A Fast Field Cycling NMR Study of Soil

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Motivation

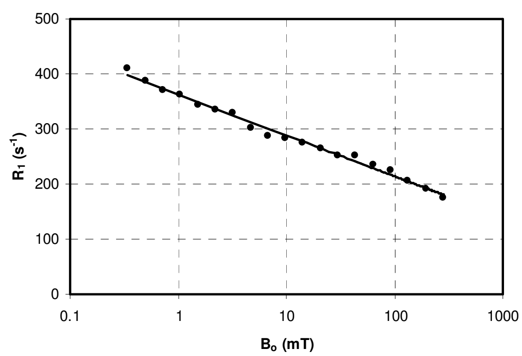
In 1962, Varian proposed the use of NMR to prospect for water in deep gravel layers.[1] This technique has since been improved for use at depths down to 100m.[2] We are interested in applying a similar technique to extract spatial information of the water content in soil nearer the surface of the earth. A first step in determining the feasibility of such a technique is to study the NMR signal from the water in soil. This work concentrates on the contribution to the NMR signal from the spin-lattice relaxation rate, R_1. R_1 studies of soils and synthetic soils at a single high frequency have been performed.[3,4] This study focuses on R_1 values as a function of magnetic field strength B_o.

Methods

Surface soil samples were collected from five locations in the USA. (See Table 1.) Samples were hydrated with HPLC water to the point of saturation for at least six months.

A Spinmaster-FFC 2000 (Stelar s.r.l., Mede, ITALY) fast field cycling NMR relaxometer was used to obtain 16-point relaxation curves at 20 magnetic field values between $0.2<B_o<280$ mT for the five soil samples. Relaxation curves were fit with both monoexponential (ME) and biexponential (BE) functions with an offset.

Optical microscopy (OM), thermal gravimetric analysis (TGA), and atomic absorption (AA) spectroscopy were used to determine the physical and chemical properties of the samples. (See Table 1.) OM was used to determine the particle size distribution and shape. The mean diameter ($\bar{d}$) and standard deviation (σ_d) are presented in Table 1. TGA provided the weight ratio (WR) of bulk water to dry soil by weight loss at ~100 °C, and the weight ratio of water of hydration to dry soil weight by weight loss at > 100 °C. AA spectroscopy was used to examine for Cr, Ni, Mn, Co, Cu, and Fe in the free water.



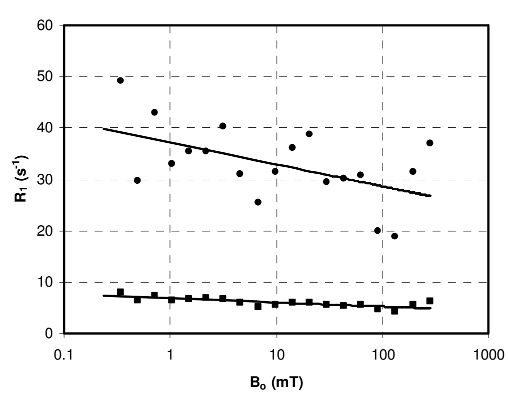


Figure 1. Relaxograms of the: (A) Combalache and (B) Spring Hill samples.

Table 1. Soil Sample Characteristics.

Location	Soil Class	WR_{bulk}	WR_{hyd}	$\bar{d}$ (μm)	σ_d (μm)
Brighton, NY	Silt	18	3	6.9	5.8
Combalache, PR	Clay	50	9	2.1	1.2
Richland, WA	Sand	25	1	446	144
Cheyenne, WY	Silt	24	5	3.4	2.8
Spring Hill, FL	Sand-Silt	37	3	*	*

* 2<d<450 μm particles, and 5μm diameter 200 μm long organic fibers

Results

AA - Concentration of paramagnetic metals in the supernate from all samples were negledgeable, except in the Spring Hill sample where [Mn]=680 ppb.
OM - The Spring Hill sample had a wide range of particle diameters as well as 200x5μm organic fibers
TGA – WR_{hyd} is indicative of the quantity of water of hydration and hence the clay content.
NMR – Relaxation curves from two of the five samples were better fit with a biexponential function. The calculated relaxation rates for all samples displayed an approximately linear and decreasing relationship as a function of $\ln(B_o)$ over the B_o range. (See Table 2.) Figure 1 displays the relaxograms for the Combalache and Spring Hill samples.

Table 2. Properties of the $R_1 = A \ln(B_o) + C$ trend line.

Location	A (s^{-1}/ln T)	C (s^{-1})
Brighton, NY	-8.441	149.6
Combalache, PR	-32.21	140.0
Richland, WA	-3.425	5.893
	-0.3891	0.8141
Cheyenne, WY	-13.53	73.39
Spring Hill, FL	-1.852	37.18
	-0.3312	6.737

Discussion

The soil samples are composed of microscopic particles and water-filled voids between the particles. The hydrophilic nature of the particles varies from sample to sample as does the distribution of void sizes. These physical characteristics influence the relative amount of structured and free water components in each sample. The observed R_1 values should be dependent on these two properties.[5]

Within the available precision of the measurements, some of the relaxation curves better match a BE fit, while others match a ME fit. The observed ME match correlated with small particle size. The calculated R_1 values displayed a decreasing trend with increasing B_o, and an approximately linear relationship as a function of $\log(B_o)$ over the B_o range. The Combalache sample had the largest R_1 value (400 s^{-1} at 0.2 mT to 175 s^{-1} at 280 mT), and also the smallest particles and the most water of hydration.

The decreasing R_1 with increasing B_o indicates that when designing a field based MRI system, it will be preferable to use larger B_o values for more favorable relaxation rates. Since the spin-spin relaxation rate, R_2, will be $\geq R_1$, many of the soils will have a structured water signal component that will be unobservable with a moderate cost detection system associated with a portable field based MRI system.

References

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