

## Response to Referee 2

First of all, we would like to thank the reviewer for careful reading the manuscript and for numerous useful suggestions. In revised manuscript, we changed the structure, adding more information about fluorescence in Introduction. We also strongly revised the chapter, containing analysis of particle fluorescence in the cloud.

Below we provide detailed response to the reviewer comments

*General: The paper contains new and very interesting observations obtained with a new approach of a fluorescence lidar for aerosol characterization. This lidar feasibility study is clearly worthwhile to be published in AMT. Nevertheless, the interpretation of the observations needs to be improved. A clear and more systematic separation of the different fluorescence contributions would be helpful to better follow the discussion. The argumentation is partly weak and a bit speculative. Minor revisions are requested.*

*The abstract has to be updated and adjusted: after all the suggested improvements.*

Abstract is revised and shortened

*P2, L39: Burton et al. 2012. Only one reference here? What about own papers: Veselovskii et al., 2015, 2020, what about Tesche 2011, Tellus, SAMUM 2, what about all the efforts within the ACTRIS EARLINET group on aerosol typing during the last five years.*

In revised manuscript we added:

“e.g. Tesche et al., 2011; Burton et al., 2012, Luís Guerrero-Rascado et al., 2018; Veselovskii et al., 2020 and references therein”

Definitely, there are a lot of important papers, showing potential of lidar technique for aerosol studies. We just can't mention them all, because we focus on the fluorescence measurements.

*P2, L44-47: I have my doubts that aerosol particles can be clearly identified and quantified in cloud layers. Ok, you can detect them, but it is already well known that interstitial aerosol particles are always present in clouds. It is impossible to have aerosol particle free clouds.*

*P3, L76-84: These are confusing statement. I am puzzled by the wording ..'external' vs 'internal' mixing of aerosol particles within liquid water droplets. There is only ONE scenario: It is impossible to have droplets without a CCN, and it is also impossible to have clouds without interstitial aerosol particles (non-activated particles). So, there is only this ONE scenario: a mixture of interstitial aerosol particles (not acting as CCN) and droplets, each of the droplets nucleated on a CCN. The CCNs may be completely dissolved in the droplet, or survived as a solid particle within the droplet, as is the case for dust or soot CCN.*

*The interstitial aerosol particles (in the cloud) may be much larger than the particles outside the cloud (because of strong water uptake at 100% rel. humidity), so the aerosol backscatter efficiency of particles within the cloud may be larger by a factor of 5 and even more, compared to the aerosol backscatter outside the cloud layer.*

*I recommend to avoid to introduce : internal and external mixtures! There is only this ONE scenario: interstitial aerosol particles and cloud droplets. Now we need a clear differentiation: What is the contribution of dry particles to fluorescence? What is the contribution of fully deliquescent (dissolved, solution) aerosol particles? Sulfate*

*particles are fully dissolved at high humidities? Can we be sure that the fluorescence signal in clouds is exclusively from interstitial aerosol particles? No contribution by cloud droplets? That needs to be carefully discussed.*

This is important comment and we agree with reviewer. In revised manuscript we don't use "internal or external mixture". Numerous modifications are introduced in the text. In particular, in Introduction we added paragraph:

"Interpretation of fluorescent measurements in a cloud is even more challenging. The liquid cloud is a mixture of interstitial aerosol particles (non-activated particles) and droplets, formed on the cloud condensation nucleus (CCNs). The CCNs may be completely dissolved in the droplet, or survived as a solid particle within the droplet, as is the case for dust or soot. The relative contributions of interstitial aerosol and activated CCNs in the droplets to the total cloud fluorescence backscatter are unknown, and the need to estimate these contributions was one of the motivations of this study"

In revised manuscript we strongly modified the section, describing fluorescence measurements in the clouds and Conclusion as well. The discussions that looked too speculative are removed.

*Dust particles with liquid shell produce an enhanced fluorescence signal (lens effect)! Is that checked? Is there a reference for that?*

To our knowledge, nobody discussed lens effect in respect to fluorescence. But physically, it may take place.

*P5, L157: Please keep in mind that RH increases from dry conditions (e.g., RH of 40%) to moist conditions (e.g., 80%, 90%, 95%) already a few hundred meters below cloud base, and then to 100% above cloud base. The aerosol particles grow by water uptake, change their backscatter efficiency and the fluorescence capability, some get liquid, some remain dry.*

Yes, influence of RH on fluorescence is an important question. RH strongly influences elastic scattering, but fluorescence is altered much less. We added paragraph in Introduction:

"One of the factors that intricate obtaining the quantitative information about aerosol properties from fluorescence measurements, is influence of the relative humidity (RH). The aerosol particles grow by water uptake, changing their elastic scatter cross-section, but the change in water percentage within an aerosol particle, normally does not alter the chemical components, so total amount of fluorescent molecules within a particle does not change. However the illumination intensity distribution within a particle, as well as the emission angle distribution will be altered by the change of particle size, shape and refractive index, and this modification may affect the fluorescence measurement. The phase functions of the microspheres for the incoherent scattering (fluorescence is an example of incoherent scattering), were computed in works of Kerker and Druger (1979) and Veselovskii et al. (2002a). Results demonstrate, that fluorescence of particles dissolved in water microspheres can be increased in the backward direction by factor ~2, comparing to fluorescence of a bulk material (calculated per gram of solid matter). This enhancement, however, occurs for relatively big microspheres with size parameter  $x = \frac{2\pi r}{\lambda}$  exceeding approximately 10 (Veselovskii et al., 2002a). For the

wavelength  $\lambda=532$  nm corresponding radius  $r$  is about  $1.0 \mu\text{m}$ , so fluorescence of the fine mode particles should be affected less by the hygroscopic growth. We should mention also that for insoluble particles, the presence of the water shell, at the condition of high RH, in principle, can lead to an additional increase of the fluorescence, due to the water droplet lens effect. Similar effect is well known for the soot particles covered by non-absorbing shell (Schnaiter, 2005)."

*Then in the cloud, cloud droplets come into play, backscatter efficiency of interstitial aerosol particles (at 100% humidity) may be much larger than for the aerosol particles below the cloud, or before the cloud formed. All this needs to be considered: in the cloud observations of backscatter and fluorescence signals.*

As we mentioned, fluorescence is less altered by droplets formation than elastic scattering. Estimated (from numerical modeling) increase of fluorescence backscattering should be about factor 2. Fig. 8a demonstrates that fluorescence of aerosol in the cloud increases about twice, when elastic backscattering is increased above 3 orders.

*Is all this known well enough to quantify the aerosol-related (non-droplet) fluorescence signal in clouds? To my opinion this is not the case. We do not know much about this. So, I have my doubts about Eq.(7).*

Definitely, there are a lot of questions, when we try characterize aerosol inside the cloud from fluorescence. Still we think, that for the aerosol outside of the cloud such estimations can be done, at least at the condition of low RH. Corresponding comment is added to the manuscript.

*P6, L176, the particle fluorescence capacity is introduced. I would recommend to do that in form of an equation.*

Done

*Now, the fluorescence signal will change with increasing humidity and water uptake and this in a different way as the total backscatter signal.*

*Again, I think the knowledge about water uptake and the link to fluorescence signal changes is just qualitative. So there is no clear knowledge about the increase of the capacity  $G$  with water uptake:*

We agree, that altering the fluorescence by water uptake is not completely understood and results, at least for the clouds, are qualitative. Corresponding comments are added to the text..

*P6, L176,  $\beta_L^a$  is introduced in Eq. (1) but not  $\beta_L$  or  $\beta^a$ .*

Yes, but on page 7 we write “Here and below, for simplicity, we will use notation  $\beta^a \equiv \beta$ .” So we think here is no misunderstanding.

*P6, L176: The capacity  $G_F$  expresses what? The fluorescence signal changes probably when aerosol particle get a wet coating, the backscatter signal changes by water uptake, so there is no clear reference (denominator), and thus, what does  $G_F$  indicate?*

For the fine mode particles water uptake should not alter significantly fluorescence backscattering. For example, on 29-30 November variation of RH from 70% to 20% is accompanied by decrease of elastic scattering by factor 40 while fluorescence backscattering is decreased less than twice. So drop of fluorescence capacity is directly related with water uptake and this is important parameter when we compare different aerosols at low RH. Besides, at low RH the fluorescence capacity is used to compare fluorescent properties of different aerosol types.

*P6, L185 and L187: Again, because of the not well-known impact of water uptake, I do not believe that you can quantify  $N$  and  $V$  at conditions with rising humidity just below cloud base or even within the cloud? : So that you can not estimate fluorescence cross sections accurately*

*enough. If you want to present it please clearly state that there are many questions how trustworthy this estimation is.*

In the revised manuscript we describe the challenges of interpretation the fluorescence measurements. Estimations of the fluorescence cross section are presented only for low RH, when water uptake does not alter the results.

*3. Observations: : .:*

*A general comment: Trajectory analysis would be helpful for all cases discussed. There is no need to show them all, but it would improve the discussion .... to know more about the origin of air masses, and the kind of aerosol mixtures*

Trajectory analysis is added.

*And it would also be helpful to have something like a bullet point list or an overview table, what aerosol produces fluorescence, what does not cause fluorescence, the same for droplets or water in aerosol particles, what is producing fluorescence, and what does not. And please provide references that support these statements*

*I ask for such a table because I learned more and more about fluorescence in detail :from page to page of the manuscript, without having a complete picture right in the beginning of the discussion. Such an overview would facilitate all discussions and complex interpretation of the shown observations.*

In revised manuscript we moved the information about fluorescence measurements to the Introduction, which should facilitate the process of manuscript reading. We wouldn't like to provide the table, because the information about fluorescence of different atmospheric aerosols in ambient conditions is quite rare. For the same reason it is not easy to support our conclusions with references: there are quite few publications on fluorescence lidars, providing quantitative results.

*P7, L205-206: Do you mean external mixing of dust and biological /organic particles, or do you mean internal mixing, this would mean coating or partly coating of dust particles with organic material.*

It can be both. Unfortunately, at this stage we can not separate these two possible scenarios.

*P7, L215: Pure water is not fluorescing, but what about the aqueous solution of dissolved aerosol particles (before becoming a droplet when acting as CCN). Again, what about the change in fluorescence efficiency with increasing water uptake and finally even change of phase (from dry and solid to totally liquid-acid aerosol particle)?*

Dissolved aerosol particles should provide the fluorescence. From our expectations, fluorescence efficiency in dissolved state should be increased by approximately factor 2. However, in some measurements, when cloud was formed at the top of aerosol layer, this enhancement was up to factor 5. At a moment we can not identify the mechanisms, responsible for such strong enhancement.

*P8, in general and to mention again: would be nice to have HYSPLIT backward trajectories to learn more about aerosol mixtures observed and what kind of aerosol are candidates for causing significant fluorescence.*

HYSPLIT analysis is added

*P9, L266-280: Again the discussion part with N and V, I am not convinced that this is a fruitful part. Yes, there are numbers, but can we trust them?*

We think, that such estimations can be used, at least for low RH. We compared results of such estimations with regularization inversion and agreement is reasonably good.

*Discussion paper*

### *3.2. Fluorescence of aerosol particles within clouds*

*This section is very interesting but, at the same time, a bit confusing. A more systematic way of presentation would be useful: What causes fluorescence, what not, what is the impact of water uptake, what happens with fluorescence when droplets are formed, with 'liquid' CCN and with solid CCN, etc. So, a bullet point list or a Table would be nice. We added a section in Introduction, trying to explain these issues.*

The section is strongly modified and some of unsupported statements are removed.

*P10, L290-299: Again, this separation of externally and internally mixed cloud: As mentioned above, there is only ONE scenario: In all clouds, there is just a mixture of interstitial aerosol particles (not acting as CCN) and cloud droplets nucleated on the available CCNs. Furthermore: In the cloud we have 100% relative humidity, so the interstitial aerosol particles are not dry, and most of them are just solution droplets (before activation to become cloud droplets). And the water droplets, on the other hand side, are formed on part of the solution droplets (CCN) but now consist almost entirely of water. So please rephrase, and avoid external and internal mixing*

We agree with reviewer. "Internal or external mixing" is not used in the revised manuscript.

*P10, L311: What do you mean here? Fluorescent aerosol particles are inside the water particles. Ok, but must they be solid? If they are dissolved in the aqueous solutions, will there still be a fluorescence signal? May be droplets and CCN in the droplet do not produce any fluorescence signal, and fluorescence is only caused by the interstitial aerosol particles, and the increase in the fluorescence signal arises from water uptake effects?*

We think that dissolved CCN provides the fluorescence signal. As mentioned, in dissolved state the signal should be about factor 2 stronger than in solid. Still this signal is probably rather weak. In particular, Fig.8b demonstrates, that fluorescence of the cloud at 2500 m is low, when the aerosol below the cloud base is not detectable. This is in contrast with results in Fig.8a, where strong fluorescence is probably provided by interstitial aerosol

*So, what shows Fig4? in contrast to Fig5? If there is a difference, what is the reason?*

In Fig.4 oscillations of elastic backscattering don't lead to synchronous oscillations of fluorescence, while in Fig.5 they do. We have no ultimate explanation for such difference, but looks like in Fig.5 the vapor is condensed in the aerosol layer, while in Fig.4 the weak water cloud layers are just mixed with aerosol.

*P11, L322: Please, do not switch from one wavelength to another. That makes comparisons confusing. If  $\beta_{1064}$  is  $0.07 \text{ Mm}^{-1} \text{ sr}^{-1}$ , then the  $532 \text{ nm}$  backscatter coefficients below the cloud is probably about  $0.15$  to  $0.2 \text{ Mm}^{-1} \text{ sr}^{-1}$ . That should be mentioned. And then we have an increase by a factor of roughly 3000 when you measure cloud a cloud  $\beta_{532}$  value of  $500 \text{ Mm}^{-1} \text{ sr}^{-1}$ , and the fluorescence signal increases just by a factor of 5. that is a good proof that water does not produce a fluorescence*

*contribution. Please state that, if my comment is true, and if there is definitely no cross talk: : :*

In revised manuscript we provide backscattering at 532 nm prior and after cloud formation. We believe that there is no cross talk, because we had observations (e.g. Fig.8b) with strong cloud backscattering, which were not accompanied by increase of fluorescence.

*P11, L327-328: Again almost the same increase in beta 532 when we start from about 0.04 Mm-1 sr-1 for 532nm (estimated from 1064 nm information) and end up at 130 Mm-1 sr-1. All this should be given in more clearly way : : : by using ONE wavelength.*

Done

*But can we trust an increase by factor 5 of the aerosol-related fluorescence backscatter when the elastic backscatter increase by a factor of 3000? Can we be sure that there is no cross talk, not stray light somewhere, nothing?*

We believe that there is no cross talk, because we had observations (e.g. Fig.8b) with strong cloud backscattering, which were not accompanied by increase of fluorescence.

*What causes the increase: : :? The lens effect? Is there another explanation?*

At a moment we can not identify the mechanism

*P11, L342 For insoluble particles increase of fluorescence by lens effects. Yes that can be, but it remains speculations, most of urban aerosol is sulfate aerosol (and not BC-containing haze) and sulfate particles dissolve completely and then there is no lens effect*

Yes, we can not prove it and we just mention such possibility. To our knowledge nobody considered lens effect in respect to fluorescence. But physically this is possible, for example for soot or dust particles covered by water shell. And definitely no lens effect for dissolved aerosol.

*P12, L358-362: This is again a non-acceptable speculation. The two cloud layers may have formed in two different air masses with different aerosol types, and the different aerosol types caused different levels of fluorescence.*

Yes, we agree that two cloud layers can be different. We just wanted to emphasize, that in some cases aerosol fluorescence in the cloud is very low (Fig.8b), while in others fluorescence is strong (Fig.8a), meaning significant content of aerosol in the cloud.

*Figure 2, would be nice to have backward trajectories: : : and thus origin of air masses for the two cases.*

We added information about back trajectories in the text.

*Figure 3, again: what is the origin of the aerosol (according to HYSPLIT trajectories)?*

HYSPLIT analysis is added

*Figure 4, strong increase of cloud beta532 but not of fluorescence beta, what can we conclude? Strong increase of beta532 by droplet backscatter, and at least significant increase of the fluorescence signal because of water uptake of interstitial particles*

We think that cloud layers, characterized by small content of aerosol (and so by low fluorescence), are mixed with aerosol particles. High RH in these layers doesn't alter significantly the fluorescence efficiency of aerosol, so oscillations of elastic backscattering is not accompanied by synchronous oscillation of fluorescence.

*And again, HYSPLIT trajectories would be nice to all the cases discussed. The trajectories must not be shown in detail, but information about origin and mixture of aerosol particles would be helpful.*

We added HYSPLIT analysis in the text for cases with clouds and elevated aerosol layers.

*Final remark:*

*This is a good paper and needs only some minor clarifying information and a clear definition of the cloud environment (with interstitial non-CCN aerosol particles and CCNbased cloud droplets). Afterwards (in the comparison: :before vs within the cloud ) a clear definition and systematic separation of the contributions by dry aerosol particles, wet aerosol particles, dissolved aerosol particles, cloud droplets nucleated on sulfate aerosol, and cloud droplets formed on soot and dust particles to fluorescence and to backscatter would be good and would make the discussion easier.*

We tried to follow these suggestions in the revised manuscript.