Response to Anonymous Referee #2

The manuscript 'Characterization of atmospheric trace gases and particle matters in Hangzhou, China' by G. Zhang et al. reports the observational results from one-year monitoring of several trace gases and particulate matter at an urban site in the YRD region. The characteristics of these trace gases and particulate matter are discussed in association with meteorological conditions. Process analysis is also performed for case studies under photochemical pollution and haze condition. The measurement data are valuable, but the manuscript needs to be more concise and more logically structured. Further proofreading is also needed to correct grammar mistakes and inappropriate description.

Response: Thanks for your approval and presenting the valuable comments on our manuscript. According to your suggestions, we restructured our manuscript logically, shortened some redundant description and corrected grammar mistakes in the revised version. We expect this version would meet the requirement for publication in ACP.

Specific comments:

1. 'Particle matter' is used almost through the entire manuscript, it should be particulate matter.

Response: According to your suggestion, we replaced "particle matter" with "particulate matter" in the revised manuscript.

2. Was the air sample dried when measuring $PM_{2.5}$? How about the drying system?

Response: As described in the manuscript, ambient $PM_{2.5}$ samples were collected using co-located Thermo Scientific (formerly R&P) Model 1405D samplers. This sampler has no dried unit in our study.

3. What is the temporal resolution of the meteorological data in the HYSPLIT model? Will the temporal resolution and also the spatial resolution as $0.5^{o}\times0.5^{o}$ influence your conclusions?

Response: As described in Section 2.4.1 in the manuscript, the six hourly final archive data with $1^{o}\times1^{o}$ spatial resolution were obtained from the National Center for Environmental Prediction's Global Data Assimilation System (GDAS) wind field reanalysis. Such designated data have been widely used in numerous previous studies (Li et al., 2015; Yu et al., 2014; Zhang et al., 2013). As you know, the numbers of back trajectories starting from a selected site during the appointed period are probably dependent of temporal and spatial resolution of the meteorological data. Nevertheless, the trajectory cluster analysis is based on the statistical results of air masses back trajectories, and it should don't change a lot. Thus they don't lead to a significant effect on the conclusion.

References:

Li, P. F., Yan, R. C., Yu, S. C., Wang, S., Liu, W. P., and Bao, H. M.: Reinstate regional transport of $PM_{2.5}$ as a major cause of severe haze in Beijing, Proc. Natl. Acad. Sci., 112(21), 2739-2740, 2015.

Yu, S. C., Zhang, Q. Y., Yan, R. C., Wang, S., Li, P. F., Chen, B. X., Liu, W. P., and Zhang, X. Y.: Origin of air pollution during a weekly heavy haze episode in Hangzhou, China, Environ. Chem. Lett., 12, 543-550, 2014.

Zhang, R, Jing, J., Tao, J., Hsu, S. C., Wang, G., Cao, J., Lee, C. S. L., Zhu, L., Chen, Z., Zhao, Y., and Shen, Z.: Chemical characterization and source apportionment of PM2.5 in Beijing: seasonal perspective, Atmos. Chem. Phys., 13, 7053-7074, 2013.

4. P9 L246-249, the author suggested comparable photochemical levels in different regions only based on measurements of NO_2 and O_3, I am afraid it is insufficient to draw this conclusion.

Response: After careful examination throughout the manuscript, we didn't find these sentences in this version of the manuscript. These sentences were possibly included in the previous version and have been removed in this version.

5. The discussion on NO_x or VOCs limitation of ozone photochemical production is based on measured CO. The author stated that VOCs and CO share common origins and play similar roles in ozone production in this region. Is there any data or previous study in this region to support this assumption?

Response: For VOCs and CO in the typical urban regions, their common origin and similar behavior in ozone production have been explicitly elucidated (Atkinson, 2000) and widely validated in the previous studies (Baker et al., 2008; Schneidemesser et al., 2010; Ding et al., 2013). Moreover, based on the data of VOCs and CO obtained at Lin'an site, a regional station located in the east Zhejiang Province (50 km away from Hangzhou) in eastern China, Guo et al. (2004) found the common sources of VOCs and CO were vehicle emissions and biofuel burning, biomass burning and industrial emissions. In addition, we Therefore, we added the previous publications behind this sentence to support our assumption in the revised manuscript.

References:

Atkinson, R.: Atmospheric chemistry of VOCs and NO_x, Atmos. Environ., 34, 2063–2101, 2000.

Baker, A. K., Beyersdorf, A. J., Doezema, L. A., Katzenstein, A. K., Meinardi, S., Simpson, I. J., Blake, D. R., and Rowland, F. S.: Measurements of nonmethane hydrocarbons in 28 United States cities, Atmos. Environ., 42, 170-182, 2008.

Ding, A. J., Fu, C. B., Yang, X. Q., Sun, J. N., Zheng, L. F., Xie, Y. N., Herrmann, E., Nie, W., Petäjä, T., Kerminen, V. M., and Kulmala, M.: Ozone and fine particulate in the western Yangtze River Delta: an overview of 1 yr data at the SORPES station, Atmos. Chem. Phys., 13, 5813-5830, 2013.

Guo, H., Wang, T., Simpson, I. J., Blake, D. R., Yu, X. M., Kwok, Y. H., and Li, Y. S.: Source contributions to ambient VOCs and CO at a rural site in eastern China, 38(27), 4551-4560, 2004.

6. The correlations of O_3 and $PM_{2.5}$ in warm and cold seasons were analyzed. The author attributed the positive correlation in warm seasons to secondary aerosol formation under high O_3 levels and negative

correlation in cold seasons to NO titration effect. However, the ambient level of either O_3 or $PM_{2.5}$ is a result of emission, sinks, physical processes and complicated chemical reactions. The explanation has no solid foundation and also needs other supporting data.

Response: Your suggestions are really valuable. Unfortunately, in this study we didn't conduct the chemical elements, ion, and OC/EC analysis of particulate matters and thus no available data could directly support this assumption. However, we find another reliable evidence based on the available data of the observed $PM_{2.5}$ and gaseous pollutants in our measurement to support our conclusion. To judge whether the secondary aerosol formed during the warm seasons and was further related with high O_3 concentrations, we chose two typical O_3 exceedances (OE) cases under air temperature on 10 and 12 July (OE1: 95 ppbv for average O_3 and 35.9 ^oC for average T) and 10-11 August (OE2: 92.7 ppbv for average O_3 and 38.7 ^oC for average T), respectively, together comparison with their nearby non-O_3 exceedances periods (NOE) from 7-8 July (NOE1) and 13-14 August (NOE2). Note that these data were both selected as the time period of 9:00-17:00 BLT, to reflect the photochemistry as possible. As can be seen from Table 1 below, the average $PM_{2.5}$ concentrations in OE1 and OE2 were both higher (ca. 2-4 folder) than those in NOE1 and NOE2, respectively. It suggested a significant formation of $PM_{2.5}$ in the OE event. Furthermore, to further distinguish the primary and secondary contribution to $PM_{2.5}$, we compared the ratio of the averaged $PM_{2.5}$ concentrations in OE to that in NOE events ($PM_{2.5(OE)}$/ $PM_{2.5(NOE)}$) with the ratios for other gaseous pollutants. If the ratio of $PM_{2.5(OE)}$/$PM_{2.5(NOE)}$ was comparable with that for other primary pollutants, it probably indicated that a significant contribution of primary particulate matter to the observed $PM_{2.5}$ in OE event. As clearly shown in Table 1, the ratios of $PM_{2.5(OE1)}$/ $PM_{2.5(NOE1)}$ and $PM_{2.5(OE2)}$/ $PM_{2.5(NOE2)}$ were 2.08 and 4.12, respectively, both higher than those for the other primary gaseous pollutants during these two episodes (1.20-1.61 and 1.62-2.58), indicating a significant contribution of secondary particulate matter to the observed $PM_{2.5}$ in warm seasons.

Table 1 Average concentrations of $PM_{2.5}$ and gaseous pollutants and their average ratios in the O_3 exceedances period on 10 and 12 July (OE1) and 10-11 August (OE2), and the nearby non-O_3 exceedances period from 7-8 July (NOE1) and 13-14 August (NOE2), respectively.

	Same time period (9:00-17:00 BLT)					
Species	OE1*	NOE1*	OE1/NOE1	OE2*	NOE2*	OE2/NOE2
$PM_{2.5}$	50.65	24.36	2.08	41.96	10.17	4.12
O_3	95.43	53.23	1.79	92.69	42.71	2.17
SO_2	12.73	7.89	1.61	5.18	2.01	2.58
CO	0.46	0.38	1.20	0.48	0.30	1.62
NO_y	35.72	23.95	1.49	29.30	16.22	1.81

*$\mu g/m^3$ unit for $PM_{2.5}$, ppmv unit for CO, and ppbv unit for the other gases, respectively

In addition, we find other simultaneous/previous observations implemented in urban Hangzhou to support our supposition. Sun et al. (2013) conducted an intensive field campaign in Hangzhou during

Sep. 2010-July 2011 and found that molar ratios of sulfate to total sulfur and nitrate to total oxidized nitrogen frequency exceeded 10%, suggesting significant effects of photochemical reactions on $PM_{2.5}$ pollution in the urban Hangzhou. Thus, secondary particulate formation may be related to high conversion rate of SO_2 and NO_x to sulfate and nitrate under a high concentration of oxidants (Khoder, 2002; Sun et al., 2013). Note that it's necessary to implement more detailed investigations related with chemical elements, ion, and OC/EC analysis of particulate matters.

In the revised manuscript, we made corresponding corrections as mentioned above.

References:

Khoder, M. I.: Atmospheric conversion of sulfur dioxide to particulate sulfate and nitrogen dioxide to particulate nitrate and gaseous nitric acid in an urban area, Chemosphere, 49, 675-684, 2002.

Sun, G. J., Yao, L., Jiao, L., Shi, Y., Zhang, Q. Y., Tao, M. N., Shan, G. R., and He, Y.: Characterizing $PM_{2.5}$ pollution of a subtropical metropolitan area in China, Atmos. Climate Sci., 3, 100-110, 2013.

7. The backward trajectory and PSCF analysis is not suitable for short-lived species such as O_3 and is especially not suitable in urban area with high local emission. So it's strange that those clean mountain area in south of Hangzhou could have more contributions? As well as that air masses coming from open seas contained higher concentrations of NO_x and O_3?

Response: We thank the referee for his/her valuable comments. We divide this comment into four questions in details:

1) The backward trajectory and PSCF analysis is not suitable for short-lived species such as O_3

At first, we have to clarify that this WPSCF analysis has its limitation. In principle, it's just a statistical method correlating air masses origin with the pollutants concentrations measured in a selected site. We agree with referee that the PSCF analysis used for so-called short-lived species such as O_3 might adds uncertainty to our results, but it will not lead to the wrong results. The method is based on the theory that those map grid cells that get much "probability" of high concentration will have an increased importance in the source area maps. A significant area will get more "probability" when a trajectory passes it again but from a slightly different direction when the length of air masses trajectory was longer than life time of the pollutant. Areas behind the source areas will have smeared concentration probability and will be mixed also with clean trajectories that have gone around the source area, thus it might arise broadening "tails" behind the significant source area with high concentration. Similar phenomenon was also found in other studies by using trajectory statistical method (Riuttanen et al., 2013).

However, this method also has significant advantage. It is a useful, widely-used, and simple way to see

where the higher concentrations (relative to a set value) come from, and thus it could represent the potential/relative source contribution fields. As mentioned in the Response 3 above, this method has been employed to elucidate the potential source contributions of particulate matters. In addition, apart from the application in investigating the potential source contributions of the trace gases such as SO_2, CO, and NO_x (Kaiser et al., 2007; Riuttanen et al., 2013; Yu et al., 2014), it has been increasingly applied to identify the origin of O_3 pollution (Stohl and Kromp-Kolb, 1994; Dickerson et al., 1995; Poirot and Wishinski, 1998; Kaiser et al., 2007; Riuttanen et al., 2013; Vellingiri et al., 2016; Sharma et al., 2017), and even extended to a more complicatedly secondary pollutant of atmospheric peroxyacetyl nitrate (PAN) (Siroris and Bottenheim, 1995). As you know, O_3 has variable precursors and complex sink mechanisms. In fact so complex that a statistical method such as PSCF has been proven to perform better compared to deterministic trajectory based method (Schlink et al., 2003). Therefore, this method has been validated to be suitable not only for particulate matters but also for trace gases such as O_3, SO_2, CO, and NO_x.

2) The backward trajectory and PSCF analysis is especially not suitable in urban area with high local emission.

With respect to the applicability of this method in urban area, we have to clarify again that it just provides a general indication of the potential source probability areas **in statistical sense** and thus it's free of turbulence, dry and wet deposition, and chemical reactions (Kaiser et al., 2007). The back trajectory and PSCF method have been widely used in the analysis of atmospheric NO_2 and O_3 in urban Hangzhou (Wu et al., 2016) and the other typical urban sites in Toronto and Montreal in eastern Canada (Johnson et al., 2007), Naples in southern Italy (Riccio et al., 2007), Korea (Vellingiri et al., 2016), and New Delhi (Sharma et al., 2017). Even, this method could be used to assess the effects of transboundary ozone pollution between Ontario, Canada and New York (Brankov et al., 2003). For NRCS site, a typical urban site located in Hangzhou, it is an ideal receptor to capture the mixed signature of local emission and regional transport, with the short and long cluster-mean trajectories, respectively.

3) So it's strange that those clean mountain area in south of Hangzhou could have more contributions?

To answer the question about high contribution from the south of Hangzhou, we first view the terrain and geographical distribution in Zhejiang Province. For Zhejiang Province, its terrain inclines from southwest to northeast, and geographically many cities (i.e., Shaoxing, Jinghua, Lishui, and Quzhou city) located in the south of Hangzhou. High O_3 is expected to be produced in these urban regions and carried to the NRCS site by the dominant southwesterly wind. Thus these areas could act as potential source regions. In addition, we think that biogenic VOCs (BVOCs) emitted from the mountain area in the south of Hangzhou might play a certain role in the formation of local O_3 during the whole year except

winter. This supposition was well evidenced by seasonal and spatial distributions of O_3 volume mixing ratio (VMR) simulated by MOZART-4/GEOS-5 (See the Figure 1 below). Cleary shown in this figure, high concentrations of O_3 distributed in the south of Hangzhou including the mountain area during the whole year except winter.

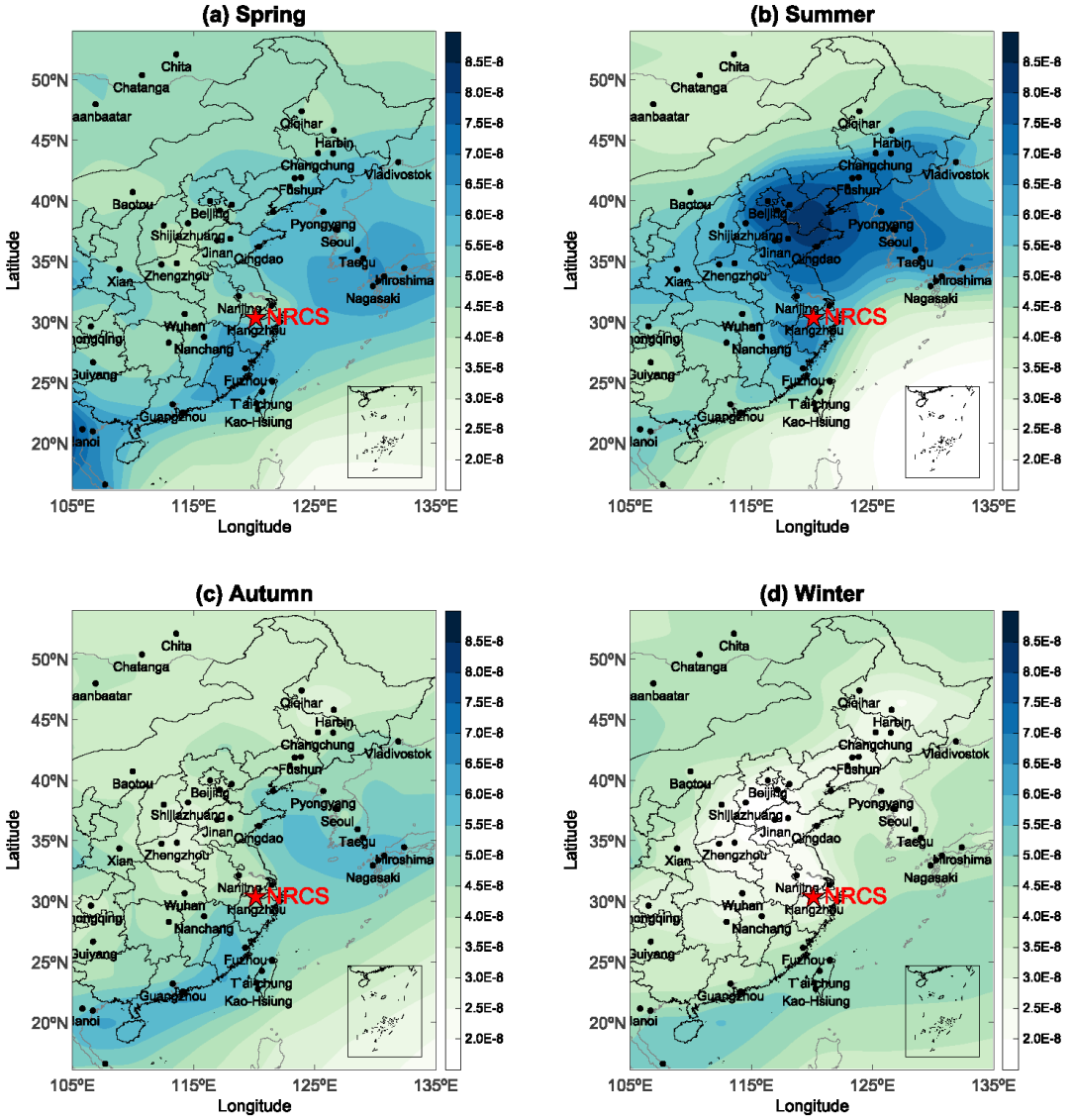

Figure 1 Seasonal and spatial distributions of O_3 volume mixing ratio (VMR) simulated by MOZART-4/GEOS-5. The sample site is marked in pentacle.

4) As well as that air masses coming from open seas contained higher concentrations of NO_x and O_3?

As responded to the Anonymous Referee #1, we are so sorry for the incorrectly expression "long transports from Yellow Sea, East Sea, and South Sea were also important potential sources for NO_x and O_3" in the initial manuscript. After careful examination, we found that air masses with the seemed high WPSCF values for NO_x were not originating far from these open seas. They were just the broadening "tails" of high values contained in the areas with intensive anthropogenic NO_x emissions from inland well-industrialized cities. This phenomenon was also found in other studies by using trajectory statistical method (Riuttanen et al., 2013).

Similar with NO_x, air masses containing the high WPSCF values of O_3 also didn't come from the open seas. Indeed, such air masses were mostly from the offshore area of East China Sea, Yellow China Sea, or South China, respectively on southeastern Zhejiang, Jiangsu, and Fujian Province. We speculated the recirculation of pollutants by sea- and land-breeze circulations around the cities along the YRD and Hangzhou Bay which has been confirmed by Li et al. (2015, 2016b), was largely responsible for the increased concentration of O_3 at NRCS site. Also, such an increase in O_3 concentrations in urbanized coastal areas have been observed and modeled in a number of studies (Oh et al., 2006; Levy et al., 2008; Martins et al., 2012). Moreover, to further judge whether air masses came from open seas contained higher concentrations of NO_x and O_3, we used the results of MOZART-4/GEOS-5 simulation to draw the distribution maps of NO_x and O_3 concentrations within the identical domain (15-55 ^oN and 105-135 ^oE) with WPSCF analysis. As clearly seen from the Figure 2 below, high NO_x mainly distributed in terrestrial regions, especially in industrialized cities, but very low NO_x were found in open seas. In comparison, significantly high O_3 were elucidated covering the offshore regions of either East China Sea, Yellow China Sea, or South China (Fig. 1). Then, along with the seasonal cluster analysis of back trajectories from NRCS site in Hangzhou, it's well confirmed that our speculation about the contribution of the recirculation of pollutants by sea- and land-breeze circulations in the offshore area to the observed O_3 at NRCS site.

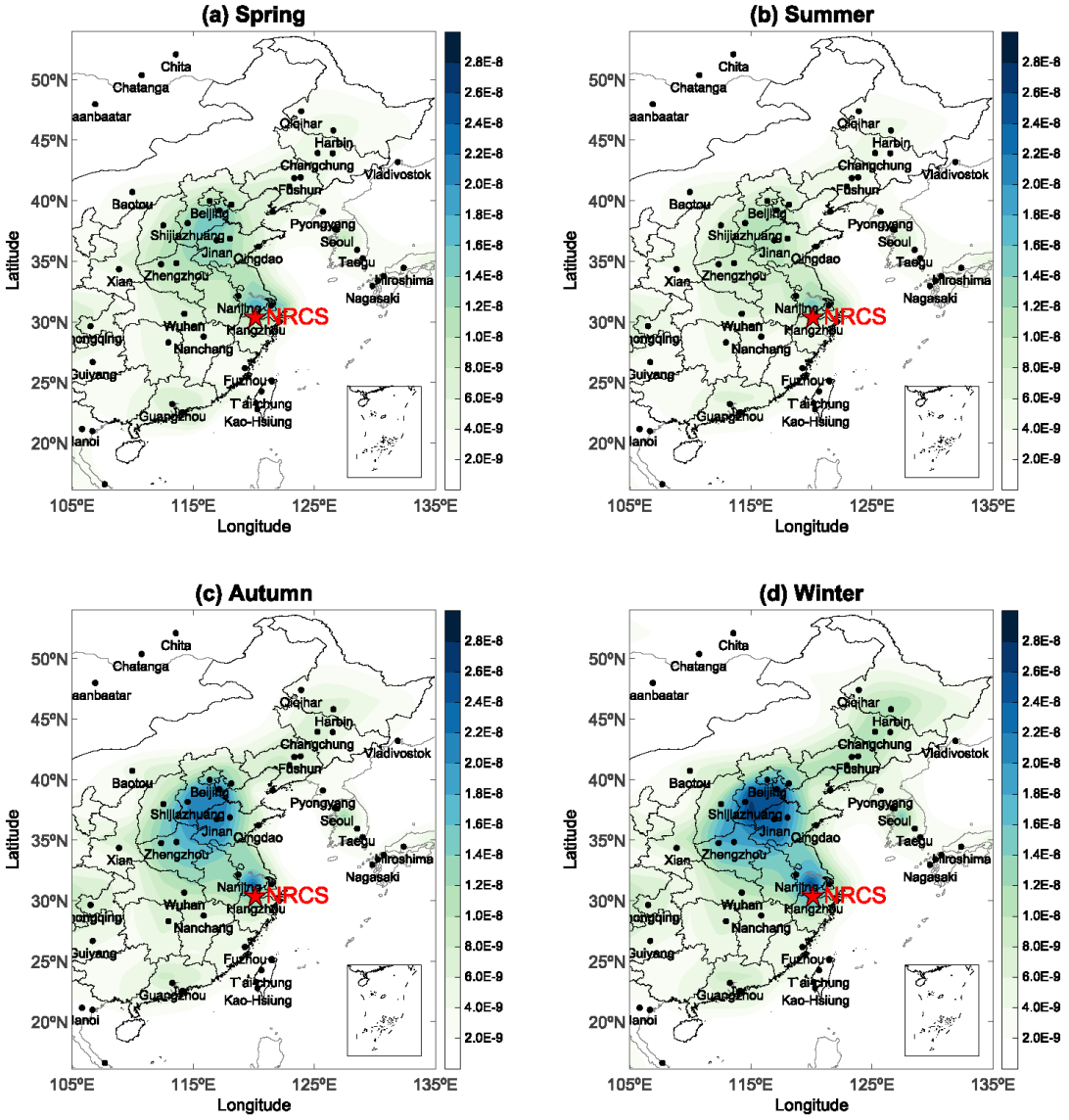

Figure 2 Seasonal and spatial distributions of NO_x volume mixing ratio (VMR) simulated by MOZART-4/GEOS-5. The sample site is marked in pentacle.

In summary, we made the corresponding corrections in the revised manuscript.

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Brankov, E., Henry, R.F., Civverlo, K.L., Hao, W., Rao, S.T., Misra, P.K., Bloxam, R., and Reid, N.: Assessing the effects of transboundary ozone pollution between Ontario, Canada and New York, USA, Environ. Pollut., 123, 403-411, 2003. Dickerson, R. R., Doddridge, B. G., and Kelley, P.: Large-scale pollution of the atmosphere over the remote Atlantic Ocean: Evidence from Bermuda, J. Geophys. Res., 100, 8945-8952, 1995.

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