

Determination of Interstitial Water Chemistry and Porosity in Consolidated Aquifer Materials by Diffusion Equilibrium-Exchange

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Diffusion equilibrium exchange (DEE) is presented as a novel, practical alternative to centrifugation for the recovery and chemical analysis of interstitial water in contaminated core samples from consolidated rocks and aquifers. The methodology is suitable for sampling organic and inorganic compounds, including redox sensitive species such as SO_4^{2-} , NO_3^- , NO_2^- , Mn(II) , Fe(II) , and sulfide (HS^-). DEE also permits analyte extraction from kilogram quantities of core, which avoids extended centrifugation or sample amalgamation and provides analyte masses appropriate for stable isotope analysis. The procedure involves simple and rapid on-site sectioning of representative core samples, which are preserved in the field by storage in airtight bottles filled with deoxygenated deionized water containing a conservative tracer (Br^-). Equilibration times for individual solutes can be estimated in advance to reduce the need for time-series analysis; for an effective diffusion coefficient of $2.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ (Br^- in chalk rock) equilibration was >90% completed after 30 h, consistent with the predicted equilibration time. The DEE method presented minimizes sampling errors from temperature changes, oxidation of reduced chemical species, and loss of volatile compounds, which can occur with other interstitial water sampling techniques. It also gives superior resolution of in situ solute distributions and geochemical processes in consolidated sediments than centrifugation and can provide estimates of aquifer porosity in core samples. Laboratory experiments using chalk rock core and simulated extraction procedures confirm the superior performance of the DEE method over centrifugation for a range of solutes. The method has been used to generate detailed interstitial water profiles of electron acceptor and contaminant concentrations along the flow path of a petroleum hydrocarbon plume in the U.K. Upper Chalk aquifer as part of a natural attenuation assessment.

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Introduction

Analyses of interstitial waters in geological media provide an understanding of in situ hydrochemical variations in the subsurface and enable the aqueous chemistry to be related directly to the composition of the host material (1). Data on interstitial water chemistry are important for correlating in situ spatial distributions of dissolved chemical species with sediment properties (2–4), relating dissolved solute concentrations to the distribution of sorbed species (5), determining chemical gradients and solute fluxes across sediment–water interfaces (2, 6–8), estimating sedimentation rates (6), deducing chemical reactions affecting mineral equilibria and element speciation during early diagenesis (6, 8–10), and interpreting geochemical processes controlling the fate of organic compounds and other species in these settings (4–9). There is also increasing application of interstitial water analyses in studies of groundwater pollution in aquifers (3–5).

The in situ and ex situ methods used to recover interstitial water samples from geological materials have been recently reviewed (11). These procedures include hydraulic and gas-pressure squeezing (12–15), centrifugation (1, 3), porous suction samplers (2, 7), and dialysis extraction (16, 17). In situ methods preserve the structure, dissolved solute distribution, and chemical gradients in the sampled sediment (11). These methods are typically used to sample interstitial water in cores from freshwater lakes, deep oceans, and contaminated aquifers (4, 7, 13, 17). The key criteria is the need to extract interstitial water samples at in situ temperatures, limit atmospheric exposure of samples, and maximize the volume of interstitial water recovered (11). This is required to minimize sampling artifacts, ensure samples are representative of the location from which they were collected, and provide adequate sample volumes for chemical analysis. The importance of temperature on interstitial water chemistry is not well-known, and samples must be extracted at in situ temperatures to avoid changing the ion-exchange equilibria and kinetics of biological processes that influence solute concentrations (11, 18–20). Similarly, anaerobic interstitial water samples should be recovered and preserved in an inert atmosphere. Precipitation of ferric hydroxides may otherwise occur, with loss of dissolved Fe(II) and coprecipitation or adsorption of other reactive species in samples, such as nutrients and trace heavy metals (11, 21–23). Degassing and loss of volatile compounds from small volume samples may also occur during the extraction procedure (11). These processes affect the acid–base equilibria and redox status of samples, with changes in pH and dissolved gas concentration (e.g. CO_2 , H_2 , H_2S , CH_4), which influence the geochemical equilibrium controlling the concentration of other dissolved species, including Ca^{2+} , HCO_3^- , and trace heavy metals (7, 11, 19). Volatile organic compounds in samples from contaminated aquifers are also lost through volatilization. These artifacts can be reduced or minimized in most methods through sample collection, manipulation, and interstitial water extraction in an inert, temperature-controlled atmosphere (7, 11, 15). However, this may be impractical for routine use in many cases (1).

On grounds of practicality and cost-efficiency centrifugation is commonly used to extract interstitial water from consolidated sediments, including aquifer materials (1, 3). Extraction methods using hydraulic squeezing have been devised for consolidated mudrocks and aquifer materials, but this requires specialist equipment and is not routinely attempted (24, 25). Porewater recovery by centrifugation is often limited to a few milliliters by small sample sizes and

partial recovery of the interstitial fluid (*I*). Interstitial water samples from successive core samples must usually be combined to form a bulked composite, depending on the number and type of chemical analyses required. The sampling resolution for centrifugation is then limited by the efficiency of the extraction procedure and sample volume required by different analytical methods. Improvements in extraction efficiency for centrifugation have been developed using displacement of interstitial water by dense immiscible organic fluids, but these may not be suitable in studies of contaminated aquifers (3). There is also potential for the interstitial water composition to be changed by volatilization, degassing, and oxidation of anaerobic water samples arising from agitation and atmospheric exposure during centrifugation. Centrifugation in an anaerobic glovebag will minimize oxidation artifacts, but loss of volatile constituents, including dissolved gases and volatile organic compounds (e.g. BTEX and solvents), will limit the application in contaminated aquifer settings.

This paper describes a new method for the recovery and analysis of interstitial water samples in consolidated rocks and aquifer materials by diffusion equilibrium exchange (DEE) with anaerobic deionized water containing a conservative tracer. The performance of the DEE method is compared with centrifugation, using chalk rock core samples. The application of the DEE method in a contaminated consolidated aquifer is illustrated for a petroleum hydrocarbon and MTBE-contaminated site on the Upper Chalk aquifer in the U.K.

Experimental Section

Aquifer Setting. The Cretaceous Chalk aquifer is a soft, white limestone (ca. 99% CaCO₃), which forms a deep consolidated, fractured, dual porosity aquifer. The aquifer matrix has a high primary porosity (ca. 30–50% in the Upper Chalk (26)) but low effective permeability, and the matrix interstitial water is essentially immobile. The matrix is dissected by fractures, which contribute minor secondary porosity (~1%), but which have very high permeability and may dominate groundwater flow and solute transport (27–29). Solute transport between the matrix and fractures occurs by diffusion. The petroleum hydrocarbon-contaminated site in this study is located on the Upper Chalk aquifer in SE England. Groundwater beneath the site is contaminated with benzene, toluene, ethylbenzene, xylenes (BTEX), methyl *tert*-butyl ether (MTBE), and *tert*-amyl methyl ether (TAME) (30). Interstitial water compositions at this site have been used to assess solute exchange between the matrix and fractures as part of fate and transport modeling of the contaminant plume.

Collection of Rock Core and Chemical Analysis. Three continuous rock cores (10 cm diameter) were recovered at the petroleum hydrocarbon-contaminated chalk site. These core samples were used to determine the interstitial water chemistry by DEE and to compare the performance of DEE with centrifugation as a method for interstitial water extraction. Two cores were from the petroleum plume (MW17, MW23), and the other core was from an uncontaminated borehole (MW20) (30). Cores in the saturated zone were collected using water flush rotary drilling, whereas rock core in the unsaturated zone at MW23 was collected by cable and tool percussion drilling. A fluorescein tracer was added to the drilling fluid to assess its migration into the core (*I*). The drilling fluid entering and leaving the core barrel at the completion of each core run was sampled to correct the interstitial water chemistry for contamination by the drilling fluid. All core processing described below was completed onsite. After collection, cores were quickly sectioned with a bench-mounted rotary stone saw to minimize sample oxidation. Each core was divided into 1 m transverse sections, followed by longitudinal sectioning and removal of an inner

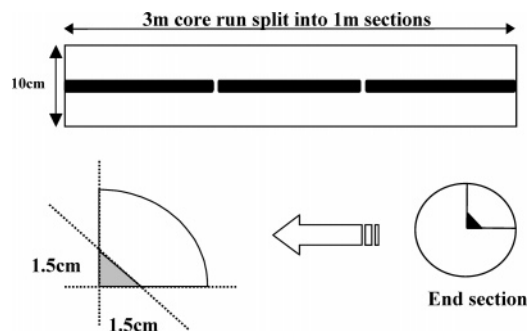


FIGURE 1. Schematic of core section procedure showing strip sample removed from center of core and quadrant subsample removed from strip samples.

quadrant from the sections (Figure 1). A continuous “strip” sample from the entire 1 m-core section was obtained, ensuring no concentration “hotspots” were missed through subsampling. The strip sample (~0.4 kg) was broken into short sections and placed in a preweighed bottle of known volume (~0.6 L in this study). Collection of the inner quadrant strip sample for interstitial water analysis minimized potential contamination of samples by the drilling fluid. As a further precaution, bottles of sectioned core were filled twice and rinsed with deoxygenated distilled water to remove surface debris. Solute loss during this procedure is insignificant for consolidated material (calculated to be <1%, see below); samples of poorly consolidated chalk marl were not rinsed, to limit sample disintegration. The bottles were then weighed to determine the mass of rock added, filled completely with deoxygenated distilled (“equilibration”) water containing a tracer (25 mg L⁻¹ Br⁻ as KBr), and sealed with a plastic cap fitted with a PTFE-faced butyl septum. Bottles were then reweighed to determine the mass of water added and left inverted in the dark for a week at 4 °C prior to analysis of the equilibration water. In the laboratory, the bottles were briefly shaken every 24 h to aid mixing. Total water content of core samples was determined after interstitial water equilibration, from the weight loss on vacuum-drying at 100 °C for ca. 48 h. A biocide can be used in the equilibration water but was omitted in this study to prevent analytical interference during the determination of NO₃⁻.

Samples of equilibration water and interstitial water extracted by centrifugation were analyzed for major anions and cations by ion-chromatography (IC) using a Dionex DX120 ion chromatograph. Dissolved petroleum compounds (BTEX, MTBE, and TAME) were determined by gas-chromatography mass-spectrometry (GC-MS) (31). Analytical precision was evaluated using certified standards during sample runs and was ± 4% RSD for IC and ± 3% RSD for GC-MS analyses, respectively. Experimental precision was evaluated from analyses of triplicate experiments (see Table 1).

Interstitial Water Solute Equilibration. The chalk core equilibration rate was monitored by periodic analysis of the equilibration water. Profiles of Br⁻ concentration in the equilibration water as a function of equilibration time show that ~100% equilibrium was attained after 30 h (Figure 2). This was confirmed by reanalysis of the equilibration water in bottles after 1 month. The theoretical equilibration of a chalk sphere by diffusion in a Br⁻ solution was evaluated to test if a 30-h equilibration time is valid. Diffusion into a sphere from a solution of known volume may be modeled using eqs 1–3 (31)

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{6\alpha(\alpha + 1) \cdot \exp(-D_{\text{Br}}^* q_n^2 t/a^2)}{9 + 9\alpha + q_n^2 \alpha^2} \quad (1)$$

TABLE 1. Interstitial Water Chemistry for Chalk Core Samples Determined by Diffusion Equilibrium Exchange (DEE) and Centrifugation (C)

analyte	sample A ^a		sample B ^a		sample C ^a		means ^b		%R.S.D. ^c		target, ^d mg L ⁻¹
	DEE, mg L ⁻¹	C, mg L ⁻¹	DEE, mg L ⁻¹	C, mg L ⁻¹	DEE, mg L ⁻¹	C, mg L ⁻¹	DEE, mg L ⁻¹	C, mg L ⁻¹	DEE, %	C, %	
chloride	108.5	106.3	105.5	120.7	104.5	121.3	106.2	116.1	1.96	7.31	115.5
nitrate	41.7	39.9	41.8	46.6	41.4	47.4	41.6	44.6	0.5	9.23	44.4
nitrite	20.4	20.7	20.1	23.9	19.8	24.9	20.1	23.2	1.49	9.46	21.8
sulfate	171.7	103.3	170.5	116.0	168.0	116.2	170.0	111.8	1.11	6.61	117.1
MTBE	2.21	1.47	2.13	1.42	2.09	1.43	2.14	1.44	2.86	1.84	2.36
TAME	2.30	1.41	2.18	1.34	2.09	1.27	2.19	1.34	4.81	5.22	2.49
benzene	2.19	0.83	2.16	0.71	2.01	0.71	2.12	0.75	4.55	9.24	2.39
toluene	2.27	0.70	2.23	0.57	2.11	0.58	2.20	0.62	3.78	11.67	2.56
p-xylene	2.64	0.58	2.63	0.44	2.51	0.45	2.59	0.49	2.79	15.94	2.85

^a All samples were analyzed in duplicate; mean values are quoted. ^b Mean of triplicate experiments. ^c Relative standard deviations (R.S.D.) calculated from triplicate experiments. ^d Target concentration represents the composition of the "test" solution in contact with the chalk samples after the initial 4-day equilibration.

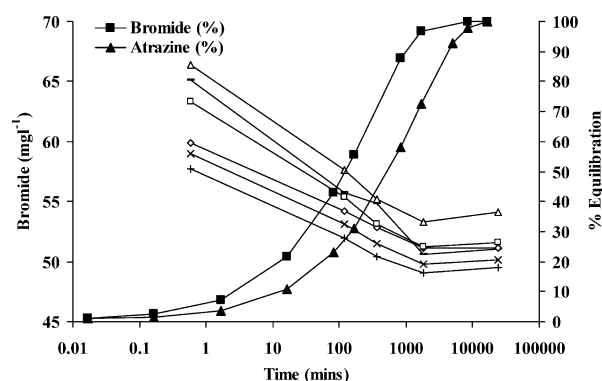


FIGURE 2. Model-predicted equilibration time for Br⁻ and the herbicide atrazine by aqueous diffusion into chalk spheres vs Br⁻ concentration in equilibration water as a function of equilibration time for six Upper Chalk core samples. In the case of Br⁻, equilibration is complete after ~1700 min (~30 h).

where the q_n values are the n th roots of

$$\tan q_n = \frac{3q_n}{3 + \alpha q_n^2} \quad (2)$$

and

$$\alpha = \frac{3V_s}{4\pi a^3} \quad (3)$$

The following assumptions were made in this analysis: (1) The equilibrating systems have 50 equally sized chalk spheres of 0.01 m radius, equilibrating in 0.4 L of water, such that each sphere is equilibrating with 0.008 L of water. (2) No concentration gradients are present in the equilibration water during equilibration (i.e. the systems are well mixed). (3) The core samples have a uniform effective diffusion coefficient (D_{Br^*}) for Br⁻ of $2.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ (mean value from experimental data ((33), using method of ref 34)).

M_t/M_∞ is the mass of Br⁻ in sphere at time t /mass of Br⁻ in sphere at equilibrium ($t = \infty$), V_s is the volume of equilibration water associated with one sphere (0.008 L), t is the time from start of equilibration, D_{Br^*} is the effective diffusion coefficient for Br⁻ in chalk ($2.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$), and a is the radius of the chalk sphere (0.01 m).

A spreadsheet model based on eq 1 was used to obtain values of M_t/M_∞ for a range of equilibration times (Figure 2). From the profile the characteristic equilibration time for Br⁻ is ~1700 min (30 h), in agreement with the experimental data (Figure 2). A similar equilibration time is expected for

other ionic species of comparable size, but for larger organic molecules, such as the herbicide atrazine ($D^* \sim 5 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$), the equilibration time is ~8400 min (6 days). The model also indicates that solute loss during rinsing of the core fragments prior to equilibration is insignificant (<1% for a 10 s rinse, cf. Figure 2).

Calculation of Rock Porosity and Interstitial Water Solute Concentrations. The change in Br⁻ concentration during equilibration was used to estimate the interstitial water volume and saturated porosity of the core and also to correct measured solute concentrations for dilution during equilibration (see eqs 4–7 below). At equilibrium Br⁻ is partitioned between interstitial water and equilibration water. A mass balance for Br⁻ before and after equilibration gives the relation

$$V_{EW} \cdot Br_{(I)}^- = (V_{EW} + V_P) \cdot Br_{(F)}^- \quad (4)$$

where V_{EW} is the volume of equilibration water added to the bottles, V_P is the interstitial water volume subject to diffusive exchange with the equilibration water, $Br_{(I)}^-$ is the Br⁻ concentration in the distilled water added to the equilibration bottles, and $Br_{(F)}^-$ is the final Br⁻ concentration after equilibration. By rearrangement of eq 4, V_P (the interstitial water volume) can be found (eq 5):

$$V_P = \frac{V_{EW} Br_{(I)}^-}{Br_{(F)}^-} - V_{EW} \quad (5)$$

The interstitial water volume accessed by the Br⁻ tracer (V_P) can be expressed as a percentage (θ_{Br^-}) of the total core volume (empty bottle volume – volume of water added), V_C (eq 6):

$$\theta_{Br^-} = \frac{100V_P}{V_C} \quad (6)$$

The total interstitial water volume, calculated from the weight loss on vacuum-drying (Δ_C), can also be expressed as a percentage (θ_W , eq 7):

$$\theta_W = \frac{100\Delta_C}{V_C} \quad (7)$$

The interstitial volume not accessed by the Br⁻ tracer comprises gas (V_G) and also water contained in closed pores (V_{CP}). The volume and contribution of these components to

the porosity (θ_G and θ_{CP} , respectively) can be found using the core sample weight loss on vacuum-drying (Δ_C , eqs 7 and 8)

$$V_G = V_C - \Delta_C - \left(\frac{M_D}{\rho_{Ca}}\right) \quad \theta_G = \frac{100V_G}{V_C} \quad (8)$$

$$V_{CP} = \Delta_C - V_P \quad \theta_{CP} = \frac{100V_{CP}}{V_C} \quad (9)$$

where V_G is gas volume, V_{CP} is the closed porosity volume, M_D is the mass of vacuum-dried core, Δ_C is the mass of wet core minus mass of vacuum-dried core, and ρ_{Ca} is the density of calcite (chalk is >99% CaCO_3).

Eq 7 assumes that the density of chalk can be modeled as a three-component mixture: CaCO_3 ($\rho=2670 \text{ kg m}^{-3}$), water ($\rho=1000 \text{ kg m}^{-3}$), and air ($\rho\sim 0 \text{ kg m}^{-3}$), with the density of the residual nongaseous component in the dried core being that of calcite. This assumption has been tested for >2000 U.K. chalk samples (29), which indicates that chalk dry density is linearly related to porosity, and at zero porosity the dry density is 2670 kg m^{-3} (within 1.5% of the expected value for calcite (2710 kg m^{-3})). Measured solute concentrations were corrected for dilution during equilibration using eq 10

$$X_{PW} = \frac{X_{EQW} \cdot \text{Br}^-_{(I)}}{\text{Br}^-_{(I)} - \text{Br}^-_{(F)}} \quad (10)$$

where X_{PW} is the pore water solute concentration corrected for dilution and X_{EQW} is the measured solute concentration in the equilibration water.

The solute mass transferred to the equilibration water during equilibration is a function of core porosity, core volume, and bottle volume. For stable isotope analysis it is important that solute yields are maximized. Equation 11 allows calculation of the optimum rock volume for equilibration at any given core porosity and bottle volume. The chalk sampled in this study has porosity of ~45 vol %, and the optimum rock volume for a 0.6 L bottle is 0.36 L (ca. 0.75 kg core). In practice it is difficult to fit 0.75 kg of rock into a 0.6 L bottle; for lower porosities the optimum mass increases, and so in general bottles should always be filled with rock fragments prior to equilibration

$$V_R = \frac{V_T}{1 + \sqrt{\frac{\theta_{AV}}{100}}} \quad (11)$$

where V_R is the rock volume, V_T is the total bottle volume, and θ_{AV} is the average rock porosity (vol %).

Experimental Determination of Interstitial Water Chemistry in Chalk Core Samples by DEE vs Centrifugation.

DEE Methodology. A laboratory experiment was undertaken to determine the concentrations, by DEE and centrifugation, of inorganic and volatile organic compounds in saturated chalk core equilibrated with "test" solution of known composition. The DEE methodology used in the experiment is analogous to that used in the field, with the omission of the core sectioning procedure. However, the time that samples were exposed to the atmosphere was comparable to that in the field (~5 min). Fragments (~1–2 cm diameter) of uncontaminated (MW20) chalk core were initially equilibrated in three 500 mL bottles with an aqueous "test" solution of anions, selected BTEX compounds, MTBE and TAME. After 4 days samples of the test solution were collected for analysis. The bottles were then drained so that a sub sample (~50g) of core material could be collected for centrifugation. The remaining chalk was rinsed twice with distilled water and the bottles were then refilled with distilled water containing a tracer ($25 \text{ mg L}^{-1} \text{ Br}^-$ as KBr). Bottles were capped and left inverted in the dark at 4°C to equilibrate. Samples of the "equilibration" water were analyzed after 4 days.

Centrifugation Methodology. Samples of chalk from the equilibration bottles were centrifuged in 50 mL HDPE centrifuge tubes for 10 min at 8000 rpm. Whole core fragments were centrifuged, and the extracted water accumulated in a pad of glass fiber at the base of the tube. Water samples were recovered using a syringe from a fine PTFE tube that extended into the glass fiber pad. 0.6 mL samples for GC-MS analysis were immediately dispensed into 2 mL vials; samples for IC analysis were dispensed into 1 mL vials. All samples were analyzed within 24 h of collection using the methods previously described.

Results

Comparison of Interstitial Water Chemistry Sampled by DEE and Centrifugation. Solute concentrations obtained by DEE and centrifugation were compared with the "test" solution composition, with 100% ratio representing the composition of the test solution in contact with the chalk core after the initial 4-day equilibration period. The results are summarized in Table 1 and Figure 3. All solute concentrations are in mg L^{-1} .

Anion concentrations for the centrifuged samples are within 10% of the test solution. Recovery by DEE is within 10% of the test solution for Cl^- , NO_2^- , and NO_3^- . However, >140% SO_4^{2-} was recovered by DEE, consistent with SO_4^{2-} release from the matrix during equilibration (see Discussion).

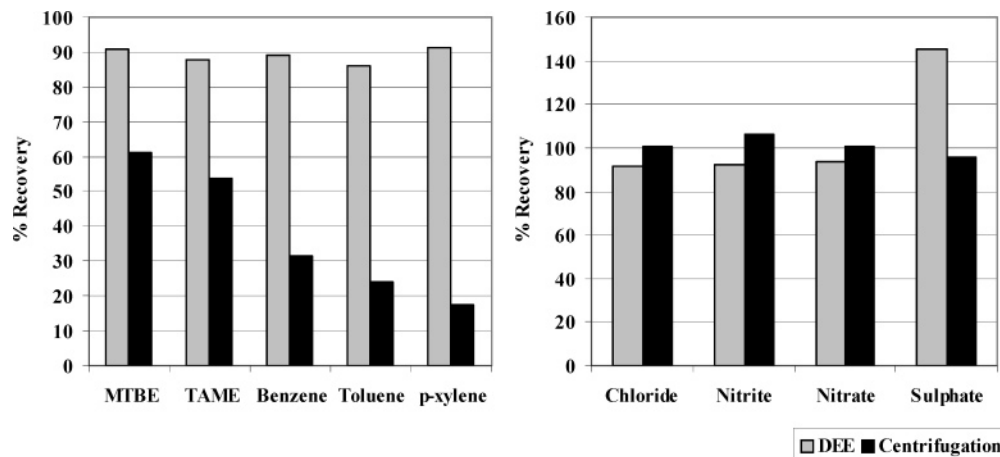


FIGURE 3. Recovery of analytes from interstitial water in chalk core material by DEE and centrifugation. Note that SO_4^{2-} recovery >140% indicates release of bound SO_4^{2-} during the equilibration procedure (see text for Discussion).

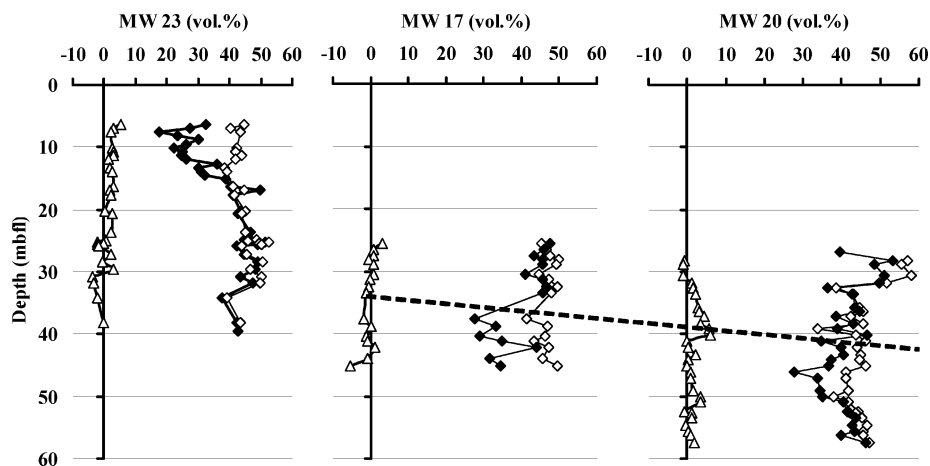


FIGURE 4. Profiles of air and water-filled porosity in rock core from petroleum hydrocarbon-contaminated Upper Chalk aquifer: plume source (MW23), plume (MW17), and downstream-untamated aquifer (MW20). The dashed line shows the inferred upper surface of a hardground. Symbols are as follows: vacuum-dried porosity, θ_w : (open diamond); tracer-determined porosity, θ_{Br^-} : (closed diamond); gas filled residual porosity, θ_G : (open triangle).

The mean of the triplicate extractions is close to the test solution for the centrifuged samples. Mean values by DEE are lower (except for SO_4^{2-}), which may be attributed to incomplete equilibration of the larger core fragments used in this experiment prior to analysis. The relative standard deviation of triplicate DEE experiments is excellent (<5%) and better than that for centrifugation.

The recovery of benzene, toluene, *p*-xylene, MTBE, and TAME is consistently around 90% by DEE, whereas the recovery of these compounds by centrifugation is 31%, 24%, 18%, 61%, and 52%, respectively (Figure 3). The recovery by centrifugation decreases with increasing hydrocarbon volatility, despite the centrifuge tubes being sealed during centrifugation. High recoveries of hydrocarbon compounds by DEE confirm that these fractions were not lost by volatilization. Minimal loss of volatiles also indicates that exposure to the atmosphere was minimized, thereby limiting the potential for sample oxidation. The test solution was pH 8, which increased to pH 8.5 in the equilibration water, indicating that pH buffering by the chalk was not significant.

Gas and Water-Filled Porosity Profiles for Chalk Core Samples. The determination of gas filled porosity (θ_G) and water filled porosity (θ_w , θ_{Br^-} , θ_{CP}) in aquifer materials using DEE was evaluated with core samples from the following locations and depths: MW23: unsaturated and saturated zone within plume source area, cored from 22 to 40 mbfl; MW17: saturated zone within mixed BTEX/MTBE/TAME plume 76 m downgradient of plume source, cored from 22 to 45 mbfl; MW20: saturated zone within uncontaminated aquifer 152 m downgradient of plume source, cored from 22 to 57 mbfl. Depths are given as meters below forecourt level (mbfl), using the elevation of MW23 as a datum. Profiles of porosity values determined by DEE and vacuum-drying of these core samples are shown in Figure 4. The gas-filled porosity (θ_G) for MW17 is within $\pm 3\%$ of zero, the average being $-0.28 \pm 0.88\%$ (95% confidence interval) for 16 core samples (effectively zero). A value of zero or close to zero is expected for θ_G in core from the saturated zone unless in situ gas production has occurred, the core sample includes the capillary fringe, or is close to the water table and is intermittently saturated. For MW23, θ_G has an average of $-0.61 \pm 1.08\%$ for 14 samples taken from the saturated zone (>22 mbfl), and $2.47 \pm 0.55\%$ (95% confidence interval) for 14 samples from the unsaturated zone (<22 mbfl). Higher values in the unsaturated zone indicate that small quantities of gas may be present, with this component accounting <6% of the total porosity.

Figure 4 also shows total rock porosity, θ_w (determined by vacuum-drying of core samples), and porosity accessed by the Br^- tracer, θ_{Br^-} (calculated using eq 9), for MW17, MW20, and MW23. The profiles diverge from 30 to 42 mbfl at MW17 and 40–50 mbfl at MW20, indicating that the tracer did not fully penetrate the core. These features are associated with a hardground in the Chalk aquifer at this site. The structural dip of this feature is evident across two of the profiles, which are located along the plume flowpath in the order they appear (Figure 4). Another divergence between total and tracer-derived porosity profiles occurs in the unsaturated zone at MW23 (6–15 mbfl). This is associated with calculated interstitial water BTEX concentrations which exceed solubility, consistent with the presence of free-phase in the core samples at this location. The presence of free-phase may prevent entry of the Br^- tracer, thereby reducing the apparent volume of the water-filled porosity measured by DEE.

Discussion

Practicality and Data Quality Control Provided by Extraction Method. The “standard” DEE method recommended for the extraction of interstitial water samples in consolidated rocks is summarized in Figure 5, which includes the relevant quality control procedures and measurements required to ensure reliability in the chemical data. The method presented is devised for onsite sample processing with subsequent laboratory analysis and has been verified with the results of the laboratory study. Alternative methods of onsite core cutting can be used, provided atmospheric exposure of samples is minimized. This method offers significant advantages in practical application and improvements in data quality, which cannot be easily achieved with conventional methods, such as centrifugation (1, 3) or squeezing (24, 25). The main sources of error when sampling interstitial water chemistry in sediment are sample contamination during core recovery, post-sampling compositional changes (including volatile and evaporative loss during fluid extraction), and compositional changes or evaporative loss during storage prior to chemical analysis (1). In anaerobic aquifers these errors can result in changes in the in situ redox state and distribution of redox-sensitive species, which compromises interpretation of the interstitial water chemistry. The DEE method minimizes or eliminates these problems and provides an estimate of their significance for chemical analyses of interstitial water samples. The use of a deoxygenated drilling fluid containing a tracer during core collection allows invasion

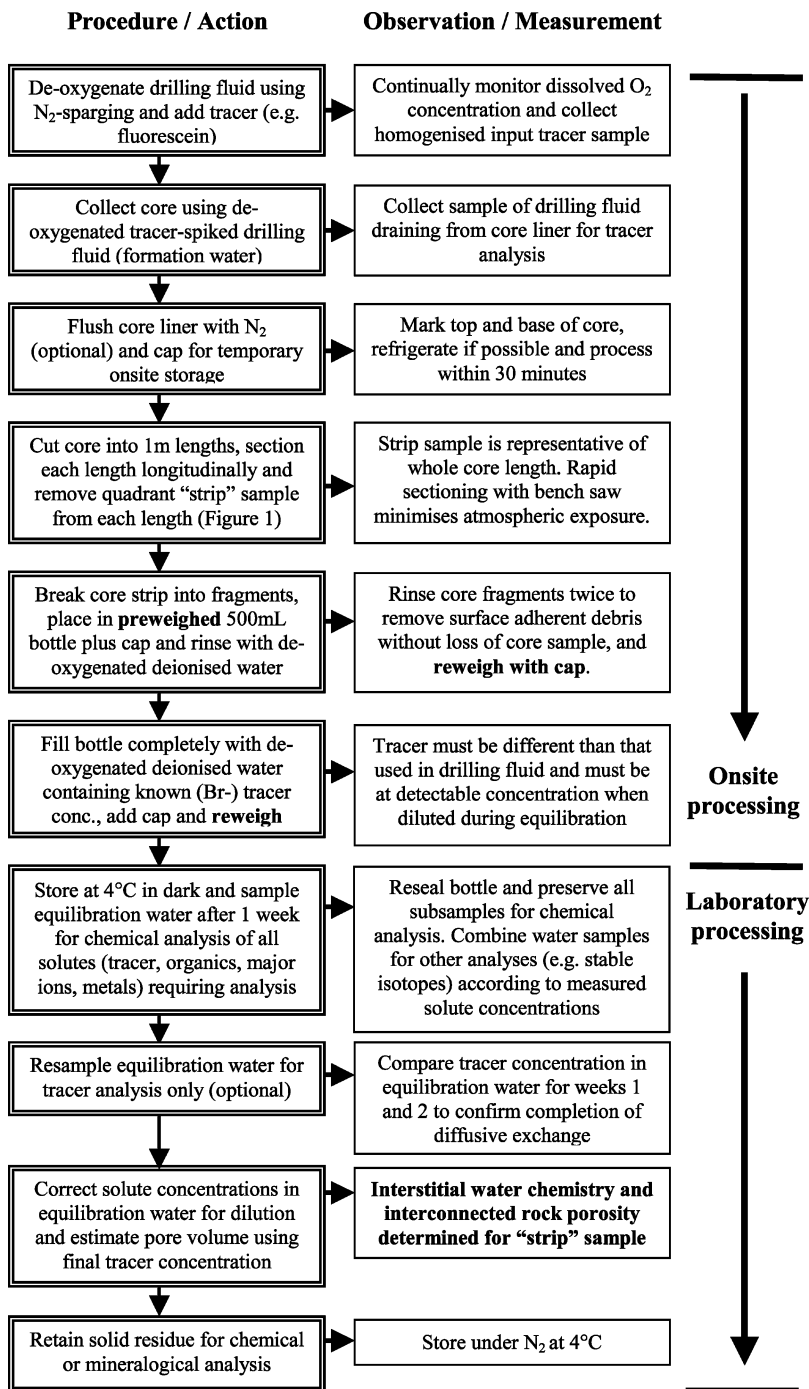


FIGURE 5. Procedure for extraction of interstitial water from consolidated sediment using DEE.

of the core by the drilling fluid to be assessed and provides an anaerobic flushing medium during the coring process. In turn, chemical analyses of interstitial water samples can be corrected for contamination by the drilling fluid, and oxidation of redox-sensitive species (including dissolved and solid-phase components) is minimized during coring. These errors will vary according to the lithology being cored and are likely to be more significant for anaerobic cores collected in coarse-grained, highly permeable strata. Previous studies show that contamination of interstitial water samples by water-based drilling fluids is more extensive and frequent in sandstone cores than Chalk cores, even after removal of the outer 2 cm of a 10 cm diameter core sample (1). In this study, fluorescein tracer was only detected in two Chalk core equilibration samples, indicating minimal contamination with drilling fluid. This is partly due to the collection of a thin

sample strip from the center of the core, which removes the potentially contaminated outer layer.

Post-sampling changes in interstitial water chemistry include artifacts from warming and atmospheric exposure of samples during extraction. This occurs during centrifugation unless the extraction is performed under temperature controlled conditions in an inert atmosphere (1, 3, 15). Ideally, interstitial water should be sampled as soon as possible after core collection to minimize chemical changes (11). In this study, core samples were either processed immediately after collection or temporarily stored in an onsite cool store but with a maximum processing time of 30 min recommended by other workers (1). The interstitial water samples were also stored at 4 °C for the duration of the extraction after addition of the equilibration water. Post-sampling oxidation of interstitial water samples is a key problem overcome by the

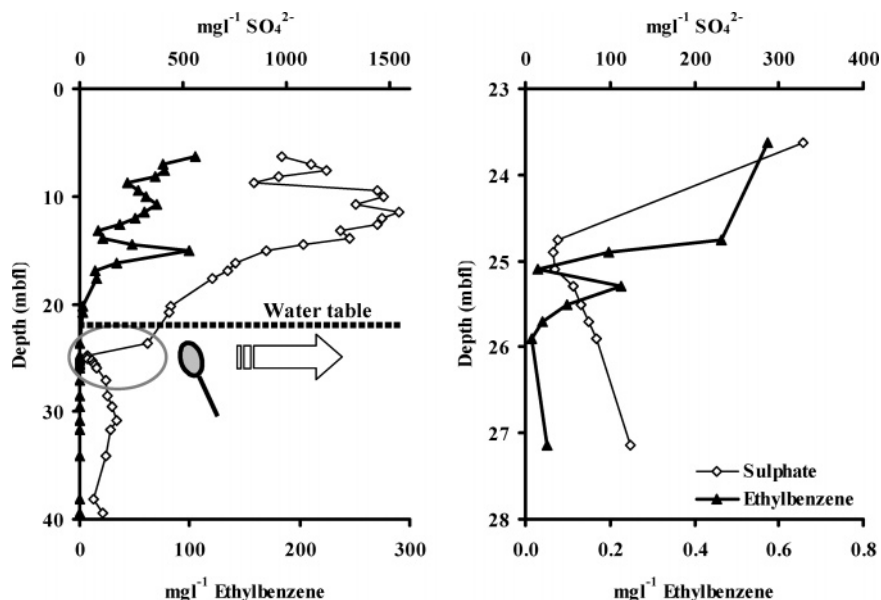


FIGURE 6. Profiles of matrix interstitial water chemistry from different locations in petroleum hydrocarbon-contaminated Upper Chalk aquifer, showing higher resolution sampling in zones of bacterial SO_4^{2-} -reduction (right-hand image).

DEE method. Core samples are maintained anaerobic in N_2 -flushed, sealed core liners onsite or a glovebag until processing and then sealed in glass bottles containing deoxygenated equilibration water. Loss of dissolved volatile components (e.g. gases and organic compounds) into the headspace cannot be avoided during centrifuge extraction of interstitial waters (11). This problem is avoided using the DEE method, by elimination of the headspace volume with the equilibration water, as demonstrated in the laboratory experiment using the test interstitial water solution (Figure 3). Furthermore, centrifugation may cause chemical fractionation of interstitial water composition (1). This is a function of the fluid volume recovered, producing nonrepresentative interstitial water compositions (1). This fractionation does not occur with the DEE method, as full recovery of the interstitial water is achieved by equilibration through diffusion (independently confirmed from the periodic Br^- tracer analysis).

Data Resolution Provided by Extraction Method. Quantitative recovery of interstitial water is seldom possible by centrifugation, and so the volume of interstitial water collected from consolidated sediments usually limits the number and type of chemical analyses that can be performed (1). This is a particular problem for coarse sediments (e.g. sands and sandstone), which may have naturally low interstitial water content, and also very fine-grained but highly porous materials (e.g. Chalk), where capillary forces may trap the interstitial water. Many key chemical analyses, such as stable isotope distributions (commonly used in studies of natural processes or contaminant degradation), need relatively large aqueous samples for analysis. This means that samples extracted by centrifugation may have to be combined to provide sufficient interstitial water for analysis. These practical limitations restrict the scope of investigation, resolution of in situ processes, and detail of interpretation that can be achieved from interstitial water samples recovered by centrifugation.

Many of these problems are avoided or minimized by the DEE method, with a significant improvement in data resolution. A representative interstitial water sample is obtained using the "strip" sampling technique included in the DEE method. The length of the strip sample and hence desired data resolution can be adjusted to suit individual study objectives, but in all cases, this technique provides a continuous profile of interstitial water chemistry, subject to

core recovery. It ensures that the full core length is sampled and that particular horizons are not missed in the sampling process, unless this is desired. Localized zones of bacterial SO_4^{2-} -reduction in the Upper Chalk aquifer were profiled at high resolution by processing the core into 20 cm strip samples. Figure 6 shows profiles of ethylbenzene and SO_4^{2-} through the unsaturated and saturated zone at MW23 in the contaminant plume source, including a data subset from the SO_4^{2-} -reducing zone sampled at higher resolution. The detailed sampling demonstrates the absence of steep SO_4^{2-} -concentration gradients close to the zone of SO_4^{2-} -reduction. This confirms that a coarser core sampling resolution (1 m) is appropriate for the purposes of this study. Alternatively, conventional sampling of cores in a series of discrete slices along the core length can be undertaken, although this will produce data gaps in the final interstitial water chemical profile. With DEE, the data resolution will only be limited by the quality of core recovery and sampling frequency over the drilled interval. Each 600 mL sample bottle provides ~300 mL equilibration water for chemical analysis, which is adequate for a wide range of conventional analytical methods. An initial analysis of the interstitial water chemistry will determine if enough mass is available for stable isotope analysis and indicate if successive samples must be combined for this purpose.

Application of the Extraction Method. Analyte recovery data from the chalk core equilibration experiment indicates that the DEE method provides significantly improved data quality compared with centrifugation, but without the practical problems and potential sampling artifacts of centrifugation. Atmospheric exposure of hydrocarbon-contaminated chalk during centrifugation resulted in up to 80% loss by volatilization of some hydrocarbon compounds from the interstitial water (Figure 4), which was avoided using the DEE method. An appropriate application of the DEE method is the sampling of interstitial water chemistry in anaerobic contaminated aquifers, as illustrated by the study of the petroleum hydrocarbon plume in the Upper Chalk aquifer. In this case, the DEE method provided unique advantages over all other interstitial water extraction procedures available for consolidated sediments. It can also be used (with similar advantages in data quality over centrifugation) for interstitial water studies in aerobic aquifers.

TABLE 2. Saturation Indices for Mineral Phases in Test Solution and Equilibration Water, Modeled Using PHREEQC

mineral phase	saturation indices	
	test solution ^a	equilibration water ^b
anhydrite	-1.69	-2.43
aragonite	-0.29	-0.25
calcite	-0.14	-0.10
dolomite	-1.01	-1.06
gypsum	-1.46	-2.20

^a Modeled mineral equilibria in the "test" solution in contact with the Chalk core samples after the initial 4-day equilibration. ^b Modeled mineral equilibria in "equilibration" water after recovery of the "test" solution by DEE (see text for discussion).

The DEE method is suitable for sampling interstitial water in consolidated rocks and aquifers in which target analytes are not affected significantly by sorption to the rock matrix. This will usually be satisfactory for the analysis of relatively mobile organic compounds in contaminated aquifers, which typically have a low (<0.1 wt %) particulate organic carbon content. Alternative methods are available to sample interstitial water chemistry in soils (12, 15), where sorption of organics analytes may be important. The application of DEE may be limited where addition of equilibration water affects the interstitial water-sediment ion-exchange equilibrium or causes dissolution of soluble mineral phases containing the target analytes. If ion-exchange processes are of interest, then interstitial water extraction by squeezing methods developed for consolidated sediment applications may be more appropriate (24, 25). Laboratory equilibration experiments simulating interstitial water extraction, such as those undertaken in this study, can be useful in identifying any changes in solute chemistry that may affect the application of the DEE method. In the laboratory study the recovery of SO₄²⁻ by DEE exceeded 100% of the target concentration. Pyrite or other iron sulfide compounds are not present in these core samples, and geochemical modeling using PHREEQC indicates that the test and equilibration solutions are significantly undersaturated with respect to anhydrite (S.I. of -1.7 to -2.4) and gypsum (S.I. of -1.5 to -2.2) (Table 2). This implies that excess SO₄²⁻ recovered in the equilibration water by DEE cannot arise from dissolution of S-bearing mineral phases in the core samples. Other studies have shown that SO₄²⁻ may be adsorbed onto calcite surfaces and that this adsorption decreases at alkaline pH due to competition with CO₃²⁻ ions (35). The modest pH change from 8 to 8.5 observed in the equilibration water during the laboratory experiment may have contributed to release of SO₄²⁻ from the aquifer matrix. A detailed interpretation of this behavior is beyond the scope of this study, but the result is important as it suggests that more SO₄²⁻ is available in the aquifer matrix than is recovered by centrifugation, despite the absence of S-bearing minerals in this part of the aquifer.

The DEE method offers significant advantages over centrifugation; these include practicality of use (simplified onsite core processing and sample handling), minimization of sampling artifacts, and improvement in data resolution. In turn, it provides a better understanding and interpretation of in situ solute distributions and geochemical processes. The DEE method yields high quality data and allows reliable sampling of dissolved volatile organic contaminants and redox-sensitive species, which would be difficult to achieve by centrifugation. The DEE method is currently being used to interpret matrix-fracture solute exchange, contaminant-electron acceptor mixing at plume fringes, contaminant degradation, and the reactive properties of aquifer materials in natural attenuation studies.

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