



## A brief note on FFC NMR relaxometry of soils

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A soil is composed of rock grains of varying sizes and porosity, humus particles (huge organic molecules containing aromatic rings and a lot of hydrophilic hydroxyl and carboxyl groups), and water (humidity). The detectable proton NMR signals are essentially those of water (plus the exchangeable hydrogens of the humus). Protons belonging to the solid matrix are sometimes also visible but these fast-decaying signals can be easily discarded and shall not be discussed here.

There are at least two distinct water environments in every soil sample:

- Water on the outside of the rock grains which is partially bound to (adsorbed on) the outer surface of the grains and which interacts strongly with humus particles.
- Water inside the possibly porous rock grains which is partially bound to the inner surface of the rock pores but which does not interact with the humus.

In both cases the “bound” water is characterized by lowered mobility (dimensionally restricted motion) and thus exhibits long correlation times and a relatively strong field- dependence of  $R_1$  relaxation rates. Moreover, the relaxation rates are often shortened – and their field dependence made more complex – by contact with paramagnetic components and/or impurities in the rock grains.

The “free” water has very short correlation times and its relaxation rate  $R_1$  is low and field-independent. However, the resulting signals are not a simple superposition of the two types. The “bound” water is in fact probably just a tiny mono-molecular layer which makes itself felt by an efficient exchange of magnetization with the rest of the liquid phase. The exchange itself occurs through a combination of three mechanisms:

- spin diffusion (the  $T_2$  process propelled by dipolar spin-spin interactions),
- chemical exchange (through the hydrogen bonds), and
- mass self-diffusion

Depending upon the particular system, the final result may be either an apparently mono-exponential decay at some intermediate  $R_1$  rate or an even markedly non-exponential decay. The theory of these processes is still in development and there is a number of models being tested. There are two main groups of models based on i) phenomenological descriptions by means of continuous, apparent  $R_1$  (or  $T_1$ ) distributions [Borgia,Brown,Fantazzini] and ii) relaxation on liquid-solid interface controlled by magnetization diffusion to the rock surface [Korb,Petit].

Testing by means of the  $B_1$  dependence of the relaxation curves should be always combined also with their temperature dependence. Notice, for example, that spin diffusion generally becomes *slower* at higher temperature and thus exhibits opposite temperature dependence than chemical exchange and self-diffusion.

The interaction of water with humus particles is an additional phenomenon present in soil but not in 'clean' rocks and sands. It behaves much like interaction of water with hydrophilic macromolecules and thus should exhibit an approximately Lorentzian  $R_1$  field-dependence. Again, whether this behavior is actually observed or whether it is obscured by concurrent mechanisms depends on the particular system.