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► **To cite this version:**

Dang-Mao Nguyen, Sabine Caré, Denis Courtier-Murias, Meng Zhou, Philippe Coussot. Mechanisms of liquid imbibition in Douglas-fir inferred from ^1H Nuclear Magnetic Resonance methods. *Holz-forschung*, 2021, 75 (3), pp.225-236. 10.1515/hf-2020-0051 . hal-02878893

HAL Id: hal-02878893

<https://enpc.hal.science/hal-02878893>

Submitted on 3 Jun 2021

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1 Soumis et accepté à HOLZFORSHUNG (18 Juin 2020)

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3 Short title: **Imbibition in softwood observed by ^1H NMR methods**

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6 **Mechanisms of liquid imbibition in Douglas-fir inferred from ^1H Nuclear**
7 **Magnetic Resonance methods**

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14
15 **Abstract:** This study aims at identifying the mechanisms of oil and water imbibition in
16 heartwood and sapwood of Douglas-fir through a combination of original experiments with
17 Magnetic Resonance Imaging (MRI) and Nuclear Magnetic Resonance (NMR) relaxation
18 measurements for oil and free water, and deformation measurements for bound water.
19 Experiments by weighing are performed to verify whether the imbibition process is also
20 consistent with Washburn law. All the results are discussed taking into account the structure of
21 wood (tubular tracheids closed at their tips, but possibly connected to each other via open pits
22 on the side faces) and the preparation of samples.

23 The observation of relatively fast oil flow imbibition confirms that sapwood exhibits a
24 connected hydraulic network through which a liquid can a priori flow and climb along the
25 structure. However, the spontaneous water imbibition is strongly damped by its very poor
26 wetting when in contact with cell-walls only partially saturated with bound water, so that the
27 diffusion of bound water control the uptake dynamics. However, due to preferentially closed
28 pits, the heartwood does not exhibit a continuous hydraulic network and water essentially
29 penetrates into wood by diffusion through the cell walls.

30
31 **Keywords:** Free and bound water, Magnetic Resonance Imaging, Nuclear Magnetic Resonance
32 Relaxation, oil, permeability, softwood, Washburn.

34 **Introduction**

35 Water transport in wood material plays a major role with regard to its physical properties in
36 various situations, leading to a possible deterioration in performance of the timber elements.
37 Moreover, liquid (oil or water) impregnation to make the wood more resistant to decay or to
38 improve the process of peeling of wood logs for new product design (e.g. Plywood) is an
39 important subject in wood sciences. Therefore, it is crucial to understand how liquid penetrates
40 in the wood material. Liquid transfer in wood materials has been widely studied (Bao et al.
41 1986, Siau 1995, Elaieb 2014 and 2016, Johansson et al. 2011, Duplex et al. 2013), it depends
42 on the permeability of wood, the viscosity of liquid as well as its wetting ability (Kučerová
43 2012, Schenk et al. 2018). But the physical mechanisms are not well understood yet. Thus, to
44 estimate lifetimes, to propose methods of maintenance through oil impregnation or to better
45 impregnate wood logs with aqueous liquid for peeling, it is necessary to continue the research
46 efforts for improving the understanding of the mechanisms of liquid transport in relation with
47 the structure of wood.

48 Wood is composed of tubular cells, with different void (i.e. lumen) sizes and arrangements
49 (essentially tracheids for softwoods and vessels and fibers for hardwoods), eventually
50 connected by pits on the side faces, and with characteristics depending on the localization
51 within the growth ring (latewood or earlywood) in the case of wood from temperate regions.
52 Moisture Content (MC) depends on the sorption mechanisms and water uptake (Almeida et al.
53 2007, Kekkonen et al. 2014) and is defined as the ratio of water mass to dry wood mass. Water
54 in cell walls is named bound water and when cell walls are saturated with bound water, MC is
55 called the Fiber Saturation Point (FSP). Water present in cell lumens is identified as free water.
56 Considering oil imbibition tests, only lumens are filled with oil.

57 For most porous materials, liquid transport is basically described by the Darcy's law, which
58 indicates that the pressure gradient is equal to the flow rate times the fluid viscosity divided by
59 the medium permeability and the imbibition mechanism follows the Washburn law (Washburn
60 1921). This model predicts that the total liquid uptake is proportional to the square root of time
61 and that a uniform liquid front advances linearly with the square root of time. In wood, either
62 in softwoods or in hardwoods, these characteristics have been observed, for example for the
63 front of penetration (Kučerová 2012) or for the proportionality between the total liquid uptake
64 and the square root of time (Sedighi-Gilani 2014). However, even if some deviations from the
65 Washburn law are observed, capillary effects are usually considered.

66 In Zhou et al. 2018 and 2019, for oils of different viscosities, the Washburn model is
67 effectively in agreement with the dynamics of the process using the parameters (permeability,
68 contact angle, pore size) of the system as deduced from direct measurements for poplar
69 heartwood. However, this is not the case for water: spontaneous water imbibition is several
70 orders of magnitude slower than expected from the Washburn prediction using the effective
71 parameters of the system. In particular, observations with Magnetic Resonance Imaging (MRI)
72 showed that bound water progresses faster than free water and that the dynamics of imbibition
73 in poplar heartwood is partly governed by bound water progression, and then not by capillary
74 effects.

75 Actually, for the comprehension of the physical mechanisms of liquid imbibition into wood,
76 the critical point is to be able to measure its spatial distribution in time, taking into account its
77 state. For this purpose, ¹H Nuclear Magnetic Resonance (NMR) is a helpful technique. In the
78 special case of water, it allows to discriminate free and bound waters through the spin-lattice
79 (T₁) and spin-spin (T₂) relaxation times (Zhou et al. 2018, van Meel et al. 2011, Gezici-Koç et
80 al. 2017 and 2018, Bonnet et al. 2017, Rostom et al. 2019). Although T₁ can provide an insight
81 in the two types of bound water (Bonnet et al. 2017), T₂ is best suited to discriminate bound
82 water –regarded as a whole- and free water. Bound water, through the hydroxyl groups of wood

83 components to form the hydrogen bonds, has a short T_2 -value. Free water behaves as bulk water
84 confined in a submillimeter pore and usually exhibits a longer T_2 -value (Gezici-Koç et al. 2017
85 and 2018), all the more long than the cell diameter is large. In some previous studies, NMR was
86 used to distinguish and quantify bound water and free water contents by T_2 measurements
87 (Telkki et al. 2013, Menon et al. 1987, Labbé et al. 2002). As based on the T_2 -value, the dynamic
88 of bound and free water imbibition profiles, through MRI technique, along poplar wood sample
89 as a function of time were identified during water uptake (Zhou et al. 2018), and also the
90 moisture profiles of water states in yellow poplar under drying condition (Zhang et al. 2013).

91 In this paper, we focus on the imbibition mechanisms, i.e. how aqueous liquid tends to
92 spontaneously penetrate into softwoods in contact with it. Through an original approach
93 coupling quantitative information obtained from mass and deformation measurements, NMR
94 relaxation measurements and MRI observations, we are able to quantify bound and free water
95 dynamics. To discuss these results, standard imbibition tests by weighing are also performed
96 with water and oil and are analyzed through Washburn model.

97

98 **Materials and Methods**

99 **Wood materials**

100 Wood samples are collected from Douglas-fir (*Pseudotsuga menziesii*) planks, which had been
101 left drying naturally under ambient conditions. Studied samples come either from the outer part
102 of the trunk (sapwood) or from the inner part (heartwood). The average density of all specimens
103 measured at 44% Relative Humidity (RH) is $590 (\pm 40) \text{ kg.m}^{-3}$ for heartwood and $620 (\pm 030)$
104 kg.m^{-3} for sapwood and the proportion of latewood related to the annual ring width is estimated
105 as $45 \pm 5\%$ for all studied samples subjected to imbibition tests. These values are consistent with
106 literature (Lachenbruch et al. 2010, Osborne et al. 2016) for Douglas-fir with a high proportion
107 of latewood or for this RH. For instance, in Lachenbruch et al. 2010, the density at 12% MC is
108 783 kg.m^{-3} with a latewood proportion of 56%.

109 Density essentially finds its origin in different proportions of latewood and earlywood while
110 the general qualitative features of the material remain the same. The microstructural properties
111 explain the physical origin of liquid transfers. Heartwood and sapwood materials are mainly
112 composed of tracheids and a small percentage of rays is observed. The tracheids exhibit smaller
113 diameter in latewood compared to earlywood, with a ratio between them of about 2. The
114 average cell diameters are as follows: (heartwood) $39.4 \pm 4.2 \mu\text{m}$ in earlywood and 21.4 ± 5.2
115 μm in latewood, and (sapwood) $44.7 \pm 4.7 \mu\text{m}$ in earlywood and $20.9 \pm 4.8 \mu\text{m}$ in latewood.
116 These measured lumen diameters are consistent with those given in (Ramage et al. 2017, Vahey
117 et al. 2007) for Douglas-fir. The cell length (along the L-axis) is approximately equal to a few
118 millimeters and the tubular tracheids are closed at their tips but connected to each other via
119 bordered pits on their lateral sides. The pits are located regularly along the tracheid cells. Most
120 of bordered pits of adjacent tracheid cells in heartwood are closed in the earlywood and opened
121 in the latewood, whereas in sapwood they are opened both in the early and latewood (Almeida
122 et al. 2008, Sedighi-Gilani et al. 2014). Through a quantitative analysis with Douglas-fir, it has
123 been shown in (Elaieb 2014) that about 65% of pits are open in sapwood but only 23% in
124 heartwood. Note that the rays contain a smaller number of pits in the crossing-field which are
125 connected to the tracheid cells. They may provide a path for internal flow, but since they are
126 perpendicular to the main flow direction of the present study, we assume that their role is here
127 negligible as considered in (Wardrop et al. 1961).

128

129 **Wood samples and liquid**

130 Two kinds of samples have been used: on the one hand, small cubes sawn along the anisotropic
131 directions, R, T and L ($1 \times 1 \times 1 \text{ cm}^3$ or $2 \times 2 \times 2 \text{ cm}^3$), for NMR relaxation measurements and

132 characterization of the wood properties and, on the other hand, for the liquid imbibition tests,
133 large samples with about 10 cm in longitudinal (L) direction, parallel to the imbibition axis, and
134 about 4cm and 2cm in the tangential (T) and radial (R) direction respectively, with several
135 visible growth rings. Tests have been duplicated to check the reproducibility of the results.
136 Samples are all pre-conditioned in desiccators at 20°C and at 44% Relative Humidity (RH)
137 before testing. Note that for liquid imbibition tests, four of six sides of large samples are sealed
138 with a water impermeable coating along the vertical sides parallel to the imbibition direction in
139 order to avoid capillary effects between the external wood surface and the water bath, or
140 possible water uptake from the lateral sides (Zhou et al. 2018). In this work, imbibition tests are
141 performed with (deionized) water and three oils whose density, viscosity and surface tension at
142 25°C are respectively: Water (1000 kg.m⁻³, 0.001 Pa.s, 0.073 N m⁻¹), Dodecane (740 kg.mm⁻³,
143 0.00134Pa.s, 0.025 N m⁻¹), silicone oil 47V20 (950 kg.m⁻³, 0.02 Pa.s, 0.0206 N m⁻¹) and silicone
144 oil 47V350 (970 kg.m⁻³, 0.35 Pa.s, 0.021 N m⁻¹).

145 As water and dodecane have close viscosities, the differences in dynamics of imbibition, if
146 any, find their origin in differences in wood-liquid interactions or in penetration mechanisms.
147 To compare these two liquids, small cubes are prepared and conditioned at two RH levels with
148 saturated salt solutions (44%RH: Potassium carbonate, K₂CO₃ and 97%RH: potassium
149 sulphate, K₂SO₄) or immersed in water or dodecane oil for 3 days. MC of wood is given in
150 Table 1. The values are obtained by drying all specimens at 103°C, in an oven, until reaching a
151 constant mass. For samples immersed in water or oil for 3 days, the accessible porosity Φ is the
152 volume of total water or oil to sample volume (at 44%RH) ratio. These results show that the
153 values seem to be quite similar for heartwood and sapwood. However, these results are related
154 to the scale of the used samples and the sample preparation by sawing may slightly increase the
155 accessibility of fluid inside wood by opening some tracheids (Choong et al. 1975). Moreover,
156 swelling coefficients are measured for samples subjected to RH (Table 2). These swelling
157 coefficients are in accordance with literature (MacLean 1958, Jamaoui 2017). Concerning
158 dodecane oil, no swelling is observed.

159

160 **NMR Relaxation measurements**

161 For NMR measurement, small sample is inserted in a 18-mm diameter glass tube in which the
162 humidity level is imposed (same value as for sample preparation) during the NMR relaxation
163 experiment. This glass tube is then inserted into a Bruker Minispec MQ20 spectrometer at 0.5
164 T, corresponding to a resonance frequency of 20 MHz for ¹H. The T₂ relaxation measurements
165 of the wood sample are performed using a Carr–Purcell–Meiboom–Gill (CPMG) NMR
166 sequence by carrying out 10000 echoes with an echo time of 0.5ms. A repetition time of 12
167 seconds was used (much higher than 5 times T₁ in order to prevent sample heating), 8 averages
168 were used. The NMR data are post-treated by means of an Inverse Laplace Transform (ILT)
169 algorithm, which converts relaxation signal into a continuous distribution of T₂ values. For
170 more details on the used homemade computer program and the artifacts of this technique, see
171 (Faure et al. 2008).

172

173 **Free water and oil distribution from MRI**

174 Large wood samples are immersed in liquid to a depth of about 5 mm. In case of oil, the wood
175 sample is placed in a glass Petri dish and MRI profiles are determined continuously. For water,
176 the imbibition test is performed outside the MRI apparatus and MRI measurements are carried
177 out at different times. The sample is put on a plastic sample support whose vertical position can
178 be adjusted in order to be placed inside the MRI system. Measurements are performed at a
179 vertical MRI spectrometer (DBX 24/80 Bruker) operating at 0.5 T and equipped with a ¹H
180 birdcage radio frequency coil of 20 cm inner diameter, with the sample located at the magnetic

181 center of the gradient coil (a BGA26 Bruker, 26 cm inner diameter, 50mT/m gradient strength).
182 As NMR relaxation times depend on the magnetic field strength, they are in principle the same
183 in NMR relaxation and MRI experiments since both equipments have the same magnetic field.

184 The water or oil 1D profiles along the sample axis (Supplementary Material, Figure 1.1) are
185 measured by means of a spin-echo sequence, with an imaging gradient in the vertical direction,
186 and repeating the profiling process over 16 successive echoes created by a series of π pulses
187 separated by a fixed echo-time $TE=3.47ms$, and selected by means of 32-step duplex cogwheel
188 phase cycling scheme (Levitt et al. 2002). One measurement then provided a series of 16
189 profiles recorded at successive times $TE, 2TE, \dots, 16TE$ during the spin-spin relaxation process,
190 with a field of view of 16 cm and a space resolution of 1.25 mm. A repetition time of 7 seconds
191 was used and 32 averages were measured. Signal intensity was calibrated using a glass tube of
192 known diameter filled with water or oil (using a repetition time of 12 seconds and 128
193 averages). In the case of water, due to the short relaxation time of bound water regarding TE ,
194 only free water is detected. A monoexponential or biexponential fit was then used to quantify
195 the amount of liquid inside wood taking into account the relaxation times T_2 (see below).

196 The 2D distribution (image) of free water or oil was observed by means of multi-slice 2D
197 MRI during the imbibition test. 2D MRI vertical slices of 2 mm thickness with 2-mm interval
198 between them (parallel to RL plane) passing through the wood sample with space resolution
199 equal to 0.47 (radial and tangential) \times 2.19 (longitudinal) mm are taken at different times during
200 imbibition (Supplementary Material, Figure 1.1). A multi-slice multi-echo (MSME) pulse
201 sequence acquiring 8 echoes was used with an echo time of 10 ms and a recycle delay of 600
202 ms. On purpose of enhancing the signal to noise ratio without increasing the measurement time,
203 images intensities owing the each of the 8 echoes were added to produce the final picture. This
204 picture can only be used for the qualitative purpose of seeing where the fluid is. Note that in the
205 case of water, this weighing enhances the signal intensity of water in the large lumens of the
206 earlywood due to longer T_2 time, which will be of key importance for data interpretation.

207

208 **Bound water distribution from swelling measurements**

209 To identify and quantify bound water distribution along the wood samples during water
210 imbibition tests with large samples, it is proposed to use swelling measurements after some
211 preliminary analysis providing the relation between the deformation to the bound water content
212 for small samples subjected to RH as done by (Zhou et al. 2018). The sample swelling is
213 measured along the radial (R) and tangential (T) directions every 5 mm along the longitudinal
214 direction (L) using a micrometer (Mitutoyo) with a precision of 0.01 mm for large samples
215 subjected to imbibition tests. For each distance, two different locations along the longitudinal
216 direction are considered to obtain an average value for both directions R and T.

217 Figure 1 shows the linearity of the relation observed between the bound water mass and the
218 corresponding sample volume increase on small samples. This result allows to determine a
219 “coefficient” of bound water mass per unit volume increase, which we will use later on to
220 translate the sample deformation during imbibition tests in bound water. Furthermore, the
221 calculated swelling coefficients (Table 2) show that the variation of the volume may be only
222 evaluated from the measurements of the dimensions along the radial and tangential directions,
223 as the swelling coefficient is negligible along the longitudinal direction. As no swelling is
224 observed during oil imbibition tests, this further supports the idea that strains are strictly related
225 to bound water during water imbibition, and this means that MRI profiles for oil imbibition will
226 in principle show the full amount of oil impregnating the sample. The total water mass entering
227 the samples measured by weighing is compared to the bound water mass evaluated from volume
228 variations plus the free water mass in wood determined from integration of the MRI 1D profiles
229 (Figure 2). It appears that the total water content entering the sample during imbibition test is

230 very close to the amount of bound water and free water inside wood. This confirms a very good
 231 accuracy in quantifying the total free water in wood from 1D MRI method as well as in
 232 computing bound water amount from deformation measurements.

233

234 **Standard imbibition tests by weighing**

235 A bottom open surface of the sample is placed (along a height of about 5 mm) in contact with
 236 a bath of liquid (water or oil) covered by a film to avoid evaporation (Supplementary Material,
 237 Figure 1.2). Liquid can then progress inside wood along its longitudinal direction. The other
 238 open surface is connected to a precision balance via a hanging wire. The mass evolution of the
 239 sample is recorded by a precision balance through an automatic recording system. The
 240 imbibition test is carried out at room temperature (20°C). Note that the apparent mass has to be
 241 corrected to get the effective mass due to a buoyancy force varying with the liquid level in the
 242 bath (Supplementary Material, section 1).

243 A quantitative analysis of the imbibition tests may be done through the Washburn model as
 244 explained below (for more details, see Zhou et al. 2018 and 2019). At the front of penetration
 245 inside the sample (interface), the average capillary ascent of a liquid in a porous material (with
 246 cylindrical conduit of radius R) is driven by the capillary pressure (neglecting ambient
 247 pressure): $\Delta p = -2\sigma\cos\theta/\alpha R$, where σ is the surface tension, α a factor related to the pore shape
 248 and θ the contact angle. This driving force acts over a distance of penetration h , which induces
 249 a pressure gradient p/h . The Darcy's law then expresses the balance between the pressure
 250 gradient and the viscous resistance with $\Delta p/h = \mu V/k$ where μ is the liquid viscosity, V the mean
 251 flow velocity through the sample, and k the permeability of the porous medium. Assuming that
 252 the liquid advances as a front saturating the lumens below a distance $h = \Omega/\varepsilon S$ increasing in time
 253 (where Ω is the volume of water entered in the sample and S the section of the sample),
 254 $V = (d\Omega/dt)/S = \varepsilon(dh/dt)$, with ε the (accessible) medium porosity. Integrating the Darcy's law we
 255 deduce that in a first regime controlled by capillary effects (negligible gravity effects) we have:

$$256 \quad \varepsilon h = \Omega/S = \lambda\sqrt{t/\mu} \quad (1)$$

257 with $\lambda = \sqrt{2k\varepsilon\sigma\cos\theta/\alpha R}$, which is independent of the liquid viscosity.

258 In a second regime controlled by gravity effects, h tends to a plateau h_{max} determined by:

$$259 \quad h \rightarrow h_{max} = \frac{\sigma\cos\theta}{\alpha R\rho g} \text{ when } t \rightarrow \infty \quad (2)$$

260 Then, since the main geometrical characteristics of the hydraulic system are known, the
 261 fundamental unknown of the problem is the contact angle, which may be fitted to either the
 262 dynamics or the maximum height of ascent. Note that if the porosity ε is not taken into account
 263 in the previous relationships, this amounts to just consider an "apparent" height for the
 264 progression of liquid.

265 For the flow through a cylindrical capillary, we have $\alpha = 1/2$ (the meniscus is a spherical
 266 cap) and the velocity profile can be computed exactly (Poiseuille law), which directly gives the
 267 relation between the pressure gradient and the mean velocity, from which we deduce the
 268 permeability for a set of parallel capillaries:

$$269 \quad k = \varepsilon R^2/8 \quad (3)$$

270

271 **Results and discussion**

272 **NMR Relaxation times for dodecane and water**

273 Figure 3 presents the distribution of NMR intensity as a function of T_2 for heartwood and
 274 sapwood at 44%RH and 97%RH and after 3 days of immersion in water or dodecane.

275 In the case of immersion in water, three main peaks are observed for heartwood and
 276 sapwood. The first peak with a T_2 value surrounding 1 ms corresponds to the bound water at

277 44%RH and 97%RH and after 3 days of immersion in water (Gezici-Koç et al. 2017). This peak
278 is located at the very limit of T_2 times that can be measured with the CPMG sequence, and is
279 just a -non quantitative - clue of a - true - fast relaxing peak of bound water existing for $T_2 < 1$ ms.
280 When the bound water content increases, the true peak increases in intensity and is shifted to
281 higher T_2 due to the increased mobility of water molecules in cell walls (Bonnet et al. 2017),
282 thus leading to an increase and a small shift of the apparent peak which can be clearly observed.
283 Two other wide peaks are identified for both heartwood and sapwood. As admitted in literature
284 (Almeida et al 2007 and Gezici-Koç et al. 2017), these peaks are attributed to free water. They
285 are located at roughly 10 and 50 ms for heartwood and 17 and 70 ms for sapwood. These two
286 peaks depend on the lumen sizes, and the longer T_2 is attributed to earlywood (Kekkonen et al.
287 2014, Menon et al. 1987). Note that, for heartwood, the two peaks are well-separated, but not
288 for sapwood. Variability in pore sizes maybe simply related to uncertainty in the ILT processing
289 but also to the seasonal variability of the wood structure. For sapwood, the T_2 distribution may
290 reflect the polydispersity of the pore sizes (Gezici-Koç et al. 2017) and the presence of a
291 transition zone between earlywood and latewood.

292 In the case of dodecane immersion, essentially one peak is obtained, situated at relatively
293 large T_2 -values (about 955 ms and 992 ms for heartwood and sapwood respectively). Here the
294 surface relaxivity (i.e. the proportionality constant between T_2 decay time and pore size) is very
295 small so that the influence of pore size on the T_2 relaxation time of dodecane is weak (Zhou et
296 al. 2018). Also, a small peak at low relaxation time is visible in each case, which likely
297 corresponds to bound water as the sample is pre-conditioning at 44%RH.

298

299 **Distribution of dodecane and free water from MRI and of bound water from swelling** 300 **measurements**

301 Figure 4 shows MRI 2D images of dodecane and water entering in heartwood and sapwood
302 samples at different times. Furthermore, the 1D curve profiles (Figure 5) provide a
303 quantification of their penetration into samples as a function of time. In the case of water
304 imbibition, as explained previously, only free water is observed with MRI, and bound water
305 profiles are obtained from swelling measurements.

306 In the case of dodecane imbibition for heartwood (Figure 4a) its penetration in earlywood is
307 very limited (up to about 3-5 mm) and dodecane content seems to increase in this layer with
308 time. Above 5 mm, dodecane seems to preferentially penetrate in latewood along the vertical
309 axis of the sample up to the top of the sample. However, it remains that the MRI signal for the
310 2D images is very weak (same order of magnitude as the signal-to-noise ratio), and effectively
311 the 1D profiles show a very limited amount of dodecane entering into the sample (Figure 5a).
312 As the relaxation time is the same in early- and latewood, then a monoexponential fit is used to
313 quantify the total amount of oil and it is not possible to distinguish in both latewood and
314 earlywood. In the case of sapwood, the 2D images clearly show that some dodecane reaches
315 the top of the sample after only 3 hours of imbibition test, in agreement with the 1D profiles
316 with higher content of dodecane oil (Figure 4b and Figure 5b). Moreover, dodecane seems to
317 preferentially penetrate in the earlywood, but there may be some penetration in latewood, not
318 well visible on these images. The differences of dodecane penetration into heartwood or
319 sapwood may be explained by the fact that there are more open pits in sapwood, as explained
320 in the section "Wood materials".

321 These results also show that for both types of wood, dodecane apparently does not progress
322 in the form of a uniform (straight) front saturating the sample at larger heights in time, as
323 expected from the standard Washburn imbibition process. However, dodecane imbibition
324 profiles showing a liquid profile extending widely throughout the material but of level
325 increasing in time, suggest that the material imbibition proceeds by a progressive increase of

326 the local saturation throughout the material. This aspect of the liquid profile results from the
327 heterogeneity of the material, while in each tracheid the liquid progresses as a straight front:
328 the dynamics of climbing varies from one tracheid to another, so that along some axis the liquid
329 may have already reached the sample top while in another place the liquid is much less
330 advanced. Such a heterogeneous distribution of front advances can predict this profile aspect.

331 According to the 2D images for free water (Figures 4c and 4d), the water front is climbing
332 in a jagged manner and clearly corresponds to the location of earlywood and latewood layers.
333 The heartwood provides an extremely slow water uptake which seems limited to a height of
334 about 5 mm after 6 days, with a progression front slightly higher in latewood. For sapwood, a
335 higher water uptake is observed with a water front reaching up to 35-40 mm over the same
336 duration. However, as explained previously, two T_2 relaxation times for free water are observed
337 due to the presence of different lumen sizes. By this means we can now distinguish the
338 distribution of free water in each type of wood in time using a bi-exponential fit (Figures 5c
339 and 5d). It appears that in sapwood the free water advances over significant distance in both
340 wood types (earlywood and latewood); in contrast, in heartwood, the free water seems to hardly
341 be able to reach a height larger than a few millimeters. These observations are consistent with
342 the qualitative observations from 2D MRI images.

343 Furthermore, according to the profiles of bound water, the most important result is that the
344 bound water distribution extends farther than the profile of free water, an effect particularly
345 clear for heartwood. So it can be considered that bound water at least partly propagates by itself
346 longitudinally through the cell walls. In particular, bound water uptake seems to be quite
347 constant up to the front of penetration of free water, with a moisture content close to the FSP
348 (taking into account the moisture content at 44%HR, Table 1). This suggests that basic
349 characteristics of water transport in softwood qualitatively similar to that in hardwoods (Zhou
350 et al. 2018), i.e. a dynamics of imbibition mainly governed by the longitudinal progression of
351 bound water in the sample: free water can advance through the vessels (considered as opened
352 capillary tubes with unlimited length) only when cell walls are saturated with bound water.
353 However, in the case of softwood, the mechanisms for liquid water transport may be quite
354 different as the structure is different with tracheids, with limited length, closed at their ends and
355 connected to each other by pits.

356 To conclude, in coherence with Sedighi-Gilani et al. 2012 and 2014, the water uptake is
357 significantly larger for sapwood than for heartwood. This result is similar for oil penetration.
358 The liquid transport penetration in heartwood and sapwood may depend on open or closed pits.
359 Furthermore, for both materials, larger oil and water contents are localized in the first 5 mm,
360 due to possible effect of preparation of sample. Indeed, sawing may slightly increase the
361 accessibility of fluid inside wood by opening tracheids (Choong et al. 1975). The aim of the
362 next section is to precise the involved mechanisms for both materials, through Washburn model
363 and from the standard imbibition tests.

364

365 **Discussion through standard imbibition tests by weighing**

366 Imbibition results for water and oil are expressed in terms of the liquid volume entering into
367 wood, per sample area (expressed as “apparent height”) as a function of the time rescaled by
368 the liquid viscosity (Figure 6). This representation is useful to discuss the imbibition dynamics
369 of different liquids with regards to the Washburn model (Equation (1)). The data deduced from
370 MRI experiments are also shown in the same graph and an excellent agreement is found
371 between these data and those obtained from mass measurements. In Supplementary Material
372 (section 2), the volume of water or oil per sample area as a function of time and 2D MR images
373 for the three oils at the end of the imbibition tests are also shown for further discussions. Note
374 that for a cylindrical capillary containing, from place to place perturbations (e.g. pits) of its

375 shape over very short distance, the maximum height of ascent is that of the main cylinder, since
376 the liquid must be able to climb between two successive perturbations, and thus Equation (2) is
377 still valid with R the main cylinder radius. Furthermore, the permeability may be affected
378 (decreased) by these perturbations as they induce further viscous dissipation during the liquid
379 flow through the whole system. It follows that the dynamics may be damped with regards to
380 that expected for the flow through a simple straight conduit but the Washburn law remains
381 valid.

382 Concerning sapwood (Figure 6a), the curves for oils of different viscosities (with only slight
383 differences in surface tension and likely close contact angles) superimpose along a master curve
384 when the time is rescaled by the viscosity. This demonstrates the validity of the assumption of
385 a viscous flow through a given hydraulic network at the origin of liquid uptake (for example in
386 consistency with the form of Equation (1)). In contrast, the imbibition curve for water, with a
387 surface tension different from that of oil by a factor about 3, is situated at rescaled times about
388 100 larger than the master curve for oils. The point may be more directly appreciated from the
389 representation of water uptake as a function of time (Supplementary Material, section 2):
390 dodecane and water have a similar viscosity but a surface tension different by a factor 3, but
391 the water uptake is slower by several orders of magnitude than that of oil. This means that in
392 that case the flow is not dependent on the same physical effects underlying the Washburn
393 approach for imbibition. This result is discussed in the following through Washburn model. A
394 plateau in the imbibition curve is clearly observed for Dodecane around $\Omega/S=1.3$ cm (Figure
395 6a, Equation (2)). Considering the accessible porosity of sapwood determined on small samples
396 (Table 1) for oil (i.e. 29.7%), this corresponds to an effective average maximum height of ascent
397 around $h_{\max} = (\Omega/\varepsilon S) = 4.4$ cm. This may be in agreement with the 2D MRI images of Dodecane
398 oil, which show liquid signal at larger height, if we assume that the tracheid diameters are
399 somewhat dispersed around a mean value, allowing different final heights of ascent around this
400 one, up to the sample height (i.e. 10 cm). It is also possible that the accessible porosity,
401 determined from oil impregnation in small samples, was somewhat overestimated due to
402 tracheid opening when sawing, as explained previously. Finally, note that the results for oils of
403 different viscosities are consistent with the 2D MRI images providing the qualitative aspect of
404 liquid ascent (Supplementary Material, section 2). From Equation (2), using $R = 15\mu\text{m}$ for the
405 average radius of tracheids (without distinguishing latewood and earlywood), a contact angle
406 of $\Theta \approx 84^\circ$ is calculated. Then, from the slope λ of the imbibition curve (Equation 1), the
407 permeability value of the Washburn model may be deduced, i.e. $k = 0.35 \times 10^{-12} \text{ m}^2$. It is worth
408 noting that this value is of the same order as the permeability of a set of simple capillaries with
409 the same mean radius (Equation (3)), i.e. $k = \varepsilon R^2/8 = 8.4 \times 10^{-12} \text{ m}^2$, which confirms assumption
410 of oil flow through tracheids. The smaller permeability value obtained here would then likely
411 be explained by the existence of pits and direction changes all along the hydraulic network
412 leading to additional pressure drops. Finally, this tends to confirm that in sapwood the hydraulic
413 network is made of tracheids connected by open pits. As explained above, the oil imbibition
414 process maybe due to the heterogeneity of the tracheid sizes, which leads to a distribution of
415 Washburn imbibition with different characteristic times. It might alternatively be due to an
416 imbibition process involving the fast ascent of some fluid towards large heights coupled with a
417 more progressive imbibition in smaller pores at the different heights. To sum up: Washburn
418 model is valid along each series of connected tracheids, which explain that the observed
419 dynamics is consistent with the theoretical prediction, associated with a front step propagation
420 in this series, but the different dynamics in each of them may give the impression of a partial
421 saturation at different levels.

422 For water imbibition in sapwood, we observe a maximum apparent height (Ω/S) of ascent
423 similar to that found for oils, which leads to a similar value for the contact angle. Since from

424 such tests, as water (bound or free) cannot be distinguished, the total accessible porosity of the
425 system for water is considered (about 41.9%, Table 1), to compute the maximum height of
426 ascent, which resumes to considering that both phases approximately fill their own porosity at
427 the same rate. The predicted front of penetration (Equation 2) is then: $h_{\max} = (\Omega/\epsilon S) = 3.0$ cm.
428 This value is in agreement with the (average) front of propagation determined with MRI 1D
429 profiles for both free and bound water, for about 3 days of imbibition tests (Figure 5d). A contact
430 angle of $\Theta \approx 88^\circ$ is then obtained, which is the hallmark of a poor wetting. Then, from the slope
431 λ of the imbibition curve, we deduce the permeability value of the Washburn model, i.e.
432 $k = 3 \times 10^{-15}$ m². This permeability is several orders of magnitude lower than that expected for
433 a set of simple capillaries with the same mean radius (Equation 3), i.e. $k = \epsilon R^2/8 = 11.8 \times 10^{-12}$
434 m². It is also several orders of magnitude smaller than the permeability observed with oil, which
435 cannot solely be explained by the difference of accessible porosity to water. It is worth noting
436 that, although there is some significant uncertainty on the effective maximum height of ascent
437 in the tracheids, this does not affect this conclusion, i.e. using a different value for the accessible
438 porosity during the process would still lead to this very large discrepancy between the apparent
439 permeability and that associated with a standard Washburn ascent along the tracheids.

440 Imbibition results for heartwood strongly differ from those in sapwood (Figure 6b). First of
441 all, the maximum height reached is significantly lower (about three times) than that in sapwood
442 over similar duration, both for oil and water. Another remarkable point is that the curves for the
443 different oils or water do not superimpose when the time is rescaled by the viscosity. These
444 results may not be explained by the variability of samples (for instance the density due to
445 different proportions of latewood as mentioned above). In fact, the shift between them
446 approximately correspond to the viscosity factor, which means that the curves would roughly
447 superimpose if represented as a function of time (without rescaling by the viscosity). And
448 effectively, when the volume of oil per sample area entering into sample is represented as a
449 function of the (non-rescaled) time the curves superimpose (Supplementary Material, Figure
450 2.1). This implies that in that case the uptake of oil is independent of viscous effects, and thus
451 cannot be described by the standard Washburn approach which relies on a balance between
452 capillary and viscous effects. The estimation of the permeability gives value of the same order
453 as that observed for water in sapwood. Altogether these different observations confirm that here
454 the pits are preferentially closed, so that there is only negligible flow through the hydraulic
455 system up to the top of the sample. Concerning water, as for sapwood, from MRI measurements,
456 the bound water profile progresses in advance of free water, but in this case, the dynamics of
457 free water imbibition seems not to be mainly governed by the longitudinal progression of bound
458 water in the sample. Then only a small amount of water can penetrate in the structure,
459 essentially by diffusion through cell walls. However, it is not clear how it can occur for oil,
460 considering that oil essentially penetrates in the first 5mm, the amount above 5mm being
461 significantly lower due to closed pits. The preferential penetration in the first 5mm layer may
462 be explained by the existence of open tracheids following cutting during the sample preparation.
463 Above a few millimeters, liquid hardly progress in the tracheids because of preferentially closed
464 pits and with their limited length.

465

466 **Discussion on the mechanisms of free water imbibition**

467 All these results obviously mean that the propagation of water does not rely on the basic
468 physical assumptions underlying the Washburn model. Instead we have to consider that the
469 capillary transport may be damped by some effect. Since the pits are moist sensitive it may be
470 suggested that pits could tend to close when in contact with water while letting oil move
471 through. However, in that case we would expect some similar dynamics between heartwood
472 (for which pits are preferentially closed) and sapwood. This is not what we observe (Figure 6b):

473 the dynamics of water imbibition is apparently about six times faster in sapwood than in
474 heartwood. Moreover, in the case of heartwood, there is almost no free water penetrating the
475 sample within the duration of the test (Figure 5c), as a result of closed pits, whereas a significant
476 amount of free water apparently penetrates the sapwood region, meaning that in contrast pits
477 effectively remain open in sapwood (Figure 5d).

478 Actually, it is worth noting that bound water progresses through the sample more rapidly
479 than free water in heartwood and sapwood (Figures 5c and 5d) and water uptake seems to be
480 governed by bound water diffusion and not by capillary flow as expected by the Washburn law.
481 This is similar to an effect suggested for aspen heartwood by (Johansson et al. 2011) but not for
482 aspen sapwood. This result is still not fully understood. However, as explained above, the
483 climbing of free water is allowed only when the free water is in contact with cell-walls which
484 MC is close to the FSP, otherwise there is a negligible displacement of free water; under such
485 conditions the dynamics is governed by the coupling between the longitudinal diffusion of
486 bound water and the progressive advance of free water.

487 According to Zhou et al. 2019, this is associated with a strong change of the wetting
488 properties with the concentration of bound water: X-Ray synchrotron images indeed showed
489 that the apparent contact angle during imbibition was close to 90° while it was seen to be much
490 lower when the cell walls are saturated with bound water, which explains the need of sufficient
491 longitudinal diffusion of bound water before the water can further progress through the lumens.
492 Finally, note that these results seem to be supported by the MRI observations of Dvinskikh et
493 al (Eng. Structures, 2011) and Eitelberg et al (2011) for a spruce sample simply put in contact
494 with air at a large RH. In that case, even in the absence of free water in contact with the sample,
495 bound water was observed to rapidly propagate in the longitudinal direction, showing its ability
496 to diffuse relatively rapidly thus keeping the possibility to control the liquid transport in an
497 imbibition process.

498

499 **Conclusion**

500 The aim of this study was to analyze the mechanisms of liquid transport in Douglas-fir,
501 especially in heartwood and in sapwood. To answer to this question, two kinds of tests have
502 been performed to identify the mechanisms of water and oil penetration: NMR methods and
503 standard imbibition tests by weighing.

504 Concerning the oil penetration, our results show that the Washburn law is only verified for
505 sapwood. In the case of heartwood, our results show that the uptake of oil is independent of
506 viscous effects, and thus cannot be described by the standard Washburn approach which relies
507 on a balance between capillary and viscous effects.

508 For the case of water, the phenomena are more complex, as it is necessary to take into
509 account free water and bound water, and the Washburn law is not available for sapwood and
510 heartwood. Indeed, our results show that the front penetration of liquid water is mainly
511 governed by the longitudinal progression of bound water in the sample.

512

513 **Acknowledgements**

514 This work has benefited from a French government grant managed by ANR within the frame
515 of the national program Investments for the Future ANR-11-LABX-022-01 (Labex MMCD,
516 <http://mmcd.univ-paris-est.fr/>).

517

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TABLES

621

622 **Table 1:** Moisture Content MC (%) and accessible porosity Φ (%). Mean and Standard
 623 Deviation (SD) values are given (three samples).

	MC at 44% RH	MC at 97% RH	MC (3 days in water)	Φ (3 days in water)	Φ (3 days in oil)
Sapwood	10.2 (± 0.1)	25.3 (± 0.35)	79.4 (± 3.7)	41.9 (± 1.2)	29.7 (± 0.1)
Heartwood	10.5 (± 0.1)	20.5 (± 0.25)	75 (± 0.15)	39.1 (± 3.2)	23.9 (± 2.0)

624

625 **Table 2:** Swelling coefficients α (%/%) along the anisotropic directions R, T, L. Mean and
 626 Standard Deviation (SD) values are given (three samples).

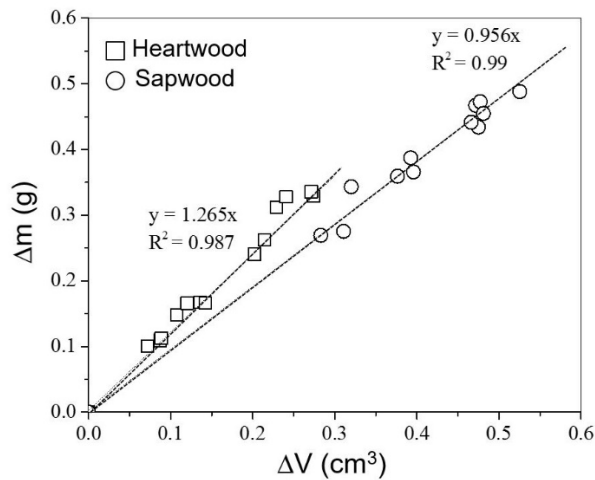
	α (R)	α (T)	α (L)
Sapwood	0.17 (± 0.02)	0.40 (± 0.01)	0.007 (± 0.004)
Heartwood	0.14 (± 0.02)	0.20 (± 0.003)	0.02 (± 0.01)

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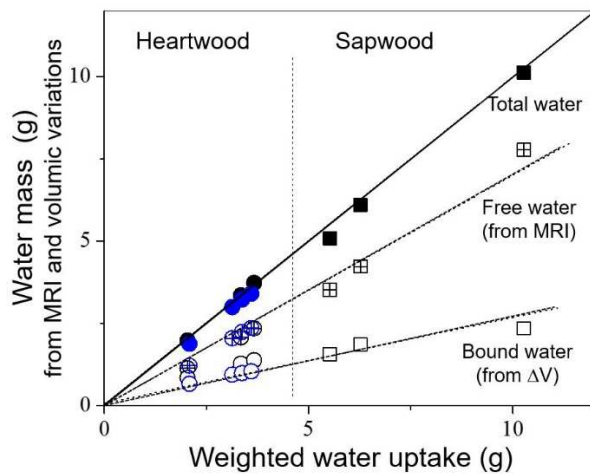
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FIGURES



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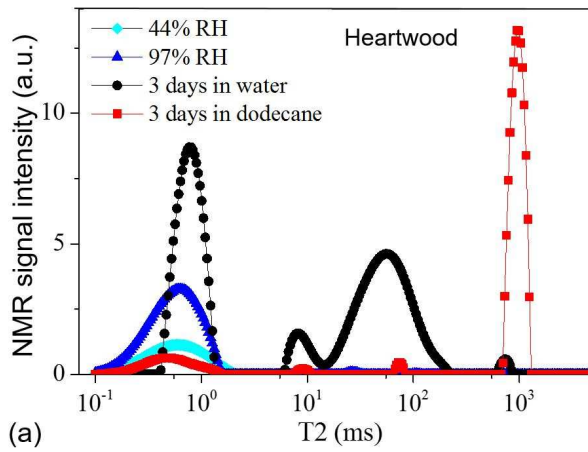
Figure 1: Additional mass Δm of bound water recorded by weighing as a function of volume increase ΔV (determined on small samples) for heartwood and sapwood between 44% RH to 97% RH.



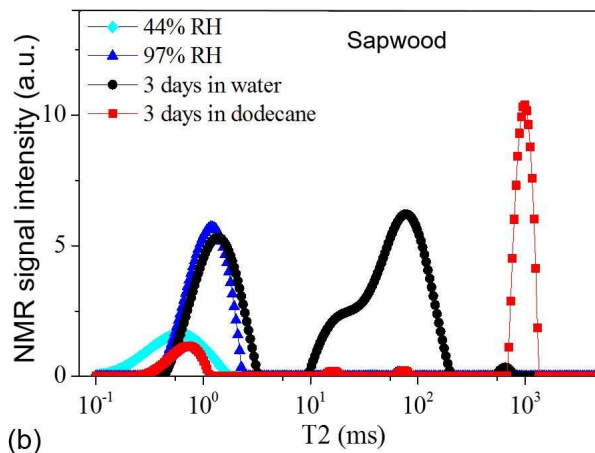
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Figure 2: Free water mass (from MRI) plus bound water (from swelling measurements ΔV) compared to the total water uptake determined by weighing, at different times during imbibition tests with large samples for heartwood (black or blue circle symbols for two tests) or for sapwood (black square symbols).

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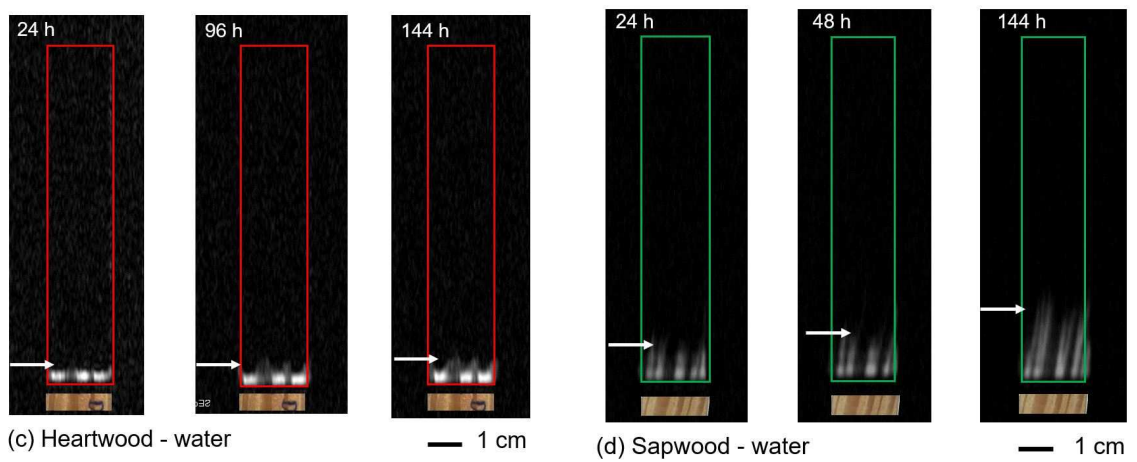
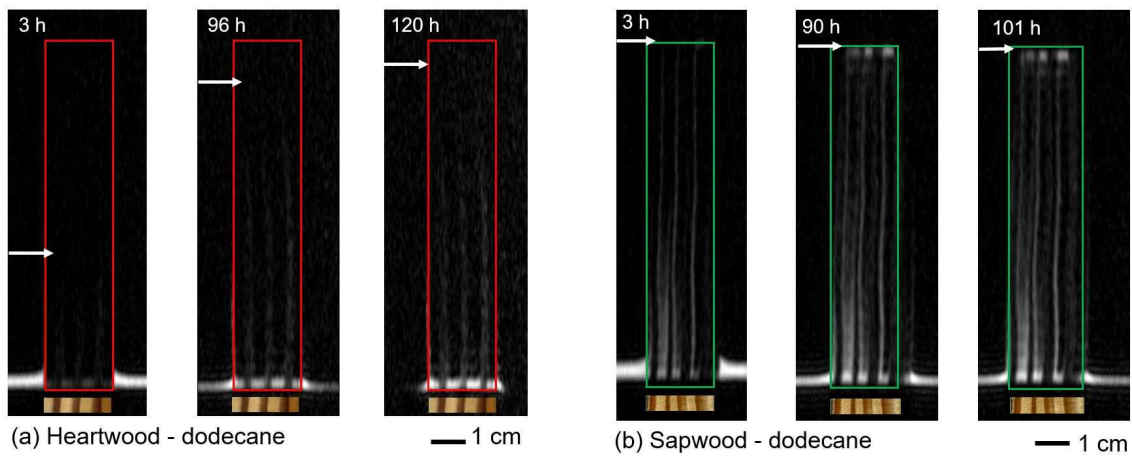
648 **Figure 3:** NMR T₂ relaxation times for heartwood (a) and sapwood (b) under 44% or 97% RH

649 and after 3 days of immersion in water or dodecane.

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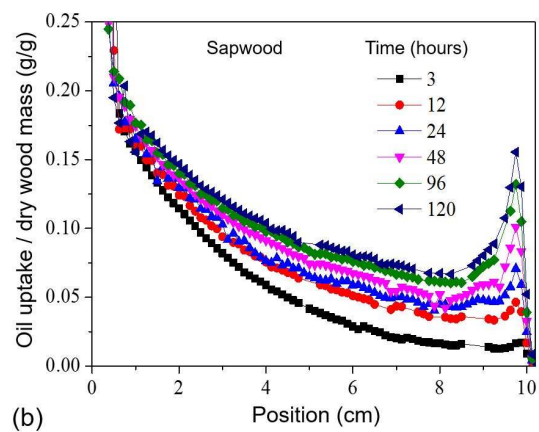
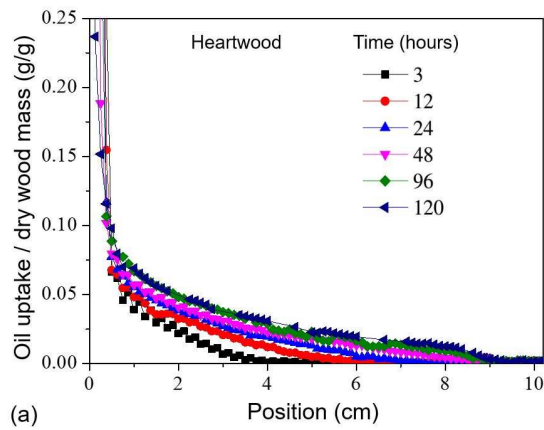


655 **Figure 4:** 2D MRI images (longitudinal-radial plane) of dodecane oil and free water distribution
656 in wood samples at different times during imbibition tests for heartwood (a, c) and (b, d) for
657 sapwood. The front of liquid penetration is indicated by a white arrow according to the 1D
658 profiles given in Figure 5. A view of the sample cross section is inserted showing the
659 correspondence between the main liquid paths and the sample structure (latewood and
660 earlywood).

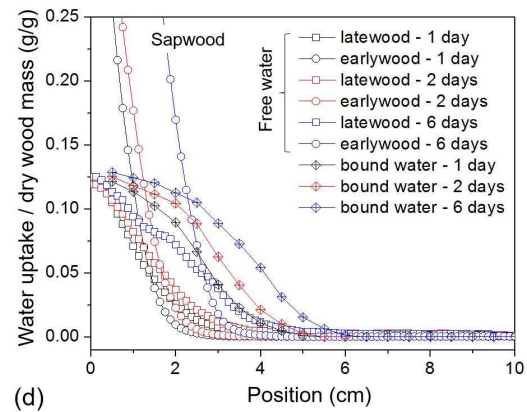
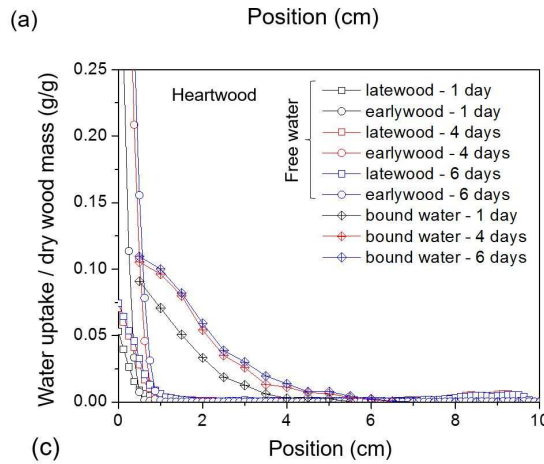
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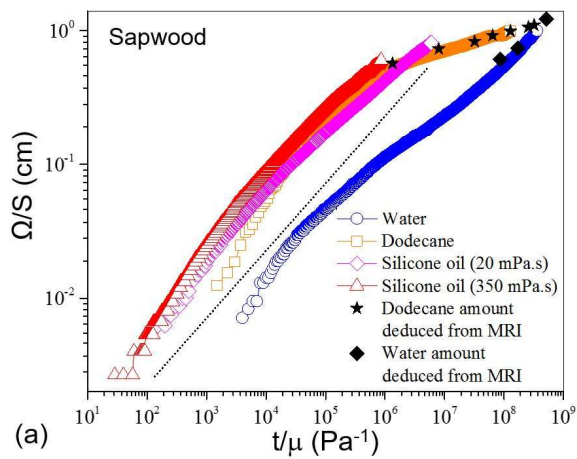
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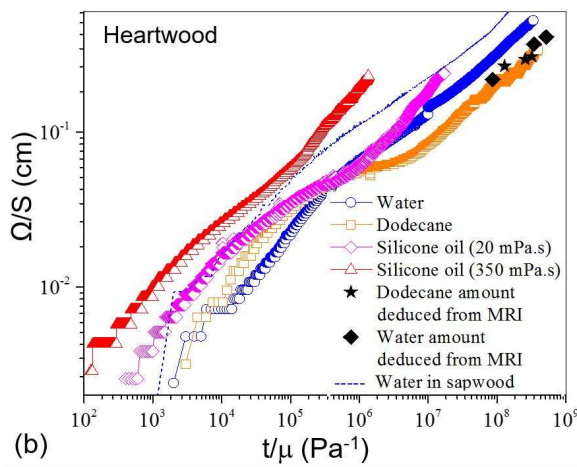
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Figure 5: 1D MRI profiles of oil (dodecane) and water uptake at different times for heartwood (a, c) and sapwood (b, d).

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Figure 6: Absorbed liquid volume per unit cross-section Ω/S area against the time per viscosity t/μ of water, dodecane oil and two silicone oils for sapwood (a) and heartwood (b) samples. The dashed line of slope 2 in Fig. a is a guide for the eye.

677

SUPPLEMENTARY MATERIAL

678 Mechanisms of liquid imbibition in Douglas-fir inferred from ¹H Nuclear Magnetic
679 Resonance methods

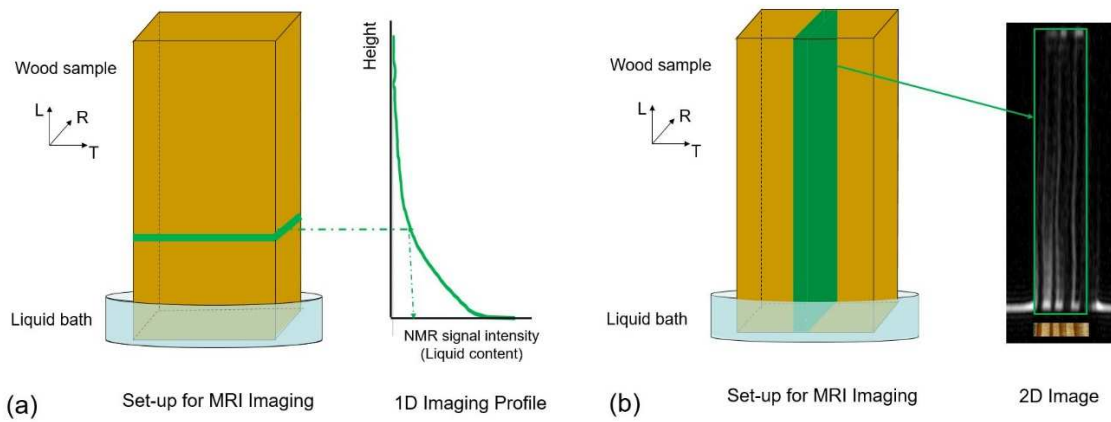
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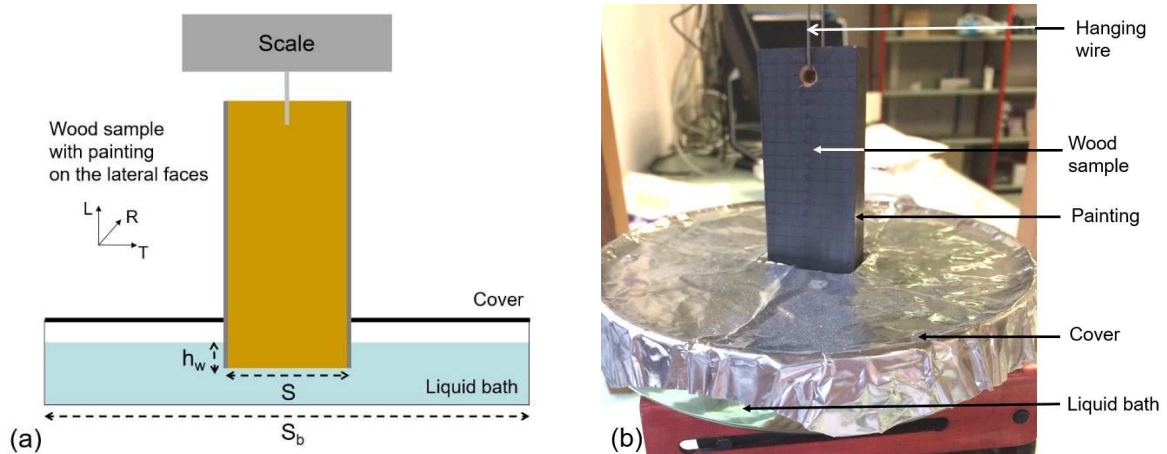
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684 SECTION 1: IMBIBITION TESTS

685 Principles of MRI measurements and of standard imbibition tests by weighing



686 **Figure 1.1:** Principle of the imbibition experiments, showing the orientation of the wood
687 sample, whose vertical faces have been sealed with paint and of the different MRI
688 measurements (for more details, see Zhou et al. 2018, 2019): a) Projection of transverse signal
689 for 1D profiles along sample axis. Every point corresponds to the integrated signal in the
690 horizontal slice with 1.25 mm of thickness. b) Slice selection for 2D NMR imaging. Examples
691 are given for dodecane oil imbibition.
692



693 **Figure 1.2:** Scheme of the standard imbibition test by weighing. a) Principle of the
694 measurements. b) View of the experiments. See below for the definitions of S_b , S and h_w .

695

696 Correction of buoyancy force

697 The variation of buoyancy force referred to the initial state can be written as $-\rho S \Delta h_w$, with
698 ρ the liquid density, S the cross-section area of the wood sample and Δh_w the variation of
699 wetted height.

700 The apparent mass of liquid entered in the sample thus writes

$$m_0 = m - \rho S \Delta h_w \tag{S.1}$$

701 where m is the effective entered mass.

702 Furthermore, the variation of liquid level in the bath results from this mass entrance:

$$m = \rho (S_b - S) \Delta h_w \tag{S.2}$$

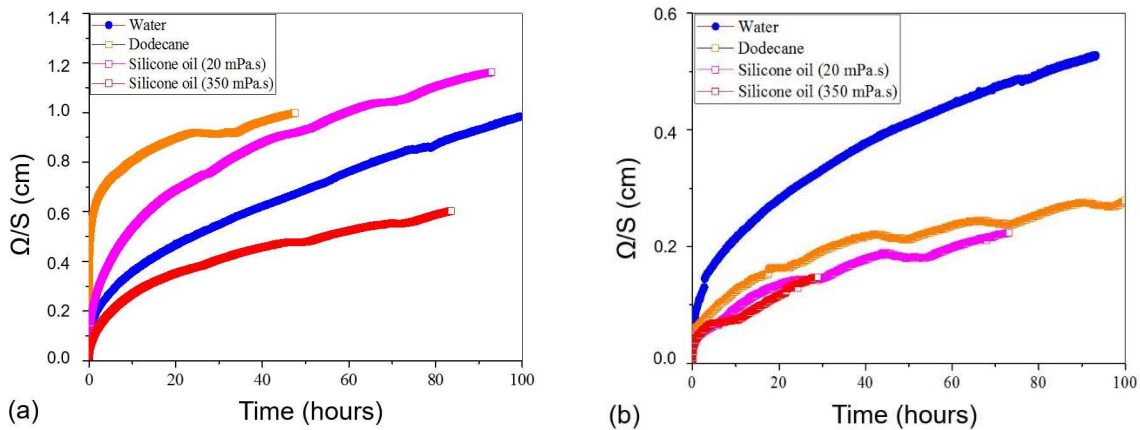
703 where S_b is the cross-section area of the liquid bath.

704 Using the value for Δh_w deduced from equation (S.1), in the expression (S.2) we find the
705 expression for the effective entered mass of liquid:

$$m = m_0 (1 - S/S_b) \tag{S.3}$$

706 SECTION 2: RESULTS

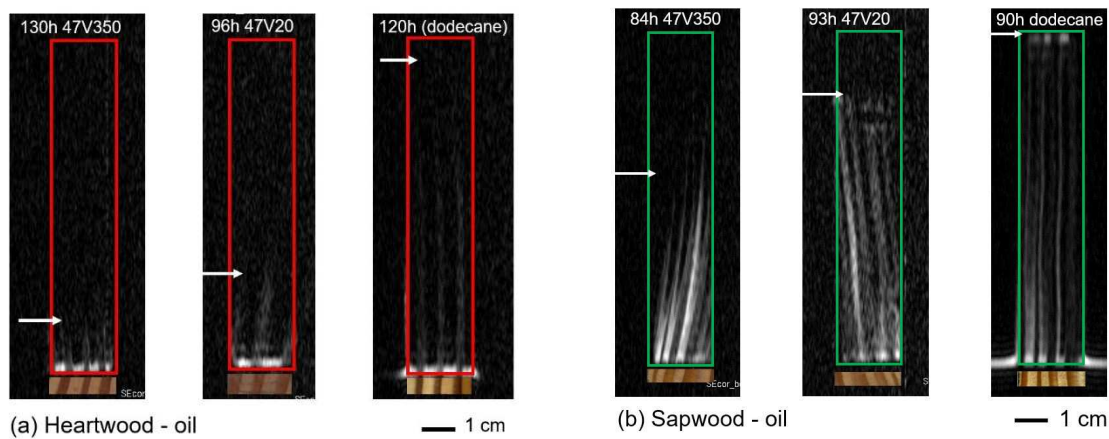
707 Liquid volume per sample area against time



708 **Figure 2.1:** Liquid (oils and water) volume per sample area (cm) against time (hours) for
709 sapwood (a) and heartwood (b). Initial state for all samples: 44% RH. Tests have been
710 duplicated for heartwood to confirm these “unexpected results”.

711

712 **MRI 2D images for the three oils (47V350, 47V20 and dodecane)**



713

714 **Figure 2.2:** 2D MRI images of the oil imbibition test along the longitudinal direction at the end
715 of the test for three oils (47V350, 47V20 and dodecane). Longitudinal-radial plane images: (a)
716 for heartwood and (b) for sapwood. A view of the sample cross section is inserted showing the
717 correspondence between the main oil paths and the sample structure (presence of latewood
718 or earlywood). The front of oil penetration is indicated by a white arrow.

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