Response to Referee #1

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.

- One concern relates to the fits given in Fig. 6: Here the authors present their measured diffusion constants of water into different aqueous matrices, with fits for each matrix to a Vogel-Fulcher-Tamman expression. First, I feel the authors should show the whole water activity range (i.e. from 0.0 to 1.0) on the x-axis. Obviously, the fits for all substances need to converge into the diffusion constant for water in water at a water activity of 1.0. My impression from what is presented in the figure is that this is not being the case now and refitting is needed. It is more difficult to do a reasonable fit to water activities approaching a water activity of 0, since the measurement with the technique used by the authors limit the accessible range to water activities of about 0.2 and higher. However, it is clear that even in a matrix containing no water at all, there will be a finite diffusion constant of water. Thus the authors have to check whether their fits lead to unreasonable low water diffusion constants for the pure substances. This seems especially critical for the fit of levoglucosan. In addition, I feel strongly that the authors should provide the reader with the coefficients of the fit (I suggest giving this in an appendix).

The fits are purely empirical, and we realise that the use of the Vogel-Fulcher-Tamman expression may have implied that they were physically motivated and the various parameters were constrained to be physically realistic. Given that our measurements were performed at a single temperature and are limited to water activities greater than 0.2, the resulting VFT fits are not physically based. Our reasoning for using the VFT approach was to be consistent with Zobrist et al., but given the referee's valid criticism we have opted to represent the data with an empirical polynomial fit. In order to avoid confusion we have simplified the form of our fit functions for D (at 296.5 K) *vs* a_w as follows:

$$\log_{10} D = a + b\,a_w + c a_w^2 + d a_w^3$$

	a	b	c	d
Sucrose	-20.89	25.92	-26.97	13.25
Levoglucosan	-18.41	31.10	-44.43	23.12
Raffinose/M5AS	-17.21	24.00	-32.50	17.02

The fits for all substances converge to the diffusion coefficient for water in water at a water activity of 1.0; the x-axis in Fig. 6 has been extended to show this. Given that all of the measurements made in this study are at water activities above 0.2, and given the lack of literature data for drier conditions, we feel it would be inappropriate (and also of limited atmospheric relevance) to extrapolate to lower water activities. The coefficients of the fit are now provided in Table 1 and Section 3 of the paper has been modified with the new fitting equation.

- My next major concern applies to Eq. (4) on page 29390: This equation hold only for the case of linear diffusion, i.e. if the diffusion constant is **independent** of concentration, but not for the cases studied in this paper! Hence, also the data presented in Fig. 8 as well as the discussion up to line 7 on page 29290 is not correct. In order to calculate a time scale for diffusion where the diffusing species acts a plasticizer you need always to specify the conditions from which you start to the ones where you wait to come into equilibrium again. These means that you have to take into account the history of relative humidity and temperature changes, since those will be manifesting themselves in concentration gradients within the particle. But even when you start with a homogeneous particle at the beginning and do a step change in relative humidity you need to solve the full non-linear equation to calculate time scales. This may be best illustrated using an example: I presume the authors mean in their sentence (line 5, page 29390): “Figure 8a shows these timescales for water diffusing into sucrose, levoglucosan and raffinose/M5AS aqueous spherical droplets of radii between 100nm and 1 _m at 20% RH.” actually the half time needed to reach equilibrium upon a change from a homogeneous particle at 0% RH exposed to rapid change to 20% RH. Here neither the diffusion constant at aw=0.0 (what constant would the authors use as they provide no fit down to aw=0?) nor the diffusion constant at aw=0.2 allows to calculate the time response, but you need to put the concentration dependence of the diffusion constant into a model like KM-GAP (Shiraiwa et al., 2012) or the one used by Zobrist et al., 2011 to get the time response right. If you use simply eq. (4) and the diffusion constant at aw=0.2 you can easily be orders of magnitude to fast (depending on the magnitude of the diffusion constant at aw=0.0) and if you would use the one at aw=0.0 and put it into eq. (4) you may be orders of magnitudes to slow. Of course the problem of applying Stokes-Einstein is an independent one from using wrongly eq. (4) and correctly discussed by the authors. The authors have to rethink how they want to discuss the problem of Stoke-Einstein. Easiest would be to compare just the diffusion constants measured with those derived via Stokes-Einstein. However, the numbers given in Fig. 8 need to be corrected, most significantly for the lower range in RH.

Our original manuscript has incorrectly given the referee the impression that the timescales we report are for a step change in humidity. In a similar way to Bones et al. (2012), the timescales we calculate using Eq. (4) are half-lives for diffusion at constant water activity, i.e. without any step change in relative humidity. We intend these timescales to give information about the rate at which water molecules diffuse within a droplet at a given relative humidity, rather than as a measure of equilibration timescales following a change in environmental conditions. We appreciate that this was not clear given the wording in the article, and have thus changed phrases such as “equilibration timescales” (abstract), “timescales for equilibration” (heading of section 3.2) and “H_2O equilibration” (p29390, l7) to “water diffusion timescales”.

We acknowledge that these diffusion half-lives are perhaps not the most atmospherically relevant measures of timescale and, as the reviewer mentions, a model of the time response of a droplet undergoing water uptake and loss would be much more appropriate. This is the subject of ongoing work, which we intend to publish in future when we report our more recent experiments on water diffusion in secondary organic material.

- The authors provide the value of the diffusion constant of aqueous sucrose in the abstract, but do not state the water activity for this diffusion constant (presumably 0.2?).

Yes, this was 0.2, it has been added to the abstract.

- In the paragraph starting on line 21 on page 29377 Zobrist et al., 2011 should be cited as well as Koop et al. 2011, since experimental evidence of the core-shell structure has been given in this paper already.

This citation has been added.

- In line 8, page 29379: I feel the citation of Bones et al., 2012 is inappropriate since those authors also measured essentially water diffusion and not viscosity.

This citation has been removed.

- Section starting line 26, page 29379: I think the technique used by Zobrist et al., 2011 allows the determination of density as shown in the paper of Lienhard et al., 2012 of the same group. They seemed to have used literature data for the study of Zobrist et al., 2011 simply because literature data were available.

The last sentence of this section has been removed.

- Sentence starting line 3, page 29380: Zhu et al., 2011 deserve a citation at this point, I feel the authors should acknowledge explicitly that they are adapting the Zhu et al. approach right at the beginning of the paragraph and not somewhere hidden later in the paragraph. In the context I also feel that the statement in the summary on line 25 page 29392 (".. we describe a new experimental system: : :") should be changed to something like: "we adapted the technique pioneered by Zhu et al. to an experimental system allowing measuring aqueous solutions of atmospheric relevance at different water activities: : :".

It is important to bear in mind that while Zhu et al.'s experiment was similar there are some major differences which make our technique unique. The key difference between the two techniques is that Zhu et al. bring two aqueous maltose solution droplets together – one containing H_2O and the other D_2O. Diffusion is then observed between the two using Raman microscopy. In contrast we have a single disk and control its composition via the vapour pressure of water, and then supply the D_2O via the gas phase.

In response to the referee we have added at the beginning of the paragraph at line 3, page 29380:

"We have used a similar technique to Zhu et al. (2011) to determine the diffusion coefficient of water in aqueous solutions. Zhu et al. (2011) brought a H_2O-maltose and a D_2O-maltose droplet together until they touched, and used a Raman microscope to quantify diffusion between the droplets. Our approach relies upon the observation of the diffusion of gas phase isotope tracer into a disk of aqueous solution."

and removed the sentence from lines 16 to 18, page 29380.

- Fig. 7 and discussion of this figure: Again, the authors should plot the full range of water activity, i.e. from aw=0 to aw=1. Then it should be noted that Zobrist et al., 2011 estimates that their parameterization at room temperature carries an uncertainty of a factor of three below a water activity of 0.6 and about 30% for aw larger than 0.6. That means that there is agreement within uncertainty with the Zobrist et al. parameterization, but not with the He et al., 2006 parameterization for the driest data point. This discussion needs to be made carefully, since it influences strongly the estimate of the diffusion constant at aw=0. Also note that the parameterization of the authors has a point of inflection at about aw=0.8. Do the authors think that is real? In addition, I feel it would make sense to add the data of Zhu et al., 2011 and the ones of Parker and Ring, 1995 and Tromp et al., 1997 to this figure even though those measured water diffusion in maltose and not sucrose. From a first rough view those seem to strongly support the data of the present paper.

The water activity range in the revised Fig. 7 has been plotted between 0.1 and 1; we have not extrapolated our fit below 0.2 because it is beyond the range of our measurements. Assuming an uncertainty of a factor of three in the Zobrist et al. (2011) parameterisation below a water activity of 0.6, we do not find agreement with our data at the driest data point. (At a water activity of 0.22 and temperature of 296.5 K, the Zobrist et al. parameterisation predicts a water diffusion coefficient of 6.46×10^{-16} m^2/s. The lower limit of the parameterisation at this water activity is therefore 2.15×10^{-16} m^2/s. The upper end of our error bar at this point is 1.36×10^{-16} m^2/s.)

The point of inflection in the parameterisation around a water activity of 0.8 may be due to underestimations of the water diffusion coefficient using our technique when diffusion is fast. This is discussed on page 29389, lines 15 to 23.

The reviewer is correct: the maltose literature data does agree well with our sucrose data. However, maltose and sucrose are different substances and it is therefore not clear to us that they should be compared in this way. Sucrose is a disaccharide of glucose and fructose; maltose is also a disaccharide, but made of two glucose units. They may have the same chemical formula ($C_{12}H_{22}O_{11}$), but their structures differ.

- Section 3.4: The authors show interesting morphology maps for the gel of MgSO4. Do they believe their finding also hold for accumulation mode size particles?

The inhomogeneities that we observed in the magnesium sulfate disk were on the order of tens of microns in size – it is unclear how these features would translate to smaller particles. More work (beyond the scope of the current paper) is required in this area.

References

Bones, D. L., Reid, J. P., Lienhard, D. M., and Krieger, U. K.: Comparing the mechanism of 25 water condensation and evaporation in glassy aerosol, P. Natl. Acad. Sci. USA, 109, 11613–11618, 2012.

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.

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;

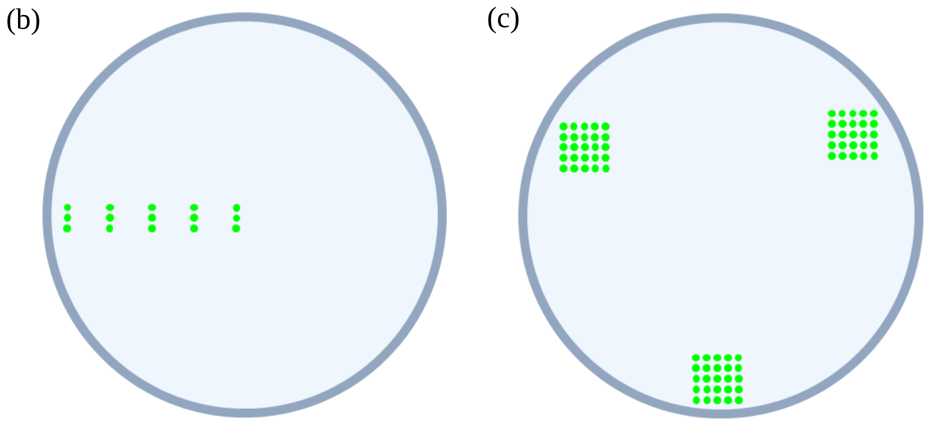
We have modified and expanded the discussion in section 2.3 to cover these points in addition to including another explanatory panel in Fig 2:

"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 D_2O 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 D_2O exposure time required to collect enough information to determine a diffusion coefficient was about 10 minutes for a D_{water} of 10^{-10} m^2s^{-1}, about 2 hours for a D_{water} of 10^{-12} m^2s^{-1}, about 20 hours for a D_{water} of 10^{-14} m^2s^{-1}, and about 8 days for a D_{water} of 10^{-16} m^2s^{-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 D_2O 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 D_2O 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* laser wavelength) / (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.