;0.008</td>
<td>0.25</td>
<td>0.002</td>
<td>3.7</td>
<td>0.2</td>
<td>0.14</td>
</tr>
<tr>
<td>F1 1h before NPs injection</td>
<td>272</td>
<td>6.84</td>
<td>13</td>
<td>0.87</td>
<td>1.01</td>
<td>0.03</td>
<td>0.31</td>
<td>0.40</td>
<td>-</td>
<td>&lt;0.008</td>
<td>-</td>
<td>0.001</td>
<td>942</td>
<td>0.06</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>F1 16h after NPs injection</td>
<td>282</td>
<td>6.65</td>
<td>13.7</td>
<td>3.06</td>
<td>0.93</td>
<td>1.12</td>
<td>0.03</td>
<td>0.32</td>
<td>0.41</td>
<td>0.81</td>
<td>0.008</td>
<td>0.27</td>
<td>-</td>
<td>434</td>
<td>0.06</td>
<td>0.06</td>
</tr>
<tr>
<td>DNS1 24h before Br injection</td>
<td>210</td>
<td>6.54</td>
<td>13.7</td>
<td>5.9</td>
<td>0.71</td>
<td>0.75</td>
<td>0.03</td>
<td>0.24</td>
<td>0.38</td>
<td>0.76</td>
<td>0.034</td>
<td>0.28</td>
<td>0.002</td>
<td>3.0</td>
<td>&lt;0.04</td>
<td>&lt;0.04</td>
</tr>
<tr>
<td>DNS1 16 h after NPs injection</td>
<td>221</td>
<td>6.39</td>
<td>13.2</td>
<td>6.1</td>
<td>0.72</td>
<td>0.78</td>
<td>0.03</td>
<td>0.24</td>
<td>0.38</td>
<td>0.76</td>
<td>0.016</td>
<td>0.27</td>
<td>0.001</td>
<td>21</td>
<td>&lt;0.04</td>
<td>&lt;0.04</td>
</tr>
</tbody>
</table>
Table 2: Parameters used into the CATTI model to simulate Br and Ti BTCs. For the mass, 3 kg of NaBr were expressed as Br = 3 kg * M_{Br} / (M_{Br} + M_{Na}) = 3*79.9/(79.9+22.99) = 2.33 kg of Br homogeneously distributed in both media. For Ti, 0.2 kg of TiO\textsubscript{2} were expressed as Ti = 0.12 kg homogeneously distributed in both media. A slight variation of the flow rate was noticed during the experiment.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Fissure - low permeability</th>
<th>Fracture - high permeability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br</td>
<td>2.46·10^{-4} 1.165 25 7.26·10^{-3} 2.45 0.00095 0.313 0</td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>2.33·10^{-4} 0.06 25 7.26·10^{-3} 2.45 0 0.001 5-104</td>
<td></td>
</tr>
</tbody>
</table>

Table 3: Apparent zeta potential, electrophoretic mobility, pH, electrical conductivity (EC), derived count rate, Z average and PdI for size measurements before and after TiO\textsubscript{2} NP injection in Well F1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Apparent zeta potential, mV</th>
<th>Electrophoretic mobility, (\mu) m s(^{-1}) cm(^{-1})</th>
<th>pH</th>
<th>EC (mS cm(^{-1}))</th>
<th>Derived Count rate (kcps)</th>
<th>Z-average (mm)</th>
<th>PdI</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO\textsubscript{2} NPs (uls) in MilliQ water</td>
<td>44.8</td>
<td>3.17</td>
<td>3.9</td>
<td>0.09</td>
<td>3,479,978</td>
<td>136</td>
<td>0.29</td>
</tr>
<tr>
<td>Initial F1 water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6,645-9,700</td>
<td>5,858</td>
<td>1</td>
</tr>
<tr>
<td>TiO\textsubscript{2} 5 min after mixing with F1 water</td>
<td>-13.2</td>
<td>-0.93</td>
<td>6.7</td>
<td>0.28</td>
<td>830,067</td>
<td>3,074</td>
<td>0.34</td>
</tr>
<tr>
<td>TiO\textsubscript{2} 1h20 min after mixing with F1 water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>481,860</td>
<td>2,319</td>
<td>0.43</td>
</tr>
<tr>
<td>1 h after injection</td>
<td>-15.6</td>
<td>-1.11</td>
<td>6.9</td>
<td>0.26</td>
<td>138,652</td>
<td>1,189</td>
<td>0.33</td>
</tr>
<tr>
<td>4 h after injection</td>
<td>-16.0</td>
<td>-1.14</td>
<td>6.7</td>
<td>0.27</td>
<td>175,260</td>
<td>1,420</td>
<td>0.40</td>
</tr>
<tr>
<td>16 h after injection</td>
<td>-14.5</td>
<td>-0.99</td>
<td>6.6</td>
<td>0.26</td>
<td>75,900</td>
<td>1,038</td>
<td>0.31</td>
</tr>
<tr>
<td>19 h after injection</td>
<td>-15.9</td>
<td>-1.12</td>
<td>6.5</td>
<td>0.26</td>
<td>59,970</td>
<td>935</td>
<td>0.33</td>
</tr>
<tr>
<td>72 h after injection</td>
<td>-14.9</td>
<td>-1.09</td>
<td>6.5</td>
<td>0.28</td>
<td>6,650-8,700</td>
<td>1,351</td>
<td>0.76</td>
</tr>
<tr>
<td>168 h after injection</td>
<td>-14.9</td>
<td>-1.05</td>
<td>6.5</td>
<td>0.26</td>
<td>5,000</td>
<td>2915</td>
<td>1</td>
</tr>
</tbody>
</table>

30