

New applications of low field NMR in Soil Science

By: **Etelvino H. Novotny**

*Embrapa Soils, Rua Jardim Botânico 1024,
CEP 22460-000, Rio de Janeiro-RJ, Brazil.
e-mail: etelvino.novotny@embrapa.br
Currently on a sabbatical with Prof. Galvosas.*

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Petrik Galvosas

*Victoria University of Wellington,
PO Box 600, Wellington, New Zealand.
e-mail: petrik.galvosas@vuw.ac.nz*

Despite the wide application of low field NMR in different fields, from petrophysics to food science and industry, its use in Soil Science is still inconspicuous. To demonstrate opportunities for low field NMR in this area we will present a few examples of so far unpublished new applications of this powerful and more affordable technique in Soil Science.

Soil plays a vital role in the ecosystem. For humankind, it provides food, fuels, fibres, medicines and some essential construction and manufacturing materials. Some examples of how soil renders environmental services are: provision of root support, water and nutrients for plants; support of the lives of a myriad of micro-organisms; maintenance of water quality, buffering against organic and inorganic contaminants, thus protecting groundwater quality; regulation of the discharge of excess rainwater, preventing flooding; contribution to the equilibrium of carbon stocks, being the main terrestrial surface carbon deposit, with more than three times the carbon in the atmosphere and in the biosphere (mainly represented by vegetation); and mitigation of emissions of greenhouse gases [1-3].

Methods

Low field (and low cost) NMR lends itself to time domain NMR (^1H relaxometry and diffusometry) where distributions of relaxation times or diffusivities are obtained from the time domain data by Inverse Laplace Transformation (ILT). In the examples below we will be using Carr-Purcell-Meiboom-Gill (CPMG) experiments for obtaining T_2 relaxation time distributions and Decay due to Diffusion in Internal Field (DDIF) for obtaining pore sizes distributions. Furthermore, Principal Component Analysis (PCA) will be used for the classification of agricultural products by the virtue of their characteristic relaxation times.

Fertiliser shelf life

Fertilisers play a key role in providing essential nutrients in crop production. Within this context, the

development of fertiliser technologies, in addition to increasing their efficiency, aims to improve their physicochemical characteristics, such as reducing hygroscopicity to facilitate fertiliser storage and its application. For the evaluation of these products, through kinetic studies measuring the moisture content as a function of the exposure time to the saturated atmosphere of water vapor, as well as its partitioning into different domains (^1H populations) of the fertiliser is only possible using NMR relaxometry. One example of this application is the study of a fertiliser made from urea (80%) and zeolite (20%) as desiccant. CPMG experiments have been performed consecutively over 83 hours every 10 minutes. Obtained T_2 distributions are plotted in Figure 1 vs the

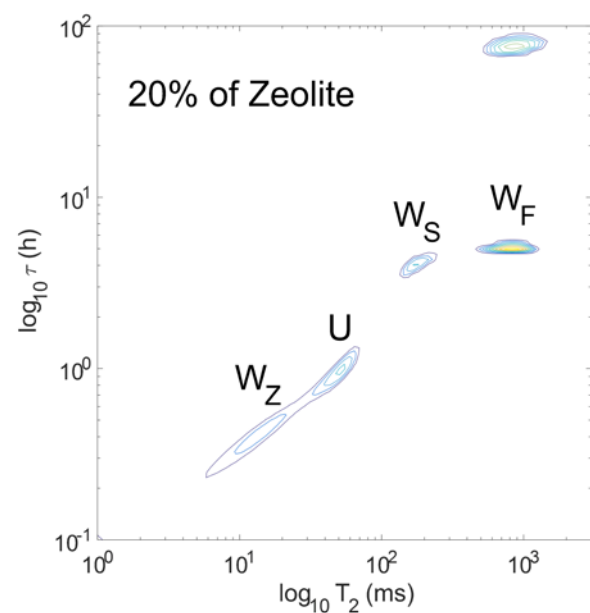


Figure 1. Time constant distribution map (2D-ILT). Horizontal axis: transverse relaxation time (T_2) distributions. Vertical axis: distributions of exponential time constant of the ^1H signal growth due to the exposure of the fertiliser to a water saturated atmosphere.

time constants of water uptake and ^1H signal of dissolved urea (both of which are expressed by an exponential increase of the ^1H signal). Based on T_2 it is possible to identify at least four domains, being the shortest T_2 (~ 15 ms), the water inside the zeolites (W_Z); the second one ($T_2 \sim 55$ ms), from the Urea ^1H (U); the third one ($T_2 \sim 200$ ms), the solvation water (W_S); and the longest ($T_2 \sim 1$ s), the free water (W_F). During the exposure time, the water goes first into the pore system of the zeolites with an uptake time constant of about 30 min. Only after the zeolite pores are fully saturated does the water begin to dissolve the urea, thus its ^1H become detectable (U). This process is linked to a time constant of about 1 h. After another 4 h the humidity begins to fully solvate the urea (W_S) and begins to condensate as free water (W_F), with two time constants, one about 5 h and

a potentially slower process with time constant of about 80 h, however, the latter likely to be an experimental artefact. For the caking to occur, resulting in the loss of the fertiliser, urea crystal solubilisation is necessary first which depends on the formation of W_p with later stages of drying and recrystallisation.

Due to the characteristics of this technique (non-invasive; analysing the total sample volume; and being insensitive to non-metallic materials, e.g. plastic and paper packaging) these same determinations could be made in packed samples which could even include the evaluation of the packing material itself.

Soil and charcoal water content and porosity

Soil's ability to store water for plant growth and development is directly related to various physical

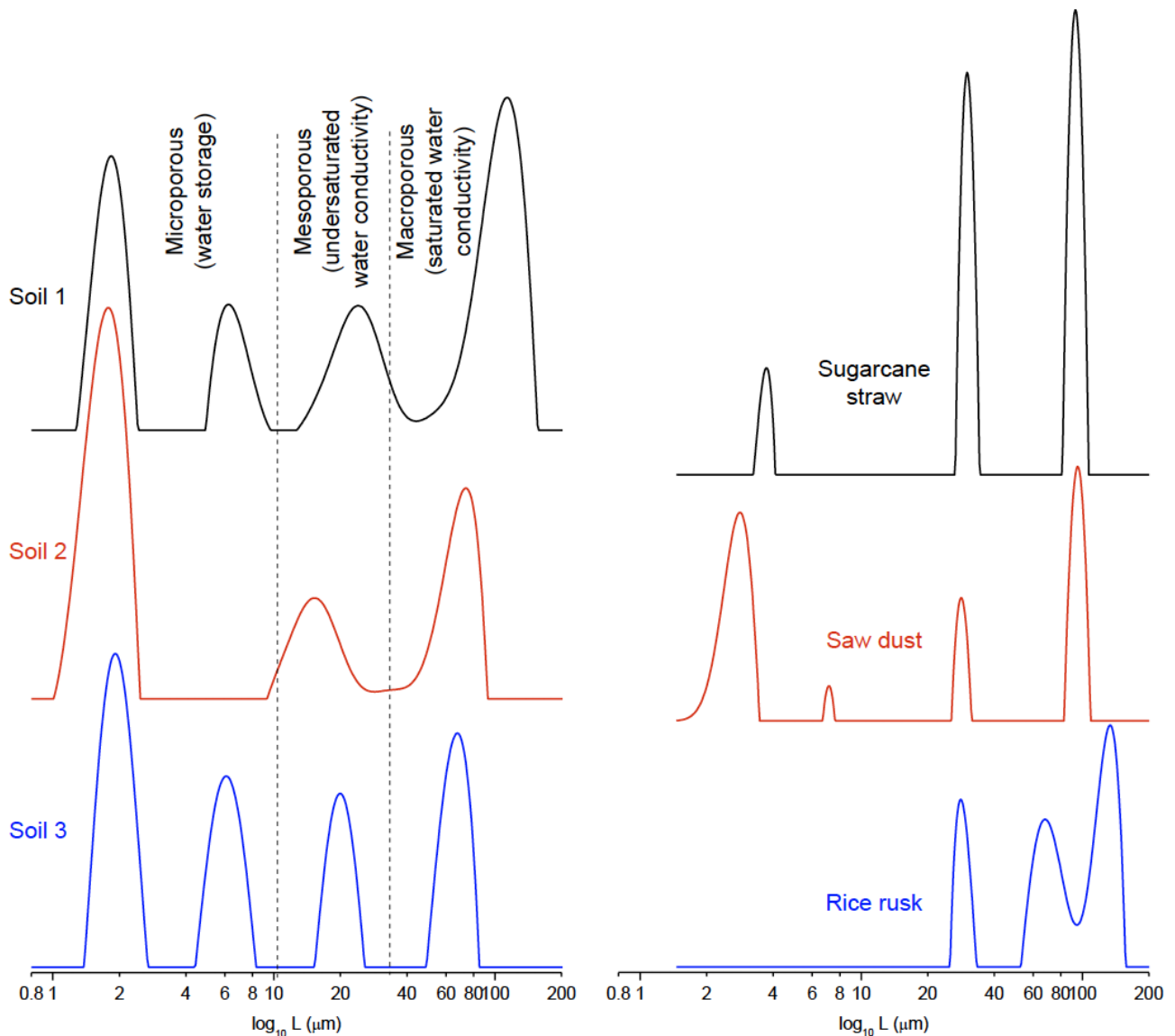


Figure 2. Porous size distribution obtained with the method Decay due to Diffusion in Internal Field. Left: three soil samples water saturated. The dashed lines indicate the general borders used in Soil Science. The macroporous ($> 50 \mu\text{m}$) are important to the soil aeration and the water infiltration; the mesoporous (between 15 and $50 \mu\text{m}$) are important to the water redistribution; and the microporous ($< 15 \mu\text{m}$) to the water storage for the plants. Right: three charcoal samples obtained from different biomass pyrolyzed at 450°C during 1 h.

attributes of soils, including porosity and the water retention. To date it remains difficult and time-consuming (sometimes up to months) to determine these physical properties experimentally. This explains the growing interest in other methods to estimate soil water retention capacity as well as the pore distribution.

This also applies to the determination of charcoal porosity. In this sense, ^1H NMR relaxometry is a tool with great potential [4]. Examples of soils and charcoal samples are provided in Figure 2.

Metal ions sorption

Some charcoals have the ability to adsorb metal ions. Since T_2 is very sensitive to the presence of paramagnetic ions in the solution, it is possible use time domain NMR for the fast screening of potential adsorbents for ion removal by just analysing the percolated solutions prepared with some suitable paramagnetic ion with known concentration as is shown in Figure 3.

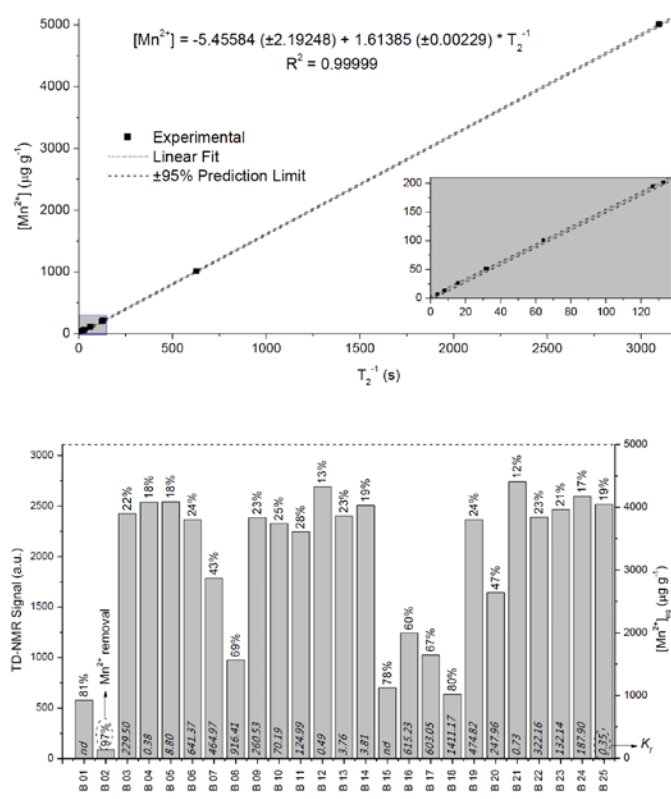


Figure 3. Top: calibration curve for Mn^{2+} test solution. Bottom: Content of Mn^{2+} found in the percolated solution through 25 different charcoals. The test solution had 5 mg g^{-1} of Mn^{2+} . The percentages in the top of the columns are the Mn^{2+} removal from the test solution and the italic numbers are the Freundlich constants (K_f), some charcoals adsorbed all the Mn^{2+} up to the concentration of 1 mg g^{-1} , making it impossible to determine the Freundlich constant (nd). These are very interesting for decontaminating water with metal ions, such as sewage and wastewater.

Organic products certification

Another interesting application is in product certification. To date there is no analytical method to certify organic agricultural products, this is done so far by process certification. However, with the use of low field NMR it appears possible to discriminate perfectly organic from conventional potatoes, regardless of the huge diversity in potato variety, soil or site of cultivation. This was done using potatoes T_2 distributions after principal component analysis (PCA) applied to the mean centred data. The highest variability (PC1, 65.9% of total variance) is due to the great diversity of potatoes (cultivars; soils; sites, etc.), but since the principal components (PCs) are, by definition, orthogonal, the second PC (30.9% of total variability) accounted only for the differences between organic and conventional potatoes (Figure 4, left).

But what differentiates these potatoes? The answer can be obtained by analysing the PCA loads (Figure 4, right), since they are the regions of the T_2 distributions that contributed most to this differentiation, with samples with high scores presenting more water in regions with positive loads and less water with T_2 's that present negative loads and vice versa for samples with negative scores. Seeking to help in the understanding, the average distributions for organic and conventional potatoes were plotted together with the PC2 load. In this particular case, the loads plot should be very similar to the subtraction of average organic minus average conventional T_2 distributions. Having that in mind, the organic potatoes present the different waters (intracellular; vascular; and starch associated) with shorter T_2 's than the conventional ones, since the loads from each domain present positive values for shorter T_2 and negative for longer (the loads plot looks like a distribution with each domain showing positive and negative lobes). Furthermore, the organic potatoes present a higher content of intracellular water than the conventional potatoes. These could be due to a minor vegetative growth, resulting in smaller cells and tissue organelles (shorter T_2 due to higher surface/volume ratio) and also due to the different fertilisation practices, resulting in a higher ions concentration in the organic potatoes fluids (shorter bulk relaxation) and higher osmotic pressure inside the cells.

These are only few examples of the enormous and underexplored potential of applications of this

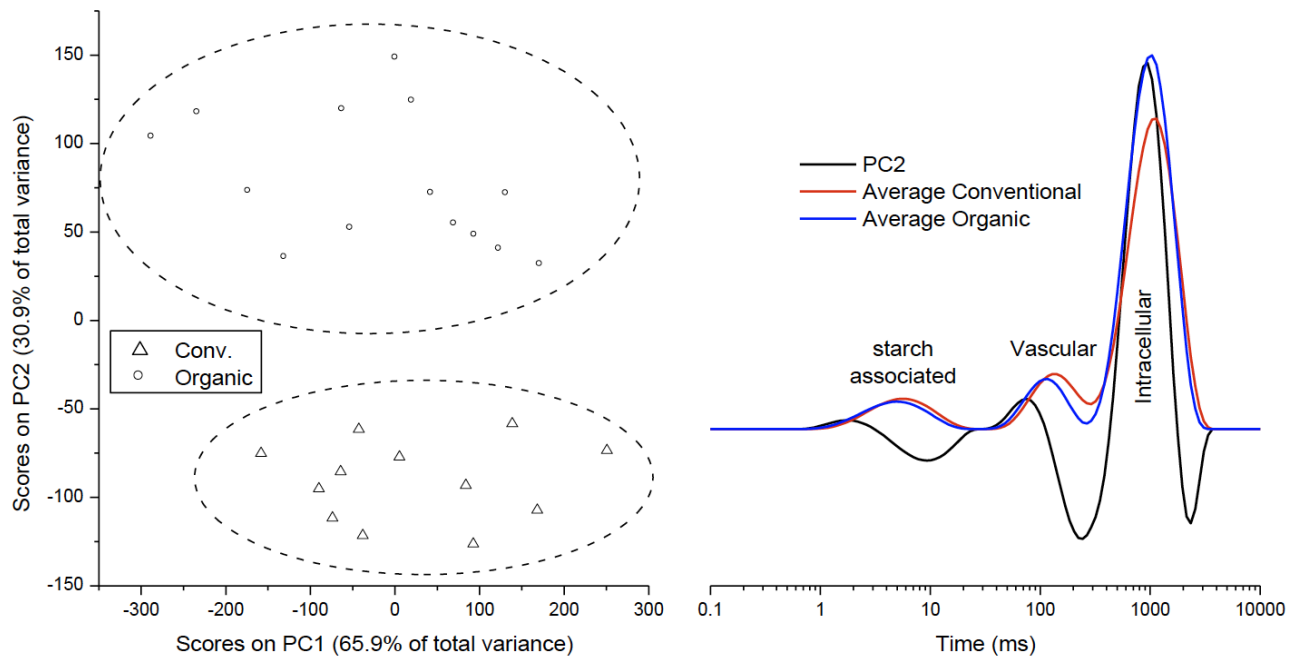


Figure 4. Principal Component Analysis (PCA) of mean centred T_2 distribution curves (ILT) obtained of whole potatoes (non-destructive). Left: PCA scores, the dashed line ellipses are the 95% confidence region for organic and conventional potatoes; right: PC2 loads.

versatile and powerful technique in Soil Science. We hope this will help to spark interest in new applications.

References

1. Maia, C. M. B. F., Novotny, E. H., Rittl, T. F. & Hayes, M. H. B. (2013) Soil organic matter: chemical and physical characteristics and analytical methods - a review. *Curr Org Chem.* 17, 19-24.
2. Blum, W.E.H. (1988). Problems of soil conservation. *Nature and environment series No. 39 Council of Europe, Strasbourg, France.*
3. Lal, R. (1997). Degradation and resilience of soils. *Philos Trans R Soc B* 352, 997- 1010.
4. Meyer, M., Buchmann, C. & Schaumann, G. E. (2018). Determination of quantitative pore-size distribution of soils with ^1H NMR relaxometry. *Eur J Soil Sci.* 69, 393-406.