Reply to the comments of anonymous reviewer #2 on manuscript entitled "Variability of depolarization of aerosol particles in Beijing mega city: implication in interaction between anthropogenic pollutants and mineral dust particles"

The authors appreciate very much for reviewing our manuscript and your insight comments. As suggested, we carefully revised the manuscript thoroughly according to the valuable advices. We will response to all the comments as follows:

The authors present a study of aerosol particles in Beijing, China, with a polarization optical particle counter (POPC). They present 8 months of statistics and 3 case studies of polluted conditions, dust conditions and a dust-pollution mixture. Especially the results presented in Fig. 7 are of interest, because they give insight in the mixing process of dust and pollution and help in the discussion about external and internal mixture. While reading the manuscript, I was missing the main new points. In the revision process, I would strongly recommend to strengthen the impact of the study: the separation of dust and pollution with a POPC and the discussion about internal or external mixture. Then, this can be applied to the statistics collected over an East Asian megacity, which lies in a global hot spot of dust and pollution mixtures.

The main point, why I have to reject the paper is that the retrieved depolarization values are questionable. I further checked the publication by Kobayashi et al., AE 2014, and I could not find any information on the calibration process of the depolarization ratio measured with the POPC. Especially the depolarization ratio can be influenced by multiple factors. I am sure, that the authors developed a calibration process to check the trustworthiness of the measured data, but it is missing in the publication. Also there are no comparisons of the retrieved depolarization ratios at 120◦ scattering angle to existing measurements or simulations of spherical or non-spherical particles. The uncertainties of the depolarization ratio values are not given. These points are essential to present trustworthy results. And as the depolarization ratio is one of the main quantities measured in this study, I have to insist on a proper calibration. Therefore, I recommend resubmitting the paper after clarifying the uncertainties of the depolarization ratio.

Reply: We greatly appreciate the reviewer for insight comments on the manuscript. To respond to the reviewer's major concerns, we made thoroughly revisions and corrections according to all the insight comments of the reviewers. Besides, more crucial information and analysis will be added in the revised manuscript, as follows:

(1) A detailed description and specification of calibration system of POPC and calibration results in this study will be added in the revised manuscript.

(2) Comparison between observation and the simulation result with T-matrix method on randomly-oriented Voronoi aggregation and elongated ellipsoid particles will be added.

(3) A comparison result of measurement of size-resolved number concentration of particles between POPC and KC52 optical particle counter will be added in the revised manuscript.

(4) Comparison of observation results between POPC measurement and LIDAR observation during several dust events in Beijing will be discussed. The cross validation on the dust events provide more

direct evidence of variation in the depolarization properties of dust particles.

Besides, to make the conclusions more pertinent to this study, we revised the expression and concise the discussion about specific chemical composition and reaction. Our conclusions were useful for understanding the long-term depolarization property of aerosols in East Asia, interaction between anthropogenic pollutions and mineral dust in East Asia and their impacts on local air quality, and the sensitive relation between particle morphology and meteorological parameter. This long-term study in Beijing motivate revisit on decades of Lidar data in dust-pollution interactions, and it indicates the necessity of a reliable optical model of internally mixed polluted dust for a detailed analysis of polarization remote sensing observations.

As fas as we known, this was the first study that long-term observation on the single particle polarization properties performed in China, the aim of this study is to investigate the long-term morphology properties of particles in North China because this region has long experienced serious air pollution and dust events due to its special geographical location and industrial activities. As suggested, in the revised manuscript, we will strengthen discussion about the separation of dust and pollution and their internal or external mixture. Comprehensive study with previous studies using the polarization optical particle counter will be performed, for instance the Lidar measurement. Single particle depolarization ratio measure is able to quantitatively investigate the evolution of the mixing of dust particles during their transport. According to the depolarization ratio of their scattering signals, every mineral dust aerosols and anthropogenic pollutants can be distinguished because the direction of polarization of scattering light was identical with the incident light for spherical particle; for the non-spherical particles, a vertical polarization signal will be produced (Pan et al., 2015). Based on this characteristic, a number of studies in East Asia have been conducted that focued on the depolarization ratio of single particles. Sugimoto et al. (2015) found that backscattering depolarization ratio in polluted dust was smaller compared to pure Asia dust for the measurement at Seoul. Pan et al. (2017) reported coating processes such as heteorogeneous reaction and hygroscopic growth on the surface of dust particles play a vital role in decreasing of depolarization ratio (DR) of particles in coarse mode. There were also lots of direct evidences of internally mixed dust particle on the basis of electronic microscopy (Li and Shao, 2009; Li et al., 2011). Note that, these studies were just a case study, and long-term measurement of their mixing states and seasonal varibility in China was still lacking. Therefore we performed an eight-month observe experiment in urban Beijing. At the present stage of this manuscript, the description about instrument calibration and uncertainty assessment was not shown, we will add relavent important information and make an detailed explanation in the revised manuscript.

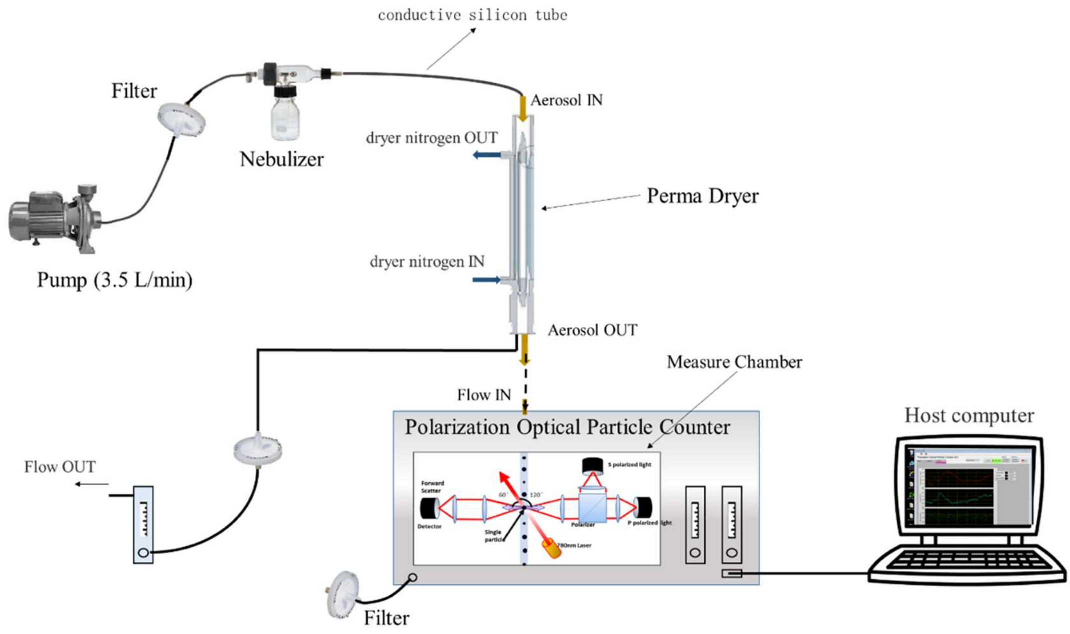

Figure 1. A schematic diagram of the laboratory calibration process

Figure 1 shows the schematic diagram of the laboratory calibration process of POPC. The spherical polystyrene standard aerosols were Dp = 0.5, 1, 3, 5, 7, 10 µm (JSR Life Sciences Corporation). Aerosols were generated by a nebulizer at an flow rate of 3.5 L/min, desiccated by passing through a vrtically placed 45 cm Perma casing tube (MD–110–24P, GLSciences). Depolarization ratio of typical spherical particles at Dp = 5 µm, 7 µm and 10 µm were found to be 0.075, 0.085 and 0.102 with an pervasive uncertainty of ± 0.01,and was almost zero for the fine particles (Dp = 0.5 µm, 1 µm) (Figure 2). In this study, the DR values of aerosols in coarse mode were found to be centered on 0.3 respectively, much larger than calibration results, indicate that coarse mode aerosol particles at the site was non-spherical generally.

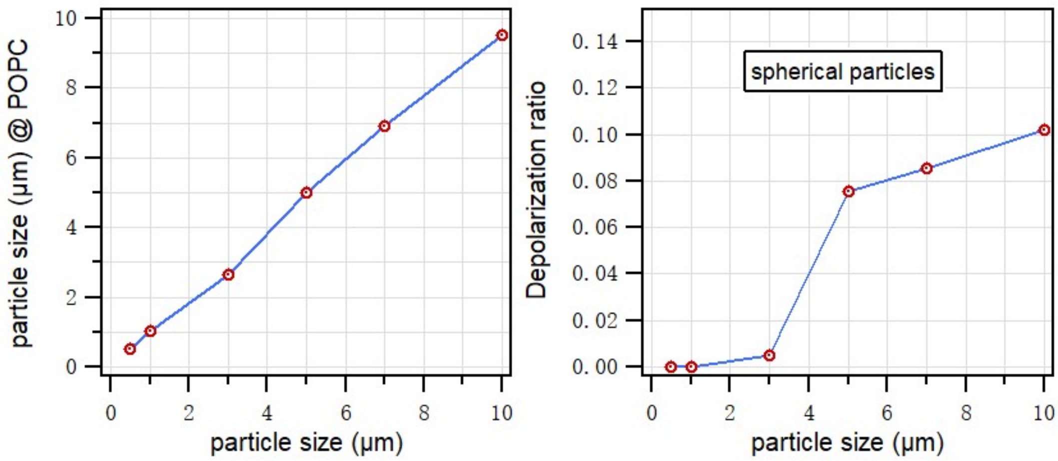

Figure 2. The calibration results of POPC using spherical polystyrene standard aerosols at Dp = 0.5, 1, 3, 5, 7, 10 µm. Optical size of the particle converted from a forward scattering signal at 60 degree (left); Depolarization of the standard particles detected from a backward scattering signal at 120 degree (right).

Due to the limitation of standard aerosols, we only did the calibration of the spherical particles. For non-spherical aerosols, we did some simulation to show the depolarization ratio at a scattering angle of 120 °. The polarization property of randomly oriented elongated ellipsoid particles was simulated on the basis of the T-matrix methodology (Dubovik et al., 2006). The non-sphericity is indicated by the aspect ratio (the ratio of long axis to its orthogonal short axis). As indicated in Figure 3, the observed depolarization ratio (range from 0.1-0.5, and centered on 0.3) in this study corresponded to an aspect ratio of 1.20 - 1.70 for coarse mode dust particles, with mode value 1.50. During the dust-dominant period on April 10, the aspect ratios of the dust particles were estimated to be 1.51 as the depolarization ratio of the dust particles was 0.34. While on polluted dust period on March 4, the aspect ratios of the dust particles were estimated to be 1.45 as the depolarization ratio of the dust particles was 0.30, providing that the dust particles has a great possibility to underwent partial deliquescent and hygroscopic growth on the surface in mixed pollution period.

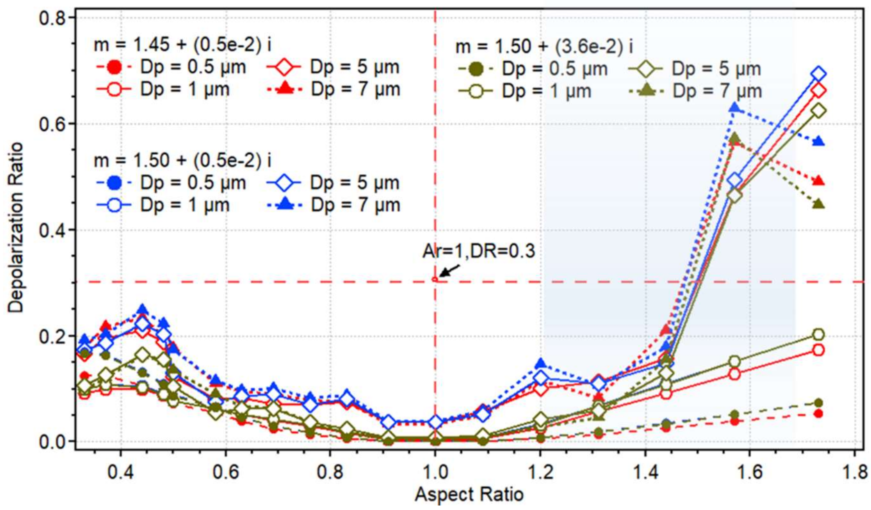

Figure 3. Theoretical simulation of the depolarization ratio of randomly oriented elongated ellipsoid particles as a function of the aspect ratio at fine mode: Dp = 0.5 µm,1 µm, and Dp = 5 µm, 7µm and on the basis of the T-matrix methodology.

Such characteristic was also well predicted by optical model considering particles of Voronoi aggregation (Ishimoto et al., 2010) (Figure 4). Theoretical simulation showed that an change in refractive index could affect the DR value evidently, for the coarse modal particles observed in this observation experiment, the simulation results showed that the depolarization ratio showed a leveling off tendency at 0.31 ± 0.02, confirmed with the depolarization ratio observed in our study.

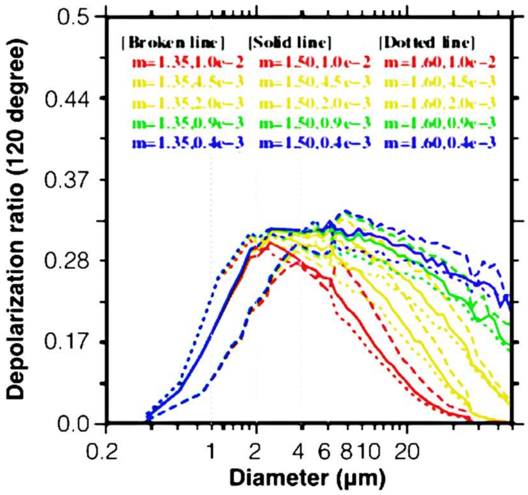

Figure 4. Theoretical calculation of depolarization ratio (at 120 backward direction) as a function of particle size for different refractive index.

As the reviewer suggested, providing the comparison that between the retrieved depolarization ratios at 120◦ scattering angle to existing measurements would better enhance the credibility of our data. The reality is that we are the first study that focused on the single particle polarized optical spectrometer in China. As far as I know, Lidar measurement and satellite on-board remote sensing (CALIPSO) (Glen et al., 2013) could provide tempo-spatial profile of volumn integrated depolarizaiton ratio, however the defination of Lidar's depolarizaiton ratio (S/P, backward at angle of180°) is different from POPC and the two methods all persuming externally mixed of spherical particles and dust aerosols. Beyond that, there is no relevant comercial instrument that can make such measurement. Mass concentration of PM was reconstructed on the basis of number concentration of particles measured by POPC and particles density. The particle density was assumed to increase linearly from 1.77 g/cm3 (0.5 µm) to 2.2 g/cm3 (10 µm). The result compared well with commercial optical particle counter (KC52, RION, as shown in Figure 5), especially in the coarse mode size range observation. We will add relevant literatures and additional remarks in the context.

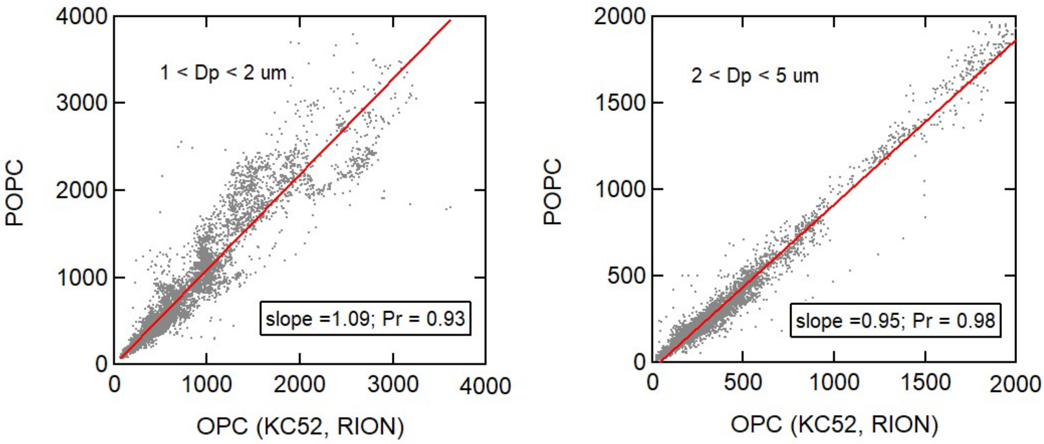

Figure 5. The comparison of number concentrations measured by POPC and OPC (KC52, RION).

The uncertainties of the depolarization ratio values was affected by various factors, including voltage variance of power supply (σ_{vol}^2), emvironment water content (σ_{WC}^2) and complex refraction index (σ_{nf}^2) of the aerosol. Light scattering signals are stored in the form of electrical impulses, the voltage instability will affect the pulse signals. The power supply voltage of POPC was set 15 V, and have a fluctuation by 5% on test. The residence time of diluted air mass in POPC was estimated to be 0.7 s, which was generally sufcient for aerosol particles to achieve equilibrium before measurement in the detecting chamber. It suggested that the wet particles tend to shrink due to loss of water. Zhang et al. (2015) reported aerosol backscattering coefficient increased 25% as the RH increased from 40% to 85 %. The measurement uncertainty in DR was estimated to be 10% caused by humidy change. Theoretical simulation also indicated that an increase in the imaginary part of the refractive index could reduce the DR value evidently (Ishimoto et al., 2010), according to the simulation experiments variations in the particle's refractive index (the real and imaginary part) can explain 6% depolarization variability (Figure 4). Under the calculation method ($\sigma_{DR} = \sqrt{\sigma_{vol}^2 + \sigma_{nf}^2 + \sigma_{WC}^2}$), we estimate the uncertainty of depolarization ratio was < 13%. As indicate in Figure 14 in the manuscript, the depolarization ratio has a decrease of 50% and 43% for 3 μm and 5 μm aerosols, we conclude that dust particles in the atmosphere does contain hygroscopic component.

Pan, X., Uno, I., Hara, Y., Kuribayashi, M., Kobayashi, H., Sugimoto, N., Yamamoto, S., Shimohara, T., and Wang, Z.: Observation of the simultaneous transport of Asian mineral dust aerosols with anthropogenic pollutants using a POPC during a long-lasting dust event in late spring 2014, Geophysical Research Letters, 42, 1593-1598, 10.1002/2014gl062491, 2015.

Sugimoto, N., Nishizawa, T., Shimizu, A., Matsui, I., and Kobayashi, H.: Detection of internally mixed Asian dust with air pollution aerosols using a polarization optical particle counter and a polarization-sensitive two-wavelength lidar, Journal of Quantitative Spectroscopy & Radiative Transfer, 150, 107-113, 10.1016/j.jqsrt.2014.08.003, 2015.

Pan, X., Uno, I., Wang, Z., Nishizawa, T., Sugimoto, N., Yamamoto, S., Kobayashi, H., Sun, Y., Fu, P., Tang, X., and Wang, Z.: Real-time observational evidence of changing Asian dust morphology with the mixing of heavy anthropogenic pollution, Sci Rep, 7, 335, 10.1038/s41598-017-00444-w, 2017.

Li, W. J., and Shao, L. Y.: Observation of nitrate coatings on atmospheric mineral dust particles, Atmos Chem Phys, 9, 1863-1871, DOI 10.5194/acp-9-1863-2009, 2009.

Li, W. J., Zhang, D. Z., Shao, L. Y., Zhou, S. Z., and Wang, W. X.: Individual particle analysis of aerosols collected under haze and non-haze conditions at a high-elevation mountain site in the North China plain, Atmos Chem Phys, 11, 11733-11744, 10.5194/acp-11-11733-2011, 2011.

Dubovik, O., Sinyuk, A., Lapyonok, T., Holben, B. N., Mishchenko, M., Yang, P., Eck, T. F., Volten, H., Munoz, O., Veihelmann, B., van der Zande, W. J., Leon, J. F., Sorokin, M., and Slutsker, I.: Application of spheroid models to account for aerosol particle nonsphericity in remote sensing of desert dust, Journal of Geophysical Research-Atmospheres, 111, 10.1029/2005jd006619, 2006.

Ishimoto, H., Zaizen, Y., Uchiyama, A., Masuda, K., and Mano, Y.: Shape modeling of mineral dust particles for light-scattering calculations using the spatial Poisson–Voronoi tessellation, Journal of Quantitative Spectroscopy and Radiative Transfer, 111, 2434-2443, 10.1016/j.jqsrt.2010.06.018, 2010.

Glen, A., and Brooks, S. D.: A new method for measuring optical scattering properties of atmospherically relevant dusts using the Cloud and Aerosol Spectrometer with Polarization (CASPOL), Atmos Chem

Phys, 13, 1345-1356, 10.5194/acp-13-1345-2013, 2013.

Zhang, L., Sun, J. Y., Shen, X. J., Zhang, Y. M., Che, H., Ma, Q. L., Zhang, Y. W., Zhang, X. Y., and Ogren, J. A.: Observations of relative humidity effects on aerosol light scattering in the Yangtze River Delta of China, Atmos Chem Phys, 15, 8439-8454, 10.5194/acp-15-8439-2015, 2015.

Further comments for improving the manuscript:

1. *Add an outline of the paper at the end of the introduction*

   Reply: As the reviewer suggested, we will add an outline of the paper at the last paragraph of the introduction as follows:

   "In this study, mineral dust-dominant, anthropogenic pollutants and polluted dust were classified according to its size distribution and depolarization ratio, as well as trajectory analysis, the seasonal characteristics of depolarization ratio of atmospheric aerosols were explained. Besides, air quality of community in the observation period were reviewed according to observed key pollutants, including the mass concentrations of $PM_{2.5}$ and PM_{10} came from the Olympic Sport Centre state control station (Longitude: 116.40E; Latitude: 39.98N; 2.7 km northeast of LAPC). During this period, three pollution events were chose to investigate the interactions between dust particles and pollutants, together with an analysis of meteorology parameters obtained from the Beijing Chaoyang district meteorological station (Longitude: 116.48E; Latitude: 39.95N; 9.5 km kilometers northeast of LAPC). To study the variability in depolarization ratio of particles, meteorological factors including wind degree, environment water content, and dominant synoptic system which was well known has an impact on atmospheric heterogeneous reaction was discussed. The objective of this study focuses on the seasonal variation of the depolarization ratio of aerosol particles and its relationship with secondary pollutants. This represents the first time that the long-term variability of ambient aerosol morphology in the megacity of Beijing has been studied based on data of single particle polarization properties, and this study has high scientific value for understanding the mixing processes of atmospheric aerosols and their climate impact."

2. *Mention, which size range is covered with your optical particle counter.*

   Reply: The effective size range of the optical particle counter was 0.5-10 µm, we will add it into the manuscript.

3. *The term "fine mode particles" normally refers to particles with a diameter smaller than 1 µm. PM1 data would be helpful to assess the fine mode particles.*

   Reply: Thanks for the reviewer's suggestion, we carefully checked relevant studies on atmospheric aerosols, and find that fine mode particles usually refers to particles with an aerodynamic diameter below 2.5 microns (Adams et al., 2001; Rathnayake et al., 2017a; Rathnayake et al., 2017b) and PM_1 (Bari et al., 2015; Shi et al., 2014) was often referred to as the sub-micron scale.

Adams, H. S., Nieuwenhuijsen, M. J., and Colvile, R. N.: Determinants of fine particle (PM2.5) personal exposure levels in transport microenvironments, London, UK, Atmospheric Environment, 35, 4557-4566, 10.1016/s1352-2310(01)00194-7, 2001.

Rathnayake, C. M., Metwali, N., Jayarathne, T., Kettler, J., Huang, Y., Thorne, P. S., amp, apos, Shaughnessy, P. T., and Stone, E. A.: Influence of rain on the abundance of bioaerosols in fine and coarse particles, Atmos Chem Phys, 17, 2459-2475, 10.5194/acp-17-2459-2017, 2017a.

Rathnayake, C. M., Metwali, N., Jayarathne, T., Kettler, J., Huang, Y. F., Thorne, P. S., O'Shaughnessy, P. T., and Stone, E. A.: Influence of rain on the abundance of bioaerosols in fine and coarse particles, Atmos Chem Phys, 17, 2459-2475, 10.5194/acp-17-2459-2017, 2017b.

Bari, M. A., Kindzierski, W. B., Wallace, L. A., Wheeler, A. J., MacNeill, M., and Heroux, M. E.: Indoor and Outdoor Levels and Sources of Submicron Particles (PM1) at Homes in Edmonton, Canada, Environmental Science & Technology, 49, 6419-6429, 10.1021/acs.est.5b01173, 2015.

Shi, Y., Chen, J., Hu, D., Wang, L., Yang, X., and Wang, X.: Airborne submicron particulate (PM1) pollution in Shanghai, China: chemical variability, formation/dissociation of associated semi-volatile components and the impacts on visibility, Sci Total Environ, 473-474, 199-206, 10.1016/j.scitotenv.2013.12.024, 2014.

4. *State clearer the difference between the depolarization ratio used in lidar studies (s-polarized to p-polarized ratio at 180◦ backscatter) and the depolarization ratio used in the POPC study (s-polarized to s+p polarized ratio at 120◦ backscatter). To add value to the lidar studies by using single particle analyses, it would be better to use the same depolarization ratio or at least to present a method to convert the POPC depolarization ratio to a lidar retrieved depolarization ratio. But I dare, that this would be rather complicated for non-spherical particles.*

Reply: The main difference between the depolarization ratio (δa) used in LIDAR and the POPC was: Lidar measured was all the particles' depolarization ratio in backward scattering angle 180° in a beam volume. The overall depolarization ratio of dust particles might be underestimated due to substantially presence of small spherical particles in the dust plume. It means external mixing of a large amount of fine particles with mineral dust aerosols also results in a lower δa; POPC measured all the single particle's depolarization ratio in the backward scattering without interference. According to theoretical simulation and optical lens design, POPC only measure depolarization ratio of scatter light at angle of 120°. Considering that the scattering phase function of particles was not linearly varying at different angles, especially for non-spherical particles, depolarization ratio at backscatter 120 ° was difficult to switch to the results of 180 °. Now we are working on a project of remould the light road of POPC, in the new version, we design to detect the scattered light information at around 180 °. In our next research, we would like to follow the review's suggestion to try provide a comparison for LIDAR result.

5. *Add the distance and the direction (north, east,...) to the description of the two additional measurements sites (Olympic Sport Centre state control site and meteorological station) and not just the coordinates. It makes it easier for the reader.*

Reply: Thanks to the reviewers' suggestions, we will add information about the distance and the direction to the description of the two additional measurements sites.