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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Direct quantification of total and biological ice nuclei in cloud water" *by* M. Joly et al.

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The work described in this paper is based on a simple and powerful idea: a direct way to determine the potential for ice formation in a cloud is to collect cloud water and determine the content of ice-forming nuclei in it. Furthermore, whether those ice nucleating particles (INPs) are of biological origin can be determined via some direct and some indirect tests. The authors' practical approach to this idea was to collect cloud water from a mountain peak when a cloud envelops it. Not surprisingly, it is difïňĄcult to realize the idea in its pure form. Complications arise from a number of directions. The main ones can be put in question form: 1. How complete is the transfer of all potential INPs from the air in the which the cloud forms? 2. How many ice particles have already

formed in the cloud and have fallen out before sampling? 3. Is the exclusion of other modes of ice nucleation, other than immersion freezing, justiïňĄed? 4. Is there any evidence for aging of the sample after collection? In spite of the fact that answers to the questions raised are missing in the paper, or are minimal, it is a valuable contribution. The paper demonstrates that detection of INPs in cloud water is a promising approach to shedding light on long-standing questions.

1) The main shortcoming of the paper is that little information is provided about the clouds that were sampled. Was there precipitation occurring at the same time? Were the clouds forming in the uplift forced by the mountain slope or were they part of extensive cloud layers? How deep were the clouds? What can be said about the age and history of the cloud parcels? Clearly, it would take a project of much greater complexity to gain information on these aspects, the lack of even some broad descriptions and possible sorting of the data according to these variables weaken the results obtained.

We agree that any information concerning cloud's history, IN partitioning and process by which freezing occur is important for data interpretation. In the original paper, in addition of ice nucleation data, we considered in our analysis sampling temperature, liquid water content, pH, ion composition and backtrajectories. For the revised version of the manuscript, we gathered and included the following additional data or information:

- Sampling times and the periods of time during which clouds were present at the sampling site based on continuous measurements of relative humidity. From these, we obtained information such as cloud duration at the sampling site and the time spent in cloud before and after sampling (did we sample the "edge" or the inside of the clouds?).

- The amount of precipitation cumulated downwind the puy de Dôme Station during the sampling period.

- Satellite visible images (Eumetsat) during the sampling period, showing an overview of the meteorological situation over Europe. These are available for academic purposes on the Wokingham Weather's website (http://www.woksat.info/wwp.html).

All these are now presented in Table 1 and supplementary material (Figure S1). Text sections have also been inserted accordingly in “2.1 Materials and Methods – Cloud water sampling and meteorological measurements” (Lines 132-148).

2) At what temperatures were the collections made? It is mentioned that some samples froze onto the plate, but it is not clear if that made any difference.

The information about whether or not samples were collected frozen was already present in the original paper (indicated in italic in Table 1): sampling temperature ranged from -1.5°C to 13.3°C, and 5 of the 12 samples were collected as ice formed by supercooled droplets on the impaction plate (#80- #84). As suggested by the reviewer, we examined whether the fact that samples were collected frozen or liquid impacted ice nucleation data (concentration of total and biological IN and proportion of biological IN at each temperature, and onset temperature of freezing, i.e. the highest temperature at which at least one droplet froze during IN assays). The number of samples analyzed was < 30 and data were not normally distributed, so the non-parametric test of Mann-Whitney was utilized for comparing the two groups (frozen vs liquid). We found the following significant differences (95% confidence):

- the concentration of total IN at -8°C, -9°C and -10°C was significantly higher in samples collected frozen (n = 5) than in liquid samples (n = 7): at -8°C, z = -2.621; p = 0.009; at -9°C, z = -2.298; p = 0.022; at -10°C, z = -2.2; p = 0.028. (Medians: 10.9, 17.6 and 19.9 vs 3.2, 8.5 and 14.4 mL-1, respectively).

- Logically, the concentration of biological IN at -8°C and -9°C was also significantly higher in samples collected frozen (n = 5) than in liquid samples (n = 7): at -8°C: z = -2.621; p = 0.009; at -9°C: z = -2.212; p = 0.027. (Medians: 10.9 and 14.3 vs 3.2 and 8.5 mL-1, respectively).

- The proportion of biological IN at -9°C was lower in samples collected frozen (n = 5) than in liquid samples (n = 7): z = -2.276; p = 0.035. (Medians: 95% vs 100%, respectively).

- The onset temperature of freezing was warmer in samples collected frozen (n = 5) than in liquid samples (n = 7): z = -2.5618; p = 0.028. (Medians: -6 vs -8°C, respectively).

So overall, samples collected frozen had higher IN activity. This information has been added in the manuscript and discussed. (From line 264)

3) How long were the sampling periods?

This information is now included in Table 1.

4) Some information on the sampling intake and the general setup of the apparatus would be helpful.

The reference describing it has been included (Kruisz et al., 1992) (Line 133).

5) The absence of data on cloud liquid water content is handled in the paper by using historical data with three different values assigned according to the collection rate of the sample. One wonders why the sample collections rates were not considered reliable enough to be used as a measure of cloud liquid water content. Changing droplet size distributions and variable collection efïňAçiencies due to different wind conditions clearly weaken the reliability of such an evaluation. To what degree? The authors' reasoning for not using that approach should perhaps be in the paper.

We rephrased the section “2.1 Materials and Methods – Cloud water sampling and meteorological measurements” for trying to make it clearer and add information about the additional parameters taken into account.

6) The presentation of the results of the measurements is not always clear. Do expressions such as “ . . . samples froze at -8âŮęC . . .. “ (3715/6), “. . . none remained supercooled ..” refer to one drop (sample tube) from the sample or some other measure?

We agree that these sentences were confusing, so we rephrased it as for example “In

11 of the 12 cloud samples (92%), the onset temperature of freezing (i.e. temperature at which the first droplet froze) was -8°C or warmer. Only sample #87 started to freeze at colder temperature (-11°C)." (Line 228).

7) Comparisons based on "maximum freezing temperature" and "highest temperature" are subject to large errors and should be viewed as rough indications. More extensive use of the concentration functions and comparisons of concentrations at ïňĄxed temperatures, as in Table 2, would improve the paper. What is the reason for stating -11âŮęC as the lowest observed freezing temperature (3715/7) when Table 2 and the ïňĄgures show data to lower temperatures?

We think that the sentence "Eleven of the 12 cloud samples (92 %) froze at −8°C or warmer, and none remained supercooled at temperatures below −11°C" was confusing. In fact, we meant that in eleven of the samples, freezing occurred at -8°C or warmer in at least one of the droplets testifying of the IN presence. For the last sample, the first freezing event occurred at -11°C. This does not mean that all of the droplets were frozen at this temperature, but it is the lowest temperature at which freezing was initiated in a sample. This sentence was modified (lines 228).

8) How can the data in Fig. 4 extend to -14âŮęC when the last points on Fig. 3 are at -13âŮęC? The impression is that the low number of samples that provided data at -13âŮęC and -14âŮęC lead the authors to some hesitation about the data presentation. It would improve the paper if the results were presented in a more consistent way. In Fig. 4, the substitution of lower bound values for those not detected introduces an upward bias in the data. How would the analysis look if only samples with measured values were included at all temperatures?

Both Fig. 3 and Fig. 4 were constructed using data presented in Table 1. However, in Fig. 3 the values above the detection limit were omitted. On the contrary, in Fig. 4 we included the lowest possible bounds of these values, as indicated in the legend. We fully agree that this can be confusing and decided to consistently show data only

down to -13°C in Figure 4, i.e. when at least 3 absolute values were available. We still included the lowest possible bounds for concentrations above the quantification limit in order to avoid to artificially decreasing the values by ignoring them, but still showing conservative estimates.

9) The data in Table 2 gives the impression that the most heat-labile samples had relatively low total concentrations of IN. Could the authors comment on this? Non-parametric Spearman's rank correlations were calculated between the different variables. The corresponding matrices (p-values, , and n) are shown in Table S2. This impression would mean, if we understand it correctly, that the concentration of total IN at given temperature would be inversely correlated with the proportion of biological (heat-labile) IN.

In reality there is a trend in that direction (see the correlation matrix in Table S2), but no significant relationship between these 2 parameters at any temperature was detected. So we do not think that it is relevant to comment more on this. A sentence stating that "The proportion of biological IN in samples did not depend on the absolute total IN concentration (Table S2; $p > 0.05$)." was inserted in the text (line 252).

10) The higher values of INPs detected in cloud water compared to precipitation (3715/17) is a signiïňĄcant result and, if conïňĄrmed by more data, calls for an intensive search for explanations. Even as an early indication, it is a strong motivation for more work with cloud samples even if they are considerably more difïňĄcult to obtain. It would be good to know whether the correlation stated on 3717/10 would also hold between bacterial concentration and total INP concentration.

We reanalyzed data, and stats have been redone. It appears that a mistake was done in particular here, and the concentration of bacteria is actually not correlated with IN data. This is now indicated in the text (line 319) and shown in Table S2.

11) Minor points (page/line): 3711/8 "all" and "throughout" are redundant. We removed the word "all" in this sentence.

3711/9 “high-temperature IN” is difïňĄcult to replace with better wording, yet is awkward to call sub-zero temperatures ‘high’ We agree but did not find better expression, so we used terms such as “high negative temperature IN” or “high subzero temperature IN” to be more precise.

3713/12 CIN instead of CIN We modified this.

3713/18-19 Fewer signiïňĄcant ïňĄgures would be sufïňĄcient (1.6 rather than 1.59 etc.) We agree and corrected it in the manuscript.

3716/2 As shown in Table 2 “at least 77%” should be “as low as 77%” This sentence was modified.

3722/27 Initials for ïňĄrst author missing. There is no initial for the first author of this reference (Stephanie and Waturangi, 2011).

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 3707, 2014.

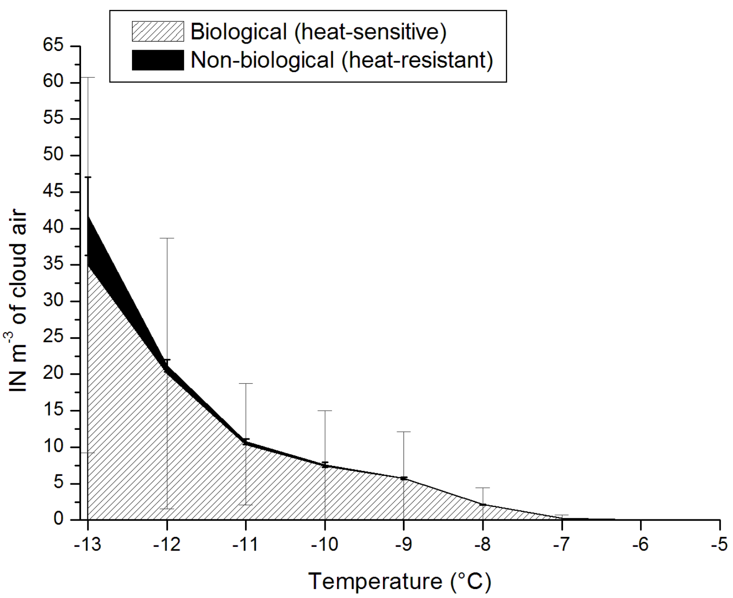


Fig. 1. Fig 4. Mean cumulative concentrations of biological (heat-sensitive. shaded area) and non-biological (heat-resistant, black area) IN in clouds (n=12) per volume of air.

Table 1. Main characteristics of the cloud events sampled. Samples recovered as ice formed upon impaction in the sampler are indicated in italic. See detailed ion composition in Table SM1.

Sample	Date	Sampling period (UTC)		Sampling duration (h)	Volume sampled (mL)	Cloud period (UTC)[a]		Cloud event duration (h)[a]	Time in cloud before sampling (h)[a]	Time in cloud after sampling (h)[a]	Precipitation accumulated in the vicinity (mL)[b]	Mean sampling temperature (°C)	Mean LWC during sampling (g m^{-3})	Bacteria concentration (mL^{-1})
		From	To			From	To							
# 76	29-Jun-11	6:30 AM	11:45 AM	5.25	> 200	6/28/11 10:00 PM	6/30/11 0:00 AM	26	8.5	12.3	1.6	11.5	0.6	n.d.*
# 77	7-Jul-11	1:50 PM	3:00 PM	1.17	15	7/7/11 9:00 AM	7/8/11 6:00 AM	21	4.8	15	7	12.0	0.1	n.d.*
# 78	20-Jul-11	7:30 AM	9:10 AM	1.67	47	7/19/11 3:00 PM	7/23/11 4:00 PM	97	16.5	78.8	0.2	8.3	0.3[c]	12355
# 79	7-Nov-11	1:00 PM	2:30 PM	1.50	193	11/6/11 8:00 AM	11/8/11 11:00 AM	51	29	20.5	0.4	7.0	0.6[c]	10825
# 80	*20-Jan-12*	*12:45 PM*	*3:00 PM*	*2.25*	*55*	*01/18/12 11:00 PM*	*01/26/12 0:00 AM*	*169*	*37.7*	*129*	*0*	*-0.4*	*0.3*[c]	*9980*
# 81	*23-Jan-12*	*1:00 PM*	*4:00 PM*	*3.00*	*53*	*01/18/12 11:00 PM*	*01/26/12 0:00 AM*	*169*	*110*	*56*	*0*	*-1.2*	*0.1*[c]	*33724*
# 82	*19-Mar-12*	*12:10 PM*	*4:10 PM*	*4.00*	*45*	*3/17/12 11:00 PM*	*3/21/12 11:00 AM*	*84*	*37.2*	*42.8*	*0.2*	*-1.5*	*0.1*[c]	*1648*
# 83	*4-Apr-12*	*6:10 AM*	*9:20 AM*	*3.17*	*29*	*4/3/12 11:00 PM*	*4/6/12 12:00 PM*	*61*	*7.2*	*50.7*	*0.25*	*-0.4*	*0.1*[c]	*14914*
# 84	*18-Apr-12*	*8:10 AM*	*12:15 PM*	*4.08*	*31*	*4/17/12 6:00 PM*	*4/25/12 6:00 AM*	*180*	*14.2*	*161.8*	*0*	*0.2*	*0.1*[c]	*3902*
# 85	25-Jun-12	1:35 PM	5:00 PM	3.42	66	6/25/12 01:00 AM	6/26/12 12:00 AM	35	12.6	19	0	13.3	0.3[c]	4474
# 86	13-Sep-12	7:50 AM	9:50 AM	2.00	75	9/12/12 7:00 PM	9/13/12 3:00 PM	20	12.8	5.2	0.8	6.0	0.6[c]	5199
# 87	10-Oct-12	8:40 AM	9:50 AM	1.17	70	10/08/12 9:00 PM	10/11/12 0:00 AM	63	35.7	26.2	0	9.4	0.6[c]	19658

a: Defined as RH > 95% based on hourly average (see Fig. S1).
b: Sum of precipitation accumulated at 5 rain gauge stations in the vicinity of puy de Dôme (Royat, Farnette, Sayat, Trois Ponts and Blanzat) (see Fig. S1).
c: Estimation from sample collection rate and puy-de-Dôme data archive.

* n.d.: not determined.

Fig. 2. Table 1. Main characteristics of the cloud events sampled. Samples recovered as ice formed upon impaction in the sampler are indicated in italic. See detailed ion composition in Table SM1.

Table 2. Total IN concentration and proportion of heat-sensitive IN in the cloud water samples between -5°C and -14°C. Values below the detection limit are presented as '0' for visual clarity, and '>' indicates values higher than our quantification limit.

Sample	n =*	Onset freezing temperature (°C)	Onset freezing temperature after heat treatment (°C)	Decrease of onset freezing temperature by heat treatment (°C)	IN mL^{-1} [total *(% heat sensitive)*]									
					Temperature (°C)									
					-5°C	-6°C	-7°C	-8°C	-9°C	-10°C	-11°C	-12°C	-13°C	-14°C
# 76	32	-8	-12	4	0 (- %)	0 (- %)	0 (- %)	4.9 (100%)	18.7 (100%)	31.6 (100%)	45.0 (100%)	118.4 (99%)	n.d.	n.d.
# 77	32	-8	<-12	>4	0 (- %)	0 (- %)	0 (- %)	4.9 (100%)	12.3 (100%)	14.4 (100%)	92.8 (100%)	138.6 (100%)	n.d.	n.d.
# 78	32	-8	-11	3	0 (- %)	0 (- %)	0 (- %)	1.6 (100%)	8.5 (100%)	16.5 (100%)	26.1 (94%)	69.3 (88%)	n.d.	n.d.
# 79	32	-8	<-12	>4	0 (- %)	0 (- %)	0 (- %)	3.2 (100%)	8.5 (100%)	12.3 (100%)	16.5 (100%)	16.5 (100%)	n.d.	n.d.
# 80	32	-8	-11	3	0 (- %)	0 (- %)	0 (- %)	4.2 (100%)	12.3 (100%)	16.5 (100%)	18.7 (92%)	53.4 (91%)	n.d.	n.d.
# 81	32	-7	-8	1	0 (- %)	0 (- %)	8.5 (100%)	63.4 (97%)	>173.3 (<99 %)	>173.3 (<97%)	>173.3 (<95%)	>173.3 (<92 %)	n.d.	n.d.
# 82	32	-6	-9	3	0 (- %)	1.6 (100%)	6.7 (100%)	10.4 (100%)	18.7 (74%)	21.1 (66%)	28.8 (70%)	53.4 (77%)	n.d.	n.d.
# 83	160	-6	-10	4	0 (- %)	0.6 (100%)	7.4 (100%)	73.2 (100%)	184.4 (100%)	219.1 (99%)	>253.8 (<97%)	>253.8 (<93%)	n.d.	n.d.
# 84	64	-6	-9	3	0 (- %)	1.6 (100%)	2.4 (100%)	11.4 (100%)	16.5 (90%)	18.7 (92%)	30.2 (95%)	41.3 (88%)	110.6 (66%)	>207.9 (<55%)
# 85	160	-8	-12	4	0 (- %)	0 (- %)	0 (- %)	2.2 (100%)	3.2 (100%)	5.3 (100%)	34.7 (100%)	138.6 (99%)	>253.8 (<91%)	>253.8 (<45%)
# 86	32	-7	-10	3	0 (- %)	0 (- %)	1.6 (100%)	3.2 (100%)	8.5 (100%)	14.4 (89%)	14.4 (89%)	18.7 (83%)	49.0 (93%)	>173.3 (<56 %)
# 87	32	-11	-13	2	0 (- %)	0 (- %)	0 (- %)	0 (- %)	0 (- %)	0 (- %)	3.2 (100%)	28.8 (100%)	83.7 (72%)	>173.3 (<46 %)
Median		-8	-10,5	3	0 (- %)	0 (- %)	0 (- %)	4.9 (100%)	>12.3 (100%)	>16.5 (100%)	>29.5 (<96 %)	>61.4 (<92%)	>97.2 (<82%)	>190.6 (<51%)
Min		-11	-13	1	0 (- %)	0 (- %)	0 (- %)	0 (- %)	0 (- %)	0 (- %)	3.2 (70%)	16.5 (91%)	49.0 (66%)	>173.3 (<45%)
Max		-6	-8	>4	0 (- %)	1.6 (100%)	8.5 (100%)	73.2 (100%)	184.4 (100%)	219.1 (100%)	>253.8 (100%)	>253.8 (100%)	>253.8 (93%)	>253.8 (<56%)

*Number of 20 µL droplets assayed by immersion freezing assays

n.d.: not determined.

Fig. 3. Table 2. Total IN concentration and proportion of heat-sensitive IN in the cloud water samples between -5°C and -14°C. Values below the detection limit are presented as '0' for visual clarity [...]

Figure S1: A- Maps locating (**left**) the sampling site (puy-de-Dôme Mountain, 45° 46' 20'' North, 2° 57' 57'' East) (Source: Google Earth) and (**right**) the rain gauge sites around puy-de-Dôme.
B- Table recapitulating meteorological data (relative humidity, LWC, downwind precipitation), backtrajectories and satellite visible images of each cloud event sampled. 72-hours backtrajectory plots were made using HYSPLIT model on GDAS1 meteorological data archive and default settings (Draxler and Rolph, 2010). Eumetsat satellite visible images were obtained from http://www.woksat.info/wwp.html.

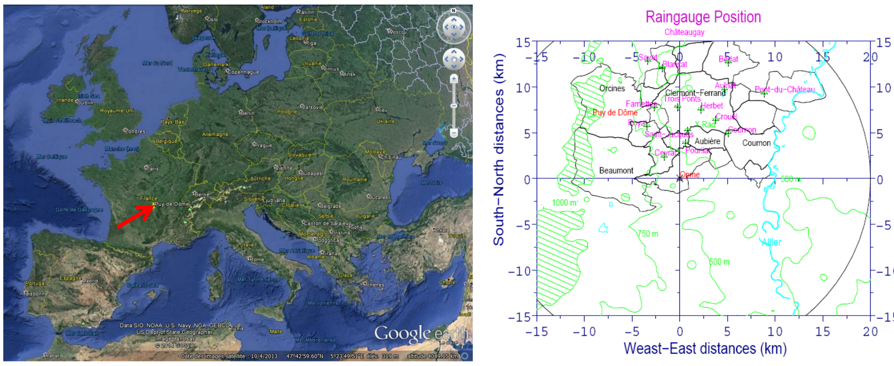
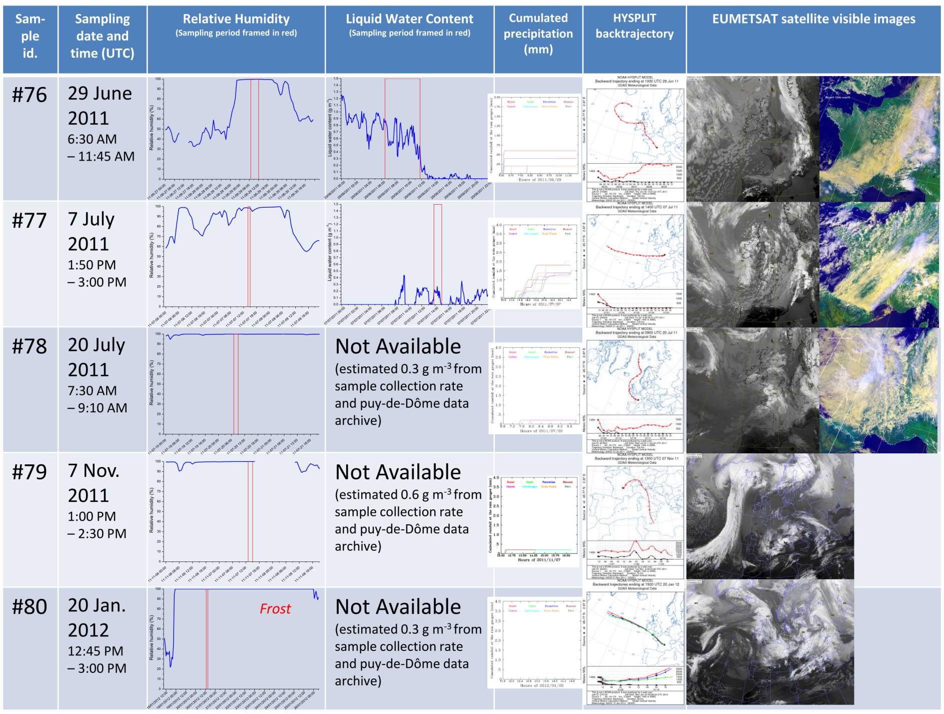


Fig. 4. Fig S1. A- Maps locating (left) the sampling site (puy-de-Dôme Mountain, 45°Âă46'Âă20" North, 2°Âă57'Âă57" East) (Source: Google Earth) and (right) the rain gauge sites around puy-de-Dôme.



Sam-ple id.	Sampling date and time (UTC)	Relative Humidity (Sampling period framed in red)	Liquid Water Content (Sampling period framed in red)	Cumulated precipitation (mm)	HYSPLIT backtrajectory	EUMETSAT satellite visible images
#76	29 June 2011 6:30 AM – 11:45 AM					
#77	7 July 2011 1:50 PM – 3:00 PM					
#78	20 July 2011 7:30 AM – 9:10 AM		Not Available (estimated 0.3 g m^{-3} from sample collection rate and puy-de-Dôme data archive)			
#79	7 Nov. 2011 1:00 PM – 2:30 PM		Not Available (estimated 0.6 g m^{-3} from sample collection rate and puy-de-Dôme data archive)			
#80	20 Jan. 2012 12:45 PM – 3:00 PM	Frost	Not Available (estimated 0.3 g m^{-3} from sample collection rate and puy-de-Dôme data archive)			

Fig. 5. Fig S1. B- Table recapitulating meteorological data (relative humidity, LWC, downwind precipitation), backtrajectories and satellite visible images of each cloud event sampled [...]

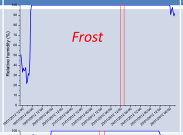
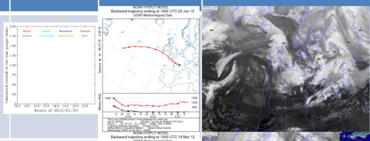
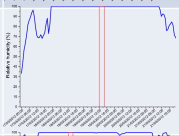
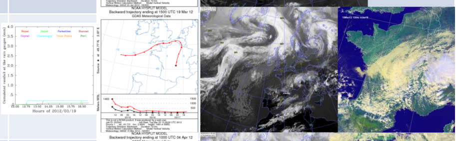
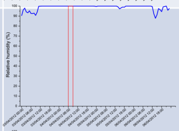
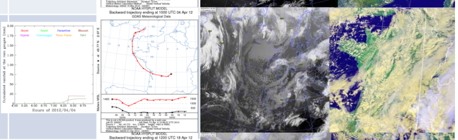
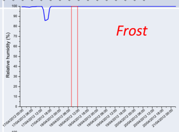
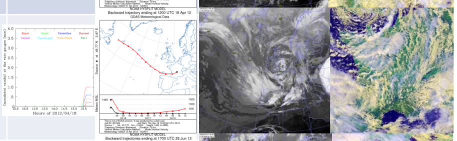
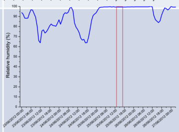
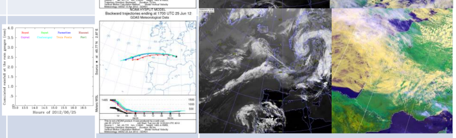
Sam-ple id.	Sampling date and time (UTC)	Relative Humidity (Sampling period framed in red)	Liquid Water Content (Sampling period framed in red)	Cumulated precipitation (mm)	HYSPLIT backtrajectory	EUMETSAT satellite visible images
#81	23 Jan. 2012 1:00 PM – 4:00 PM		Not Available (estimated 0.1 g m^{-3} from sample collection rate and puy-de-Dôme data archive)			
#82	19 Mar. 2012 12:10 PM – 4:10 PM		Not Available (estimated 0.1 g m^{-3} from sample collection rate and puy-de-Dôme data archive)			
#83	4 Apr. 2012 6:10 AM – 9:20 AM		Not Available (estimated 0.1 g m^{-3} from sample collection rate and puy-de-Dôme data archive)			
#84	18 Apr. 2012 8:10 AM – 12:15 PM		Not Available (estimated 0.1 g m^{-3} from sample collection rate and puy-de-Dôme data archive)			
#85	25 June 2012 1:35 PM – 5:00 PM		Not Available (estimated 0.3 g m^{-3} from sample collection rate and puy-de-Dôme data archive)			

Fig. 6. Fig S1.

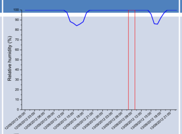
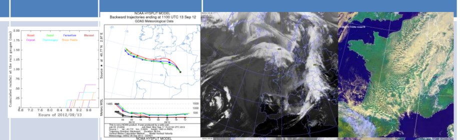
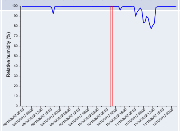
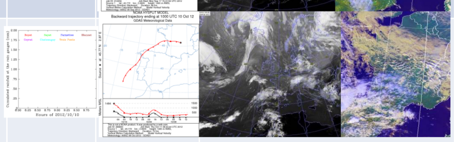
Sam-ple id.	Sampling date and time (UTC)	Relative Humidity (Sampling period framed in red)	Liquid Water Content (Sampling period framed in red)	Cumulated precipitation (mm)	HYSPLIT backtrajectory	EUMETSAT satellite visible images
#86	13 Sep. 2012 7:50 AM – 9:50 AM		Not Available (estimated 0.1 g m^{-3} from sample collection rate and puy-de-Dôme data archive)			
#87	10 Oct. 2012 8:40 AM – 9:50 AM		Not Available (estimated 0.1 g m^{-3} from sample collection rate and puy-de-Dôme data archive)			

Fig. 7. Fig S1.