

Response to Referee #2

We thank the referee for their remarks on the manuscript and for taking the time to review it. The referee's comments are shown in red, and our responses follow in black.

(1) The authors should provide some further details of the grid of experimental measurements made (both in radial coordinate and in time) and consider how they might better represent the fitting of the data, currently presented in the form of Figures 5(b) and 10. In these figures, it is not possible for the reader to clearly discern what is experimental data and what is a fit. If all of the data recorded is of the form shown in Figure 5(a), I would prefer to see fits to a simple 2-d plot of this form rather than the full surface shown in Figure 5(b). This would allow the reader to make a more informed judgement on the quality of the fit.

It should have been mentioned in the description of Fig. 5(a) that this data came from a one-off experiment, the setup of which was slightly different to that used for the calculation of diffusion coefficients from the surface fits. In this particular experiment, we chose to repeatedly collect data at five specific radial positions, so that a 2D plot could be obtained and the change in concentration at each point easily visualised. This was not how the vast majority of data was collected (as detailed below).

We have added the following to the caption of Fig. 5 to clarify:

“This was a one-off experiment in which data was repeatedly collected at five specific radial positions, for the purpose of visualising how concentration changed at a fixed location over time.”

We have modified Fig. 5 (b) to show the surface fit for levoglucosan at 50% RH, rather than 60% RH, as it is perhaps easier to differentiate between the experimental data (the points) and the fit (the grid). We have also added Fig. 5 (c), which is a one-to-one plot showing the measured ϕ vs ϕ according to the fit, also for levoglucosan at 50% RH.

Can the authors state:

- how many points the retrieval is fit to;
- what the time resolution is and how many radial coordinates were measured;

We have modified and expanded the discussion in section 2.3 to cover these points in addition to including another explanatory panel in Fig 2:

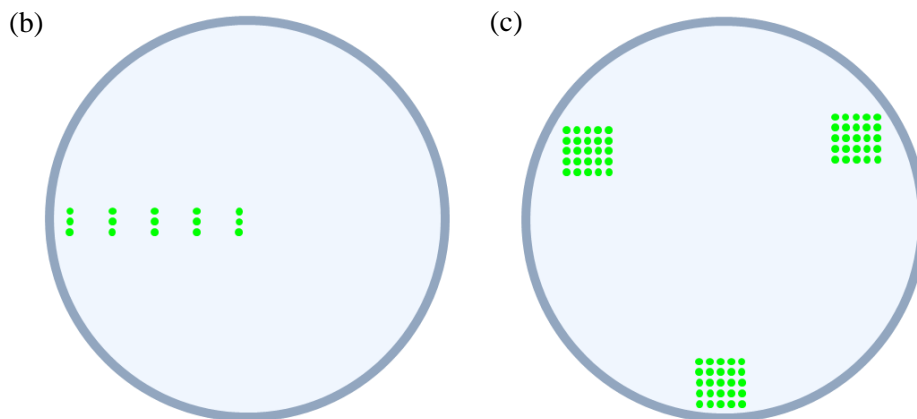
“The spectrometer was configured to collect Raman spectra after chosen time intervals at locations across a grid covering a portion of the sample disk (see Fig. 2). The spatial and temporal separations of the spectra were chosen such that, as far as possible, a broad range of D₂O concentrations could be observed over the entire disk radius during the experiment. Each spectrum was measured at a new XY coordinate (and hence radial position), chosen according to the rate of diffusion in each experiment. The D₂O exposure time required to collect enough information to determine a diffusion coefficient was about 10 minutes for a D_{water} of $10^{-10} \text{ m}^2\text{s}^{-1}$, about 2 hours for a D_{water} of $10^{-12} \text{ m}^2\text{s}^{-1}$, about 20 hours for a D_{water} of $10^{-14} \text{ m}^2\text{s}^{-1}$, and about 8 days for a D_{water} of $10^{-16} \text{ m}^2\text{s}^{-1}$.

The Raman software could be used to define a rectangular grid across which spectra could be collected in a raster fashion. At high diffusion coefficients, it was important to collect data across the entire radius of the disk in a short space of time. For this reason, a grid such as that shown in Fig. 2(b) was configured, with a 25 μm spacing in the x direction and a small (up to 5 μm) spacing in the y direction. Limitations existed at low RH because diffusion was so slow as to make it impractical to

wait for high D₂O concentrations at the disk centre; it was nevertheless possible to determine diffusion coefficients using the concentration measurements near the edge of the disk (see Fig. 2(c)). At these slow diffusion coefficients, where many spectra could be collected without the concentration gradient changing significantly, it was less important to cover the entire radius of the disk in a short space of time. This allowed us to collect clusters of more spectra at higher spatial resolution (typically with X and Y spacing of 5 μm), with time breaks between each cluster (Fig. 2(c)). As diffusion progressed, and the O-D band was visible across greater proportions of the radius, the size and number of spectra in each cluster was increased to cover more of the radius.

The time taken to collect each spectrum was typically 1 s, with a further 1 s period required between spectra for the motorized XYZ stage to move to the next location. This therefore defined the upper limit to the diffusion coefficients which could be measured where diffusion occurred on a minute timescale. Some spectra were longer in duration (up to 40 s per spectrum) – these longer acquisitions were used where the extra duration did not compromise the time resolution but did improve the quality of the spectral data. For very slow experiments (e.g. sucrose 20% RH, which involved a 3 week D₂O exposure), there were breaks between several series of spectral acquisitions in order to avoid wear on the laser.

The number of points used in each surface fit varied according to the duration of each experiment, which was directly influenced by the rate of diffusion at each relative humidity. Experiments where diffusion coefficients were large typically involved the collection of several hundred spectra (and thus data points in the surface fit); experiments with the smallest diffusion coefficients usually generated several thousand spectra.”



New Fig. 2(b) and (c). The configuration of the grids over which spectra were collected for (b) fast and (c) slow diffusion experiments.

- how the radial values were aggregated from what must be a x-y Cartesian coordinate set of measurements (for example, it is not exactly clear how figure 2(b) is arrived at from measurements on the particle of cylindrical symmetry and simply presenting a clear explanation of this would suffice);

The old Fig. 2(b) has caused some confusion. This is not experimental data, but is a representation of what we might expect. However, we give a similar plot of the actual data in Fig 5. We have removed the old Fig. 2(b).

The XY coordinate of the centre of each disk, as well as its radius, was determined using the method discussed on page 29385, lines 11 to 20. With this information, basic trigonometry was used to determine the radial position of each spectrum from its XY coordinate.

- a metric for the quality of the fit determined.

The fit was determined by minimising χ^2 . The random error in the surface fit due to errors in ϕ was included in the calculation of the errors in the diffusion coefficients, plotted in Figs. 6 and 7. As this was not the sole source of error in the diffusion coefficient, we do not feel it is of benefit to report it separately.

The authors should also provide more detail on how they arrived at the estimate of the spatial resolution of the technique of 1.3 microns.

The manufacturers of our Raman spectrometer state that the diameter of the laser spot and hence the lateral region probed is given by $(0.61 * \text{laser wavelength}) / (\text{lens numerical aperture})$ (see e.g. Murphy (2001) for further details). The laser wavelength in this case was 514 nm, and the lens numerical aperture was 0.25. We now state that this value is “estimated by the manufacturer” in section 2.4.

(2) The authors should present the coefficients for the VFT fits shown in Figure 6 in a tabulated form.

As mentioned in the response to referee #1, we have simplified the form of the equations used for the fit. The coefficients for the new fit are now presented in Table 1.

(3) When considering the diffusion timescales shown in Figure 8(b), given the inherent problems of assuming a Stokes Einstein treatment, the authors should also include the parameterization of the diffusion constant provide by Zobrist et al. (2011) for direct comparison with the values reported from the new measurements.

Diffusion timescales calculated using the Zobrist et al. (2011) parameterisation have been added to Figure 8 (b). These timescales agree much more closely with the diffusion timescales calculated using the water diffusion coefficients measured in this study than with those calculated from viscosity measurements.

(4) All of the Figures have text labels that are far too small for publication in a two column journal format - they are quite hard to read even in the format of the ACPD article.

The figures and their text labels will be adjusted during the preparation of the ACP manuscript.

References

Murphy, D. B.: Fundamentals of Light Microscopy and Electronic Imaging, Wiley-Liss, New York, NY, 2001.

Zobrist, B., Soonsin, V., Luo, B. P., Krieger, U. K., Marcolli, C., Peter, T., and Koop, T.: Ultra-slow water diffusion in aqueous sucrose glasses, Phys. Chem. Chem. Phys., 13, 3514, 2011.