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Modelling surface NMR spin-echo experiments in a heterogeneous B_1 field

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SUMMARY

Surface nuclear magnetic resonance (NMR) measurements show great promise for characterization of subsurface water content, pore-sizes and permeability. The link between surface NMR and pore-size/permeability is founded in the connection between the NMR signal's time dependence and the geometry of the pore-space. To strengthen links between the NMR signal and pore-geometry multipulse surface NMR sequences have been developed to estimate the parameter T_2 , which carries a strong link to pore-geometry and has formed the basis for NMR-based permeability estimation in the petroleum industry for decades. Producing reliable subsurface characterizations from multipulse surface NMR measurements that measure T_2 requires that the forward model is able to accurately predict the transverse magnetization at the time when the measurement occurs. Traditional surface NMR T_2 forward models employ an analytic expression for the transverse magnetization, an expression developed in the context of laboratory NMR experiments conducted under conditions significantly different from surface NMR and which require several assumptions to simplify the underlying Bloch equation. To investigate the reliability of this analytic expression under surface NMR conditions, a synthetic comparison is performed where the analytic expression is contrasted against the transverse magnetization predicted from a solution of the full-Bloch equation without the same simplifying assumptions and which can appropriately weight heterogeneity in the applied and background magnetic fields. The comparison shows that the analytic expression breaks down in a range of conditions typical to surface NMR measurements.

Key words: Hydrogeophysics; Numerical approximations and analysis; Permeability and porosity.

INTRODUCTION

Surface nuclear magnetic resonance (NMR) is a non-invasive technique that measures the properties of a magnetization at depth, which originates from the immersion of water molecules within the Earth's magnetic field (Legchenko & Valla 2002). Two attractive features of the surface NMR method are its direct sensitivity to water content and its potential to make quantitative estimates of pore-size and permeability (Schirov *et al.* 1991; Mohnke & Yaramanci 2008). Direct sensitivity to water content stems from the fact that the amplitude of the measured magnetization is related to the quantity of water within the sensitive volume of the measurement (Hertrich 2008). Links to pore size and permeability stem from a dependence of the NMR signal's duration on the geometry of the pore space (Brownstein & Tarr 1979). The relation between the parameters governing the signal's time dependence, which are called relaxation times, and the pore geometry allow empirical equations to be developed to make quantitative pore size and permeability estimates (Kenyon *et al.* 1988; Howard & Kenyon 1992).

The staple surface NMR measurement, which is performed using the Earth's magnetic field as the background magnetic field (B_0), is called a free-induction decay (FID). An FID consists of measuring the NMR signal following a single excitation pulse. The time-dependence of the signal in this case is governed by the effective transverse relaxation time T_2^* . The challenge is that there exists an inherent uncertainty about which relaxation mechanism controls T_2^* (Grunewald & Knight 2011). In some cases, T_2^* is closely linked to a related parameter called the transverse relaxation rate T_2 , in which case T_2^* carries strong ties to pore geometry. In other cases, T_2^* can be strongly impacted by the presence of background magnetic field inhomogeneity that obscures the link to pore-geometry. The difficulty is that one cannot typically determine which scenario is present, resulting in large uncertainties in estimated pore-sizes/permeabilities and lithology estimates. As such, several recent works have aimed to develop surface NMR transmit schemes focused on measurements of the relaxation times T_2 (Shushakov 1996; Legchenko *et al.* 2010; Grunewald & Walsh 2013; Grunewald *et al.* 2014) and T_1 (Legchenko *et al.* 2004;

Walbrecker *et al.* 2011a; Muller-Petke *et al.* 2013), which carry more direct links to pore geometry. In this work, we focus on measurement of T_2 .

Schemes to measure T_2 require the use of measurements that employ multiple pulses, in contrast to the FID scheme that uses a single pulse. Two approaches have been proposed for T_2 measurement in surface NMR. The first, called spin-echoes, involves measuring the amplitude of an echo—a signal produced by a pulse sequence consisting of two pulses where the second pulse occurs a time t_d after the first pulse, and has twice the strength of the first pulse (Hahn 1950) (which typically corresponds to a pulse of equal peak current amplitude and twice the duration). The amplitude of the echo is measured for multiple times t_d in order to sample a decay whose time-dependence is governed by T_2 . An alternative approach called a multi-echo acquisition, which is an approximation of the CPMG sequence (Carr & Purcell 1954; Meiboom & Gill 1958), involves the use of many pulses (typically <6 in surface NMR) in order to measure multiple echoes within a single acquisition (Grunewald & Walsh 2013). This allows multiple points of the decay to be sampled at once and greatly reduces acquisition times in the field.

Regardless of the pulse sequence employed, a surface NMR T_2 measurement involves repeating the sequence for variable peak current amplitudes. Manipulating the peak current amplitude alters the spatial origin of the observed signals and is critical to encoding information about the spatial variability of subsurface parameters into the measured data cube. This allows an inversion to be used to estimate depth profiles of water content and the relevant relaxation times. A key component of producing reliable images of subsurface properties is that the behavior of the magnetization during the experiment is modelled accurately (Grombacher *et al.* 2017). This requires predicting the magnitude of the transverse magnetization at each location in the subsurface at the times when the measurement occurs—at the peak of the spin-echo or spin-echoes for T_2 measurements. In the following, we consider only two-pulse spin-echo experiments in order to simplify the discussion.

Previous surface NMR spin-echo measurements have predicted the transverse magnetization at each location in the subsurface using an analytic expression. This expression was developed within the context of laboratory NMR applications where pulses can be tailored to produce specific manipulations of the magnetization (Bloom 1955). In the lab precise 90° or 180° rotations can be produced within the entire sensitive volume of the measurement depending on intended function of the pulse. The difference between the conditions under which these expressions were derived and surface NMR conditions is that the surface NMR experiment employs an extremely heterogeneous applied magnetic field (B_1) that spans multiple orders of magnitude in strength and uses long pulse durations compared to laboratory conditions. In the weak- B_1 /long-pulse limit, off-resonance effects can become significant (Walbrecker *et al.* 2011b). These effects have been demonstrated to significantly perturb single pulse surface NMR experiments (Grombacher & Knight 2015). Strong heterogeneity in B_1 and B_0 also affects multipulse experiments such as logging-based CPMG measurements (Hürlimann & Griffin 2000) and saturation-recovery measurements (Duan *et al.* 2017). As such, it is imperative to ensure that the currently used analytic expressions for spin-echoes can be extended to surface NMR conditions. In the following we investigate the ability of the analytic expressions to reproduce the results based on a solution of the Bloch equation, where B_1 amplitudes, off-resonance effects and relaxation are directly accounted for during the solution for the transverse magnetization. The results of the Bloch solved

transverse magnetization are contrasted against the analytic expressions to investigate the reliability of this expression under surface NMR conditions.

BACKGROUND

Modelling the transverse magnetization

Of critical importance to the surface NMR forward model is the ability to accurately predict the transverse magnetization at each location in the subsurface. The value of the transverse magnetization immediately following the single excitation pulse is needed for modelling of free-induction decay measurements, while two-pulse spin-echo measurements require the value of the transverse magnetization at the time when the echo forms. Predicting the transverse magnetization requires solving the Bloch equation, which describes the behavior of the magnetization during the course of the NMR experiment (Bloch 1946).

$$\frac{\partial \mathbf{M}}{\partial t} = \gamma \mathbf{M} \times \mathbf{B}_{\text{eff}} - \frac{M_x + M_y}{T_2} - \frac{M_z - M_0}{T_1} \quad (1)$$

γ is the gyromagnetic ratio of the hydrogen nuclei. Note that $\mathbf{M}$ and $\mathbf{B}_{\text{eff}}$ are both functions of time. M_x , M_y and M_z are the x-, y- and z-components of $\mathbf{M}$. In this work we consider the solution of the Bloch equation in the rotating reference frame, a frame which rotates at the instantaneous transmit frequency. In this case, the $\mathbf{B}_{\text{eff}}$ field is given by

$$\mathbf{B}_{\text{eff}} = \begin{bmatrix} B_{1x} \\ B_{1y} \\ (\omega_0 - \omega_t)/\gamma \end{bmatrix} \quad (2)$$

and describes the effective magnetic field responsible for perturbing the magnetization. The B_1 terms represent the magnitude of the applied corotating magnetic field and are oriented in the x - y plane. In the following, a pulse with B_1 oriented along x is referred to as having a phase of 0, while a pulse with B_1 along the y -axis is referred to as having a phase of $\pi/2$. In the presence of an offset between the transmit (ω_t) and Larmor frequency (ω_0) the magnetization will precess about the z -direction in the rotating frame at a rate determined by the magnitude of the offset. This precession can be described by including a z -component B_z into the effective magnetic field, where $B_z = \Delta\omega/\gamma$ and $\Delta\omega = \omega_0 - \omega_t$. The last two terms in eq. (1) are called the relaxation terms, and act to return the magnetization to equilibrium following perturbation. T_2 and T_1 are termed the transverse relaxation time and the longitudinal relaxation time, respectively. In this work we set T_1 equal to T_2 in order to reduce the dimensionality of the following analysis. In practice, T_1 is typically within one to three times the magnitude of T_2 (Kleinberg *et al.* 1993).

To determine the transverse magnetization at a time t' [i.e. the x - and y -components of $\mathbf{M}(t')$], eq. (1) is solved from $t = 0$ until $t = t'$ given an initial condition describing a unit magnetization at equilibrium $\mathbf{M}_0$ (represented numerically as a 3 by 1 unit vector oriented in z -direction).

Many approaches may be used to solve eq. (1). A first approach is to seek a solution in the no-relaxation limit, a simplification allowing analytic solutions to be found in certain cases. A second approach is to solve the full equation, which can be done using a variety of solvers. In this work we use a 4th-order Runge–Kutta solver when solving eq. (1). This approach is a time stepping algorithm that predicts the magnetization at a time t_{i+1} given the known magnetization at time t_i and a change in the magnetization described

by eq. (1). Once t_{i+1} is known, the process can be repeated to predict t_{i+2} and so on.

Note that eqs. (1) and (2) correspond to a single Larmor frequency. If an inhomogeneous B_0 field is present, it leads to the measurement of a signal with multiple Larmor frequency components. One approach to model the transverse magnetization in this multiple Larmor frequency scenario is to consider the static dephasing limit (Hürlimann 1998). This limit describes the scenario where the diffusion length of the water molecule (during the time when the equation is being solved) is less than the scale of B_0 heterogeneity; that is, the magnetization associated with each Larmor frequency component experiences a single B_0 throughout the measurement. In this case, the net magnetization $\mathbf{M}$ can be calculated from the weighted sum of the magnetizations corresponding to each individual Larmor frequency component $\mathbf{M}_j$.

$$\mathbf{M} = \sum_j A_j \mathbf{M}_j \quad (3)$$

A_j represents the relative abundance of the j th Larmor frequency, and the sum of all A_j equals 1. Each $\mathbf{M}_j$ is found by solving eq. (1) with the relevant $\mathbf{B}_{\text{eff}}$. We consider the static dephasing limit in the following.

The no relaxation limit

A first approach to solve eq. (1) is to consider the no-relaxation limit, where the relaxation terms are neglected and only the cross-product term remains on the right-hand side of eq. (1). In this limit, if $\mathbf{B}_{\text{eff}}$ is constant over a time period τ , the perturbation of $\mathbf{M}$ over this time period can be described by a rotation about the $\mathbf{B}_{\text{eff}}$ axis through an angle ϕ_{eff} , which is determined by the magnitude of $\mathbf{B}_{\text{eff}}$ and τ (Mansfield *et al.* 1979).

$$\phi_{\text{eff}} = \gamma \tau \sqrt{B_{1x}^2 + B_{1y}^2 + B_z^2} \quad (4)$$

The rotation $\mathbf{R}_{\mathbf{B}_{\text{eff}}}(\phi_{\text{eff}})$ can be described using a 3 by 3 matrix that acts to rotate a 3 by 1 vector through an angle ϕ_{eff} about the $\mathbf{B}_{\text{eff}}$ direction (Mansfield *et al.* 1979). An alternative but equivalent solution involves a spinor representation, which simplifies the solution by considering 2 by 2 spinor matrices in place of 3 by 3 rotation matrices (Jaynes 1955). In both schemes one must define the orientation of the $\mathbf{B}_{\text{eff}}$ axis, which can be done using an angle α where the $\mathbf{B}_{\text{eff}}$ field forms an angle α with respect to the x-y plane.

$$\tan(\alpha) = \frac{\gamma B_1}{\Delta\omega} \quad (5)$$

Further details surrounding the rotation matrix and spinor representation approaches to solving the Bloch equation in the no-relaxation limit can be found in Mansfield *et al.* (1979) and Jaynes (1955), respectively.

To predict the magnetization at a time t using the rotation matrix or spinor approaches involves discretizing the measurement into segments where $\mathbf{B}_{\text{eff}}$ is constant. Fig. 1 illustrates three examples. For the single pulse constant ω_t experiment (Fig. 1A), the magnetization at the end of the pulse (at the time marked by the x on the time axis) can be estimated using a single rotation matrix or spinor. This corresponds to advancing the magnetization from time 0 (start of pulse) to the end of pulse (dashed vertical line) using a single rotation. For a single pulse variable ω_t experiment, (Fig. 1B) such as an adiabatic half-passage pulse (Tannus & Garwood 1997), the pulse is discretized into many segments where the transmit frequency (and therefore $\mathbf{B}_{\text{eff}}$) can be assumed to be constant over the segment. The

Figure 1. Schematic illustration of three surface NMR acquisition schemes—(a) a single pulse described by a fixed transmit frequency, (b) a single pulse described by a variable transmit frequency and (c) a two-pulse experiment described by two fixed transmit frequency pulses separated by a delay time t_d (i.e. t_d is the time between the two left-most vertical dashed lines in C). Black solid lines indicate whether B_1 is present (On) or not (Off), while x's indicate the time at which an estimate of the transverse magnetization is desired.

magnetization at the end of the pulse (at the time marked by the x) can then be estimated by applying a series of rotation matrices or spinors. Each rotation or spinor advances the magnetization from the state at the beginning of the time segment to its state at the end of the time segment (i.e. from one dashed line to the next dashed line in Fig. 1B). For a two pulse constant ω_t experiment (Fig. 1C), such as a spin-echo experiment, the magnetization at the time when an echo forms (marked by the x) can be estimated by applying four rotation matrices or spinors. The first, second, third and fourth rotations advance the magnetization to its state at the end of pulse 1, the end of the delay first time, the end of pulse 2 and the time when the echo forms, respectively. The Runge–Kutta solution used in this work is similar to the approach shown for the single pulse variable ω_t in Fig. 1(B), where small time steps (20 μs steps in this work) are taken over which $\mathbf{B}_{\text{eff}}$ is assumed to be constant. Larger time steps ($>20 \mu\text{s}$) were observed to lead to instability in the large B_1 limit.

Previous modelling of the spin-echo amplitude in surface NMR

Previous surface NMR spin-echo studies have predicted the transverse magnetization at the time the echo forms using an analytic expression given by

$$m_{\perp} = \sin(\gamma B_1 \tau_1) \sin^2(\gamma B_1 \tau_2/2), \quad (6A)$$

or

$$m_{\perp} = \sin^3(\gamma B_1 \tau_1) \quad (6B)$$

In eq. (6A), τ_1 and τ_2 are the length of the first and second pulses, respectively. Both pulses are of equal peak current amplitude. eq. (6A) reduces to (6B) in the case where $\tau_2 = 2\tau_1$. eq. (6A) is derived using the approach Bloom (1955) used to arrive at eq. (15) in his manuscript. This involves solving for the transverse magnetization at the time when the echo forms using a set of four rotations; Bloom (1955) used the spinor representation. This echo scenario is the same as the two-pulse scenario illustrated in Fig. 1, where the second pulse is separated from the first by a delay time

t_d , and the echo forms a time t_d after the end of the second pulse. To form the analytic expression given in eq. (6) requires imposing two assumptions (Bloom 1955),

- 1) a near-resonance condition and
- 2) that terms carrying a negative time dependence with respect to the first delay time may be neglected.

The near-resonance condition assumes that $\mathbf{B}_{\text{eff}} \sim \mathbf{B}_1$, which requires that $\alpha \sim 0$ (equivalent to $\mathbf{B}_{\text{eff}}$ lying in the x - y plane). The terms carrying a negative time dependence with respect to the first pulse (referred to in the following as b), are given by

$$b = \sum_j A_j e^{-i\Delta\omega_j t_d}. \quad (7)$$

eq. (7) sums over all Larmor frequency components, where the contribution of the j th Larmor frequency is weighted by its relative abundance A_j and its phase developed over the delay time t_d .

The advantage of these assumptions is that the transverse magnetization at the time when the echo forms, $\mathbf{M}_{\text{echo}}$, is described by a compact analytic expression dependent on only the local magnitude of $\mathbf{B}_1$ and the duration of the two pulses. This equation does not require one to specify the extent of B_0 heterogeneity (i.e. to define the A_j values for each Larmor frequency component) and does not depend on any relaxation time values (T_2^* or T_2 or T_1). The lack of relaxation time dependence allows the surface NMR inversion to be linearized, requiring only a single kernel calculation for each inversion, greatly accelerating inversion times. However, eq. (6A) was originally proposed under very different conditions than those present in the surface NMR experiment. Bloom (1955) considered laboratory NMR conditions, where one typically has more homogeneity in B_1 , works at different B_1 strengths, and deals with very different magnitudes of background magnetic field (B_0) heterogeneity (because laboratory NMR measurements often are performed at much larger magnitude B_0 compared to surface NMR). Given the magnitude of these differences, it is imperative to evaluate whether the echo amplitude described by eq. (6), and the applicability of these two assumptions, remain valid under conditions representative of that expected in a surface NMR experiment.

RESULTS

Evaluating the near-resonance criteria

Two factors determine if the near-resonance condition is satisfied (i.e. if $\alpha \sim 0$). The first is the magnitude of the offset (which controls B_z in eq. 2) and the second is the magnitude of B_1 . To define a plausible range of offsets in surface NMR one can consider the range of typical T_2^* that may be encountered, which often range from 20 to 500 ms in magnitude (Schirov *et al.* 1991). These values represent fast and slow decays, respectively. Fig. 2(A) illustrates the Larmor frequency distributions associated with $T_{2\text{IH}}$ values that span the same range, from 20 ms (red) to 500 ms (purple); $T_{2\text{IH}}^{-1} = T_2^{*-1} - T_2^{-1}$. $T_{2\text{IH}}$ is a parameter describing signal loss due to dephasing in an inhomogeneous B_0 field, where $T_{2\text{IH}}$ and T_2 combine in parallel to form T_2^* (Grunewald & Knight 2011). Small $T_{2\text{IH}}$ correspond to wide distributions, while large $T_{2\text{IH}}$ correspond to narrow distributions. Each distribution is normalized by its peak amplitude to emphasize width variations. The width of the Larmor frequency distribution is approximated from $T_{2\text{IH}}$ by calculating the Lorentzian whose width corresponds to exponential decay controlled by $T_{2\text{IH}}$ (Sukstanskii & Yablonskii 2001; Chen *et al.* 2005; Grunewald &

Figure 2. a) Peak-normalized Larmor frequency distributions for a range of different $T_{2\text{IH}}$ values (u). $T_{2\text{IH}}$ varies from 20 ms (red) to 500 ms (purple) in steps of ~ 50 ms. (b) Black, blue, and red curves illustrate the offset at which more than 25, 50 and 75 per cent of the Larmor frequency distribution lies at larger offsets for a range of $T_{2\text{IH}}$ values.

Knight 2012), as an exponential decay in the time-domain corresponds to a Lorentzian distribution in the frequency-domain. To further emphasize the widths of each distribution, Fig. 2B illustrates the 25th (black), 50th (blue) and 75th (red) percentiles as a function of $T_{2\text{IH}}$. The 25th percentile corresponds to the value at which 25 per cent of the distribution lies at larger offsets, and equivalent for the 50th and 75th percentiles. As a reference, for $T_{2\text{IH}}$ equal to 200 ms more than 25 per cent of the distribution will correspond to offsets larger than 2 Hz (black circle), while for $T_{2\text{IH}}$ equal to 100 ms more than 25 per cent of the distribution has offsets larger than 4 Hz (black cross). Overall, Fig. 2(B) indicates that it is likely to encounter offsets on the order of several Hz in non-negligible proportions in many scenarios. Of importance is whether these offsets constitute a violation of the near-resonance condition.

Consider next the role that $\mathbf{B}_1$ plays in the near-resonance condition, as $\mathbf{B}_1$ also affects α . In surface NMR, $\mathbf{B}_1$ is extremely heterogeneous and varies by several orders of magnitude. As such, an offset may satisfy the near-resonance condition over a certain range of $\mathbf{B}_1$ amplitudes but not in others. Fig. 3(A) illustrates the offsets that correspond to α of $\pi/4$ (black, $B_z = B_1$ scenario), $\pi/6$ (blue) and $\pi/12$ (red); each of which represent violations of the near-resonance condition to varying extents. As reference, a 40 ms on-resonance pulse produces a $\pi/2$ rotation at B_1 of $\sim 1.5 \times 10^{-7}$ T; much of the surface NMR signal originates from B_1 greater than $\sim 1 \times 10^{-8}$ T, which can be seen from the $m_{\perp}$ curves discussed in Grombacher *et al.* (2017). The B_1 range investigated in Fig. 3 corresponds to the typical range of B_1 present at depth in a surface NMR experiment. At weak B_1 very small offsets lead to large α , observed by noting that the red, blue, and black profiles converge to 0 in the low B_1 limit. At strong B_1 the offset required to produce large α quickly increases, indicating that much larger offsets are required to break the near-resonance condition at strong B_1 . At $B_1 = 1 \times 10^{-7}$ T, offsets of 4.4, 2.2 and 1.1 Hz lead to α of $\pi/4$, $\pi/6$ and $\pi/12$, respectively. Overall, Fig. 3A indicates that offsets present in significant portions (e.g. the 25 per cent of offsets greater than approximately 4 Hz for $T_{2\text{IH}} = 100$ ms) may

Figure 3. (a) Black, blue, and red curves illustrate the offset required to produce a $\mathbf{B}_{\text{eff}}$ vector that is orientated at an angle of $\pi/4$, $\pi/6$ and $\pi/12$ above the transverse plane, respectively, for a range of B_1 values. At B_1 larger than 10^{-6} the curves extend above the shown offset range. (b) Curves showing the cumulative percentage of the Larmor frequency distribution that corresponds to $\alpha < \pi/12$ for a range of different T_{2IH} values (colours) over a range of B_1 amplitudes.

lead to significant deviations from the near-resonance criteria over a wide range of B_1 typical in surface NMR.

To further investigate the range of conditions that may lead to violations of the near-resonance condition consider Fig. 3(b), which illustrates the proportion of the Larmor frequency distribution that has $\alpha < \pi/12$ for a range of different T_{2IH} (colours). Values of 100 per cent indicate that the entire distribution corresponds to $\alpha < \pi/12$ (approximating the near-resonance criteria well), while values of 0 per cent indicate that the entire distribution corresponds to $\alpha > \pi/12$ (i.e. a strong violation of the near-resonance condition). For large T_{2IH} (purple, narrow B_0 distributions) the proportion curves approach 100 per cent more rapidly at smaller B_1 , with the $T_{2IH} = 500$ ms curve attaining a value of 92 per cent at $B_1 \sim 1\text{E-}7$ T. For smaller T_{2IH} significant portions of the B_0 distribution still correspond to $\alpha > \pi/12$ over a B_1 range that significantly contributes to surface NMR signals. For example, for T_{2IH} of 150 ms (light green) only 75 per cent of the distribution has $\alpha < \pi/12$ at $B_1 = 1\text{E-}7$ T. Overall, the lack of convergence to a value of 100 per cent over the B_1 range where much of the NMR signal originates from suggests that conditions violating the near-resonance condition will be encountered in surface NMR.

Magnitude of the term carrying a negative time dependence with respect to the first delay time

To evaluate the term carrying a negative time dependence with respect to the first delay time (eq. 7) the contributions of each offset must be weighted appropriately based on its abundance and the total magnitude determined by summing all individual components. For this term to be negligible, it must be approximately equal to 0. Neglecting this term stems from an expectation that the B_0 inhomogeneity and typical delay times are enough to lead to strong dephasing (i.e. destructive interference) that causes this term to be negligible. During the delay times each offset accumulates a phase,

Figure 4. Black, blue and red curves indicate the value of the b term, the term carrying a negative time dependence with respect to the first delay time that is neglected when forming eq. (6), for a range of different T_{2IH} values and three different delay times (colours).

where the relative phases between offsets increase for longer delay times. Fig. 4 illustrates the magnitude of the b term for several area-normalized Larmor frequency distributions that correspond to a range of T_{2IH} spanning from 20 ms to 2 s and three different delay times [100 ms (black), 200 ms (blue) and 300 ms (red)]. As T_{2IH} decreases (i.e. wider Larmor frequency distributions) the b term approaches 0. In this limit, strong dephasing results in incoherence that reduces the magnitude of the b term following summation. In contrast, when T_{2IH} increases (narrower B_0 distributions) the b term approaches 1. This results from improved coherence that limits destructive interference. Note also that as the delay time increases (black to red) the range of T_{2IH} where the b term is approximately 0 increases to larger T_{2IH} . Overall, the term carrying a negative time dependence with respect to the first delay time does not appear to be negligibly small for the full range of conditions likely to be encountered in surface NMR, particularly in the large T_{2IH} limit (e.g. $T_{2IH} > \sim 100$ ms). However, at small T_{2IH} and longer delay times this term becomes negligibly small.

Note that assumption 2 (i.e. that the term carrying the negative time dependence with respect to the first delay time is negligible) breaks down in the opposite limit as assumption 1 (i.e. the near-resonance condition). For large T_{2IH} the b term is non-negligible (i.e. the second assumption is violated), while small T_{2IH} (and their corresponding wide Larmor frequency distributions) strongly violate the near-resonance condition (i.e. the first assumption).

Calculating M_{echo} in surface NMR conditions

Of ultimate importance is whether a violation of these two assumptions leads to transverse magnetization at the time when the echo forms that significantly differs from eq. (6). Figs 5 and 6 illustrate the magnitude of the transverse magnetization at the time when the echo forms for a range of different T_{2IH} , T_2^* , T_2 and t_d scenarios. These profiles are formed by solving eq. (1) using a 4th-order Runge–Kutta solver given the relevant B_1 magnitude, T_2 and Larmor frequency distribution (determined from T_{2IH} and accounted for using eq. 3). Each solution of the Bloch equation produces a single point in the profile. This procedure is repeated for a range of B_1 values and the collection of results can be visualized as a profile. These profiles are treated as the best estimate of the transverse magnetization at the time when the echo forms given that they

Figure 5. The echo amplitude M_{echo} expected for a range of B_1 amplitudes for a two-pulse experiment where the second pulse is $\pi/2$ phase shifted with respect to the first ($0-\pi/2$). The first and second pulses are 10 and 20 ms, respectively. The left and right columns correspond to delay times of 100 and 300 ms, respectively. The top, middle, and bottom rows correspond to T_2 values of 125, 325 and 625 ms, respectively. Profile colors correspond to the T_2^* value (same colors in all panels). The black profile represents M_{echo} predicted using eq. (6).

are produced while accounting for all terms in the Bloch equation and calculated without the two simplifying assumptions. To investigate the accuracy of eq. (6) under surface NMR conditions, the coloured profiles in Figs 5 and 6 are compared against the black profiles. The black profiles correspond to transverse magnetization predicted using eq. (6) and a weighting based on the echo time and the value of T_2 ; that is the value M_{echo} predicted by eq. (6) is also weighted by e^{-t_{echo}/T_2} in order to account for the influence of T_2 on the echo. No additional weighting is required for the coloured profiles, as T_2 's influence directly enters eq. (1). If eq. (6) is accurate, colored profiles should converge to the black line over much of the B_1 range. Deviations from the black line indicates a breakdown of the two assumptions and that the transverse magnetization is not well described by eq. (6) under the corresponding conditions. Fig. 5 illustrates M_{echo} formed during a two-pulse sequence where the first and second pulses have a phase of 0 and $\pi/2$, respectively (i.e. the pulses are out-of-phase). Fig. 6 corresponds to a two-pulse sequence where both pulses have a phase of 0 (i.e. the pulses are in-phase). Both scenarios have been previously used in surface NMR (Legchenko *et al.* 2010; Grunewald *et al.* 2014). In the following examples, the first and second pulses have durations of 10 and 20 ms, respectively.

Each panel in Figs 5 and 6 corresponds to a T_2 - t_d pairing, where each row and column correspond to a particular T_2 and t_d , respectively. The colored profiles in each panel correspond to the T_2^* value (i.e. a particular T_2 - $T_{2\text{IH}}$ combination, meaning each color corresponds to varying widths of the Larmor frequency distribution). Profiles of the same color in each panel correspond to the same T_2^* value. Note also that the y-axis varies in each panel.

Consider first Fig. 5, the $0-\pi/2$ phase scenario. In this case, many of the profiles appear to track the black curve closely in the large B_1 limit, although some deviation near the zero-crossings is observed. In the weak B_1 limit, small T_2^* (red) profiles appear to closely approximate the black profile, although the amplitude of the main low B_1 peak is less for the red profile compared to the black profile. As T_2^* increases the profiles begin to deviate significantly from the black profile. This can be observed by noting that the colored profiles have much larger amplitudes at low B_1 than the black profile, suggesting that the echo signal may originate at weaker B_1 than predicted by eq. (6) (which would correspond to deeper depths). These trends are observed at each T_2 level (i.e. comparing rows shows similar trends). Comparing the same color profiles for different delay times (e.g. comparing columns) indicates that longer delay times produce profiles that more closely approximate the black line. Another important feature highlighted by Fig. 5 is that the transverse magnetization (computed using the full Bloch equation) at the time when the echo forms displays a dependence on T_2^* (i.e. the underlying Larmor frequency distribution). This suggests that surface NMR echo measurements are not independent of T_2^* (a lack of T_2^* dependence would correspond to no variation between the coloured profiles).

Consider next the scenario where both pulses have 0 phase (Fig. 6). In this case, the colored profiles deviate significantly from the black profiles over the full range of investigated B_1 in many of the investigated scenarios. Short T_2^* (red) profiles most closely approximate the black line, while longer T_2^* values show significant deviations. In the 300 ms delay time case (right-hand column) the red profile closely follows the black profile, while more deviation

Figure 6. The echo amplitude M_{echo} expected for a range of B_1 amplitudes for a two-pulse experiment where the second pulse is in phase with the first pulse (0–0). The first and second pulses are 10 and 20 ms, respectively. The left and right columns correspond to delay times of 100 and 300 ms, respectively. The top, middle, and bottom rows correspond to T_2 values of 125, 325 and 625 ms, respectively. Profile colors correspond to the T_2^* value (same colors in all panels). The black profile represents M_{echo} predicted using eq. (6).

is observed in the 100 ms scenario (left-hand column). In nearly all other investigated scenarios the black profile does not closely approximate the colored profiles, suggesting that eq. (6) does not present an accurate description of the echo amplitude in this case. Only in the long delay time, small T_2^* , large T_2 limit do the colored profiles converge to the black profile. Note also that a significant variation is observed for different T_2^* values. This variation indicates that the measured echoes depend on both T_2 and T_2^* . Comparing Figs 5 and 6 indicates that the 0– $\pi/2$ phase scenario is much better represented by eq. (6) than the 0–0 phase scenario. Note that the black profile in Fig. 6 has a minus sign compared to the black profiles in Fig. 5. The minus sign is necessary as the main echo (low B_1 peak) forms in the $-y$ direction for the 0–0 phase case, while the main echo forms in the $+y$ direction for the 0– $\pi/2$ phase case.

The trends observed in Figs 5 and 6 are also observed for two-pulse sequences using different pulse lengths (e.g. first pulse durations of 5 and 20 ms). Changes to the pulse length shift the profiles in Figs 5 and 6 to smaller or larger B_1 for longer and shorter pulses, respectively.

Impact on surface NMR echo amplitudes

Although the profiles in Figs 5 and 6 provide valuable insight into the accuracy of eq. (6) under surface NMR transmit conditions, they represent a single component of the surface NMR forward model (the transverse magnetization). Additional factors, such as the transmit/receive loop geometry, current strengths and subsurface conductivity also impact the observed surface NMR signals

(Weichman *et al.* 2000). In practice, deviation of the echo amplitude from that predicted by a forward model based on eq. (6) will depend strongly on a range of site specific parameters—such as the local water content, T_2^* , T_2 and their spatial distributions. To provide insight into potential variations in echo amplitudes and magnitude of the deviation from a forward model based on eq. (6), consider Fig. 7 which illustrates sounding curves showing the expected echo amplitude measured for a range of different current amplitudes for the two-pulse sequences used in Fig. 5 (the 0– $\pi/2$ case). The synthetic echo amplitudes were simulated for a 75 m square coincident transmit/receive loop, a 1000 Ω m half-space, and for current amplitudes ranging from 2 to 200 Amps. These sounding curves correspond to a 30 per cent water content half-space, and half-spaces of varying T_2^* (profile color) and T_2 (row). In all cases, T_1 is set equal to T_2 . The colored profiles represent an estimate of the spin-echo amplitude at a time t_{echo} , where $t_{\text{echo}} = \tau_1 + \tau_2 + 2t_d$. These estimates are formed using a surface NMR forward model where the transverse magnetization is based on a solution of the full-Bloch equation given the relevant T_2^* , $T_{2\text{IH}}$, T_2 , T_1 and t_d (i.e. the transverse magnetization profiles shown in Fig. 5 are used as look-up tables when calculating the relevant forward responses illustrated in Fig. 7). To investigate the accuracy of a forward model based on eq. (6), the colored profiles are compared against the black profile in each panel. The black profile is formed by a surface NMR forward model where the transverse component is described by eq. (6). An additional weighting equal to e^{-t_{echo}/T_2} is also present in each black profile.

Comparing the colored and black profiles in Fig. 7 reveals that in nearly all investigated cases the sounding curves predicted from

Figure 7. Sounding curves illustrating the echo amplitude for a $0\text{-}\pi/2$ two-pulse sequence, (the first and second pulses have durations of 10 ms and 20 ms, respectively). Colored profiles correspond to echo amplitudes estimated using a forward model based on the full-Bloch equation. Profiles of the same color in different panels correspond to the same T_2^* value. The black profile in each panel illustrates the echo amplitude estimated using a forward model based on eq. (6).

a full-solution of the Bloch equation differ significantly from the sounding curve predicted by eq. (6) (i.e. transverse magnetization based on the black lines in Fig. 5). Deviation from the black profile varies depending on T_2^* and the current amplitude. In the low current limit, larger T_2^* values appear to more closely approximate the black curve, while in the high current limit the small T_2^* values are closer to the black profile. This trend is observed for both investigated delay times (each column in Fig. 7). Note that the y-scale in each panel is different in Fig. 7.

Although Fig. 7 illustrates sounding curves for a simple half-space example, it serves to highlight that a forward model based on eq. (6) can lead to significant deviations from echo estimates formed via a solution of the full-Bloch equation. This type of deviation in data space has potential to introduce inversion artifacts in estimated water content or T_2 profiles. In practice, observed deviations and the potential inversion artifacts will depend strongly on site specific parameters.

DISCUSSION

The desire to use spin-echo measurements is rooted in an attempt to strengthen links to pore-size and permeability; T_2 carries a much stronger link to pore geometry than T_2^* . Improved links to pore-size represents a significant increase in value for the standard surface NMR survey. Yet for the full-value of spin-echo measurements to be realized we must retain the ability to produce reliable estimates of the spatial distribution of water content and relaxation times. This demands the ability to reliably predict the magnitude of the transverse magnetization at each location in the subsurface at the time when the signal is observed. Modelling errors, such as those shown in Figs 5–7, may lead to challenges in correctly

determining the signal's spatial origin, and difficulties fitting data with an accurate water content and T_2 profile. Such a loss in image accuracy may undermine the added value provided by direct T_2 sensitivity.

The modelled echo amplitudes are observed to deviate significantly from predictions based on eq. (6) in the large T_2^* and short delay time scenario. In this case, deviations are due to a violation of the assumption that the term carrying a negative time-dependence with respect to the first delay time is negligible. This conclusion stems from observations of Fig. 4, where the b term obtains its largest values in the large $T_{2\text{IH}}$ and short delay time scenario, which also corresponds to the large T_2^* short delay time limit. To improve the applicability of eq. (6) in the long T_2^* limit, long delay times should be used.

A second limit where significant deviations are observed from predictions based on eq. (6) is in the small B_1 limit. In this limit, deviations are due to a violation of the near-resonance condition. For small B_1 , even modest offsets lead to $\mathbf{B}_{\text{eff}}$ vectors that form significant angles with respect to the transverse plane. This can be observed by noting that very small offsets are required to produce large α in Fig. 3(a). A consequence of divergence in the small B_1 limit is difficulty quantifying water content at depth, where the smallest B_1 contribute a majority of the observed signals. It also suggests that echoes may have signal components that originate from greater depth than would be expected given modelling based on eq. (6).

Another conclusion that can be drawn from Figs 5–7 is that the echo amplitudes can be expected to carry a dependence on T_2^* . Previous surface NMR echo forward models based on eq. (6) involve an assumption that the echo carries only a T_2 dependence, as T_2^* does not enter the forward model. However, the differences for

profiles with differing T_2^* values indicates a residual T_2^* dependence on the echo amplitude, a dependence displaying a complex relationship on the B_1 strength and the delay time. This has potential to influence the accuracy of water content and relaxation time images produced from echo data, given that T_2^* can be expected to influence the potential contribution of each region in the subsurface to the observed signal. Even if T_2^* at a site can be constrained, forward models that use an analytic description of the echo amplitude that does not include T_2^* will struggle to take advantage of a constrained T_2^* value.

One solution to improve the ability to model the echo amplitude is to use a forward model based on a solution of the full-Bloch equation (Grombacher *et al.*, in press). Such an approach does not require the near-resonance assumption or an assumption that the term carrying the negative time dependence with respect to the first pulse can be neglected. Furthermore, a full-Bloch solution is also able to directly include the influence of the relaxation terms, thus readily allowing the complex dependence of the echo on B_1 , T_2^* and T_2 to be included. This type of workflow is also more naturally suited to coupling inversions of FID and spin-echo data as the forward model incorporates the influence T_2^* on the echo data, while also including the influence of T_2 on the FID [as Grombacher & Auken (2018) demonstrated that T_2 can strongly affect the FID amplitude and phase]. An approach based on the full-Bloch equation would also allow the observed echo signals to be modelled at arbitrary times, not only the time at which the echo forms as in eq. (6). This would allow a single forward response to predict the FID amplitude following the first pulse, the FID amplitude following the second pulse and the spin-echo amplitude—such an approach may allow for a more complete exploitation of the full surface NMR two-pulse experiment data cube. The potential of a forward model based on the full-Bloch equation for the two-pulse experiment is the subject of future research.

If eq. (6) is used to forward model surface NMR echo data, we recommend that the $0-\pi/2$ approach used by Grunewald *et al.* (2014) be employed. This acquisition scheme produces an echo that is more closely approximated by eq. (6) when compared to the $0-0$ two-pulse experiment. Furthermore, the $0-\pi/2$ scheme allows a phase-cycling approach to be used, which further allows the echo signal to be isolated from the FID produced by the second pulse. Such an isolation greatly improves the accuracy of the echo forward modelling (Grunewald *et al.* 2014), because if the FID following the second pulse has non-negligible amplitude at the time when the echo forms it can bias the observed echo amplitudes. However, if one were to use a full-Bloch solution capable of modelling both the echo and the FID generated by the second pulse, it may alleviate the need to isolate these two signals.

In this work variable width Larmor frequency distributions were considered, where off-resonance excitation occurs for all parts of the distribution not equal to the transmit frequency (the 0 Hz offset case). This situation represents an approximation of the ‘on-resonance’ scenario, where the transmit frequency for both pulses is selected to be equal to the center frequency in the Larmor frequency distribution. The scenario where the transmit frequency is distinct from the center frequency of the Larmor frequency distribution is not considered. Such a scenario is likely to occur in practice, given that unintentional off-resonance excitation commonly occurs in single pulse FID experiments in surface NMR due to a temporally varying Larmor frequency (due to diurnal B_0 variations) and resolution limits on the true Larmor frequency. The impact of this type of an offset on two-pulse surface data will be the subject of future research.

A second approach to improve T_2 sensitivity in surface NMR is multi-echo experiments, where multiple refocusing pulses are applied in quick succession allowing multiple echoes to be measured during a single acquisition. This approach has the distinct advantage that it allows the T_2 decay to be sampled at multiple points per acquisition, in contrast to the spin-echo approach that provides a single point on the T_2 decay per acquisition. Modelling the first echo in a multi-echo acquisition is identical to the scenarios considered in this work. Subsequent echoes were not considered in this work, but it is likely that these echo amplitudes will display similar deviation from eq. (6), given that their spatial distribution and coherence is also strongly affected by the first two pulses.

CONCLUSIONS

Production of reliable surface NMR images of subsurface properties using spin-echos demands that the forward model is able to accurately estimate the spatial origin and amplitude of echoes. Traditionally, this is done using a closed form analytic description of the spin-echo amplitude formed by solving the Bloch equation in the no relaxation limit, imposing a near-resonance condition and neglecting a term carrying a negative time dependence with respect to the first delay time. These two assumptions are shown to break down under a range of conditions that can be expected in surface NMR. In the large T_2^* , short delay time limit, the analytic description of the echo amplitude is shown to significantly diverge from expected amplitudes. Further breakdown of the analytic description is expected in the small B_1 limit. Of the two spin-echo acquisition schemes previously used in surface NMR, the approach where the second pulse is $\pi/2$ phase shifted with respect to the first produces spin-echo amplitudes that are more closely approximated by eq. (6). In contrast, the spin-echo experiment where both pulses are in-phase ($0-0$) leads to significant deviations over a wide range of conditions.

Although this investigation is based on synthetic echo comparisons, it serves to demonstrate that the simplified analytic description of the echo previously implemented in surface NMR echo forward models is inadequate to describe the signal in the full range of conditions expected in surface NMR. Modelling errors in the echo amplitudes have potential to bias estimated water content and relaxation time profiles, potentially undermining the benefits of the more direct T_2 sensitivity. Furthermore, it is shown that the echo amplitude is expected to retain dependence on T_2^* , a dependence that cannot be incorporated into a forward modelling scheme using an analytic description that does not depend on T_2^* . An alternative approach to spin-echo modelling involving a solution of the full-Bloch equation is recommended.

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