Response to Reviewer #1's Comments

Anonymous Referee #1:

This manuscript presents a year of continuous measurements of atmospheric Hg species at a suburban site in eastern China, which is an important anthropogenic Hg source region in China. This study combines the analysis of speciated Hg concentrations, local meteorology, receptor-based modelling, PMF and specific event, showing the sources and transformations of atmospheric Hg.

Major comments:

The authors discussed the impact of local emissions and long-range transport of Hg on observed atmospheric Hg. The analysis, however, do not generate a conclusion that which of these two processes were the dominant sources of the observations, and some of the conclusions from the analysis are contradictory to each other at times. The analysis of using PSCF model neglect the local meteorology. For example, when there is a shallow boundary layer formed at the sampling site, an analysis of long range transport could be not suitable because local to regional are more important in this case. This manuscript seems not have a clear motivating hypothesis. The authors made a brief introduction of Hg emissions in East Asia, but have not summarized the findings of many previous studies conducted in this region or in East Asia. They also have not addressed the scientific gaps existing after many previous studies in this region. Therefor, it is not clear to what extent that this study could contribute to the science. The descriptions of the materials and methods section are not clear. The collection of GOM and PBM at 2-hour interval indicates a GOM or PBM concentration could be obtained every 3 hours (1 hour thermal desorption and detection is needed after collection). This does not match the backward trajectories simulated every two hours. The operations of the speciated Tekran system did not followed the standard method very well. For example, a replacement of filter at a monthly interval is too longer under heavily PM pollution conditions. The calculation of backward trajectory is not clear. What is the arrival height used for the calculation of backward trajectories? What is the threshold concentrations of speciated atmospheric Hg and the reasons of the selection of the thresholds.

We sincerely thank for the reviewer's in-depth comments and helpful suggestions on this manuscript. Based on the specific comments, we have responded to all the comments point-by-point and made corresponding changes in the manuscript as highlighted in red color. The reviewer has raised a number of issues and we quite agree. We feel the substantial revisions based on the reviewer's comments have greatly improved the quality of this manuscript. Please check the detailed responses to all the comments as below.

Specific comments:

1. Line 26-27: a conclusion of impact of the long-range transport and local emissions on observations is meaningless. All observations could be impacted by local and long-range sources.

Response: We agree with the reviewer that this sentence is redundant. This statement has been revised as "An application of the GOM/PBM tracer method and trajectory-based source region identification distinguished the relative importance of long-range transport from northern China and quasi-local emission sources on the magnitudes of Hg species." in the revision.

2. Line 46 and 48: the citations of references are not correct. Please check the similar errors throughout the manuscript.

Response: Thanks for pointing out this. The references have been checked throughout the manuscript.

3. Line 53: as for the anthropogenic mercury?

Response: The sentence has been revised as "As for the anthropogenic emission sources of mercury, coal combustion, non-ferrous smelters, cement production, waste incineration, and mining are considered to be the main sources." in the revision.

4. Line 71-72: are you sure that atmospheric transformations such as redox reactions could not impact atmospheric GEM. There are many evidences that transformations including oxidation of GEM and foliar uptake of GEM could significantly affect GEM observations.

Response: We agree with the reviewer that the redox reactions can indeed significantly affect GEM observations and our statement was not appropriate. we have revised the original sentence as "Generally, the levels of GEM could be affected by various emission sources, redox reactions, and foliar uptake, while the GOM species from the GEM oxidation and subsequent formation of PBM by adsorption on the particulate matters can significantly affect their ambient concentrations, especially in regions with high GEM levels." in the revision.

5. Line 75-85: a detailed introduction of previous studies in eastern China should be added here. You should also introduce the progress of atmospheric Hg observations and point out the remaining questions regarding sources and transformation in this region.

Response: Thanks for the suggestion. A detailed introduction of previous studies has been added in the revision. "Early field measurements in urban Shanghai found that the sources of TGM were most likely derived from coal fired power plants, smelters and industrial activities (Friedli et al., 2011). One study in urban Nanjing indicated that natural sources were important while most sharp peaks of TGM were caused by anthropogenic sources (Zhu et al., 2012). Modeling of atmospheric mercury in eastern China simulated by the CMAQ-Hg model showed that natural emissions with a contribution of 36.6% were the most important source for GEM in eastern China (Zhu et al., 2015). One study at Chongming (an island belonging to Shanghai) observed a downward trend for GEM concentrations from 2014 to 2016 due to the reduction of

domestic emissions (Wang et al., 2016). Studies conducted in Changbai Mountain (Wan et al., 2009) and Xiamen (Xu et al., 2015) used Principal Components Analysis (PCA) to identify potential sources of atmospheric mercury, but the specific contributions of each source couldn't be quantified due to the limitation of the PCA method. Overall, studies with respect to the specific sources and their quantified contributions to atmospheric mercury in the suburbs of East China and the formation and transformation processes among Hg species in the atmosphere are still lacking."

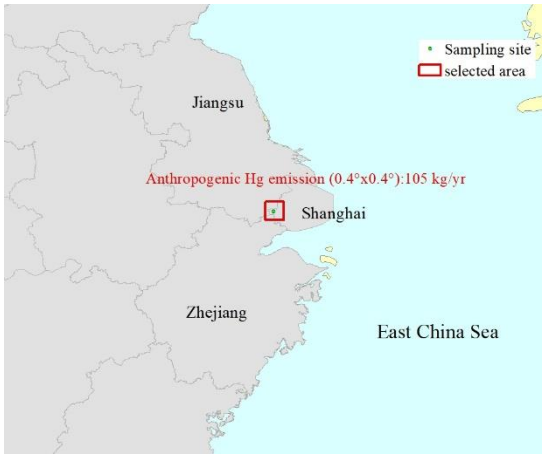
6. Section 2.1: the authors declare that there is no large point sources within 20 km of the sampling site. This seems not correct. From the Chinese inventory and global inventory, I can calculate the total GEM emission reaches more than 10 tons within 0.4◦×04◦ grid of the site (corresponding to a 20 Km cycle around the site). For such a strong local emission, is it suitable to use PSCF modelling to study the long-range transport. How could you separate the local emissions from long-range transport signals?

Response: Thank for the reviewer's carefully check on the emissions around the sampling site. Based on a mercury emission inventory of China in 2014 (Wu et al., 2016), the total GEM emission in Shanghai was approximately 5 tons/yr. Since our sampling site is located in Shanghai, it seems unlikely that the GEM emission within a 0.4◦×04◦ grid of the site can reach more than 10 tons, even higher than the total of Shanghai. To clarify this, we checked the EDGAR (Emissions Database for Global Atmospheric Research) global emission inventory (http://edgar.jrc.ec.europa.eu/overview.php?v=4tox2), which included a variety of emission sectors as shown in the table below. We also selected a 0.4◦×04◦ grid of the site as shown in the figure below. The latest year of the EDGAR mercury emission dataset is 2012.

It is calculated that the total GEM emissions in this grid box is about 105kg/yr, of which power industry and cement production are the major contributors. In this regard, the emissions around the sampling site is not significant.

The sampling site is located beside Dianshan Lake as seen in the photos below. No strong point sources and high buildings are around the site and could be regarded as an ideal suburban site in the YRD region.

Sector	Emissions (kg/yr)
Cement	28.49
Power-industry	53.87
Residential	10.05
Glass	0.03
Transportation	3.67
Waste	9.38
Total	105.49



7. Section 2.4: you should show the arrival heights of the backward trajectories and the threshold concentrations.

Response: Thanks for the suggestion. The last paragraph in Section 2.4 has been revised as "In this study, we set the threshold concentration as the mean value of the whole sampling period. The mean GEM, PBM, and GOM concentrations were 2.77 ng/m^3, 60.8 pg/m^3, and 82.1 pg/m^3, respectively. The HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) model is applied for calculating air mass backward trajectories (Draxler and Rolph, 2012). The model was run online at the NOAA ARL READY Website using the meteorological data archives of Air Resource Laboratory (ARL). The meteorological input data used in the model was obtained from NCEP (National Centers for Environmental Prediction)'s global data assimilation system (GDAS) with a horizontal resolution of 0.5° × 0.5°. In this study, 72-hours back trajectories were calculated at 500m AGL (above ground level) and the cell size was set as 0.5°×0.5°.

8. Line 193: standard errors of the means should be also presented here. You should also define the characteristic of the site. Is it a remote site or suburban site? I would prefer a suburban characteristic of the sampling site. Then, comparisons between previous observations in urban, suburban and remote areas are meaningful.

Response: The standard errors of the means have been added and the sentence has been revised as "The annual average concentrations of GEM, PBM, and GOM at DSL were 2.77±1.36 ng/m^3, 60.8±67.4 pg/m^3, and 82.1±115.4 pg/m^3, respectively." in the revision. The characteristic of the site has already been defined as suburban in Table 1.

9. Line 210: a description of elevated Hg concentrations in both cold and warm seasons is confusing. What is the statistical test for the seasonal variations?

Response: The table below shows the statistical test with the p-value among the four seasons for GEM concentration. It indicates the GEM concentration in autumn is statistically different from that of spring, summer, and winter ($p<0.05$), while there are no significant differences

among spring, summer, and winter ($p>0.05$). In this regard, we revised the description as "Statistical test showed that no significant differences of the seasonal variations of GEM concentrations among spring, summer, and winter were observed (Table S1). This was different from many urban and remote sites in China, such as Guiyang, Xiamen, and Mt. Changbai, where GEM showed significantly higher concentrations in cold seasons than those in warm seasons (Feng et al., 2004;Xu et al., 2015;Fu et al., 2012)." in the revision.

Table R1. P-value between seasons for GEM concentration

	spring	summer	autumn	winter
spring				
summer	$p>0.05$			
autumn	$p<0.05$	$p<0.05$		
winter	$p>0.05$	$p>0.05$	$p<0.05$	

10. Line 214-216: here references are needed.

Response: Thanks for the suggestion. The references have been added in the revision.

11. Line 224-225: does a highest GOM concentration observed in winter support the effect of atmospheric oxidation at the sampling site. Generally, modeling studies argued that the oxidation rate of GEM should be highest in summer. Also, GOM observed peaked in morning (10:00), similar to GEM. This is in contrast with many previous studies that showed highest concentrations at noon, which could support a strong transformation between GEM and GOM.

Response: Thanks for the comments. The atmospheric oxidation was lowest in winter due to the relatively weak solar radiation. Thus, the high GOM concentrations observed in winter probably were attributed to the influence of strong anthropogenic emissions (such as the enhanced coal combustion in winter) and unfavorable meteorological conditions.

As for similar peaks of GOM and GEM in this study, we think this is also likely attributed to the influence of anthropogenic emissions as GOM derived largely from anthropogenic emissions in addition to the secondary formation.

In the revised manuscript, we have stated more clearly about the diurnal pattern of mercury species.

12. Line 241: are there any previous studies showed the diurnal patterns of anthropogenic emissions. The difference in Hg concentrations between daytime and night needs a statistical test.

Response: To our best knowledge, no diurnal patterns of anthropogenic Hg emissions are available from previous studies. The figure below is the hourly profile of major emission sectors (including power plants, industries, residential and transportation) for allocating emissions in China (data from Prof. Qiang Zhang from Tsinghua University). It could be seen that all emissions peak during daytime, reflecting the strong influences from human activities. We also performed statistical analysis and confirmed that the difference of Hg concentrations between daytime and night was significant ($p<0.05$).

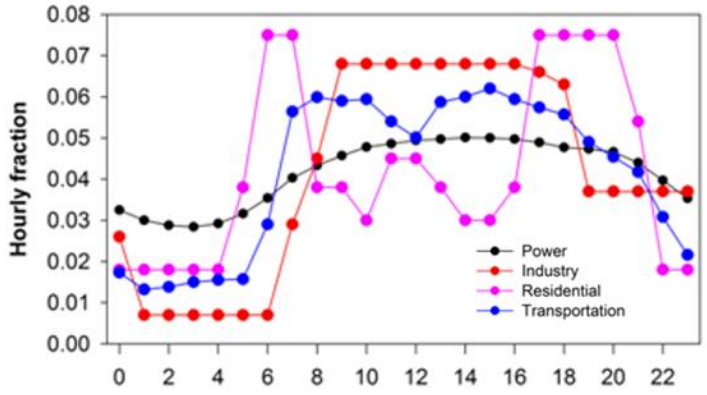


Figure R1. Hourly profile of major emission sectors in China

13. Line 257-258: PBM showed the highest in southwest, west and northwest winds, this is not consistent with the PSCF result. Please explain.

Response: Thanks for the comment. We think that there are two main reasons. 1) The wind rose plot was based on instantaneous wind directions, which revealed the relationship between PBM concentrations and wind direction/wind speed at a local scale. The PSCF analysis was based on three-days backward trajectories, which revealed the transport routes of air masses and potential sources regions at a much larger scale. Thus, it is possible that the wind rose plot and PSCF didn't show very consistent results. 2) As shown in Fig 5 (a), the frequency of the wind from southwest directions only accounted for about 6% of the total winds, which could impact the results of PSCF. As the PSCF analysis applied a weighting factor to reduce the uncertainty when a small number of trajectories crossed a particular cell. This might cause the PSCF values to be underestimated in the southwest, west and northwest wind directions.

14. Line 272: a description of PBL should be presented before the abbreviation. What methods did you use to determine the PBL? It is also appropriate to separate the shallow PBL from the PSCF analysis.

Response: We added the sentence "The data of the height of planetary boundary layer (PBL) were retrieved from the U.S. National Oceanic and Atmospheric Administration (https://ready.arl.noaa.gov/READYamet.php)." in Section 2 in the revision. When performing

the PSCF analysis, the starting heights were set as 500m, thus precluding the events under the shallow PBL conditions.

15. Line 300-301: I do not agree East China Sea is an important source region of the site given the PSCF values ranging from 0.2 to 0.4. There are also studies of atmospheric Hg in East China Sea, which highlighted that outflows of Hg from mainland China drive the increase of Hg concentrations.

Response: Thanks for the comment. The PSCF pattern in Fig. 7 of the original manuscript was based on an annual basis of Hg, indicating moderate PSCF values as the reviewer commented. If by referring to seasonal potential source regions of GEM as shown in the figure below, we did observe some high PSCF values (>0.5) over the East China Sea. We believe these signals imply the impact of ship emissions, but not the impact of ocean emissions. However, we do agree with the reviewer that East China Sea is not an important source region as the mainland evidently showed much higher and widespread PSCF signals. To avoid misunderstanding, we revised the sentence as "In addition, the East China Sea (including the offshore areas and open ocean) showed sporadic high PSCF signals of GEM in all four seasons (Fig. S1), indicating possible influences from shipping activities." in the revision.

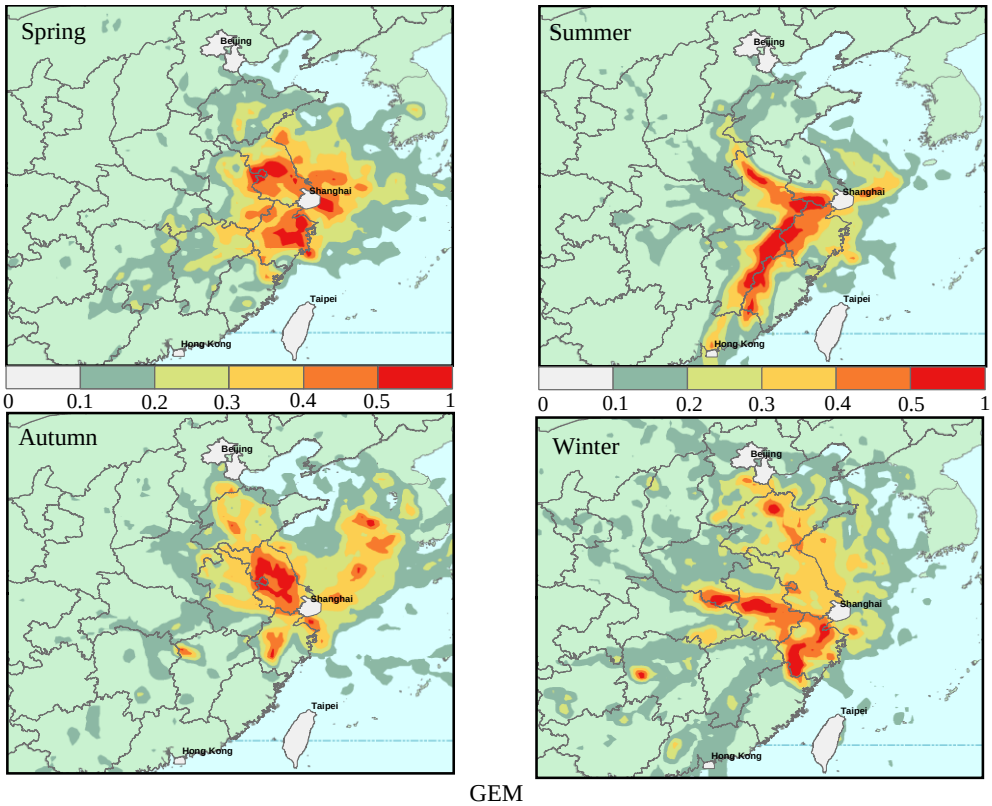


Figure S1. Potential source regions of seasonal GEM at the sampling site according to PSCF analysis.

16. Line 314-315: what I see from Figure 7 is that GOM and GEM share the similar source regions, and what is different is that of PBM.

Response: Thanks for pointing this out. We revised the description as "The PSCF pattern of GOM was as similar as that of GEM but different from that of PBM." in the revision.

17. Line 355-356: relative fraction of wind in south, southwest and west wind directions are similar in the four GOM/PBM groups, and why? Long-rang transport sources are also located in these directions.

Response: Thanks for the comment. We agree with the reviewer that the long-range transport sources could be also derived from the south, southwest and west directions. However, it is generally regarded that the long-range transport extent from the wind directions mentioned above was less than from northern China. Thus, this may explain that the frequency of south, southwest and west wind directions showed no clear trend as the GOM/PBM ratios increased. In this section, we have testified that the GOM/PBM ratio can be used as a quick tracer for identifying the relative importance of long-range transport vs. local sources. However, this is just a qualitative method, but not a quantitative solution for separating different sources. Explicit source apportionment should require chemical transport modeling, however, this is out the scope of this study.

In the revised manuscript, we have added in the end of this paragraph that "In general, the GOM/PBM ratio can be used as a qualitative tracer for identifying the relative importance of long-range transport vs. local sources. However, when the influences from long-range transport and local emission were close, the result could be ambiguous based on this method and this may require further efforts such as chemical transport modeling".

18. Line 359-382: low GEM concentrations were mostly related to high CO and SNA concentrations. Does this support that local-regional emissions are more important? This is contradictory to low GOM/PBM ratios, which indicates a progress of long-range transport.

Response: Thanks for the comments. In Shanghai, when high CO and SNA concentrations occurred, these events were generally related to the impact of long-range transport from northern China, especially in winter, but seldom from local emissions. In this study, GEM showed an increasing trend as the GOM/PBM ratios increased while both CO and SNA decreased. Thus, the low GEM concentrations were mostly related to high CO and SNA concentrations, suggesting the long-range transport from northern China was not the major cause of high GEM concentrations. In Fig. 9 of the manuscript, lower GEM concentrations corresponded to lower GOM/PBM ratios, further corroborating the influence of long-range transport was not crucial on GEM. Hence, there is no contradiction between the results based on different methods.

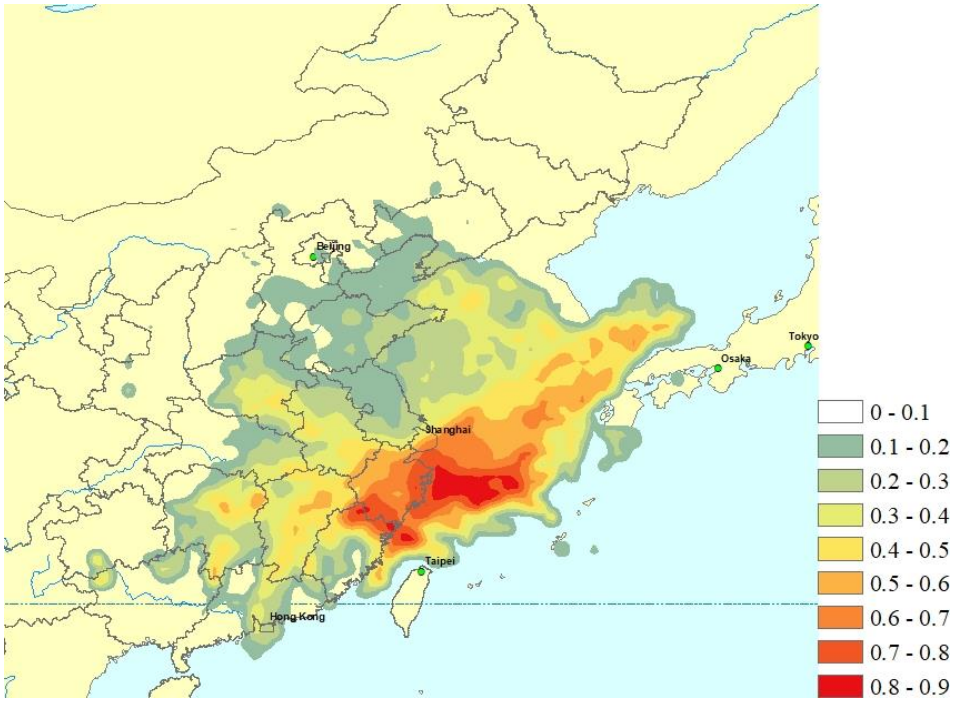
19. Section 3.3.3: why did not apportion the major sources of PBM and GOM?

Response: Thanks for this good suggestion. Actually, we've tried hard to apportion the major sources of PBM and GOM by using PMF. However, we found the results difficult to explain. We think that the possible reasons are that the concentrations of PBM and GOM fluctuated much stronger than other atmospheric species such as soluble ions, organic/elemental carbon, and elements. Due to the relatively short residence time in the atmosphere, it seems not suitable by digesting PBM and GOM into the PMF analysis. Thus, we didn't include source apportionment of PBM and GOM in this study.

20. Line 401-406: factor 2 could be mostly related to oil combustion in motor vehicle in urban areas and shipping emissions over the Dianshan Lake.

Response: Thanks for the comment. In order to determine whether factor 2 represents shipping emissions, the time-series of GEM concentrations from the shipping factor based on the PMF modeling were extracted and digested into the PSCF modeling. The figure below showed the potential sources regions were mainly located over the East China Sea, which indicated factor 2 from PMF should be representative of the shipping sector. At the same time, we recognized oil combustion in motor vehicle and shipping emissions over the Dianshan Lake certainly contributed to Hg pollution, but the existing ships in Dianshan Lake are far from being comparable to that of the adjacent East China Sea, and the proportion of mobile oil combustion is relatively small in YRD (5.34%)(Tang et al., 2018), thus we think that factor 2 should be likely related to ship emission over the offshore and open areas of the East China Sea as well as oil combustion in motor vehicles and inland shipping activities.

In the revised manuscript, we have made clarification about the explanation of factor 2 by PMF modeling.



21. Section 3.4.1: I do not agree variations of GEM and GOM concentration can support a strong conversion of GEM to GOM. Did you observe a strong negative correlation between GEM and GOM concentrations?

Response: Thanks for comments. Strong negative correlation between GEM and GOM concentrations were usually observed at remote and high-altitude sites, where the impact of anthropogenic emissions is weak. As a suburban site located in one of the most industrialized regions of China, it is difficult to see such a strong negative correlation between GEM and GOM as the reviewer mentioned. However, from Figure 11, we can still see that when GEM concentration began to decline from 6:00, the concentrations of GOM continued to rise until it reached the peak value at around 10:00, and the levels of ozone and temperature also kept rising during this period. This phenomenon has been repeatedly observed during the study period, revealing the acceleration of the conversion process of GEM to GOM under favorable atmospheric conditions of higher O_3 concentration and ambient temperature. However, we understand that GOM could be directly emitted from various emission sources and the formation mechanism of GOM is complicated and we are not trying to elucidate it based on limited measured parameters.

In the revised manuscript, we have revised the title of Section 3.4 as "Factors affecting the formation and transformation of mercury species". In the context of this section, we have adjusted the writings to focus on the crucial factors affecting the formation and transformation of mercury species but not the intrinsic mechanisms.

22. 452-469: Figure 12 is meaningless. Anyone could expect a similar trend between GOM concentrations and GOM/PBM ratios.

Response: Thanks for the comments. We do agree with the reviewer that the relationship between GOM concentrations and GOM/PBM ratios could be expected. Actually, Figure 12 more focus on the multi-relationship among GOM, GOM/PBM, O_3, and temperature. We intended to explore some crucial factors affecting the concentrations of GOM such as temperature and the levels of oxidants.

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