Analysis of water content in wood material through 1D and 2D 1H NMR relaxometry: application to te the determination of the dry mass of wood

Leila Rostom, Sabine Caré, Denis Courtier-Murias

Référence article accepté :

Analysis of water content in wood material through 1D and 2D 1H NMR relaxometry: application to te the determination of the dry mass of wood

https://doi.org/10.1002/mrc.5125

Analysis of water content in wood material through 1D and 2D ^{1}H NMR relaxometry: application to the determination of the dry mass of wood

Leila Rostom[1], Sabine Caré[1], Denis Courtier-Murias[1,2]

[1]Lab. Navier, Ecole des Ponts, Univ Gustave Eiffel, CNRS, 77420 Marne la Vallée, France
[2]GERS-LEE, Univ Gustave Eiffel, IFSTTAR, F-44344 Bouguenais, France

Correspondence
Denis Courtier-Murias
Water and Environment Laboratory, GERS Department
University Gustave Eiffel, Bouguenais, France
Email: denis.courtier-murias@univ-eiffel.fr

Abstract:

There is an increasing interest on wood as it is an environmentally sustainable product (e.g. biodegradable and renewable). Thus, an accurate characterisation of wood properties is of extreme importance as they define the kind of application for which each type of wood can be used. For instance, dry mass of wood is a key parameter itself and is needed to calculate Moisture Content (MC) of wood, which is correlated to its physical properties. Due to the limitations of commonly used drying methods, preliminary work has shown the potential of ^{1}H NMR to measure dry mass of wood but it has never been validated. Here, we performed a critical analysis of 1D and 2D ^{1}H NMR relaxometry methods for obtaining the dry mass of wood and we compared their performance to three commonly used drying methods. This showed that commonly used drying methods do not remove all water from wood. Moreover, we are able to classify them accordingly to their performance. In addition, we showed that MC values obtained by ^{1}H NMR relaxometry methods are higher (up to 20%) than values from commonly used drying methods. This empathizes the importance of accurate values of dry mass of wood and the utility of ^{1}H NMR relaxometry on wood sciences. When comparing both NMR relaxometry methods, 2D should provide the more accurate results but 1D measurements would also be a recommended choice as they are faster than 2D and their results clearly overcome commonly used drying methods in a non-invasive and non-destructive manner.

Keywords: ^{1}H NMR, 1D and 2D NMR relaxometry, wood drying, dry mass, moisture content

Introduction

Since thousands of years, wood has been used for fuel, construction, making paper, etc. In addition, nowadays there is an increasing interest of wood uses as it is an environmentally sustainable product (e.g. biodegradable and renewable). Knowing several wood characteristics (e.g. density, shrinkage/swelling, degradation and mechanical response) is of extreme importance as they define the kind of application for which each type of wood can be used, taking into account in particular its hygroscopicity. In particular, fungal attacks, insects or climatic conditions can affect wood in living trees or in building constructions. The wood structures can be damaged, so that their performances may be modified or they will be completely useless.

Wood is composed of cells with different void (i.e. lumen) sizes and arrangements (essentially tracheids for softwoods and vessels and fibers for hardwoods).Cell walls are composed of hydrophilic and hydrophobic molecules (cellulose, hemicelluloses, and lignin). Due to its hygroscopic nature and its porosity, wood can absorb water as a liquid, if in contact with it, or as vapour from the surrounding atmosphere (essentially Relative Humidity (RH)). This will modify the moisture content (MC) in wood, which is correlated to its shrinkage and swelling or density, and thus its mechanical properties. MC depends on the sorption mechanisms and water uptake of each type of wood.[1,2] Moreover, it may be useful for studies where modifications of the chemical composition or the wood structure have an impact on the sorption (and desorption) mechanisms (e.g. in the case of the study of thermal treatments on wood properties). Water in cell walls is named bound water and when cell walls are saturated with bound water, the corresponding MC is called the Fiber Saturation Point (FSP). Water present in cell lumens is identified as free water. MC is defined as the ratio of the water mass to the dry wood mass.

Dry mass of wood can be estimated by different chemical and physical methods. For instance, water can be removed from wood by chemical reactions with materials such as calcium carbide, acid chlorides, or by the Karl Fischer reagent.[3] Physical methods can use the Dean and Stark distillation, oven drying with blowing air, or high vacuum drying at temperatures up to 105°C.[4] However, these methods are time consuming for many practical applications. Moreover, completely removing all water is impossible without damaging wood.[4] Indeed, the chemical bonds between wood fiber and water are strong.[4] Thus, the obtained dry mass may depend on the used method to "dry" wood samples. Moreover, oven drying at 103°C, which is the most used method, at least for routine MC determinations, is an invasive and destructive technique.[3] In particular, for some wood species, the extractives may leak out of the sample if the temperature is too high[5] and then this drying method could overestimate MC of wood. To overcome this issue, drying at 60°C in a vacuum oven with P_2O_5 for 24 to 28 hours can be used to obtain a RH close to 0% to allow preventing extractives leaking and accelerate the drying process, but without proof of removing all water.[6] As far as the authors are aware, these commonly used drying methods have not been compared to each other, it is then difficult to know which method is the most appropriate to measure wood dry mass and then MC. Therefore, due to all the difficulties to measure dry mass of wood, it appears that it is necessary to find a non-invasive and non-destructive method to be able to obtain accurate MC values.

Low-field ^{1}H Nuclear Magnetic Resonance (NMR) has been suggested several decades ago as an interesting tool for wood and wood-derived materials for the evaluation of bound and free water[7–11] and the investigation of the presence of liquid water below the FSP.[1] Regarding lignocellulosic materials, NMR relaxometry has been also used for studying biomass–water interactions, measuring water retention values (WRV), understanding biomass recalcitrance, and high solid effects.[12–15] Two main experiments are used in literature: (i) 1D T_2 NMR relaxometry, mainly due to its short experimental time and its possibility to distinguish bound

and free water and (ii) 2D T_1T_2 correlation NMR relaxometry, as it significantly improves resolution and gives physical and chemical information on the samples.[16–19] For instance, the latter enables the resolution of two types of bound water in the wood cell walls. Note that in the case of wood analysis 1D T_1 distribution spectra are usually not considered because bound water, free water (water present in the cell lumens) and solid wood may have similar T_1 values. This signal overlapping makes it difficult to distinguish these three phases without a detailed NMR parametrization and data analysis, which may lead to misinterpretation of T_1 distribution spectra. Moreover, experimental time needed for T_1 analysis is much longer than that needed for T_2 experiments.

Among the works using various ^{1}H NMR methods, dry wood mass has been also investigated.[4] In particular, this analysis was performed by deconvoluting ^{1}H NMR spectra into three different components, weakly bonded water, strongly bonded water and wood polymers. The complexity of this type of data treatment could explain why NMR signal and MC of wood changed linearly only at values lower than the FSP. Moreover, these NMR results were not compared to commonly used drying methods to critically discuss the performance of ^{1}H NMR to estimate dry mass of wood. As far as the authors are aware, this was the only time that NMR was used to obtain the dry mass of wood. Related works have shown that free induction decay (FID) ^{1}H NMR signal can be used to obtain a linear relationship between NMR signal and MC below and above the FSP.[20–22] Thus, showing that the use of NMR for MC determination is not limited to values lower than the FSP as it was previously concluded .[4] In recent years, ^{1}H NMR relaxometry has been used to determine the MC and density of wood materials[9,22,23] .[9,22–24] However, these methods have used ^{1}H NMR to obtain water quantities but dry mass of wood was still obtained by commonly used drying methods. In general, preliminary work has showed the potential of ^{1}H NMR spectroscopy for dry mass calculation of wood,[4] but its performance needs to be evaluated (e.g. in comparison to commonly used drying methods). Moreover, the influence of dry mass calculations by ^{1}H NMR on MC calculations is also unknown.

In this paper, we used 1D and 2D ^{1}H NMR relaxometry methods, being used in wood sciences in recent years, to estimate the dry mass of wood. Then, we will analyse and compare 1D T_2 ^{1}H NMR relaxometry, if fast quantification of dry mass of the sample is needed, and 2D T_1T_2 ^{1}H NMR relaxometry, as it is also becoming routinely used in wood sciences if detailed information about the type of water is of interest. We have also compared the obtained results to "commonly used" drying methods such as oven drying at 103°C, and the use of P_2O_5 and SiO_2 as drying agents. Finally, we evaluated the performance of both 1D and 2D ^{1}H NMR relaxometry methods to obtain MC of wood in comparison to the values provided by the "commonly used" drying methods.

^{1}H NMR relaxometry is gaining popularity in the field of wood sciences in recent years. Therefore, in this paper, we propose a new procedure using 1D and 2D ^{1}H NMR relaxometry methods to estimate the dry mass of wood. Moreover, the performance of the two methods is assessed and compared to commonly used drying methods such as oven drying at 103°C or the use of P_2O_5 and SiO_2 as drying agents. Finally, we evaluated the performance of both 1D and 2D ^{1}H NMR relaxometry methods to obtain MC of wood in comparison to the values provided by the commonly used drying methods.

Experimental

Materials

The experimental samples consisted of modern oak wood provided from a sawmill located in the North of France.[18] Nine samples of about 1x1x1 cm^3 were prepared from a wooden bar

with an average volume measured at 65% RH, $V_{65\%RH}$ = 1.1 ± 0.1 cm^3. They were sawn along the anisotropic directions (Longitudinal L, Radial R and Tangential T) and were taken, as possible, side by side to minimize the variability between samples. Note that the average density of the nine samples was found to be 588 ± 8 $kg.m^{-3}$ at 65% RH (Table 1, which also gives the densities for the three groups of samples). These results show a very small variability between the three groups confirming an adequate sampling protocol.

Table 1. Density ($kg.m^{-3}$) of the studied samples at 65% RH. Mean value μ for each group of samples and for the all nine samples are presented and the standard deviation SD values are provided: μ (SD).

	"oven samples"	"P_2O_5 samples"	"$Si0_2$ samples"	all samples
μ (SD)	590 (8)	582 (7)	589 (10)	588 (8)

The samples were subjected to a cycle of adsorption and desorption in order to adjust their hydric state to 65% RH (with a saturated solution of ammonium nitrate) on an adsorption cycle. The initial state at 65 (±3)% RH and 20 (±2)°C was characterized by measuring the weight and dimensions and by ^{1}H NMR relaxometry. RH and temperature were monitored with a Testo thermo-hygrometer and dimensions were measured with a Mitutoyo electronic calliper. The wood samples were then dried (according to three commonly used drying methods, see below) and analysed in their dry state noted "dry". To be able to compare the masses of samples with slightly different volumes, each sample was normalized to its volume measured before the NMR relaxometry experiments at 65% RH, $V_{65\%RH}$. Thus, for simplification, normalized units will be used (g_* referring to g/cm^3).

Commonly used drying protocols

We compared three commonly used drying methods to ^{1}H NMR relaxometry method for the determination of dry mass and MC of wood. These "commonly used" drying methods are related to methods usually reported in literature.[17,25–27] To do so, the specimens were divided into 3 groups:

- The "oven samples" group: three samples were dried in an oven at 103 (±0.5) °C for 24 hours;
- The "P_2O_5 samples" group: three samples were dried for one week in a closed desiccator filled with Phosphorus Pentoxide (P_2O_5) (which gives a RH of about 0-1%) at 20 (±2) °C;
- The "SiO_2 samples" group: three samples were dried for one week in a closed desiccator filled with Silica Gel (SiO_2) (which gives a RH of about 2-3%) at 20 (±2) °C.

At the end of these "commonly used" drying methods, the samples were weighed to obtain the "dry" mass of wood, $M_{drywood,w}$. Samples were then analysed through ^{1}H NMR relaxometry a second time but in a "dry" state. The dry mass obtained by ^{1}H NMR relaxometry is noted $M_{drywood,NMR}$.

It is important to note that the dry mass of the samples can vary with the duration of conditioning. Indeed, for the "P_2O_5 samples" and "SiO_2 samples", other durations (two and ten weeks) have been considered to better understand commonly used drying protocols and compare them with ^{1}H NMR relaxometry, knowing that the longer the samples stay in the desiccator, the dryer they get. Therefore, depending on the volume of samples, the precision of the scale and possible RH fluctuations, the "equilibrium" dry mass can evolve. In addition, as it is a time consuming step for the study of wood samples, it is then important to set an average duration of conditioning (assessed by mass monitoring) according to current standards.[27]

The MC of wood samples was determined to assess the influence of the dry mass determination. Therefore, it is determined at 65% RH, $MC_{w,65\%RH}$ by weighing (the samples are considered

being at equilibrium) and is defined as follows:

$$MC_{w,65\%RH} = \frac{M_{wood,w,65\%RH} - M_{drywood,w}}{M_{drywood,w}} \times 100 \quad (1)$$

with $M_{wood,w,65\%RH}$ the mass of the sample at 65% RH determined by weighing.
The $MC_{65\%RH,w}$ will be compared with the value obtained with ^{1}H NMR relaxometry (see following sections).

^{1}H NMR relaxometry

We have performed 1D and 2D ^{1}H NMR relaxometry measurements on all nine samples before and after drying treatments, i.e. at 65% RH and in the "dry state". Concerning the 1D ^{1}H NMR measurements, as explained in the Introduction section, only the T_2 distribution spectra were analysed because for T_1 distribution spectra, the peak with high T_1 relaxation values corresponds to the overlapping of bound water, wood polymers and eventually to free water (if samples in the hygroscopic domain above FSP are to be studied). The NMR device used is a BRUKER MINISPEC MQ20 spectrometer, which operates at 0.5 T, corresponding to a Larmor frequency of 20 MHz for ^{1}H.

The samples were inserted in an 18 mm NMR tube with a maximum sample height of 10 mm for an optimum operating performance. The RH was controlled with a saturated salt solution inside the NMR tube (placed in a small container on the top of the NMR tube using a cap) during the NMR relaxometry measurement at 65% RH.[17, 18] For samples measured at "dry state", the container was filled with SiO_2 or P_2O_5 for the corresponding drying method. Concerning the "oven dried samples", they were dried a second time in the oven right before the NMR relaxometry analysis as this measure at "dry state" was performed after seven weeks, during which they were stored in a desiccator filled with SiO_2. Therefore, the "oven dried samples" were analyzed in an NMR tube closed with a cap and secured with parafilm to avoid as much as possible RH changes during the analysis. As the temperature of the magnetic unit is 40°C, a cooling system is used to keep the samples at 20°C (at the bottom of the NMR tubes). The temperature of the room (at the aperture of the device) was measured during analysis and corresponds to 25 (±2) °C. The estimated variation of the RH (controlled by the saturated salt solution) due to temperature is up to 3% decrease of RH at 25°C. Therefore, to take into account possible variations of the RH during the analysis which can have an effect on MC, all samples were weighed before and after NMR relaxometry measurements. Moreover, the difference in MC calculated with the mass before or after NMR relaxometry measurements was evaluated and resulted to be lower than 0.1%.[18] Thus, this minor error does not affect the results and their interpretations.

The Inversion Recovery (IR) sequence coupled with the Carr-Purcell-Meiboom-Gill (CPMG) sequence[28,29] is usually used to measure the longitudinal (T_1) and the transversal (T_2) relaxation times therefore permitting to obtain T_1T_2 2D NMR correlation distribution spectra. In this work, the recovery time of the IR sequence was increased in 60 steps as a geometric series (i.e. following a regular sampling on a logarithmic scale) from 0.01 to 1000ms. CPMG echo train comprised 200 successive echoes with an echo time TE = 60µs, among which 50 echoes were recorded, following approximately a geometric series from 60µs to 12ms. To increase the signal-to-noise ratio (SNR), the T_1T_2 sequence was repeated 288 times. Repetition delay TR needs to be five times higher than the highest T_1 value (in this case 100 ms for adsorbed water) to ensure complete equilibrium recovery between successive sequences. Here it was finally set to 1s to also avoid excessive RF power deposition of the CPMG part of the sequence on the sample, and keep sample temperature constant.

1D T_2 NMR distribution spectra for the T_2 relaxations times were obtained by using data measured during the last CPMG block of the T_1T_2 NMR sequence (i.e. data obtained for the longest IR time). These data were analyzed by means of an inverse Laplace transform (ILT) algorithm, which converts relaxation signal into a continuous distribution of relaxations (i.e. T_2 distribution spectra). This was done by using a homemade computer program based on the method described by Whittall and MacKay[30] and Provencher[31] performing the same work as the well-known CONTIN program. Further details about the technique can be found in.[32]

The T_1T_2 experiments took about 6 hours and the T_2 experiments only 5 minutes. This makes NMR relaxometry an excellent tool due to its short experimental time and non-invasive and non-destructive nature. It should be noted that, these NMR relaxometry experiments are carried out on low-field NMR permanent magnets, contrary to high-field NMR used to quantify and characterize wood polymers in solution[33] and solid-state.[34] As experiments were performed over several months, the performance of the NMR instrument was verified by running a standard reference. Small variations on signal intensity were observed and corrected for each sample.

Determination of water and dry mass of wood through ^{1}H NMR relaxometry

Since NMR signal intensity depends on the number of measured nuclei, ^{1}H NMR signal can be converted into mass of water. To do so, a standard curve was performed with different quantities of water (Figure 1), obtaining a proportional coefficient α between the NMR signal intensity and the water mass. The water mass $M_{water,NMR,x\%RH}$ determined by ^{1}H NMR relaxometry at x% RH is therefore defined by Equation 2:

$$M_{water,NMR.x\%RH} = \frac{q_{NMR.x\%RH}}{\alpha} \quad (2)$$

where $q_{NMR,x\%RH}$ is the ^{1}H NMR signal intensity at x % RH and α the proportional coefficient determined through the standard curve (Figure 1). In this study, α was equal to 161.42 (±0.64) ^{1}H NMR signal intensity/g of water.

To calculate the dry mass of wood, it is necessary to know the total mass of wood and the amount of water inside the sample. As shown in Equation 2, the latter is calculated through ^{1}H NMR at x% RH (at 65% RH or in the "dry" state obtained with the three commonly used drying methods as depicted above). Therefore, the mass of dry wood $M_{drywood,NMR}$ can be calculated as follows:

$$M_{drywood,NMR} = M_{wood,w,x\%RH} - M_{water,NMR,x\%RH} \quad (3)$$

where $M_{wood,w,x\%RH}$ is the total mass of wood determined by weighing at x% RH in two ways:

- For the T_1T_2 analysis: it is the average value of the masses weighed before and after the NMR relaxometry experiment;
- For the T_2 analysis: only the mass after the NMR relaxometry analysis is considered as the data used for T_2 analysis is acquired in the last 5 minutes of the analysis. It is therefore important to take into account possible evolution of the water content in wood during the NMR relaxometry experiments.

The Moisture Content $MC_{NMR,x\%RH}$ [%] determined by ^{1}H NMR relaxometry measurements at x% RH is then defined by Equation 4:

$$MC_{NMR,x\%RH} = \frac{M_{water,NMR,x\%RH}}{M_{drywood,NMR}} \times 100 \quad (4)$$

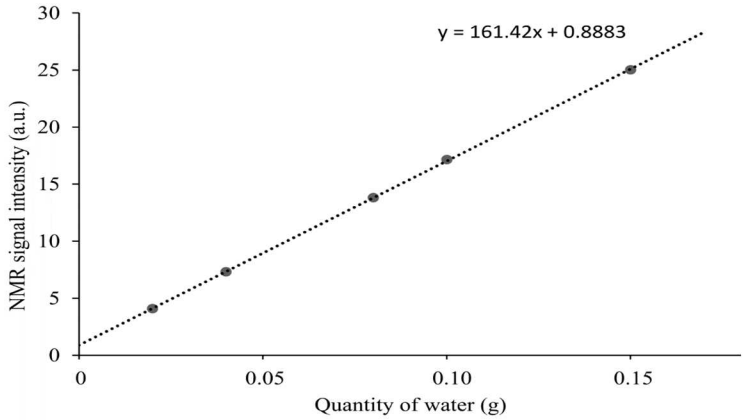

Figure 1. Standard curve showing the relationship between NMR signal intensity and water amount.

Uncertainties on the mass of samples and moisture content

The uncertainties on masses and MC are evaluated for each specimen and for the two methods used (weighing and ^{1}H NMR relaxometry). The uncertainties on masses are noted: $\Delta M_{wood,w,65\%RH}$, $\Delta M_{drywood,w}$, $\Delta M_{drywood,NMR}$, $\Delta M_{water,NMR,x\%RH}$ and those on MC are defined as: $\Delta MC_{w,x\%RH}$ and $\Delta MC_{NMR,x\%RH}$.

The uncertainties on masses $\Delta M_{wood,w,65\%RH}$ and $\Delta M_{drywood,w}$ obtained by weighing at 65% RH and at the end of the three commonly used drying methods respectively, have been evaluated considering two factors. These are the precision of the scale (0.0002g considering the tare weight) and the evolution of the mass of the samples over time due to the fluctuations of RH for all samples. The average uncertainties with normalized units were estimated for 'dry state': $\Delta M_{drywood,w} = 0.001$ g* for "SiO_2 and P_2O_5 samples" and $\Delta M_{drywood,w} = 0.003$ g* "for oven samples" and for at 65% RH: $\Delta M_{wood,w,65\%RH} = 0.002$ g* for the nine samples.

The uncertainties on the mass of water $\Delta M_{water,NMR,x\%RH}$ and the "dry" mass $\Delta M_{drywood,NMR}$ obtained through ^{1}H NMR relaxometry experiments at x% RH are expressed according to Equations 5 and 6:

$$\Delta M_{water,NMR,x\%RH} = \frac{q_{NMR.x\%RH}}{\alpha} \times \left(\frac{\Delta q_{NMR,x\%RH}}{q_{NMR,x\%RH}} + \frac{\Delta \alpha}{\alpha} \right) \quad (5)$$

$$\Delta M_{drywood,NMR} = \Delta M_{wood,w,x\%RH} + \Delta M_{water,NMR,x\%RH} \quad (6)$$

The data in the Equations 5 and 6 are evaluated according to:

- $\frac{\Delta q_{NMR,x\%RH}}{q_{NMR,x\%RH}} = 2\%$ for measurements at 65%RH and $\frac{\Delta q_{NMR,x\%RH}}{q_{NMR,x\%RH}} = 31\%$ for measurements at 'dry state' according to Bonnet et al.[17] These uncertainties have been determined from T_1T_2 distribution spectra of a Douglas-fir wood, dried with SiO_2. It is supposed that the uncertainties on the NMR signal are similar in this work, for the other drying methods and the T_2 distribution spectra and do not depend on the wood species. These uncertainties take into account some biases linked to the ILT data processing that can affect the measured values. The stability of this data processing was analyzed by adding white noise on a model signal that is close to the experimental data.[16]
- $\frac{\Delta \alpha}{\alpha} = 0.39\ \%$ with $\Delta \alpha = 0.64$ evaluated from three standard curves performed at different times.

- $\Delta M_{wood,w,x\%RH}$: the uncertainties on the measurements by weighing are the same than those determined above. For T_1T_2 measurements: the uncertainty due to eventual variations of MC during NMR relaxometry experiments has been quantified by weighing the samples before and after each NMR relaxometry experiment. For T_2 measurements, the uncertainty due to eventual variations of RH during NMR relaxometry experiments has been quantified by weighing the samples after each NMR relaxometry experiment.

The average uncertainties, determined through ^{1}H NMR relaxometry, for the nine samples are: $\Delta M_{water,NMR,x\%RH} = 0{,}001$ g* and $\Delta M_{drywood,NMR} = 0{,}003$g*. These are applied for T_1T_2 and T_2 measurements and for the two hydric states (at 65%RH and in the 'dry state').

Concerning MC calculations, the uncertainties obtained by weighing ($\Delta MC_{w,x\%RH}$) and by ^{1}H NMR relaxometry methods ($\Delta MC_{NMR,x\%RH}$) at x = 65% RH, are then determined by:

$$\Delta MC_{w,x,\%RH} = \left(\frac{\Delta M_{wood,w.x\%RH}}{M_{drywood,w}} + \frac{M_{wood,w,x\%RH}}{M_{drywood,w}^{\,2}}\Delta M_{drywood,w}\right) \times 100 \quad (7)$$

$$\Delta MC_{NMR,x\%RH} = MC_{NMR,x\%RH} \times \left(\frac{\Delta q_{NMR.x\%RH}}{q_{NMR.x\%RH}} + \frac{\Delta\alpha}{\alpha} + \frac{\Delta M_{drywood,NMR}}{M_{drywood,NMR}}\right) \quad (8)$$

The uncertainties of the different data in the Equations 7 and 8 are the same than those expressed above. The average uncertainties on MC at 65% RH are: $\Delta MC_{NMR,65\%RH} = 0.3$ % of the nine samples and $\Delta MC_{w,65\%RH} = 0.4$ % for "SiO_2 and P_2O_5 samples". Concerning the "oven samples", the uncertainties are higher (about 1%).

The determination of these uncertainties provides information about the precision of weighing and ^{1}H NMR relaxometry measurements and then allows to compare the methods against each other. The obtained results show that the accuracy of all methods is similar even if for "oven samples" the precision seems to be less good.

Moreover, to determine if the differences obtained between the methods are significant or not, we performed Student T-test. In addition, Standard Deviation (SD) for each group, expressed as the square root of the variance of the data set, was calculated to evaluate the dispersion of the results between samples. Results of Student T-tests are mentioned in Supplementary Material and SD values in Tables.

Note that, as explained previously, to compare the results of the nine samples, the masses of wood have been normalized to consider a volume equal to 1cm^3 at 65% RH. Taking into account the uncertainties on the measured dimensions with the calliper equal to 0.01mm, the uncertainties on masses and MC are higher, however they do not modify the conclusions on the results of Students T-tests and on SD values.

Results and discussion

Comparison of T_1T_2 and T_2 distribution spectra of wood at 65% RH

^{1}H T_1T_2 NMR distribution spectra of wood at 65% RH show four main peaks (Figure 2a), which have been previously labelled as A, B, C and D and assigned to free water in large pores (lumens), strongly interacting bound water, weakly interacting bound water and hydrogen atoms of wood polymers respectively.[16,17] In this work, as samples are below the FSP, signal corresponding to bound water and hydrogen atoms of wood polymers is mainly observed but also coming from traces of peak A. These traces of free water have already been observed below the FSP[35] and the position of peaks above the T_1=T_2 limit has been explained due to its very low intensity.[17] Moreover, other studies have shown that wood may contain free water below

the FSP.[35] Due to their small intensity, these peaks could be just artefacts due to the processing, but further analysis and spectral interpretation are out of scope of this work. The goal here is to obtain the total mass of water inside the sample by measuring the ^{1}H NMR signal corresponding to water. Thus, the signal intensities of all peaks expect for peak D were considered for the calculations.

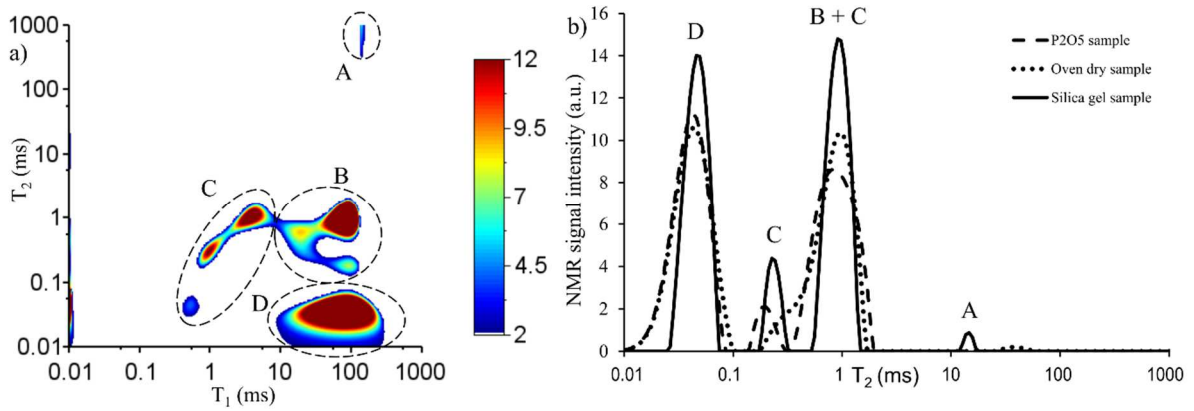

Figure 2. (a) T_1T_2 distribution spectrum for one of the specimens of the "oven sample" group and (b) T_2 distribution spectra of one sample from each drying method (right-hand side) both at 65% RH. Peaks A, B, C and D correspond to free water, strongly bound water, weakly bound water and wood polymers respectively.

^{1}H T_2 NMR distribution spectra show three main peaks (Figure 2b): a first peak for T_2 values lower than 0.1ms, corresponding to wood polymers, and two other peaks with T_2 values between 0.1 and 2ms, corresponding to bound water. It should be noted that these two peaks are not always well distinguished (e.g. T_2 NMR distribution spectrum of "oven samples"). This shows a clear advantage of T_1T_2 over T_2 NMR relaxometry analysis as the former will better separate the peaks (the distance between peaks is higher in a 2D NMR distribution spectra than in 1D NMR distribution spectra). As the analysis of NMR relaxation is carried out by post-treating time-domain NMR data using an ILT algorithm, peak resolution due to this post-treatment depends on SNR. Thus, increasing number of scans could allow to improve peak resolution. However, this is not needed for this work as it is just necessary to separate the ^{1}H NMR signal from wood polymers from the water signal, to be able to quantify the total water mass inside wood. There are some very small peaks with T_2 NMR values higher than 5ms, as for T_1T_2 NMR distribution spectrum, which again should correspond to small traces of peak A. The two peaks with T_2 NMR values higher than 0.1ms (and lower to 10ms) correspond to bound water (peaks B and C on T_1T_2 NMR distribution spectra). The one with the shorter relaxation time matches well with a part of peak C. Indeed, a previous study has already shown that peak C can split into two different peaks having a similar T_1/T_2 ratio but a different T_2 relaxation time.[18] The other peak (at 1ms), also corresponding to bound water, accounts for peak B and for the rest of peak C. To calculate the water mass, the signal of all peaks with a T_2 value higher than 0.1ms was used. It should be noted that a small peak assigned to water on the T_1T_2 NMR distribution spectra (with a T_2 value shorter than 0.1ms and a T_1 value shorter than 1 ms) overlaps with the peak corresponding to wood polymers on the T_2 NMR distribution spectra. This could lead to an underestimation of water in the T_2 NMR data processing. However, its intensity being very small, it should not affect the interpretation of the T_2 NMR relaxometry analysis.

It is important to note that NMR parameters used for T_2 NMR signal decay measurements (for both T_1T_2 and T_2 data) are only adequate for relatively short T_2 values (of the order of few ms). This could however induce some errors for the free water analysis as it has longer T_2 NMR

values (about 1 s for lumen water). However, this error will mainly affect the accuracy of T_2 NMR values (which are not used in this work) but the signal intensity will be almost unaffected. Moreover, in this particular work the amount of signal with long T_2 values is very small. If free water is to be measured, NMR parameters concerning T_2 should be modified. However, care must be taken as this could increase RF deposition and thus lead to sample heating and even RF-coil damage. To reduce RF deposition, it is possible to increase recycle delays (increasing experimental time) and/or use logarithmic echo times as this reduces the number of RF pulses by unit of time.[36] There is still concerns about use of the latter approach as unwanted signal "coherence-pathways" may not be eliminated as effectively as with linear spacing.[37] However, this approach has shown great results for practical applications in wood sciences.[38] In general, T_1T_2 NMR distribution spectra provide rich information about the different types of water and their "state" inside wood, but for water quantification and dry mass calculations, the resolution obtained by T_2 NMR relaxometry should provide the same results in just a small fraction of the time required for a T_1T_2 NMR relaxometry experiment.

Dry mass of wood obtained by 1D and 2D ^{1}H NMR relaxometry at 65%

As previously explained, ^{1}H NMR signal can be converted into water amount and then dry mass of wood may be calculated by subtracting it from the total wood mass obtained by weighing (Equation 3). Here, the results from T_1T_2 and T_2 ^{1}H NMR relaxometry experiments carried out on the nine different wood samples at 65% RH are used for the determination of the dry mass of wood (Table 2). First, mass of water is obtained by NMR relaxometry ($M_{water,NMMR,65\%RH}$) which is then subtracted from the mass of wood obtained by weighing ($M_{wood,w,65\%RH}$) (data not shown), providing dry mass of wood ($M_{drywood,NMR,65\%RH}$).

Table 2. Results of 1D T_2 and 2D T_1T_2 ^{1}H NMR relaxometry analysis of wood samples at 65% RH for the calculation of water mass $M_{water,NMR,65\%RH}$ (g*) and dry mass $M_{drywood,NMR}$ (g*) for the three "group of samples" used in this work. Mean values for the nine samples are also provided. SD values are included in parenthesis. We performed paired Student's t-tests to compare dry masses obtained by 1D and 2D NMR relaxometry methods, showing that values were not significantly different (p-value > 0.10), and to compare 2D NMR relaxometry results to commonly used drying methods, with p-values < 0.05).

	NMR method	"oven samples"	"P_2O_5 samples"	"SiO_2 samples"	all samples
$M_{water,NMR,65\%RH}$	1D	0.065 (0.002)	0.064 (0.001)	0.067 (0.003)	0.065 (0.002)
	2D	0.063 (0.002)	0.064 (0.002)	0.064 (0.002)	0.06436 (0.002)
$M_{drywood,NMR}$	1D	0.525 (0.006)	0.521 (0.010)	0.523 (0.010)	0.524 (0.008)
	2D	0.526 (0.007)	0.521 (0.008)	0.525 (0.009)	0.524 (0.007)

Table 2 presents the results obtained by 1D and 2D ^{1}H NMR relaxometry analysis for each group of drying method, in terms of mass of water and calculated dry mass of wood. These results will be compared to the dry masses obtained by the commonly used drying methods, presented in Table 3. The results obtained by 1D and 2D NMR relaxometry methods are very similar but small differences can still be noticed. For instance, the average value of mass of water is slightly lower for T_1T_2 NMR relaxometry experiment compared to average value obtained by T_2 NMR relaxometry analysis. As explained in the Experimental section, the average value of mass before and after NMR relaxometry analysis was used for the T_1T_2 NMR

relaxometry analysis, while for the T_2 NMR relaxometry analysis, the mass at the end of the NMR relaxometry experiment has been used (because the T_2 data is recorded at the end of the NMR relaxometry experiment). The mass of samples at the end of the experiments is slightly higher than the mass before the NMR relaxometry experiment, which means that there should be more water inside the wood samples during the time T_2 NMR data is recorded. This explains the small differences on the detected water amount, which is slightly lower for the T_1T_2 NMR relaxometry experiment. However, dry masses of wood obtained by 1D and 2D NMR relaxometry are very similar, showing that the ^{1}H NMR relaxometry method works well for both experiments and is able to take into account the variation of humidity in samples, due to RH variations. In general, the differences between dry wood masses calculated by 1D and 2D NMR relaxometry methods are relatively small, so it can be concluded that both 1D and 2D NMR relaxometry experiments perform equally well. In addition, it can be mentioned that the uncertainties of the calculated dry masses are similar for the 1D and 2D ^{1}H NMR relaxometry methods. The Student T-test performed on the values obtained by both NMR methods shows that the differences are not significant, meaning that the results obtained with both methods are similar (see Supplementary Material for further details).

Table 3. Dry mass (g*) determined by weighing of samples subjected to the three drying methods: in a desiccator with SiO_2 or P_2O_5 for different durations and in an oven at 103°C for 24 hours. Relative differences (%) are calculated by subtracting dry mass values from commonly used drying methods from values obtained with NMR relaxometry (Table 2) and dividing the result by values obtained with NMR relaxometry. The relative differences for 1D and 2D ^{1}H NMR relaxometry methods are provided in parenthesis (1D/2D). We performed paired Student T-tests to compare dry masses from NMR relaxometry methods and commonly used drying methods after 24 h, showing that values were significantly different (p-values < 0.05). Moreover, we performed unpaired Student T-test between relative difference values to compare the performance of commonly used drying methods, showing that they are significantly different (p-values < 0.05 except for P2O5 vs SiO2 with p-value ≈ 0.10)

drying duration	"oven samples" (24 h)	"P_2O_5 samples"	"SiO_2 samples"
one week	0.532 (0.007)	0.527 (0.008)	0.534 (0.008)
two weeks	/	0.526 (0.008)	0.533 (0.008)
ten weeks	/	0.524 (0.008)	0.535 (0.008)
Relative difference (one week) 1D / 2D	1.2 (0.3) / 1.1 (0.1)	1.2 (0.4) / 1.3 (0.1)	2.1 (0.6) / 1.7 (0.3)

Comparison of dry mass determined by ^{1}H NMR relaxometry and by weighing with commonly used drying methods

To validate the results obtained by 1D and 2D ^{1}H NMR relaxometry methods and the advantage to use them to measure dry mass of wood, we compared NMR relaxometry results to commonly used drying methods. The nine samples studied in the previous section were split in three groups and each group was dried accordingly to different commonly used protocols (oven drying, P_2O_5 and SiO_2) to obtain the dry mass of wood. Results are given in Table 3 and are compared to the values obtained with ^{1}H NMR relaxometry (Table 2). The relative differences between these two methods were also calculated.

We have applied the SiO_2 and P_2O_5 methods for different durations: one, two and ten weeks;

while the "oven dry samples" have been dried for only 24h, as long exposition to high temperature may damage the samples and/or lead to possible extractives leaking. Therefore, the value used for comparison, in Table 3, is the one right after 24 hours drying. The mass of the samples conditioned with SiO_2 and P_2O_5 continue to decrease after one week (with the exception of SiO_2 after ten weeks but we can explain this because of an increase of RH inside the desiccator due to a decrease of SiO_2 performance). However, even if there is still some water that can be removed from wood, the decrease is very small (less than 0.1% each day). Therefore, according to the standards, the mass could be considered constant and the samples dried for one week used as the reference of the protocol for comparison. Moreover, previous works have shown that this duration can be considered adequate for drying samples with these kind of dimensions.[17,18] However, this shows some of the limitations of commonly used methods. Firstly, it is necessary to follow the variation of mass until equilibrium (e.g. less than 0.1% per day) and the time needed for drying samples is closely related to the size of the samples (the bigger the samples, the longer the drying time). Secondly, even for small specimens as the ones used in this work, there is still water inside wood after one week of drying, which is already a long drying protocol. The fact that dry masses of wood obtained by ^{1}H NMR were always lower than the values obtained by the commonly used methods, confirms that these drying methods do not allow to remove all water from wood as fast as it may be needed for experiments, which may even be impossible without damaging wood.[4] This was validated by Student T-tests as shown in Supplementary Material.

When comparing the results of commonly used drying methods to the ones obtained from NMR relaxometry, it appears that there is a significant difference on the performance between all these techniques, even if the uncertainties on the calculated dry masses are slightly higher for the ^{1}H NMR relaxometry method compared to the commonly used drying methods, as mentioned in the Experimental section. Let us focus on 2D NMR relaxometry results as shown in previous section they are likely to provide more accurate results than 1D NMR relaxometry (SD values for 2D NMR relaxometry are about half of values for 1D NMR relaxometry). The highest relative difference in dry mass values compared to 2D NMR relaxometry was observed for samples conditioned in the SiO_2 with 1.7% relative difference. P_2O_5 method showed an intermediate value of about 1.3% relative difference, while the oven method provided the smallest relative difference with NMR relaxometry values (1.1%). This allows classifying these three drying methods according to their level of performance in removing water from wood: oven>P_2O_5>SiO_2. To confirm this, we performed Student T-tests by comparing results of commonly used drying methods, providing p-values < 0.05 expect for the comparison between P_2O_5 and SiO_2 with a p-value ≈ 0.10 (see Supplementary Material for more details). Although 1D NMR relaxometry methods do not clearly show the same trend as 2D NMR relaxometry, differences between 1D and 2D ^{1}H NMR relaxometry concerning dry mass calculations are very small, showing a similar performance of both NMR relaxometry methods. Thus, for this type of analysis, 1D ^{1}H NMR relaxometry, which has a shorter acquisition/analysis time than 2D ^{1}H NMR relaxometry, would be the best choice for the determination of the dry mass of wood in routine use.

1D and 2D ^{1}H NMR relaxometry of "dry" wood

Results showed on previous sections showed that commonly used drying methods do not allow to remove all water from wood (NMR relaxometry methods provide lower dry mass values than commonly used drying methods). To confirm this, we have performed additional ^{1}H NMR relaxometry experiments on samples after drying (Figure 3), looking for traces of water in wood. Figure 3 (a) presents the T_1T_2 distribution spectra of a dry sample showing small peaks corresponding to adsorbed water in wood and confirming the presence of traces of bound water

in wood. In addition to confirming the presence of water in these dried samples, a critical analysis of the ^{1}H NMR distribution spectra could help to better understand the utility of ^{1}H NMR relaxometry to obtain dry mass of wood and to calculate its MC.

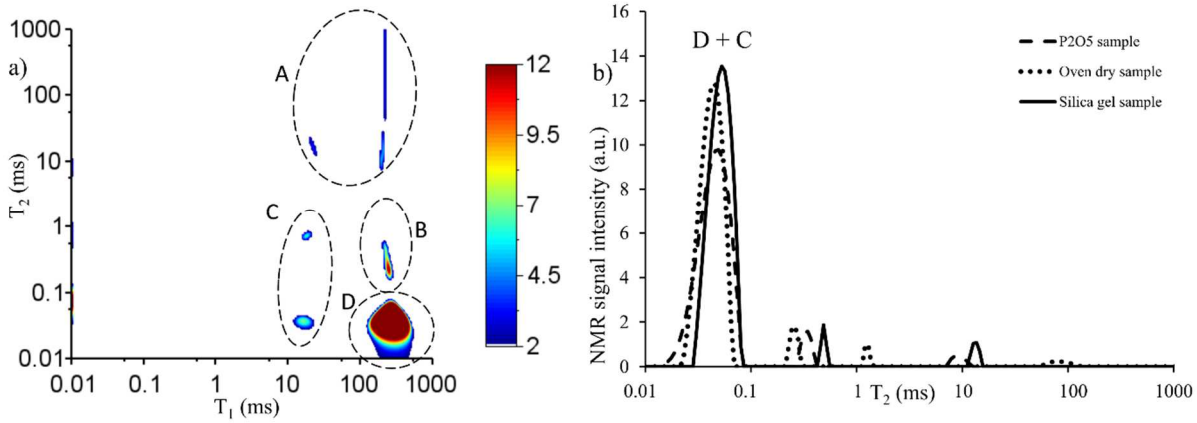

Figure 3. (a) T_1T_2 distribution spectrum for one of the specimens of the "oven sample" group treated for 24h at 103°C (left-hand side) and (b) T_2 distribution spectra of one sample from each drying method after 1 week of drying and 24h treatment for 'oven sample' (right-hand side). Peaks A, B, C and D correspond to free water, strongly bound water, weakly bound water and wood polymers respectively.

The general features of 1D and 2D NMR distribution spectra of "dry" samples are the same as for samples at 65% RH discussed in previous sections. The main difference observed is the amount of water signal, which is much smaller for "dry" samples. In addition, as previously shown in literature,[17] both T_1 and T_2 NMR values for water signal decrease along with a decrease of RH. When comparing 1D and 2D NMR distribution spectra there are some peculiarities for "dry" samples, not found for wood analysed at 65% RH. Indeed, in T_1T_2 NMR distribution spectra, the peak of water with short T_2 and T_1 values (corresponding to a part of peak C) has a higher intensity for the "dried" samples compared to their state at 65% RH. This peak represents about 25% of total water signal for "dry" samples and cannot be measured by T_2 NMR relaxometry experiments as it is overlapping with the signal from wood polymers. Thus, it is expected that T_1T_2 NMR data provide more accurate results than T_2 NMR data (as only 75% of water is measured) for the calculation of the amount of water in wood.

The difference in performance between 1D and 2D NMR relaxometry methods can be shown by looking at the values in Table 4. For instance, the amount of water found for the three drying methods vary between 1D and 2D NMR relaxometry methods. For 1D NMR relaxometry the values are very similar but 2D NMR values showed a higher variation and there is a similar trend to that observed for dry mass calculation at 65% RH. Oven drying methods had the lowest amount of water, P_2O_5 showed an intermediate value and SiO_2 the highest one. The values of dry mass are very similar (0.527 and 0.526 for 1D and 2D NMR relaxometry respectively) but the difference between these values is greater than for the values obtained at 65% RH (0.5240 for both 1D and 2D NMR relaxometry in Table 2). In the first case, the value obtained from 1D NMR relaxometry is higher than the value obtained by 2D NMR relaxometry. This should come from the overlapping occurring in the T_2 NMR distribution spectra leading to a partial measurement of water and thus an overestimation of dry mass of wood. It is also important to note that the dry mass of wood obtained by ^{1}H NMR relaxometry at 65% RH is lower than the value obtained from samples at "dry" state. This is probably due to some water at the "dry" state may have very short T_2 values, making it "invisible" to ^{1}H NMR relaxometry methods. Thus, it is recommended to study samples at high RH values but, even at low RH, ^{1}H NMR relaxometry is still able to measure most of water and overperforms commonly used drying

methods.

Table 4. Results of 1D T_2 and 2D T_1T_2 ^{1}H NMR relaxometry analysis of wood at "dry" state for the calculation of water mass $M_{water,NMR,x\%RH}$ (g*) and dry mass $M_{drywood,NMR}$ (g*) for the three "drying" methods used in this work. The notation "x%RH" has been used for water mass, as the actual RH for each "drying" method is unknown. Mean values for the nine samples are shown for $M_{drywood,NMR}$ but not for $M_{water,NMR,x\%RH}$ as the amount of water and MC should not be the same for each drying protocol. SD values are included in parenthesis.

	Method	"oven samples"	"P_2O_5 samples"	"SiO_2 samples"	all samples
$M_{water,NMR,x\%RH}$	1D	0.0038 (0.0009)	0.0039 (0.0003)	0.0034 (0.0004)	/
	2D	0.0038 (0.0002)	0.0043 (0.0004)	0.0055 (0.0009)	/
$M_{drywood,NMR}$	1D	0.526 (0.008)	0.522 (0.008)	0.533 (0.008)	0.527 (0.008)
	2D	0.525 (0.008)	0.522 (0.007)	0.531 (0.009)	0.526 (0.008)

Moisture Content

In addition to dry mass of wood, another crucial parameter of wood is the MC, which actually needs dry mass of wood for its calculation (see Eqs. 1 and 4). To emphasize the importance of obtaining accurate dry mass values, MC values obtained using dry mass from NMR relaxometry methods are compared to the MC obtained using dry mass from the three commonly used drying methods (Table 5).

Table 5. MC of samples subjected to the three drying methods: in a desiccator with SiO_2 or P_2O_5 during one week and a 24-hours drying in an oven at 103°C. $MC_{65\%RH}$ corresponds to the moisture content calculated either by weighing (Eq. 1) or by ^{1}H NMR relaxometry (Eq. 4). The relative differences (%) were obtained by subtracting weighing value from NMR value and dividing it by weighing method value. Mean and relative difference values for the nine samples are not calculated as they do not should provide the same results for each weighting method. Paired Student's t-tests were performed to compare MC values from NMR relaxometry methods and commonly used drying methods, showing that values were significant different (p-values < 0.05). Moreover, we performed unpaired Student T-test between relative difference values to compare the performance of commonly used drying methods, showing that they significantly different (with p-values < 0.05 for "oven samples" vs "SiO_2 samples" and "oven samples" vs "P_2O_5 samples" and p-values < 0.10 for "P_2O_5 samples" vs "SiO_2 samples"). *We identified a possible outlier value for 1D analysis of "SiO_2 samples" but as this difference could be explained due to sample heterogeneity and 1D NMR relaxometry measurement uncertain, it was kept for calculations. If this value is not used, the results for $MC_{65\%RH}$ for SiO_2 samples, all samples and relative difference for SiO_2 samples are 12.4 (0.1), 12.3 (0.2) and 20.7 (2.1) respectively. This does not affect to data interpretation.

	Method	"oven samples"	"P_2O_5 samples"	"SiO_2 samples"	all samples
$MC_{65\%RH}$	Weighing	10.9 (0.1)	10.8 (0.2)	10.3 (0.2)	/
	1D NMR	12.3 (0.3)	12.30 (0.1)	*12.8 (0.6)	*12.4 (0.4)
	2D NMR	12.0 (0.2	12.2 (0.1)	12.2 (0.3)	12.1 (0.2)
Relative difference	1D NMR	13 (2)	14 (3)	*24 (6)	/
	2D NMR	11 (1)	13 (1)	18 (4)	/

First, we compared the performance of the three commonly used methods. As expected from results showed in previous sections, a trend is observed when MC is compared between the three commonly used methods (Table 5). SiO_2 method shows the lowest MC value, the oven drying method provides the highest MC value and P_2O_5 has an intermediate value. Thus, they can be classified in terms of drying performance (oven> P_2O_5>SiO_2). It is important to note that when dry mass calculations were compared in previous sections, relative differences varied from 1.1 to 1.7%, which are relatively low values. However, the relative differences of MC values between commonly used drying methods and NMR relaxometry (calculated as $(\mathrm{MC_{NMR,65\%RH}} - \mathrm{MC_{w,65\%RH}})/\,\mathrm{MC_{w,65\%RH}}) \times 100$) are much more important. Relative differences for MC ranged from 11 to 24 %, meaning that even relatively small errors of dry mass lead to important differences in the MC calculated. This emphasize the importance of measuring accurate values of dry mass of wood and the limitations of commonly used drying methods.

Let us now focus on comparing 1D and 2D ^{1}H NMR relaxometry methods. Both of them provided similar results, which are significantly higher than the values obtained by commonly used methods. Moreover, we can also use the relative differences values to compare the performance of 1D and 2D ^{1}H NMR relaxometry methods. For both 1D and 2D ^{1}H NMR relaxometry experiments, relative difference values show the same trend as what it was observed for commonly used drying methods concerning drying performance. We will look first at 2D ^{1}H NMR relaxometry results as they are more accurate and trend is clearer. Relative difference values are high for the method with a poor drying performance and low for good drying performance (11 % for oven method, 13 % for P_2O_5 method and 18 % for SiO_2 method). This is not so clear for 1D NMR relaxometry experiments (13 % for oven method and 14 % for P_2O_5 method), which could be explained by the limitations of 1D ^{1}H NMR relaxometry experiments due to some signal overlapping explained on previous sections, which slightly affect water quantification and dry mass calculations. Furthermore, SD values for 1D NMR relaxometry for MC calculations are about the double than for 2D NMR relaxometry. We have confirmed it by performing a student T-test to compare 1D and 2D NMR relaxometry for MC calculations (see Supplementary Material), showing that their results are significantly different (although they are not for dry mass calculations). This empathises again the importance of obtaining accurate dry mass values and also the advantages of 2D over 1D NMR relaxometry (which are not so clearly for dry mass calculations).

In conclusion, the results presented in this work clearly show that MC values are underestimated with commonly used drying methods. Thus, results obtained by these NMR relaxometry experiments cannot be directly compared with previously published data (obtained by commonly used drying methods). A possible solution could be to scale these values by a factor equal to the relative difference values (Table 5). However, this should be tested for other types of woods and drying methods to completely validate this approach. Concerning other types of wood, as far as they have similar NMR relaxometry spectra (as it happens for other published works), this protocol should be feasible for them too. In general, both 1D and 2D approaches provided comparable results for MC calculations but 2D NMR relaxometry provided slightly more accurate results (SD values for 2D NMR relaxometry are about half of that for 1D NMR relaxometry, Table 5). However, if fast quantification of MC of the sample is needed (and detailed information about the type of water is not of interest), ^{1}H T_2 NMR relaxometry should provide good enough results which overperform commonly used drying methods in a faster way and in a non-invasive and non-destructive manner.

Conclusions

The study presented here showed that NMR relaxometry is an excellent tool for obtaining dry mass and MC of wood. Due to its short experimental time and the non-invasive and non-destructive nature of this technique, it should be increasingly used in wood sciences, as it overcomes some limitations of commonly used drying methods. Indeed, even if the oven drying method shows great performance it could however alter the sample (wood polymers and extractives).[39,40] The two other methods using saturated salt solution and silica gel show that they are not able to remove all water from wood, being NMR the unique technique able to measure dry mass of wood accurately and without damaging the samples. However, it requires a sampling/sample collection and a sample size of maximum $1cm^3$.

The experiments carried out also allowed evaluating the performance of three drying methods commonly used in wood sciences. They show that oven drying allowed to better remove water from wood, P_2O_5 showed an intermediate performance and SiO_2 provided the worst performance within the three methods for drying wood samples. Comparing the results after one week of drying (24h for oven method) to NMR relaxometry analysis permitted to obtain a relative difference for dry mass calculations, which ranged from 1.1 to 1.7 %. If these masses are used to calculate MC of wood, the relative errors increased to values from 11 to 18%, empathising the importance of measuring accurate dry mass values of wood. Due to the important differences on MC of wood between NMR relaxometry and commonly used drying methods, care should be taken when comparing them to previously published data obtained by commonly used drying methods.

A critical analysis of both 1D T_2 and 2D T_1T_2 ^1H NMR relaxometry methods has also been carried out. The main technical differences between the two techniques is the experimental time needed to carry them out, which is much higher for T_1T_2 NMR relaxometry experiments. Concerning spectral analysis, some water signal that overlaps with signal coming from wood polymers in T_2 NMR distribution spectra can be clearly measured on T_1T_2 NMR distribution spectra. This amount of water is very small and thus does not have a clear effect on dry mass but this effect is more important for MC calculations. A positive point of T_2 NMR relaxometry experiments is related to their short experimental time in comparison to T_1T_2 NMR relaxometry experiments (5 min vs. 6 hours). In practical applications for obtaining dry mass and MC of wood, T_1T_2 NMR relaxometry experiments should provide the more accurate results, but if there were no interest on studying different types of bound water, T_2 NMR relaxometry measurements would be the recommended choice, as the results still clearly overcome commonly used drying methods.

It is also important to note that we carried out these NMR relaxometry experiments with low-field NMR permanent magnets, which are relatively cheap, have very low maintenance costs (no need for cryogenic fluids) and are easy to manipulate. An important drawback of this technique is related to size constrains ($1cm^3$) and it cannot be easily performed for industrial applications. However, the potential for studying small samples at the laboratory scale makes it interesting for wood sciences. Moreover, these experiments can be applied on portable NMR devices using one-sided access instrumentation and applied for "outdoor" studies.[24] Another difficulty found for the application of NMR relaxometry methods to measure dry mass and MC of wood concerns the need of specialized personnel to recognize and overcome technical difficulties that may be encountered.[25] Thus, NMR relaxometry methods are considered not yet standardisable for normal use but the critical NMR distribution spectra analysis and the comparison with other techniques performed here should help non-NMR researchers to apply this technique for wood science research. In addition, this protocol is not restricted to wood samples but it could be applied to other porous media such as cement or soils.

Acknowledgements

This work has benefited from a French government grant managed by the French National Research Agency (ANR) within the frame of the national program "Investments for the Future" (I-site Future, http://www.future-isite.fr/accueil/, reference number: ANR- 16-IDEX-0003).

References

[1] G. Almeida, S. Gagné, R. E. Hernández, *Wood Science and Technology* **2007**, *41*, 293–307.
[2] P. M. Kekkonen, A. Ylisassi, V.-V. Telkki, *The Journal of Physical Chemistry C* **2014**, *118*, 2146–2153.
[3] H. F. A. Hergt, G. N. Christensen, *Journal of Applied Polymer Science* **1965**, *9*, 2345–2361.
[4] A. J. Nanassy, *Wood science* **1976**, *9*, 104–109.
[5] A. Alkadri, D. Jullien, O. Arnould, E. Rosenkrantz, P. Langbour, L. Hovasse, J. Gril, *Wood Sci Technol* **2020**, *54*, 1269–1297.
[6] B. Marcon, G. Goli, M. Matsuo-Ueda, L. Denaud, K. Umemura, J. Gril, S. Kawai, *iForest - Biogeosciences and Forestry* **2018**, *11*, 131–139.
[7] R. S. Menon, A. L. MaCkay, J. R. T. Hailey, M. Bloom, A. E. Burgess, J. S. Swanson, *J. Appl. Polym. Sci.* **1987**, *33*, 1141–1155.
[8] C. D. Araujo, S. Avramidis, A. L. MacKay, *Holzforschung* **1994**, *48*, 69–74.
[9] N. Labbé, B. D. Jéso, J.-C. Lartigue, G. Daudé, M. Pétraud, M. Ratier, *Holzforschung* **2002**, *56*, 25–31.
[10] P. Coussot, *Exp Fluids* **2020**, *61*, 207.
[11] D. Courtier-Murias, *eMagRes* **2019**.
[12] N. D. Weiss, L. G. Thygesen, C. Felby, C. Roslander, K. Gourlay, *Biotechnol Progress* **2017**, *33*, 146–153.
[13] T. Jeoh, N. Karuna, N. D. Weiss, L. G. Thygesen, *ACS Sustainable Chem. Eng.* **2017**, *5*, 8785–8795.
[14] N. D. Weiss, C. Felby, L. G. Thygesen, *Cellulose* **2018**, *25*, 3423–3434.
[15] N. D. Weiss, C. Felby, L. G. Thygesen, *Biotechnology for Biofuels* **2019**, *12*, 3.
[16] J. Cox, P. J. McDonald, B. A. Gardiner, *Holzforschung* **2010**, *64*, DOI 10.1515/hf.2010.036.
[17] M. Bonnet, D. Courtier-Murias, P. Faure, S. Rodts, S. Care, *Holzforschung* **2017**, *71*, 481–490.
[18] L. Rostom, D. Courtier-Murias, S. Rodts, S. Care, *Holzforschung* **2020**, *74*, 400–411.
[19] S. Hiltunen, A. Mankinen, M. A. Javed, S. Ahola, M. Venäläinen, V.-V. Telkki, *Holzforschung* **2020**, *0*, DOI 10.1515/hf-2019-0246.
[20] M. Merela, P. Oven, I. Serša, U. Mikac, *Holzforschung* **2009**, *63*, DOI 10.1515/HF.2009.050.
[21] A. R. Sharp, M. T. Riggin, R. Kaiser, M. H. Schneider, *Wood and Fiber* **1978**, *10*, 74–81.
[22] I. D. Hartley, F. A. Kamke, H. Peemoeller, *Holzforschung* **1994**, *48*, 474–479.
[23] C. Casieri, L. Senni, M. Romagnoli, U. Santamaria, F. De Luca, *Journal of Magnetic Resonance* **2004**, *171*, 364–372.
[24] B. Wolter, M. Krus, in *Electromagnetic Aquametry* (Ed.: K. Kupfer), Springer-Verlag, Berlin/Heidelberg, **2005**, pp. 491–515.
[25] D. Camuffo, *Journal of Cultural Heritage* **2018**, *31*, S10–S14.
[26] C. Gauvin, Experimental and numerical study of the hygromechanical behaviour of a wooden panel., Université de Montpellier, **2015**.
[27] EN 13183-1, Moisture Content of a Piece of Sawn Timber – Part 1: Determi-nation by Oven Dry Method, European Committee for Standardization (CEN), Brussels, **2002**.
[28] H. Carr, E. Purcell, *Physical Review* **1954**, *94*, 630–638.
[29] S. Meiboom, D. Gill, *Review of Scientific Instruments* **1958**, *29*, 688–691.
[30] K. P. Whittall, A. L. MacKay, *Journal of Magnetic Resonance (1969)* **1989**, *84*, 134–152.
[31] S. W. Provencher, *Computer Physics Communications* **1982**, *27*, 213–227.

[32] P. F. Faure, S. Rodts, *Magnetic Resonance Imaging* **2008**, *26*, 1183–1196.
[33] D. J. Yelle, J. Ralph, C. R. Frihart, *Magnetic Resonance in Chemistry* **2008**, *46*, 508–517.
[34] M. Bardet, A. Pournou, *Magn. Reson. Chem.* **2015**, *53*, 9–14.
[35] V.-V. Telkki, M. Yliniemi, J. Jokisaari, *Holzforschung* **2013**, *67*, 291–300.
[36] D. Courtier-Murias, E. Michel, S. Rodts, F. Lafolie, *Environ. Sci. Technol.* **2017**, *51*, 2602–2610.
[37] A. Valori, P. J. McDonald, K. L. Scrivener, *Cement and Concrete Research* **2013**, *49*, 65–81.
[38] T. Lerouge, B. Maillet, D. Coutier-Murias, D. Grande, B. Le Droumaguet, O. Pitois, P. Coussot, *Phys. Rev. Applied* **2020**, *13*, 044061.
[39] P. Blanchet, A. Kaboorani, C. Avila, *Wood and fiber science: journal of the Society of Wood Science and Technology* **2016**, *48*, 117–128.
[40] J. Winandy, **1996**.

Supplementary Material

Here, we show the results of student T-test analysis of our data (shown in Tables S1 and S2):

1) Dry mass 1D vs 2D NMR (paired)
p-value = 0.1345

2) Dry mass, 2D NMR vs "common" methods (paired)
Oven method: p-value = 0.0057
SiO_2 method: p-value = 0.0122
P_2O_5 method: p-value = 0.0009

3) Dry mass relative differences between 2D NMR and "common" methods (unpaired)
Oven vs P2O5, p-value = 0.0351
Oven vs SiO2, p-value = 0.0327
P_2O_5 vs SiO2, p-value = 0.1081

4) MC 1D vs 2D NMR (paired)
p-value = 0.0128

5) MC, 2D NMR vs "common" methods (paired)
Oven method: p-value = 0.0046
SiO_2 method: p-value = 0.0134
P_2O_5 method: p-value = 0.0009

6) Relative differences of MC from 2D NMR at 65% RH vs "common" methods (unpaired)
Oven vs P2O5, p-value = 0.0342
Oven vs SiO2, p-value = 0.0290
P_2O_5 vs SiO2, p-value = 0.0913

Table S1. Dry mass (g*) and MC (%) values from 1D NMR, 2D NMR and weighing for the nine samples used in this work. Value in bolds was identified as an outlier.

	Dry mass 1D NMR	Dry mass 2D NMR	Dry mass Weighing	MC 1D NMR	MC 2D NMR	MC Weighing
	0.5186	0.5187	0.5234	12.0	11.9	10.9
	0.5276	0.5293	0.5350	12.3	12.0	10.8
Oven	0.5297	0.5310	0.5371	12.5	12.2	10.9
	0.5145	0.5164	0.5250	12.4	12.0	10.2
	0.5331	0.5336	0.5411	12.5	12.0	10.4
SiO_2	0.5214	0.5249	0.5358	**13.4**	12.5	10.2
	0.5112	0.5128	0.5195	12.4	12.1	10.6
	0.5215	0.5203	0.5274	12.2	12.3	10.8
P_2O_5	0.5303	0.5288	0.5352	12.3	12.3	10.9

Table S2. Relative difference (%) values between NMR and weighing results (shown in Table S1) for the nine samples used in this work.

	Dry mass 1D NMR	Dry mass 2D NMR	MC 1D NMR	MC 2D NMR
	0.9	0.9	10.3	9.3
	1.4	1.1	14.4	11.0
Oven	1.4	1.1	14.2	11.6
	2.0	1.7	22.2	18.0
	1.5	1.4	19.3	14.8
SiO_2	2.8	2.1	31.2	22.4
	1.6	1.3	17.0	13.8
	1.1	1.4	13.3	14.0
P_2O_5	0.9	1.2	12.1	12.4