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Leila Rostom, Sabine Caré, Denis Courtier-Murias. Analysis of water content in wood material through 1D and 2D ^1H NMR relaxometry: application to the determination of the dry mass of wood. *Magnetic Resonance in Chemistry*, 2021, 59 (6), pp. 614-627. 10.1002/mrc.5125 . hal-03085690

HAL Id: hal-03085690

<https://enpc.hal.science/hal-03085690v1>

Submitted on 25 May 2021

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1 **Référence article accepté :**

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4 <https://doi.org/10.1002/mrc.5125>

5

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

9

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20

21 **Abstract:**

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

39

40 **Keywords:** ¹H NMR, 1D and 2D NMR relaxometry, wood drying, dry mass, moisture content

41

42

43

44 Introduction

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

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

67 Dry mass of wood can be estimated by different chemical and physical methods. For instance,
68 water can be removed from wood by chemical reactions with materials such as calcium carbide,
69 acid chlorides, or by the Karl Fischer reagent.^[3] Physical methods can use the Dean and Stark
70 distillation, oven drying with blowing air, or high vacuum drying at temperatures up to 105°C.^[4]
71 However, these methods are time consuming for many practical applications. Moreover,
72 completely removing all water is impossible without damaging wood.^[4] Indeed, the chemical
73 bonds between wood fiber and water are strong.^[4] Thus, the obtained dry mass may depend on
74 the used method to “dry” wood samples. Moreover, oven drying at 103°C, which is the most
75 used method, at least for routine MC determinations, is an invasive and destructive technique.^[3]
76 In particular, for some wood species, the extractives may leak out of the sample if the
77 temperature is too high^[5] and then this drying method could overestimate MC of wood. To
78 overcome this issue, drying at 60°C in a vacuum oven with P₂O₅ for 24 to 28 hours can be used
79 to obtain a RH close to 0% to allow preventing extractives leaking and accelerate the drying
80 process, but without proof of removing all water.^[6] As far as the authors are aware, these
81 commonly used drying methods have not been compared to each other, it is then difficult to
82 know which method is the most appropriate to measure wood dry mass and then MC. Therefore,
83 due to all the difficulties to measure dry mass of wood, it appears that it is necessary to find a
84 non-invasive and non-destructive method to be able to obtain accurate MC values.

85 Low-field ¹H Nuclear Magnetic Resonance (NMR) has been suggested several decades ago as
86 an interesting tool for wood and wood-derived materials for the evaluation of bound and free
87 water^[7-11] and the investigation of the presence of liquid water below the FSP.^[1] Regarding
88 lignocellulosic materials, NMR relaxometry has been also used for studying biomass–water
89 interactions, measuring water retention values (WRV), understanding biomass recalcitrance,
90 and high solid effects.^[12-15] Two main experiments are used in literature: (i) 1D T₂ NMR
91 relaxometry, mainly due to its short experimental time and its possibility to distinguish bound

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

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

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

127 ^1H NMR relaxometry is gaining popularity in the field of wood sciences in recent years.
128 Therefore, in this paper, we propose a new procedure using 1D and 2D ^1H NMR relaxometry
129 methods to estimate the dry mass of wood. Moreover, the performance of the two methods is
130 assessed and compared to commonly used drying methods such as oven drying at 103°C or the
131 use of P_2O_5 and SiO_2 as drying agents. Finally, we evaluated the performance of both 1D and
132 2D ^1H NMR relaxometry methods to obtain MC of wood in comparison to the values provided
133 by the commonly used drying methods.

134

135 **Experimental**

136 **Materials**

137 The experimental samples consisted of modern oak wood provided from a sawmill located in
138 the North of France.^[18] Nine samples of about $1 \times 1 \times 1 \text{ cm}^3$ were prepared from a wooden bar

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

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

	“oven samples”	“P ₂ O ₅ samples”	“SiO ₂ samples”	all samples
μ (SD)	590 (8)	582 (7)	589 (10)	588 (8)

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

157

158 **Commonly used drying protocols**

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

- 163 - The “oven samples” group: three samples were dried in an oven at 103 (± 0.5) °C for 24 hours;
- 164 - The “P₂O₅ samples” group: three samples were dried for one week in a closed desiccator filled
 165 with Phosphorus Pentoxide (P₂O₅) (which gives a RH of about 0-1%) at 20 (± 2) °C;
- 166 - The “SiO₂ samples” group: three samples were dried for one week in a closed desiccator filled
 167 with Silica Gel (SiO₂) (which gives a RH of about 2-3%) at 20 (± 2) °C.

168 At the end of these “commonly used” drying methods, the samples were weighed to obtain the
 169 “dry” mass of wood, $M_{\text{drywood},w}$. Samples were then analysed through ¹H NMR relaxometry a
 170 second time but in a “dry” state. The dry mass obtained by ¹H NMR relaxometry is noted
 171 $M_{\text{drywood},\text{NMR}}$.

172 It is important to note that the dry mass of the samples can vary with the duration of conditioning.
 173 Indeed, for the “P₂O₅ samples” and “SiO₂ samples”, other durations (two and ten weeks) have
 174 been considered to better understand commonly used drying protocols and compare them with
 175 ¹H NMR relaxometry, knowing that the longer the samples stay in the desiccator, the dryer they
 176 get. Therefore, depending on the volume of samples, the precision of the scale and possible RH
 177 fluctuations, the “equilibrium” dry mass can evolve. In addition, as it is a time consuming step
 178 for the study of wood samples, it is then important to set an average duration of conditioning
 179 (assessed by mass monitoring) according to current standards.^[27]

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

182 being at equilibrium) and is defined as follows:

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

183 with $M_{wood,w,65\%RH}$ the mass of the sample at 65% RH determined by weighing.

184 The $MC_{65\%RH,w}$ will be compared with the value obtained with 1H NMR relaxometry (see
185 following sections).

186

187 1H NMR relaxometry

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

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

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

227 1D T_2 NMR distribution spectra for the T_2 relaxations times were obtained by using data
 228 measured during the last CPMG block of the T_1T_2 NMR sequence (i.e. data obtained for the
 229 longest IR time). These data were analyzed by means of an inverse Laplace transform (ILT)
 230 algorithm, which converts relaxation signal into a continuous distribution of relaxations (i.e. T_2
 231 distribution spectra). This was done by using a homemade computer program based on the
 232 method described by Whittall and MacKay^[30] and Provencher^[31] performing the same work as
 233 the well-known CONTIN program. Further details about the technique can be found in.^[32]

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

242

243 **Determination of water and dry mass of wood through ^1H NMR relaxometry**

244 Since NMR signal intensity depends on the number of measured nuclei, ^1H NMR signal can be
 245 converted into mass of water. To do so, a standard curve was performed with different quantities
 246 of water (Figure 1), obtaining a proportional coefficient α between the NMR signal intensity
 247 and the water mass. The water mass $M_{\text{water,NMR},x\%RH}$ determined by ^1H NMR relaxometry at
 248 $x\%$ RH is therefore defined by Equation 2:

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

249 where $q_{\text{NMR},x\%RH}$ is the ^1H NMR signal intensity at $x\%$ RH and α the proportional coefficient
 250 determined through the standard curve (Figure 1). In this study, α was equal to 161.42 (± 0.64)
 251 ^1H NMR signal intensity/g of water.

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

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

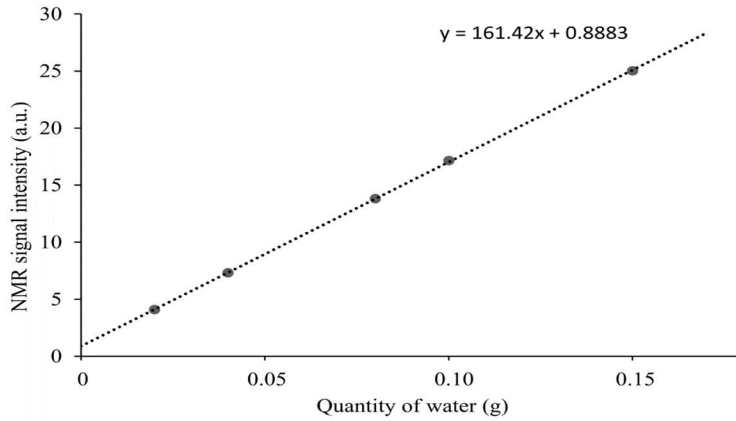
257 where $M_{\text{wood},w,x\%RH}$ is the total mass of wood determined by weighing at $x\%$ RH in two ways:

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

264 The Moisture Content $MC_{\text{NMR},x\%RH}$ [%] determined by ^1H NMR relaxometry measurements at
 265 $x\%$ RH is then defined by Equation 4:

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

266



267
268 **Figure 1.** Standard curve showing the relationship between NMR signal intensity and water amount.
269

270 **Uncertainties on the mass of samples and moisture content**

271 The uncertainties on masses and MC are evaluated for each specimen and for the two methods
272 used (weighing and ^1H NMR relaxometry). The uncertainties on masses are noted:
273 $\Delta M_{\text{wood,w,65\%RH}}$, $\Delta M_{\text{drywood,w}}$, $\Delta M_{\text{drywood,NMR}}$, $\Delta M_{\text{water,NMR,x\%RH}}$ and those on MC are
274 defined as: $\Delta MC_{\text{w,x\%RH}}$ and $\Delta MC_{\text{NMR,x\%RH}}$.

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

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

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

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

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

286 $-\frac{\Delta q_{\text{NMR,x\%RH}}}{q_{\text{NMR,x\%RH}}} = 2\%$ for measurements at 65%RH and $\frac{\Delta q_{\text{NMR,x\%RH}}}{q_{\text{NMR,x\%RH}}} = 31\%$ for measurements at
287 ‘dry state’ according to Bonnet et al.^[17] These uncertainties have been determined from T_1T_2
288 distribution spectra of a Douglas-fir wood, dried with SiO_2 . It is supposed that the uncertainties
289 on the NMR signal are similar in this work, for the other drying methods and the T_2 distribution
290 spectra and do not depend on the wood species. These uncertainties take into account some
291 biases linked to the ILT data processing that can affect the measured values. The stability of
292 this data processing was analyzed by adding white noise on a model signal that is close to the
293 experimental data.^[16]

294 $-\frac{\Delta \alpha}{\alpha} = 0.39\%$ with $\Delta \alpha = 0.64$ evaluated from three standard curves performed at different
295 times.

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

302 The average uncertainties, determined through 1H NMR relaxometry, for the nine samples are:
 303 $\Delta M_{water,NMR,x\%RH} = 0,001 \text{ g}^*$ and $\Delta M_{drywood,NMR} = 0,003 \text{ g}^*$. These are applied for T_1T_2
 304 and T_2 measurements and for the two hydric states (at 65%RH and in the ‘dry state’).

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

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

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

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

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

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

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

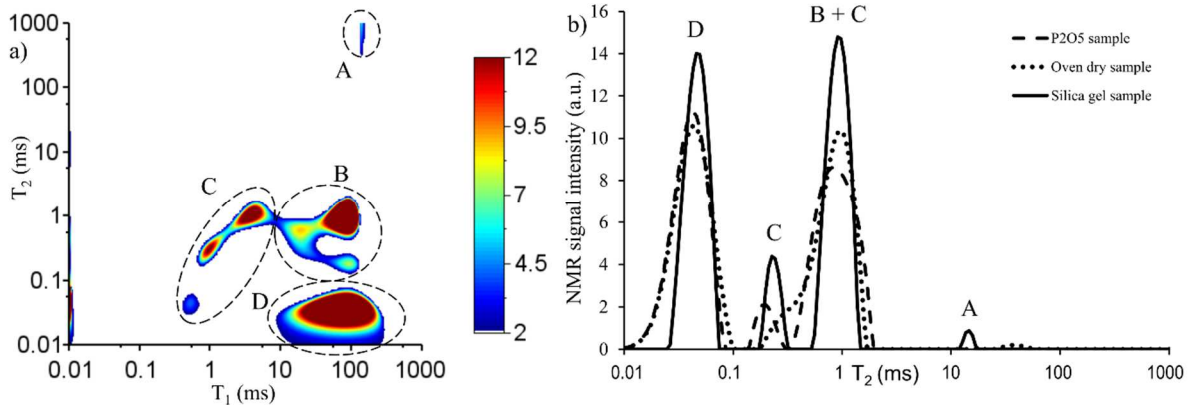
325

326 **Results and discussion**

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

328 1H T_1T_2 NMR distribution spectra of wood at 65% RH show four main peaks (Figure 2a), which
 329 have been previously labelled as A, B, C and D and assigned to free water in large pores
 330 (lumens), strongly interacting bound water, weakly interacting bound water and hydrogen
 331 atoms of wood polymers respectively.^[16,17] In this work, as samples are below the FSP, signal
 332 corresponding to bound water and hydrogen atoms of wood polymers is mainly observed but
 333 also coming from traces of peak A. These traces of free water have already been observed below
 334 the FSP^[35] and the position of peaks above the $T_1=T_2$ limit has been explained due to its very
 335 low intensity.^[17] Moreover, other studies have shown that wood may contain free water below

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



341 **Figure 2.** (a) T_1T_2 distribution spectrum for one of the specimens of the “oven sample” group and (b)
 342 T_2 distribution spectra of one sample from each drying method (right-hand side) both at 65% RH. Peaks
 343 A, B, C and D correspond to free water, strongly bound water, weakly bound water and wood polymers
 344 respectively.
 345

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

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

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

388

389 **Dry mass of wood obtained by 1D and 2D 1H NMR relaxometry at 65%**

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

397 **Table 2.** Results of 1D T_2 and 2D T_1T_2 1H NMR relaxometry analysis of wood samples at 65% RH for
 398 the calculation of water mass $M_{water,NMR,65\%RH}$ (g^*) and dry mass $M_{drywood,NMR}$ (g^*) for the three
 399 “group of samples” used in this work. Mean values for the nine samples are also provided. SD values
 400 are included in parenthesis. We performed paired Student’s t-tests to compare dry masses obtained by
 401 1D and 2D NMR relaxometry methods, showing that values were not significantly different (p-value >
 402 0.10), and to compare 2D NMR relaxometry results to commonly used drying methods, with p-values
 403 < 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)

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

412 relaxometry analysis, while for the T₂ NMR relaxometry analysis, the mass at the end of the
 413 NMR relaxometry experiment has been used (because the T₂ data is recorded at the end of the
 414 NMR relaxometry experiment). The mass of samples at the end of the experiments is slightly
 415 higher than the mass before the NMR relaxometry experiment, which means that there should
 416 be more water inside the wood samples during the time T₂ NMR data is recorded. This explains
 417 the small differences on the detected water amount, which is slightly lower for the T₁T₂ NMR
 418 relaxometry experiment. However, dry masses of wood obtained by 1D and 2D NMR
 419 relaxometry are very similar, showing that the ¹H NMR relaxometry method works well for
 420 both experiments and is able to take into account the variation of humidity in samples, due to
 421 RH variations. In general, the differences between dry wood masses calculated by 1D and 2D
 422 NMR relaxometry methods are relatively small, so it can be concluded that both 1D and 2D
 423 NMR relaxometry experiments perform equally well. In addition, it can be mentioned that the
 424 uncertainties of the calculated dry masses are similar for the 1D and 2D ¹H NMR relaxometry
 425 methods. The Student T-test performed on the values obtained by both NMR methods shows
 426 that the differences are not significant, meaning that the results obtained with both methods are
 427 similar (see Supplementary Material for further details).

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

438
 439 **Comparison of dry mass determined by ¹H NMR relaxometry and by weighing with**
 440 **commonly used drying methods**

441 To validate the results obtained by 1D and 2D ¹H NMR relaxometry methods and the advantage
 442 to use them to measure dry mass of wood, we compared NMR relaxometry results to commonly
 443 used drying methods. The nine samples studied in the previous section were split in three groups
 444 and each group was dried accordingly to different commonly used protocols (oven drying, P₂O₅
 445 and SiO₂) to obtain the dry mass of wood. Results are given in Table 3 and are compared to the
 446 values obtained with ¹H NMR relaxometry (Table 2). The relative differences between these
 447 two methods were also calculated.

448 We have applied the SiO₂ and P₂O₅ methods for different durations: one, two and ten weeks;

449 while the “oven dry samples” have been dried for only 24h, as long exposition to high
450 temperature may damage the samples and/or lead to possible extractives leaking. Therefore, the
451 value used for comparison, in Table 3, is the one right after 24 hours drying. The mass of the
452 samples conditioned with SiO₂ and P₂O₅ continue to decrease after one week (with the
453 exception of SiO₂ after ten weeks but we can explain this because of an increase of RH inside
454 the desiccator due to a decrease of SiO₂ performance). However, even if there is still some water
455 that can be removed from wood, the decrease is very small (less than 0.1% each day). Therefore,
456 according to the standards, the mass could be considered constant and the samples dried for one
457 week used as the reference of the protocol for comparison. Moreover, previous works have
458 shown that this duration can be considered adequate for drying samples with these kind of
459 dimensions.^[17,18] However, this shows some of the limitations of commonly used methods.
460 Firstly, it is necessary to follow the variation of mass until equilibrium (e.g. less than 0.1% per
461 day) and the time needed for drying samples is closely related to the size of the samples (the
462 bigger the samples, the longer the drying time). Secondly, even for small specimens as the ones
463 used in this work, there is still water inside wood after one week of drying, which is already a
464 long drying protocol. The fact that dry masses of wood obtained by ¹H NMR were always lower
465 than the values obtained by the commonly used methods, confirms that these drying methods
466 do not allow to remove all water from wood as fast as it may be needed for experiments, which
467 may even be impossible without damaging wood.^[4] This was validated by Student T-tests as
468 shown in Supplementary Material.

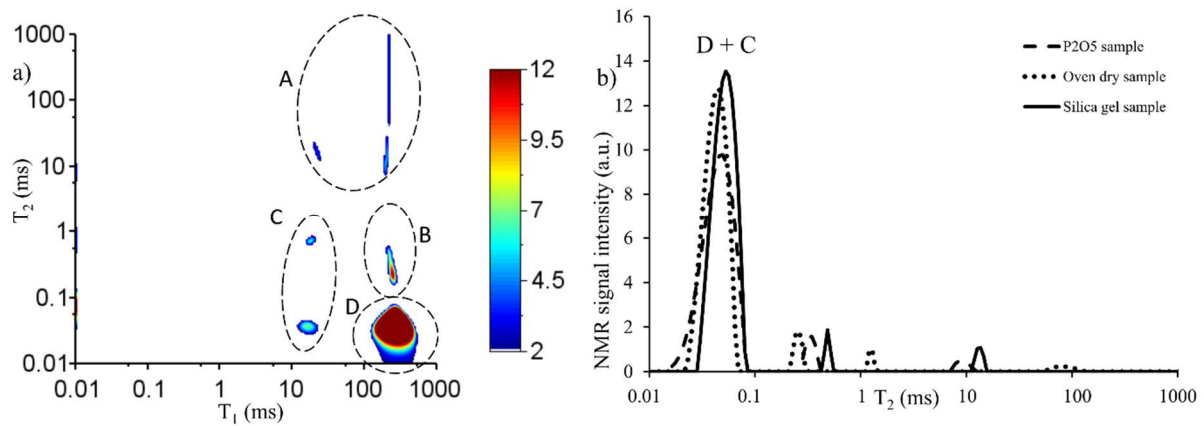
469 When comparing the results of commonly used drying methods to the ones obtained from NMR
470 relaxometry, it appears that there is a significant difference on the performance between all
471 these techniques, even if the uncertainties on the calculated dry masses are slightly higher for
472 the ¹H NMR relaxometry method compared to the commonly used drying methods, as
473 mentioned in the Experimental section. Let us focus on 2D NMR relaxometry results as shown
474 in previous section they are likely to provide more accurate results than 1D NMR relaxometry
475 (SD values for 2D NMR relaxometry are about half of values for 1D NMR relaxometry). The
476 highest relative difference in dry mass values compared to 2D NMR relaxometry was observed
477 for samples conditioned in the SiO₂ with 1.7% relative difference. P₂O₅ method showed an
478 intermediate value of about 1.3% relative difference, while the oven method provided the
479 smallest relative difference with NMR relaxometry values (1.1%). This allows classifying these
480 three drying methods according to their level of performance in removing water from wood:
481 oven>P₂O₅>SiO₂. To confirm this, we performed Student T-tests by comparing results of
482 commonly used drying methods, providing p-values < 0.05 expect for the comparison between
483 P₂O₅ and SiO₂ with a p-value ≈ 0.10 (see Supplementary Material for more details). Although
484 1D NMR relaxometry methods do not clearly show the same trend as 2D NMR relaxometry,
485 differences between 1D and 2D ¹H NMR relaxometry concerning dry mass calculations are
486 very small, showing a similar performance of both NMR relaxometry methods. Thus, for this
487 type of analysis, 1D ¹H NMR relaxometry, which has a shorter acquisition/analysis time than
488 2D ¹H NMR relaxometry, would be the best choice for the determination of the dry mass of
489 wood in routine use.

490

491 **1D and 2D ¹H NMR relaxometry of “dry” wood**

492 Results showed on previous sections showed that commonly used drying methods do not allow
493 to remove all water from wood (NMR relaxometry methods provide lower dry mass values than
494 commonly used drying methods). To confirm this, we have performed additional ¹H NMR
495 relaxometry experiments on samples after drying (Figure 3), looking for traces of water in wood.
496 Figure 3 (a) presents the T₁T₂ distribution spectra of a dry sample showing small peaks
497 corresponding to adsorbed water in wood and confirming the presence of traces of bound water

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



501
502 **Figure 3.** (a) T_1T_2 distribution spectrum for one of the specimens of the “oven sample” group treated
503 for 24h at 103°C (left-hand side) and (b) T_2 distribution spectra of one sample from each drying method
504 after 1 week of drying and 24h treatment for ‘oven sample’ (right-hand side). Peaks A, B, C and D
505 correspond to free water, strongly bound water, weakly bound water and wood polymers respectively.

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

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

535 methods.

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

	Method	“oven samples”	“P ₂ O ₅ samples”	“SiO ₂ samples”	all samples
$M_{\text{water,NMR,x\%RH}}$	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)	/
$M_{\text{drywood,NMR}}$	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)

542

543 Moisture Content

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

549 **Table 5.** MC of samples subjected to the three drying methods: in a desiccator with SiO₂ or P₂O₅ during
 550 one week and a 24-hours drying in an oven at 103°C. $MC_{65\%RH}$ corresponds to the moisture content
 551 calculated either by weighing (Eq. 1) or by 1H NMR relaxometry (Eq. 4). The relative differences (%)
 552 were obtained by subtracting weighing value from NMR value and dividing it by weighing method
 553 value. Mean and relative difference values for the nine samples are not calculated as they do not should
 554 provide the same results for each weighing method. Paired Student’s t-tests were performed to compare
 555 MC values from NMR relaxometry methods and commonly used drying methods, showing that values
 556 were significant different (p-values < 0.05). Moreover, we performed unpaired Student T-test between
 557 relative difference values to compare the performance of commonly used drying methods, showing that
 558 they significantly different (with p-values < 0.05 for “oven samples” vs “SiO₂ samples” and “oven
 559 samples” vs “P₂O₅ samples” and p-values < 0.10 for “P₂O₅ samples” vs “SiO₂ samples”). *We identified
 560 a possible outlier value for 1D analysis of “SiO₂ samples” but as this difference could be explained due
 561 to sample heterogeneity and 1D NMR relaxometry measurement uncertain, it was kept for calculations.
 562 If this value is not used, the results for $MC_{65\%RH}$ for SiO₂ samples, all samples and relative difference
 563 for SiO₂ samples are 12.4 (0.1), 12.3 (0.2) and 20.7 (2.1) respectively. This does not affect to data
 564 interpretation.

	Method	“oven samples”	“P ₂ O 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)	/

565

566 First, we compared the performance of the three commonly used methods. As expected from
567 results showed in previous sections, a trend is observed when MC is compared between the
568 three commonly used methods (Table 5). SiO₂ method shows the lowest MC value, the oven
569 drying method provides the highest MC value and P₂O₅ has an intermediate value. Thus, they
570 can be classified in terms of drying performance (oven > P₂O₅ > SiO₂). It is important to note that
571 when dry mass calculations were compared in previous sections, relative differences varied
572 from 1.1 to 1.7%, which are relatively low values. However, the relative differences of MC
573 values between commonly used drying methods and NMR relaxometry (calculated as
574 $(MC_{\text{NMR},65\%RH} - MC_{\text{w},65\%RH}) / MC_{\text{w},65\%RH} \times 100$) are much more important. Relative
575 differences for MC ranged from 11 to 24 %, meaning that even relatively small errors of dry
576 mass lead to important differences in the MC calculated. This emphasize the importance of
577 measuring accurate values of dry mass of wood and the limitations of commonly used drying
578 methods.

579 Let us now focus on comparing 1D and 2D ¹H NMR relaxometry methods. Both of them
580 provided similar results, which are significantly higher than the values obtained by commonly
581 used methods. Moreover, we can also use the relative differences values to compare the
582 performance of 1D and 2D ¹H NMR relaxometry methods. For both 1D and 2D ¹H NMR
583 relaxometry experiments, relative difference values show the same trend as what it was
584 observed for commonly used drying methods concerning drying performance. We will look
585 first at 2D ¹H NMR relaxometry results as they are more accurate and trend is clearer. Relative
586 difference values are high for the method with a poor drying performance and low for good
587 drying performance (11 % for oven method, 13 % for P₂O₅ method and 18 % for SiO₂ method).
588 This is not so clear for 1D NMR relaxometry experiments (13 % for oven method and 14 % for
589 P₂O₅ method), which could be explained by the limitations of 1D ¹H NMR relaxometry
590 experiments due to some signal overlapping explained on previous sections, which slightly
591 affect water quantification and dry mass calculations. Furthermore, SD values for 1D NMR
592 relaxometry for MC calculations are about the double than for 2D NMR relaxometry. We have
593 confirmed it by performing a student T-test to compare 1D and 2D NMR relaxometry for MC
594 calculations (see Supplementary Material), showing that their results are significantly different
595 (although they are not for dry mass calculations). This empathises again the importance of
596 obtaining accurate dry mass values and also the advantages of 2D over 1D NMR relaxometry
597 (which are not so clearly for dry mass calculations).

598 In conclusion, the results presented in this work clearly show that MC values are underestimated
599 with commonly used drying methods. Thus, results obtained by these NMR relaxometry
600 experiments cannot be directly compared with previously published data (obtained by
601 commonly used drying methods). A possible solution could be to scale these values by a factor
602 equal to the relative difference values (Table 5). However, this should be tested for other types
603 of woods and drying methods to completely validate this approach. Concerning other types of
604 wood, as far as they have similar NMR relaxometry spectra (as it happens for other published
605 works), this protocol should be feasible for them too. In general, both 1D and 2D approaches
606 provided comparable results for MC calculations but 2D NMR relaxometry provided slightly
607 more accurate results (SD values for 2D NMR relaxometry are about half of that for 1D NMR
608 relaxometry, Table 5). However, if fast quantification of MC of the sample is needed (and
609 detailed information about the type of water is not of interest), ¹H T₂ NMR relaxometry should
610 provide good enough results which overperform commonly used drying methods in a faster
611 way and in a non-invasive and non-destructive manner.

612

613 **Conclusions**

614 The study presented here showed that NMR relaxometry is an excellent tool for obtaining dry
615 mass and MC of wood. Due to its short experimental time and the non-invasive and non-
616 destructive nature of this technique, it should be increasingly used in wood sciences, as it
617 overcomes some limitations of commonly used drying methods. Indeed, even if the oven drying
618 method shows great performance it could however alter the sample (wood polymers and
619 extractives).^[39,40] The two other methods using saturated salt solution and silica gel show that
620 they are not able to remove all water from wood, being NMR the unique technique able to
621 measure dry mass of wood accurately and without damaging the samples. However, it requires
622 a sampling/sample collection and a sample size of maximum 1cm³.

623 The experiments carried out also allowed evaluating the performance of three drying methods
624 commonly used in wood sciences. They show that oven drying allowed to better remove water
625 from wood, P₂O₅ showed an intermediate performance and SiO₂ provided the worst
626 performance within the three methods for drying wood samples. Comparing the results after
627 one week of drying (24h for oven method) to NMR relaxometry analysis permitted to obtain a
628 relative difference for dry mass calculations, which ranged from 1.1 to 1.7 %. If these masses
629 are used to calculate MC of wood, the relative errors increased to values from 11 to 18%,
630 empathising the importance of measuring accurate dry mass values of wood. Due to the
631 important differences on MC of wood between NMR relaxometry and commonly used drying
632 methods, care should be taken when comparing them to previously published data obtained by
633 commonly used drying methods.

634 A critical analysis of both 1D T₂ and 2D T₁T₂ ¹H NMR relaxometry methods has also been
635 carried out. The main technical differences between the two techniques is the experimental time
636 needed to carry them out, which is much higher for T₁T₂ NMR relaxometry experiments.
637 Concerning spectral analysis, some water signal that overlaps with signal coming from wood
638 polymers in T₂ NMR distribution spectra can be clearly measured on T₁T₂ NMR distribution
639 spectra. This amount of water is very small and thus does not have a clear effect on dry mass
640 but this effect is more important for MC calculations. A positive point of T₂ NMR relaxometry
641 experiments is related to their short experimental time in comparison to T₁T₂ NMR relaxometry
642 experiments (5 min vs. 6 hours). In practical applications for obtaining dry mass and MC of
643 wood, T₁T₂ NMR relaxometry experiments should provide the more accurate results, but if
644 there were no interest on studying different types of bound water, T₂ NMR relaxometry
645 measurements would be the recommended choice, as the results still clearly overcome
646 commonly used drying methods.

647 It is also important to note that we carried out these NMR relaxometry experiments with low-
648 field NMR permanent magnets, which are relatively cheap, have very low maintenance costs
649 (no need for cryogenic fluids) and are easy to manipulate. An important drawback of this
650 technique is related to size constrains (1cm³) and it cannot be easily performed for industrial
651 applications. However, the potential for studying small samples at the laboratory scale makes
652 it interesting for wood sciences. Moreover, these experiments can be applied on portable NMR
653 devices using one-sided access instrumentation and applied for “outdoor” studies.^[24] Another
654 difficulty found for the application of NMR relaxometry methods to measure dry mass and MC
655 of wood concerns the need of specialized personnel to recognize and overcome technical
656 difficulties that may be encountered.^[25] Thus, NMR relaxometry methods are considered not
657 yet standardisable for normal use but the critical NMR distribution spectra analysis and the
658 comparison with other techniques performed here should help non-NMR researchers to apply
659 this technique for wood science research. In addition, this protocol is not restricted to wood
660 samples but it could be applied to other porous media such as cement or soils.

661

662 Acknowledgements

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

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667 References

- 668 [1] G. Almeida, S. Gagné, R. E. Hernández, *Wood Science and Technology* **2007**, *41*, 293–307.
669 [2] P. M. Kekkonen, A. Ylisassi, V.-V. Telkki, *The Journal of Physical Chemistry C* **2014**, *118*, 2146–
670 2153.
671 [3] H. F. A. Hergt, G. N. Christensen, *Journal of Applied Polymer Science* **1965**, *9*, 2345–2361.
672 [4] A. J. Nanassy, *Wood science* **1976**, *9*, 104–109.
673 [5] A. Alkadri, D. Jullien, O. Arnould, E. Rosenkrantz, P. Langbour, L. Hovasse, J. Gril, *Wood Sci*
674 *Technol* **2020**, *54*, 1269–1297.
675 [6] B. Marcon, G. Goli, M. Matsuo-Ueda, L. Denaud, K. Umemura, J. Gril, S. Kawai, *iForest -*
676 *Biogeosciences and Forestry* **2018**, *11*, 131–139.
677 [7] R. S. Menon, A. L. MacKay, J. R. T. Hailey, M. Bloom, A. E. Burgess, J. S. Swanson, *J. Appl. Polym.*
678 *Sci.* **1987**, *33*, 1141–1155.
679 [8] C. D. Araujo, S. Avramidis, A. L. MacKay, *Holzforschung* **1994**, *48*, 69–74.
680 [9] N. Labbé, B. D. Jéso, J.-C. Lartigue, G. Daudé, M. Pétraud, M. Ratier, *Holzforschung* **2002**, *56*, 25–
681 31.
682 [10] P. Coussot, *Exp Fluids* **2020**, *61*, 207.
683 [11] D. Courtier-Murias, *eMagRes* **2019**.
684 [12] N. D. Weiss, L. G. Thygesen, C. Felby, C. Roslander, K. Gourlay, *Biotechnol Progress* **2017**, *33*,
685 146–153.
686 [13] T. Jeoh, N. Karuna, N. D. Weiss, L. G. Thygesen, *ACS Sustainable Chem. Eng.* **2017**, *5*, 8785–8795.
687 [14] N. D. Weiss, C. Felby, L. G. Thygesen, *Cellulose* **2018**, *25*, 3423–3434.
688 [15] N. D. Weiss, C. Felby, L. G. Thygesen, *Biotechnology for Biofuels* **2019**, *12*, 3.
689 [16] J. Cox, P. J. McDonald, B. A. Gardiner, *Holzforschung* **2010**, *64*, DOI 10.1515/hf.2010.036.
690 [17] M. Bonnet, D. Courtier-Murias, P. Faure, S. Rodts, S. Care, *Holzforschung* **2017**, *71*, 481–490.
691 [18] L. Rostom, D. Courtier-Murias, S. Rodts, S. Care, *Holzforschung* **2020**, *74*, 400–411.
692 [19] S. Hiltunen, A. Mankinen, M. A. Javed, S. Ahola, M. Venäläinen, V.-V. Telkki, *Holzforschung* **2020**,
693 *0*, DOI 10.1515/hf-2019-0246.
694 [20] M. Merela, P. Oven, I. Serša, U. Mikac, *Holzforschung* **2009**, *63*, DOI 10.1515/HF.2009.050.
695 [21] A. R. Sharp, M. T. Riggan, R. Kaiser, M. H. Schneider, *Wood and Fiber* **1978**, *10*, 74–81.
696 [22] I. D. Hartley, F. A. Kamke, H. Peemoeller, *Holzforschung* **1994**, *48*, 474–479.
697 [23] C. Casieri, L. Senni, M. Romagnoli, U. Santamaria, F. De Luca, *Journal of Magnetic Resonance*
698 **2004**, *171*, 364–372.
699 [24] B. Wolter, M. Krus, in *Electromagnetic Aquametry* (Ed.: K. Kupfer), Springer-Verlag,
700 Berlin/Heidelberg, **2005**, pp. 491–515.
701 [25] D. Camuffo, *Journal of Cultural Heritage* **2018**, *31*, S10–S14.
702 [26] C. Gauvin, Experimental and numerical study of the hygromechanical behaviour of a wooden
703 panel., Université de Montpellier, **2015**.
704 [27] EN 13183-1, Moisture Content of a Piece of Sawn Timber – Part 1: Determination by Oven Dry
705 Method, European Committee for Standardization (CEN), Brussels, **2002**.
706 [28] H. Carr, E. Purcell, *Physical Review* **1954**, *94*, 630–638.
707 [29] S. Meiboom, D. Gill, *Review of Scientific Instruments* **1958**, *29*, 688–691.
708 [30] K. P. Whittall, A. L. MacKay, *Journal of Magnetic Resonance (1969)* **1989**, *84*, 134–152.
709 [31] S. W. Provencher, *Computer Physics Communications* **1982**, *27*, 213–227.

- 710 [32] P. F. Faure, S. Rodts, *Magnetic Resonance Imaging* **2008**, *26*, 1183–1196.
711 [33] D. J. Yelle, J. Ralph, C. R. Frihart, *Magnetic Resonance in Chemistry* **2008**, *46*, 508–517.
712 [34] M. Bardet, A. Pournou, *Magn. Reson. Chem.* **2015**, *53*, 9–14.
713 [35] V.-V. Telkki, M. Yliniemi, J. Jokisaari, *Holzforschung* **2013**, *67*, 291–300.
714 [36] D. Courtier-Murias, E. Michel, S. Rodts, F. Lafolie, *Environ. Sci. Technol.* **2017**, *51*, 2602–2610.
715 [37] A. Valori, P. J. McDonald, K. L. Scrivener, *Cement and Concrete Research* **2013**, *49*, 65–81.
716 [38] T. Lerouge, B. Maillet, D. Coutier-Murias, D. Grande, B. Le Droumaguet, O. Pitois, P. Cousot,
717 *Phys. Rev. Applied* **2020**, *13*, 044061.
718 [39] P. Blanchet, A. Kaboorani, C. Avila, *Wood and fiber science: journal of the Society of Wood*
719 *Science and Technology* **2016**, *48*, 117–128.
720 [40] J. Winandy, **1996**.
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722

723 **Supplementary Material**

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

725

726 1) Dry mass 1D vs 2D NMR (paired)

727 p-value = 0.1345

728

729 2) Dry mass, 2D NMR vs “common” methods (paired)

730 Oven method: p-value = 0.0057

731 SiO₂ method: p-value = 0.0122

732 P₂O₅ method: p-value = 0.0009

733

734 3) Dry mass relative differences between 2D NMR and “common” methods (unpaired)

735 Oven vs P₂O₅, p-value = 0.0351

736 Oven vs SiO₂, p-value = 0.0327

737 P₂O₅ vs SiO₂, p-value = 0.1081

738

739 4) MC 1D vs 2D NMR (paired)

740 p-value = 0.0128

741

742 5) MC, 2D NMR vs “common” methods (paired)

743 Oven method: p-value = 0.0046

744 SiO₂ method: p-value = 0.0134

745 P₂O₅ method: p-value = 0.0009

746

747 6) Relative differences of MC from 2D NMR at 65% RH vs “common” methods (unpaired)

748 Oven vs P₂O₅, p-value = 0.0342

749 Oven vs SiO₂, p-value = 0.0290

750 P₂O₅ vs SiO₂, p-value = 0.0913

751

752 **Table S1.** Dry mass (g*) and MC (%) values from 1D NMR, 2D NMR and weighing for the nine
753 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
Oven	0.5186	0.5187	0.5234	12.0	11.9	10.9
	0.5276	0.5293	0.5350	12.3	12.0	10.8
	0.5297	0.5310	0.5371	12.5	12.2	10.9
SiO ₂	0.5145	0.5164	0.5250	12.4	12.0	10.2
	0.5331	0.5336	0.5411	12.5	12.0	10.4
	0.5214	0.5249	0.5358	13.4	12.5	10.2
P ₂ O ₅	0.5112	0.5128	0.5195	12.4	12.1	10.6
	0.5215	0.5203	0.5274	12.2	12.3	10.8
	0.5303	0.5288	0.5352	12.3	12.3	10.9

754

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

	Dry mass 1D NMR	Dry mass 2D NMR	MC 1D NMR	MC 2D NMR
Oven	0.9	0.9	10.3	9.3
	1.4	1.1	14.4	11.0
	1.4	1.1	14.2	11.6
SiO ₂	2.0	1.7	22.2	18.0
	1.5	1.4	19.3	14.8
	2.8	2.1	31.2	22.4
P ₂ O ₅	1.6	1.3	17.0	13.8
	1.1	1.4	13.3	14.0
	0.9	1.2	12.1	12.4

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