Relaxation–Relaxation Experiments in Natural Porous Media with Portable Halbach Magnets

Nuclear magnetic resonance (NMR) relaxometry is particularly suitable for the study of water dynamics in natural porous media like soils. The recent development of one- and two-dimensional correlation Laplace NMR experiments provides new tools to investigate exchange processes between different pore classes. In particular, dynamic information can be retrieved by two-dimensional NMR relaxation exchange, where ideally an initial NMR relaxation environment is correlated with a final relaxation environment of molecules migrating from one environment to the other within a so-called NMR mixing time \( \tau_m \). In this work, transverse relaxation–relaxation \((T_2-T_2)\) exchange experiments were performed on water-saturated soil samples at a low and inhomogeneous magnetic field with a simple, portable Halbach magnet at a proton Larmor frequency of 21.85 MHz. The relaxation curves were analyzed by inverse Laplace transformation and yielded two-dimensional \( T_2 \) relaxation distribution functions from which the exchange pathways between different relaxation sites could be unraveled. Whereas fine sand exhibited long relaxation times and weak exchange of water molecules between the pores, two different silt loams were characterized by the exchange of water between pores with fast relaxation times and multisite exchange with increasing \( \tau_m \). The measured exchange dynamics were characterized by \( T_2 \) relaxation times in the range of 5 ms. They were caused by molecular diffusion of mobile water molecules between pores.

**Soil acts as a filter** for water on its way to aquifers and controls the supply of plant nutrients. These functions relate to the structure of the pore system, which is characterized by the pore size distribution, pore connectivity, water content, and water dynamics. Nuclear magnetic resonance is most suitable for investigating water in natural porous media, since NMR methods are noninvasive and directly probe the substance of interest, that is, water. In the past, such natural pore systems have mainly been characterized by one-dimensional NMR relaxometry (Dunn et al., 2002; Todoruk et al., 2003; Kleinberg and Griff in, 2005; Schaumann et al., 2005; Pohlmeier et al., 2009; Stingaciu et al., 2009), leading to pore size distribution functions by using the well-established Brownstein–Tarr relationship and with the surface relaxivity as a scaling parameter (Hinedi et al., 1997; Baric, 2000). One drawback of soil is its inherent heterogeneity in pore size, pore geometry, mineral content, and organic material. This complicates the interpretation of relaxation-time distribution functions, which may contain modes resulting from different pore sizes confounded by modes resulting from surface chemistry effects. A promising new tool are two- and three-dimensional Laplace correlation NMR (Lee et al., 1993; Godefroy and Callaghan, 2003; McDonald et al., 2005; Washburn and Callaghan, 2006; Song et al., 2008; Arns et al., 2007). In Laplace exchange NMR experiments, the magnetization of a spin system is monitored successively in two different encoding time periods, separated by a so-called mixing, exchange, or storage time, \( \tau_m \). These methods yield information far more detailed than the respective one-dimensional experiments. At present, longitudinal relaxation time \((T_1)\)–\(T_2\) and \(D\)–\(T_2\) correlation methods are gaining popularity for studying artificial porous media and rocks (Song et al., 2002; Washburn and Callaghan, 2006; Hürlimann et al., 2002).

Maps of \( T_2–T_2 \) correlation are obtained from the measured data by two-dimensional inverse Laplace transformation (Godefroy and Callaghan, 2003). Ideally in such maps, the transverse relaxation time distributions from the first and the second encoding periods are plotted vs. each other. We have determined that this simplistic view can be used for a qualitative analysis, although it is flawed by the fact that the encoding and mixing times...
are on the same order of magnitude so that a quantitative analysis needs to be based on computer simulations of the experimental data. In this simple picture, water molecules that remain in or return to the same pore-size class during the mixing interval contribute to peaks on the diagonal, while cross-peaks indicate water molecules that have exchanged between pores of different sizes. Performing such experiments at a low magnetic field is advantageous because heterogeneous structures are probed, which gives rise to local distributions of the magnetic field with so-called internal magnetic-field gradients, which are small at low field.

In this study, $T_2$–$T_2$ exchange experiments were applied for the first time to water-saturated soil systems to probe the water dynamics in the pore space. Three repacked soil materials were chosen that represent pure fine sand and two silt loams with different sand and silt contents. In the past, fast transverse relaxation times have been assigned to immobile and clay-bound water (Straley et al., 1997). The question is whether two-dimensional relaxometry can give information on whether such water is really immobile or exchanges after all.

**Materials and Methods**

Measurements were performed on one fine sand and two different soil samples. The fine sand was purchased from Quarzwerke GmbH, Frechen, Germany, and the soil materials were from Merzenhausen and Selhausen, Germany. The textural composition of each sample is presented in Table 1. The material was air dried, sieved to <2-mm grain size to remove stone particles, packed into 9- by 100-mm cuvettes, centrifuged for 30 min at 1000 × $g$, and finally saturated with tap water for 48 h. The original aggregate size was <5 mm.

Nuclear magnetic resonance measurements were performed with a Halbach magnet (Raich and Blümich, 2004; Blümich et al., 2009). This magnet is designed in such a way that the magnetic field strength is maximum inside and minimum outside. It consists of two rings with 12 hexagonal bar magnets each (Fig. 1). The rings are separated by a 2.5-cm gap, which leads to a more homogeneous field along the magnet axis. The field strength is $B_0 = 0.51$ T. It defines a proton resonance frequency of 21.85 MHz. The radio-frequency coil was wound on a hollow Teflon cylinder with an inner diameter of 11 mm using five windings of copper sheet wire across a length of 5 cm.

<table>
<thead>
<tr>
<th>Soil type</th>
<th>Sand</th>
<th>Silt</th>
<th>Clay</th>
<th>$θ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>FH31 fine sand</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0.36</td>
</tr>
<tr>
<td>Selhausen silt loam</td>
<td>15</td>
<td>68</td>
<td>17</td>
<td>0.4</td>
</tr>
<tr>
<td>Merzenhausen silt loam</td>
<td>4</td>
<td>81</td>
<td>15</td>
<td>0.43</td>
</tr>
</tbody>
</table>

The pulse sequence (Fig. 2) of the two-dimensional $T_2$–$T_2$ relaxation exchange experiment (Washburn and Callaghan, 2006) encompassed three main time periods: a $T_2$ encoding period for the indirectly detected relaxation dimension, a mixing time $t_m$, and an encoding period for read-out of the signal decay times after the mixing time. During the encoding periods, transverse relaxation was detected in the moderately inhomogeneous magnetic field of the Halbach magnet by multi-echo trains generated according to the Carr, Purcell, Meiboom, and Gill (CPMG) method (Blümich, 2004). The time between the echoes, $t_E$, was kept at a constant value. The numbers of echoes used in the first encoding period was increased logarithmically in 64 steps so that the maximum first encoding time covered the same range as the second encoding time. The echo time $t_E$ for the FH31 sand was 0.5 ms, for the Selhausen soil it was 0.3 ms, and for the Merzenhausen soil it was 0.1 ms. The mixing times used between the two $T_2$ encoding times were varied from 1 ms up to 1 s for the FH31 sand, up to 55 ms for the Selhausen soil, and up to 10 ms for the Merzenhausen soil. Each line of the two-dimensional data matrix was scanned eight times, and the repetition time between scans was set to five times the longitudinal relaxation time $T_1$. Each experiment lasted between 2 and 30 min depending on the duration of the mixing time and the repetition time. The raw data were analyzed with a two-dimensional inverse Laplace transformation program (provided by P. Callaghan, Victoria University of Wellington, New Zealand), which generated a 32 by 32 $T_2$–$T_2$ distribution matrix (Godefroy and Callaghan, 2003).

**Results and Discussion**

Initially, one-dimensional CPMG experiments were performed to obtain transverse relaxation decays, which were subsequently inverted by one-dimensional inverse Laplace transformation (Godefroy and Callaghan, 2003) to obtain a transverse relaxation time distribution (Fig. 3). The relaxation times decreased with
smaller pore sizes (Barrie, 2000). The longest $T_2$ distribution of the FH31 fine sand was bimodal, with maxima at 40 and 500 ms. The soil materials exhibited relaxation times much faster than those of the fine sand, covering ranges between 1 and 160 ms for the Selhausen soil and 0.5 to 50 ms for the Merzenhausen soil. Furthermore, the bimodal behavior found for the sand changed for the soils to multimodal distribution functions. Comparing the relaxation times with the textural composition of each sample, it can be seen that with increasing silt and clay content, the $T_2$ relaxation times decreased significantly.

To test if the two-dimensional exchange experiment and the data processing by the two-dimensional inverse Laplace transformation program worked reliably and to ascertain that the observed cross-peaks were not artifacts from poor signal/noise ratios, a reference experiment with two stacked, individual, 5-mm NMR tubes was performed. Each tube was filled with different aqueous CuSO$_4$ solutions, which gave different $T_2$ values. Figure 4 shows the results from the relaxation–relaxation exchange experiments that were performed for mixing times of 1 and 30 ms. As expected, only diagonal peaks were observed and no off-diagonal peaks were detected. The loss of intensity of the fast diagonal peak at $T_2 \sim 10$ ms at a mixing time of 30 ms is remarkable. This was due to longitudinal relaxation during the mixing time, when the magnetization was stored along the $z$ axis.

Once the measurement procedure had been tested, relaxation–relaxation exchange experiments were conducted for different mixing times for all samples (Fig. 5). In the corresponding exchange distributions, molecules residing in their original environment gave rise to signals along the diagonal, while those changing their environment during the mixing time produced off-diagonal peaks. Summarizing the results of the $T_2$–$T_2$ correlation maps for the systems with zero mixing time (Fig. 5a–5c), all signals appear as diagonal elements and the projections to the coordinate axes are very similar to the one-dimensional distributions shown in Fig. 3. As expected, no exchange is observed for zero mixing time.

For the FH31 sand, the exchange of water molecules is barely observed at mixing times of both 100 and 500 ms by the presence of very weak off-diagonal peaks (Fig. 5d and 5g). The sand was quite homogeneous, with only a small fraction of narrow pores, as evident from Fig. 3a and confirmed by $T_1$ relaxometry data (Pohlmeier et al., 2009). This is why exchange processes in the sand were caused mainly by molecular movement within pores of the same size class.

Figures 5e and 5h present the distributions for the Selhausen soil at mixing times of 10 and 35 ms. The observed values of $T_2$ are widely distributed and range between 1.6 and 160 ms, showing up to four components. Unlike the results for the FH31 sand,
cross-peaks appear at mixing times of 10 and 35 ms, indicating strong exchange between the shortest components and weak exchange to sites with longer relaxation times. These cross-peaks identify migration of water molecules between relaxation environments, which may correspond to small and large pores. It is also noted that the distribution matrix is rather asymmetric, which is a strong indication of multisite exchange (Van Landeghem et al., 2010). The fastest component on the diagonal completely vanishes at long mixing times (Fig. 5h) due to relaxation effects.

Like the Selhausen soil, the Merzenhausen soil shows a multimodal distribution with short $T_2$ components ranging from 0.5 to 50 ms (Fig. 5c, 5f, and 5i). As in the Selhausen soil, cross-peaks between the shortest components arise already at a mixing time of 2 ms (data not shown here) and became stronger at a mixing time of 4 ms (Fig. 5f). At a mixing time of 10 ms, the shortest diagonal peaks vanish due to a short $T_1$ relaxation of about 2 ms (Pohlmeier et al., 2009), and exchange with the longer components becomes observable. In addition, with increasing mixing times, the two-dimensional spectra become slightly asymmetric, which indicates the onset of multisite exchange.

**Conclusions**

The results of our experiments prove that two-dimensional exchange relaxometry methods are suitable to observe moisture migration in loose, natural, porous media like soils. For sand, only weak and slow exchange was found, while in more complex, textured soils, exchange of water molecules was observed for short mixing times between the fastest components and between slower components at longer mixing times. It is not surprising that, in such heterogeneous systems, the water molecules exchange between more than two sites as the mixing time is prolonged. By such two-dimensional experiments, the relaxation modes identified in one-dimensional experiments can be correlated and interpreted in terms of distances traveled by water molecules during the exchange experiment once the exchange rates are quantified by numerical simulation of the experimental exchange maps. This is in line with the assumption incorporated in the Brownstein–Tarr model that the observed relaxation modes can be assigned to pores of different sizes. In particular, it was shown that the existence of cross-peaks identifies the motion of the water molecules between different pore size classes in a qualitative analysis. If exchange between two pore size classes is observed, water in these classes should be regarded as mobile, not immobile. With respect to our investigated soil material, also the water in pores with sizes corresponding to $T_2$ relaxation times of about 5 ms is mobile in the sense that the pore connectivity permits exchange.

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**References**


