

General comments:

The article investigates the increase in ozone levels in Shanghai during city-wide static management measures implemented in April and May 2022 to control the spread of the Omicron variant. Despite significant reductions in VOCs and NO₂ emissions, average ozone levels rose by 23%. The study involves comprehensive observations and statistical analysis of ozone profiles categorized into four clusters based on their characteristics. It highlights the importance of radical chemistry and photochemical processes in understanding the increased ozone levels. The research concludes that Shanghai operates in a VOCs-limited regime, suggesting that controlling VOCs is vital for effective ozone pollution management. I generally agree with the structure of the manuscript and classify my recommendation as minor revision. However, there are several specific and minor points that I recommend the authors address (see below).

Firstly, we would like to express our sincere gratitude for the valuable time and effort you have dedicated to reviewing my manuscript. We have also re-examined the article and identified issues with the processing of photolysis data. Consequently, we have reran the OBM model and conducted a fresh statistical analysis and discussion of the results related to the OBM model (Section 3.3). The latest findings have not fundamentally altered the original conclusions. The responses to your comments that follow are based on these most recent results.

Specific comments:

How were the simulated radical concentrations validated against observed data, especially considering the variations in different urban and non-urban environments?

R: Thanks for your comments. Unfortunately, this study did not conduct simultaneous observations of free radicals, thus direct verification was not possible. However, there are research teams in China that have carried out comparative studies on radicals' observations and simulations.

The earliest observation of OH radicals in China was accomplished through collaborative efforts between Peking University and Forschungszentrum Juelich (FZJ), resulting in the construction of a Laser Induced Fluorescence (LIF) instrument for detecting OH and HO₂. Additionally, the Anhui Institute of Optics and Fine Mechanics (AIOFM) independently developed a Laser Induced Fluorescence (LIF) instrument. Simultaneously, comparisons with model simulations were conducted during the radical observations.

Tan et al. (2017) from Peking University's observations and simulation studies in Wangdu, China, indicate that the simulation of radicals exhibits excellent performance. Zhang et al. (2022a) from AIOFM reported good consistency between observed and simulated values of radicals. Those indicate the feasibility of applying observation-based models in the simulation of photochemical processes. Based on error analysis of models and observations, Lu and Zhang (2010) suggested that the ratio of simulated to measured values for HO_x (OH + HO₂) falling within the range of 0.4-1.6 can be considered acceptable. Applying the chemical box model to dissect photochemical processes is a mature and widely-used approach, currently adopted by teams that lack the capability to conduct radical observations.

Lu et al. (2019) categorized the observed OH radicals into three groups: urban areas, remote

regions (including continents, oceans, polar regions, and the free troposphere), and forested areas. The maximum concentrations of OH radicals observed across different categories all fall within the range of 10^6 to 10^7 molecules cm^{-3} (see Figure R1). In this study, the average peak of OH was around 5.0×10^8 molecules cm^{-3} , which is considered a moderate level in urban environments.

The team from AIOFM conducted continuous observations of radicals at the Shanghai Academy of Environmental Sciences (31.17°N, 121.43°E, urban environment) using their independently developed Laser-Induced Fluorescence (LIF) system from November 8th to November 24th, 2019 (Zhang et al., 2022a). The average concentrations of OH and HO₂ radicals during the midday hours (11:00-13:00) were 2.7×10^6 and 0.8×10^8 molecules cm^{-3} , respectively. We performed OBM simulations for the same period at the site within this study. The simulation results showed average concentrations of OH and HO₂ radicals to be 2.67×10^6 and 0.84×10^8 molecules cm^{-3} , respectively. The diurnal variation trends also demonstrated good consistency. This indirectly indicates that the free radical chemistry simulation results of this study are relatively reliable.

We hope to conduct radical observations in the future through collaborative efforts or independent research, and to conduct comparative studies on radicals in urban and non-urban environments.

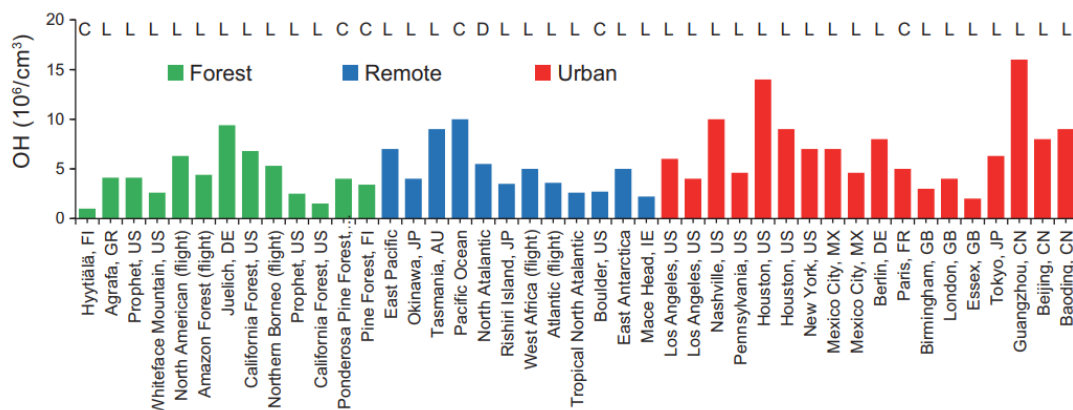


Figure R1. Typical observed daily averaged maximum OH concentrations at distinct different geographical regions (i.e. urban, remote, forest areas) with different measurement techniques (i.e. DOAS, LIF, CIMS, CEAS and CRDS). The figure is sourced from Lu et al. (2019).

The study details various sources and production rates for radicals. If possible, a deeper exploration of how these sources differ in urban settings and their specific impacts on air quality could be insightful.

R: Thanks for your comments. Over the past few decades, understanding the sources and chemical behavior of HO_x has been a focal point in air quality research. Despite the visual similarities in air pollution issues, the chemistry of radicals, particularly the relative importance of the main sources of radicals, varies across different types of regions. Generally, the primary sources of radicals include the photolysis of O₃, HONO, HCHO, and other OVOCs, as well as non-photolytic sources such as the reaction of ozone with alkenes and the reaction of NO₃ with unsaturated VOCs.

Regarding the impact of the sources of radicals in urban environments on air quality, we conducted a correlation analysis between the sources of radicals and ozone-related indices, as shown in Figure R2. The production rates of radicals P(RO_x) had a strong positive correlation with the production rates of ozone P(O₃), and both were temperature-dependent. The higher the temperature, the higher P(O₃) and P(RO_x). Additionally, we defined daily net ozone production

O_3_net as the difference between the highest ozone value at noon and the lowest value in the morning. The correlation analysis between daily O_3_net and the photolysis rates of HONO, O_3 , HCHO, and OVOCs, as well as the total radical source, reveals a significant positive relationship. This implies that the strength of different sources of modeled radicals positively contributes to ozone production. From the perspective of the slopes, the contribution of HCHO photolysis to net ozone generation is evident. This may be attributed to the enhancement of the NO_2 -NO- O_3 cycle by the HO_2 radicals produced from HCHO photolysis.

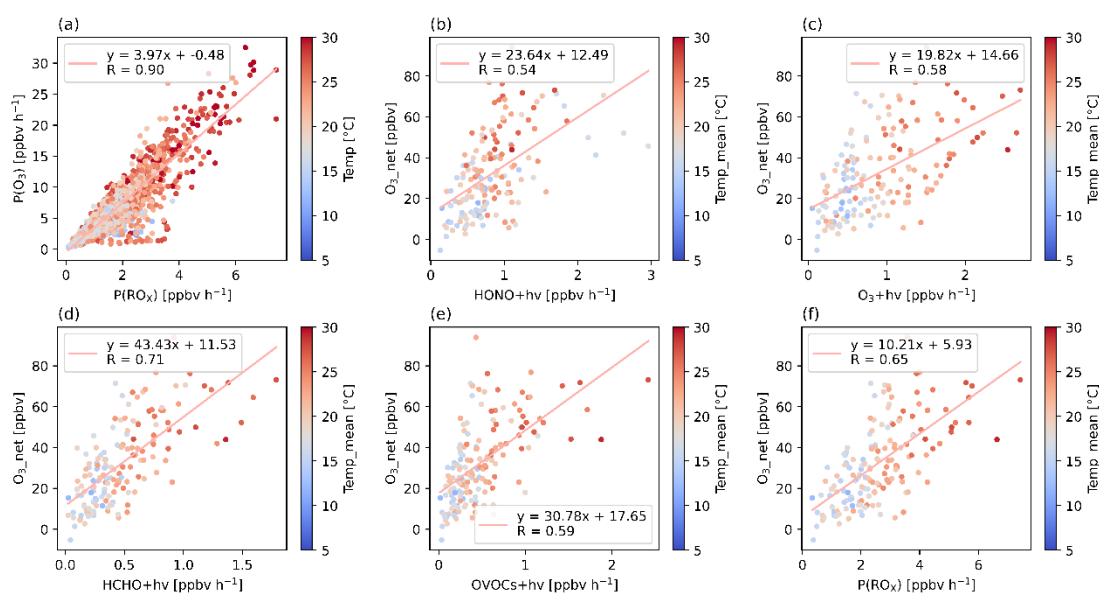


Figure R2. Correlation analysis between the sources of radicals and ozone-related indices, (a) $P(O_3)$ & $P(RO_x)$; (b) O_3_net & HONO+hv; (c) O_3_net & O_3 +hv; (d) O_3_net & HCHO+hv; (e) O_3_net & HONO+hv; (f) O_3_net & $P(RO_x)$.

We have included the above textual and graphical descriptions in the Supplement, please refer to [Text S2](#) and [Figure S15](#). Further explanations can be found in the manuscript on [Lines 310-311](#).

We have also included in the Supplement a review of the radical observation and simulation studies conducted both domestically and internationally, as shown in the following text and table. Please refer to [Text S3](#) and [Table S3](#) in the Supplement.

“We have compiled observations and simulations of radical chemistry conducted by various research teams in different environments (see Table R1). It is evident that the primary sources of radicals vary in different regions and seasons. Compared to marine boundary layer environments, forest environments, and suburban environments, the primary sources of radicals in urban environments were complex. For example, simulation work conducted in urban environments in Nashville, Houston, and Writtle indicates that the photolysis of ozone was a primary contributor to the primary source of radicals (Kovacs et al., 2003; Martinez et al., 2003; Thornton et al., 2002; Mao et al., 2010; Lee et al., 2006; Emmerson et al., 2007; Emmerson and Carslaw, 2009). And in locations like New York, Palaiseau, Shenzhen, the photolysis of HONO played a significant role (Ren et al., 2003a; Ren et al., 2003b; Cai et al., 2008; Dolgorouky et al., 2012; Michoud et al., 2012; Yang et al., 2022). It is noteworthy that within the same urban environment, the dominant sources can vary across different seasons, time periods, and conditions. In Tokyo, the primary sources of free radicals in winter were the reactions between ozone and alkenes, while in summer,

they were the photolysis of ozone and OVOCs (Kanaya et al., 2008; Kanaya et al., 2007a). In New York, during the daytime, the primary source was the photolysis of HONO, while at night, it resulted from the reaction between O₃ and alkenes(Cai et al., 2008; Ren et al., 2006). In Jülich, under high NO_x conditions, the primary source was the photolysis of HONO, whereas under low NO_x conditions, it was the photolysis of O₃ (Kanaya et al., 2012). In marine boundary layer environments, most studies indicated that the photolysis of ozone was the primary contributor to free radicals during the day, while at night, it resulted from the reaction between O₃ and alkenes. In suburban and rural environments, the primary contributor was the photolysis of HONO. Just as you mentioned the differences in radical chemistry between urban and suburban environments, historical research has also indicated this, and it is a crucial aspect of the simulation studies we conducted in Shanghai.”

Table R1. Summary of measurements and model comparisons for OH and HO₂ in different typical environments, as well as OH reactivity and HOx primary sources

campaign	year	location	Technique	OH measured	HO₂ measured	OH reactivity	HOx primary sources	comments	Ref.
Urban environment									
SOS	June-July 1999	Nashville, Tennessee, USA, 36°N, 88°W	LIF	0.8 pptv at noon	80 pptv at noon	11.3±4.8 s ⁻¹	O ₃ +hv	OH observed-to-modeled ratio: 1.33; OH observed-to-modeled ratio: 1.56; the measured OH reactivity is about 1.2 times larger than modeled.	(Thornton et al., 2002; Martinez et al., 2003; Kovacs et al., 2003)
PUMA	June 1999 & January-February 2000	Birmingham, UK, 53°N, 2°W	LIF	(2-9)×10 ⁶ molecule cm ⁻³ in summer, (0.5-4)×10 ⁶ molecule cm ⁻³ in summer,	(1.5-10)×10 ⁸ molecule cm ⁻³ in summer, ~4×10 ⁶ molecule cm ⁻³ in summer,	-	O ₃ +alkenes: 46% in summer, 62% in winter	OH modeled-to-measured ratio: 0.58 in summer and 0.5 in winter; HO ₂ modeled-to-measured ratio: 0.56 in summer and 0.49 in winter.	(Emmerson et al., 2005a; Emmerson et al., 2005b; Heard et al., 2004; Harrison et al., 2006)
TEXAQS	August-September 2000	Houston, Texas, USA, 29°N, 95°W	LIF	Maximum ~0.8 pptv	Maximum ~30 pptv	7-12 s ⁻¹	O ₃ +hv		(Mao et al., 2010)
PMTACS-NY	June-August 2001	New York, USA, 41°N, 74°W	LIF	(2-20)×10 ⁶ molecule cm ⁻³	(0.5-2)×10 ⁸ molecule cm ⁻³	15-25 s ⁻¹	HONO+hv	OH observed-to-modeled ratio: 1.10; HO ₂ observed-to-modeled ratio: 1.24; The OH reactivity measurements agree with the calculations to within 10%	(Cai et al., 2008; Ren et al., 2003b; Ren et al., 2003a)
HOxComp	9-11 July 2005	Julich, Germany (50°54'33"N, 06°24'44"E)	LIF, DOAS, CIMS	Maximum 9.4×10 ⁶ molecule cm ⁻³	Maximum 35 pptv		high-NOx: HONO+hv; low-NOx: O ₃ +hv	Good agreement between model and observations for OH under high isoprene low NOx (fresh isoprene emissions)	(Kanaya et al., 2012)
MCMA	April 2003	Mexico City, Mexico, 19°N, 100°W	LIF	(5-8)×10 ⁶ molecule cm ⁻³	15-60 pptv	25-120 s ⁻¹	HCHO+hv	(OH)model=1.2×(OH)-0.008 pptv R ² =0.80; (HO ₂)model=0.90×(HO ₂)+0.98 pptv R ² =0.64; OH reactivity in the model is about 10-20% too low	(Volkamer et al., 2010; Sheehy et al., 2010; Shirley et al., 2006)
TORCH-1	July-August 2003	Writtle, Essex,	LIF	(1.2-7.5)×10 ⁶ molecule cm ⁻³ , with	(0.16-3.3)×10 ⁸ molecule cm ⁻³ ,	2-10 s ⁻¹	O ₃ +hv	Daytime OH and HO ₂ Overpredicted by 24% and 7%, respectively; nighttime	(Emmerson and Carslaw, 2009);

		UK, 51°N, 0°E			2.6×10^6 molecule cm^{-3} at night	with 2.9×10^7 molecule cm^{-3} at night			OH and HO ₂ unpredicted 41% and 16%, respectively	Emmerson et al., 2007; Lee et al., 2006)
IMPACT IV&L	January-February and July-August 2004	Tokyo, Japan, 35°N, 139°E	LIF		In winter, daytime median was 1.5×10^6 molecule cm^{-3} and night mean was 1.8×10^5 molecule cm^{-3} ; in summer, daytime median was 6.3×10^6 molecule cm^{-3} and night mean was 3.7×10^5 molecule cm^{-3}	In winter, daytime median was 1.1 pptv and night mean was 0.7 pptv; in summer, daytime median was 5.7 pptv and night mean was 2.6 pptv		the day and night in winter: O ₃ +alkenes; in daytime during summer: O ₃ +hv and OVOCs+hv, during the early morning in summer: HONO+hv	Daytime OH well reproduced by model for both periods; daytime HO ₂ underestimated in winter and overestimated in summer.	(Kanaya et al., 2008; Kanaya et al., 2007a)
PMTACS-2	January-February 2004	New York, USA, 41°N, 74°W	LIF		maximum 1.4×10^6 molecule cm^{-3}	maximum 0.7 pptv	20-40 s ⁻¹	Daytime: HONO+hv; Nighttime: O ₃ +alkenes	OH observed to modelled ratio of 0.98; HO ₂ observed to modelled ratio of 6, with the greatest values at high NO; OH reactivity measured higher than calculated at rush hour in the morning and in the evening, possibly due to unmeasured or missing VOCs.	(Cai et al., 2008; Ren et al., 2006)
MILAGRO	March 2006	Mexico City, Mexico, 19°N, 100°W	LIF		maximum median 4.6×10^6 molecule cm^{-3}	maximum median 1.9×10^8 molecule cm^{-3}		HCHO+hv	OH overpredicted by a factor of 1.7 at midday, well reproduced after 14:30; HO ₂ underpredicted in the morning, well reproduced after 11:30	(Dusanter et al., 2009b; Dusanter et al., 2009a)
TRAMP	August-September 2006	Houston, Texas, USA, 29°N, 95°W	LIF		Daytime: 0.33 ± 0.23 pptv; Nighttime: 0.087 ± 0.066 pptv	Daytime: 22 ± 18 pptv; Nighttime: 11 ± 7.8 pptv	10-20 s ⁻¹	morning rush hour: HONO+hv; daytime: O ₃ +hv; nighttime: O ₃ +alkenes	the measured OH was generally greater than the modeled OH for all mechanisms, especially during the afternoon; For HO ₂ , Good agreement was found in the morning for the models with most mechanisms, except for SAPRC-99 (slope=0.67); This good agreement between measured and calculated OH reactivity	(Chen et al., 2010; Mao et al., 2010)
MEGAPOLI	July 2009	Palaiseau, French 48.71°N, 2.21°E	LIF		$\sim 5 \times 10^6$ molecule cm^{-3}	$\sim 1.2 \times 10^8$ molecule cm^{-3}		HONO+hv	Photo Stationary State calculations overestimate OH by 50 %, box model overestimated 12% and 5 %, for OH and (HO ₂ +RO ₂) respectively.	(Michoud et al., 2012; Dolgorouky et al., 2012)

STORM	September-October 2018	Peking University Shenzhen Graduate School, Shenzhen, China	22.60°N, 113.97°E	LIF	maximum of 4.5×10^6 molecule cm^{-3}	Maximum of 4.2×10^8 molecule cm^{-3}	18-22 s^{-1}	HONO+hv	Good agreement between the observed and modeled kOH during the several days in Shenzhen	(Yang et al., 2022)
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Marine boundary environment

EASE97	April-May 1997	Mace Head, Ireland, 10°W	53°N,	LIF	$(2.0-6.0) \times 10^6$ molecule cm^{-3}	$(0.5-3.5) \times 10^8$ molecule cm^{-3}		O_3+hv	average model-measurement ratios were 2.4 for OH, 3.6 for HO_2 between 11:00 and 15:00.	(Creasey et al., 2002; Carslaw et al., 2002)
OKIPEX	July-August 1998	Okidogobari Island, Japan, 133°E	36°N,	LIF	Below the detection limit of the instrument (0.8 pptv)	Maximum of 17 pptv		O_3+hv	Model usually overestimated HO_2 by a factor of 2	(Kanaya et al., 2000; Kanaya and Akimoto, 2002)
ORION99	August 1999	Cape Okinawa, Japan, 128°E	Hedo Island, 27°N,	LIF	Maximum of 4×10^6 molecule cm^{-3}	Daytime: maximum of 17 pptv; nighttime: 0.5-5.5 pptv		O_3+hv	OH was underestimated by model calculations but within a large uncertainty; Model underestimated daytime HO_2 by only 20%	(Kanaya et al., 2001b; Kanaya et al., 2001a; Kanaya et al., 2002a)
SOAPEX-2	January-February 1999	Cape Grim, Tasmania, 142°E	41°S,	LIF	Maximum of 3.5×10^6 molecule cm^{-3}	Maximum of 2×10^8 molecule cm^{-3}		O_3+hv	Models overestimated OH by 10%-20%; Models overestimated HO_2 by ~40%;	(Sommariva et al., 2004; Creasey et al., 2003)
RISOTTO	June 2000	Rishiri Island, Japan, 141°E	45°N,	LIF		~10 pptv at midday; mean of 4.2 ± 1.2 pptv at night		Nighttime: $\text{O}_3+\text{alkenes}$	OH overestimated by ~36%; HO_2 overestimated by ~70%, requiring 25 pptv IO to reconcile model with observations	(Kanaya et al., 2002c; Kanaya et al., 2002b)
RISFEX	September 2003	Rishiri Island, Japan, 141.12°E	45.07°N,	LIF	Daytime: maximum of 2.7×10^6 molecule cm^{-3} ; Nighttime: $(0.07-0.55) \times 10^6$ molecule cm^{-3}	Daytime: maximum of 5.9 pptv; Nighttime: (0.5-4.9) pptv		Daytime: O_3+hv ; Nighttime: $\text{O}_3+\text{alkenes}$	OH overestimated by 35%; HO_2 overestimated by 89%; median nighttime modeled-to-observed ratios were 1.29 and 0.56 for HO_2 and OH, respectively	(Kanaya et al., 2007b; Qi et al., 2007)
RHaMBLe	May-June 2007	Cape Verde, Atlantic Ocean, 24.87°W	16.85°N,	LIF	Maximum of 9×10^6 molecule cm^{-3}	Daytime: maximum of 6×10^8 molecule cm^{-3} ; Nighttime: ~0.6 pptv		Daytime: O_3+hv ; Nighttime: $\text{O}_3+\text{alkenes}$	under-predicted OH on average by 18%; under-predicted HO_2 by 39%	(Lee et al., 2010; Whalley et al., 2010)
SOS	February-March; June;	Cape Verde, Atlantic Ocean,		LIF	Maximum of $\sim 9 \times 10^6$ molecule cm^{-3}	maximum of 4×10^8 molecule cm^{-3}		O_3+hv	Concentrations in summer (June,	(Carpenter et al., 2010; Vaughan et

	September 2009	17°N, 25°W		molecule cm ⁻³	cm ⁻³ , ~10 ⁷ molecule cm ⁻³ at night			September) almost double those observed in winter (Feb, March)	al., 2012)
Forest environment									
AEROBIC	July-August 1997	Indigenous forest, North West Greece, 40°N, 21°E	LIF	(4-12)×10 ⁶ molecule cm ⁻³	(0.4-9)×10 ⁸ molecule cm ⁻³		O ₃ +hv	Model underprediction of OH by ~50%. Modelled HO ₂ was typically higher than observations. But observations showed high variability	(Creasey et al., 2001; Carslaw et al., 2001)
PROPHET-98	August 1998	Deciduous forest, North Michigan, USA, 45.6°N, 84.7°W	LIF	Daytime: 0.1-0.2 pptv; Nighttime: 0.04 pptv	Daytime: 10-25 pptv; Nighttime: 1-4 pptv		O ₃ +alkenes	OH observations 2.7 times greater than the model; HO ₂ observations and model in good agreement	(Faloona et al., 2001; Tan et al., 2001)
GABRIEL	October 2005	Suriname, South America	LIF	0.25 pptv	~(50-55) pptv		O ₃ +hv	Observed to modelled ratio of 12.2 for OH and 4.1 for HO ₂	(Kubistin et al., 2010; Butler et al., 2008; Lelieveld et al., 2008; Martinez et al., 2010)
OP3	April and July 2008	Sabah, Borneo, 5°N, 118°E	LIF	2.5×10 ⁶ molecule cm ⁻³	2×10 ⁸ molecule cm ⁻³	10-60 s ⁻¹	O ₃ +hv	Factor of 10 underprediction in OH when model constrained to OH reactivity. HO ₂ overpredicted at ground level	(Whalley et al., 2011; Stone et al., 2011; Pugh et al., 2010)
HUMPPA-COPEC-2010	July and August 2010	boreal forest in Hyytiälä, southern Finland 61.9°N, 24.3°E	LIF, CIMS	3.5×10 ⁶ molecule cm ⁻³	37 pptv	12.4 s ⁻¹	O ₃ +hv	OH _{LIF} /OH _{CIMS} = (1.31 ± 0.14); OH _{mod} /OH _{obs} = 1.00 ± 0.16; HO ₂ ^{mod} /HO ₂ ^{obs} = 0.3 ± 0.2; simulated OH reactivity does not match the observed OH reactivity	(Hens et al., 2014; Nölscher et al., 2012)
Suburban & rural environments									
CAREBeijing-2006	August- early September 2006	Suburban rural site, Beijing, China, 39.61°N, 116.30°E	LIF	(4-17)×10 ⁶ molecule cm ⁻³	(2-24)×10 ⁸ molecule cm ⁻³	10-30 s ⁻¹	HCHO+hv	A large discrepancy of a factor 2.6 is found at the lowest NO concentration encountered (0.1 ppb)	(Lu et al., 2010)
PRIDE-PRD	autumn 2014	Guangdong Atmospheric	LIF	maximum median of 4.5×10 ⁶ molecule cm ⁻³	maximum median of	22-32 s ⁻¹	HONO+hv	50 % was unexplained by the measured	(Tan et al., 2019)

2014		Supersite, China 22.73°N, 112.93°E		³	3×10^8 molecule cm^{-3}				OH reactants	
	June 2014	Wangdu, China	LIF	$(5-15) \times 10^6$ molecule cm^{-3}	$(3.14) \times 10^8$ molecule cm^{-3}	10-20 s^{-1}	HONO+hv	Model-measurement ratio was between 1.4 and 2; For HO ₂ , good agreement between modeled and observed concentrations during day and night	(Fuchs et al., 2017; Tan et al., 2017)	
BEST-ONE	January- March 2016	suburban site Huairou, Beijing, China 40.41°N, 116.68°E	LIF	2.4×10^6 molecule cm^{-3} in severely polluted air; 3.6×10^6 molecule cm^{-3} in relatively clean air	0.52×10^8 molecule cm^{-3} in severely polluted air; 0.93×10^8 molecule cm^{-3} in relatively clean air	26.9 s^{-1} in severely polluted air; 10.1 in relatively clean air	HONO+hv	OH and HO ₂ observed to modelled ratio of 1.5 during clean days; underestimated HO ₂ concentrations by factors up to 5 during pollution episodes	(Tan et al., 2018)	
CHOOSE-2019	August- September 2019	Xinjin, Chengdu, China 30.40°N, 103.85°E	LIF	Mean of 9.5×10^6 molecule cm^{-3}	Mean of 9×10^8 molecule cm^{-3}		HONO+hv	OH observed to modelled ratio of 0.8, HO ₂ observed to modelled ratio of 1.0	(Yang et al., 2021; Zhang et al., 2022b)	

The study relates different ozone profile clusters to radical chemistry variations. Further analysis of how these clusters specifically influence overall ozone levels and atmospheric chemistry would be beneficial.

R: Thanks for your comments.

Firstly, cluster analysis reveals that the ozone profiles in the Shanghai region can be classified into four clusters, each characterized by: Cluster 1 with low background concentration and low net production; Cluster 2 with low background concentration and high net production; Cluster 3 with high background concentration and low net production; and Cluster 4 with high background concentration and high net production, as shown in Table R2.

The common characteristic of Cluster 1 and Cluster 2 is a lower baseline value of ozone, primarily because a significant amount of ozone was titrated and consumed from nighttime to early morning. As depicted in Figure 5 of the manuscript, the NO_2 levels for Cluster 1 and Cluster 2 were significantly higher during the night or early morning peaks, indicating the crucial role of titration. Due to a significant reduction in NO_x emissions during the static management period in 2022, the total number of days for Cluster 1 and Cluster 2 decreased from 37 days in 2020 and 40 days in 2021 to 11 days in 2022.

The common characteristic of Cluster 2 and Cluster 4 is a higher daytime net ozone production. This is attributed not only to meteorological conditions favorable for photochemical processes, characterized by high temperatures, low relative humidity, and high radiation but also to the contribution of elevated VOCs concentrations during the early morning peak, which got consumed in the ozone production process. As clearly shown in Figure 5 of the manuscript, the VOC levels during the early morning peak for Cluster 2 and Cluster 4 were significantly higher than those for Cluster 1 and Cluster 3, contributing to the higher daytime net ozone production. Due to a reduction in VOCs emissions during the static management period in 2022, the total number of days for Cluster 2 and Cluster 4 decreased from 28 days in 2020 and 25 days in 2021 to 20 days in 2022. However, the number of days for Cluster 4 increased from 4 days in 2020 and 2021 to 16 days in 2022, as the reduction in NO_x emissions in 2022 led to an increase in the number of days with elevated ozone baseline levels.

Overall, the change in the number of days for the four ozone diurnal profiles is influenced by the differential reduction in precursor VOCs and NO_x levels. The number of days with higher ozone concentrations for Cluster 3 and Cluster 4 significantly increased in 2022. This directly resulted in an overall elevation of ozone levels during the silent management period in 2022 compared to the same period in 2020 and 2021.

In the radical cycling $\text{OH-RO}_2\text{-RO-HO}_2\text{-OH}$, the OH radical initiates a series of subsequent reactions, and RO_2 and HO_2 are the primary precursors for ozone formation in the presence of NO_x . The cycle is terminated through reactions with NO_x under high NO_x conditions and cross-reactions with RO_x under low NO_x conditions. We compiled the daytime average concentrations of radicals, sources of radicals, OH propagation and termination, as well as ozone production rates for Cluster 1-4 (see table R2). The concentrations and sources of radicals for Cluster 1-4 have been previously discussed in the manuscript. In summary, both the concentration and source strength of radicals were highest in Cluster 4, followed by relatively comparable levels in Cluster

2 and Cluster 3 as secondary, while Cluster 1 had the lowest levels. In the radical cycling, due to the increased consumption of VOCs, the OH propagation in Cluster 2 and Cluster 4 is significantly higher than in Cluster 1 and Cluster 3. Meanwhile, the low nitrogen oxide concentrations in Cluster 3 and Cluster 4 weaken the OH termination. This directly reflects that the ratio of OH propagation to termination in Cluster 4 was considerably higher, indicating a more efficient radical cycle. This higher efficiency allows for significant net ozone generation even in the presence of elevated baseline ozone levels.

We have included the relevant description in the manuscript; please refer to [Lines 310-315](#) in the track-changes manuscript.

Table R2. The ozone concentration (ppbv) characteristics, the average daytime radicals concentration (molecules cm⁻³), and the average reaction rates of the main processes for Cluster 1-Cluster 4.

	Cluster 1	Cluster 2	Cluster 3	Cluster 4
O ₃ background	22.4	16.9	40.6	33.3
O ₃ net production	14.8	45.9	17.5	50.9
OH concentration	1.4×10 ⁶	3.3×10 ⁶	3.1×10 ⁶	3.9×10 ⁶
HO ₂ concentration	0.6×10 ⁸	1.5×10 ⁸	1.9×10 ⁸	3.5×10 ⁸
RO ₂ concentration	0.3×10 ⁸	0.8×10 ⁸	0.9×10 ⁸	2.2×10 ⁸
P(RO _x)	0.92	2.09	1.35	2.23
OH propagation (OH+VOCs)	0.68	1.75	1.16	2.03
OH termination (OH+NO ₂)	0.63	1.14	0.69	0.88
propagation/termination	1.08	1.54	1.69	2.29
P(O ₃)	3.12	7.73	5.24	8.20

The dominance of radical cycling in polluted environments raises questions about its specific role in ozone formation and the potential for targeted interventions in such environments.

R: Thanks for your comments. As mentioned in the response to specific comments, an inappropriate ratio of NO_x to VOCs concentrations can enhance the radical cycle, leading to substantial ozone generation within the cycling. The current mainstream perspective on ozone control emphasizes the need to establish a scientific VOCs/NO_x emission reduction ratio, aiming to weaken the intensity of the radical cycling. This study suggests that reducing NO₂ by about 50% and VOCs by 30% in Shanghai would enhance the radical cycling, leading to an increase in ozone levels.

The spatial distribution characteristics of O₃ generation sensitivity exhibit both similarities and differences across different regions. Urban sites in the Beijing-Tianjin-Hebei and surrounding areas, the Yangtze River Delta, the Pearl River Delta, and other regions show consistent O₃ generation sensitivity, predominantly falling within the VOC control regime. (Wang et al., 2022; Wang et al., 2020a; Lyu et al., 2019; Yu et al., 2020; Wang et al., 2023). However, there are variations in the sensitivity of suburban sites. Suburban sites in the Yangtze River Delta (An et al., 2015; Xu et al., 2017; Zhao et al., 2020), Pearl River Delta (Wang et al., 2017), and Chengdu-Chongqing region (such as Chongqing) (Su et al., 2018) are mainly situated in the VOC control

regime. In contrast, suburban sites in the Beijing-Tianjin-Hebei and surrounding areas (Lu et al., 2010; Ran et al., 2011), the middle and lower reaches of the Yangtze River (such as Wuhan) (Zhu et al., 2020a), and the northwest region (such as Lanzhou) (Xue et al., 2014) are primarily located in the NO_x control regime or NO_x-VOC mixed control regime. The above emphasize that most areas in my country are still in a high NO_x environment and VOCs play an extremely important role in the O₃ production process (especially O₃ production in urban areas). At this stage, it is still necessary to implement scientific VOCs/NO_x collaborative emission reduction measures to weaken the radical cycling. Identifying and controlling key reactive VOC species in O₃ generation are essential for effectively mitigating O₃ pollution.

Minor comments:

Line 17: The statement that "the average ozone level increased by nearly 23%" lacks specific context. What does "nearly 23%" represent in terms of absolute concentrations, and how does it compare to historical averages or expected levels under similar conditions?

R: Thanks for your comments. The comparisons made here are between the static management period of 2022 and the same periods in 2020 and 2021. Therefore, the statement " the average ozone level increased by nearly 23%" refers to the average ozone concentration during the static management period of 2022 being approximately 23% higher than the same period in 2020 and 2021. We have added "Compared to 2020 and 2021" at the end of the sentence. Please refer to [Line 17](#).

Line 39: The phrase "in those countries like China that face air pollution complex" could be better structured for clarity. Consider rephrasing to "in countries like China that face complex air pollution issues."

R: Thanks for your suggestion. We have modified it according to your opinions. Please refer to [Line 40](#).

Lines 40-48: The comparison with the lockdown measures in early 2020 is useful. Could the paper elaborate on how the findings from 2020 influenced the hypotheses or research methods for the 2022 study?

R: Thanks for your suggestion. This paragraph has been reorganized and revised as follows, and please refer to [Lines 45-53](#).

"Prior to this, China had implemented a series of nationwide lockdown measures against the occurrence and spread of the virus in early 2020. This reduction in human activity is expected to significantly reduce air pollutant emissions, as confirmed by lots of studies on lockdown in 2020 (Bao and Zhang, 2020; Huang et al., 2021; Li et al., 2021; Liu et al., 2020; Tian et al., 2021; Wang et al., 2021; Zhang et al., 2022c). Reports on the impact of the lockdown on air quality most commonly focus on measuring nitrogen dioxide (NO₂) and fine particulate matter (PM_{2.5}) (Agarwal et al., 2020; Hua et al., 2021; Chu et al., 2021). According to satellite data, tropospheric nitrogen oxides (NO_x) emissions have decreased by 30-60% compared to pre-lockdown levels (Feng et al., 2020; Ding et al., 2020; Venter et al., 2020). Similarly, surface PM_{2.5} levels in northern China have also decreased by approximately 35%. Meanwhile, the average O₃ concentration has increased 1.5-2 times (Shi and Brasseur, 2020). In Wuhan, the urban area that

implemented stringent measures to limit the spread of the coronavirus, concentrations of $PM_{2.5}$, NO_2 , and ozone also exhibited similar changes (Shi and Brasseur, 2020). Most studies attribute the decrease in NO_2 and $PM_{2.5}$ to the suspension of transportation and industrial activities (Rana et al., 2021; Wang et al., 2020b). Huang et al. (2021) suggest that increase in O_3 enhances atmospheric oxidation capacity, providing favorable conditions for the formation of secondary particulate matter. Due to the lockdown taking place during winter, which is a season of high particulate matter pollution in China, the reports on the impact of the lockdown on air quality have focused more on the changes in particulate matter. The lockdown in Shanghai in 2022 was implemented in April and May during the high-ozone (O_3) season and lasted for a longer duration, providing an opportunity to study atmospheric pollution primarily caused by O_3 .”

Line 52: Ensure consistent use of punctuation, especially with regard to commas and periods. Should be “During the static management...”? Please briefly describe the definition of static management to make it clear.

R: Thanks for your suggestion. We have modified it. Please refer to **Line 59**. The static management is an epidemic prevention and control measure. Specifically, it means that individuals are prohibited from leaving their homes within the controlled area, residents within the controlled zone are prohibited from leaving their residential units, participation in nucleic acid sampling is restricted to in-and-out, and all citizens are required to stay indoors, avoid going out, and refrain from visiting public places unless absolutely necessary.

In **Lines 32 and 33** of the manuscript, it has been explained that the Chinese government, to curb the spread of the virus, implemented control measures citywide static management in Shanghai.

Line 70: Were the experimental conditions and methodologies consistent across the different years (2020, 2021, and 2022) to ensure comparability of the data?

R: Thanks for your suggestion. Yes, the experimental conditions and methods in 2020, 2021 and 2022 are consistent, and the data are comparable.

Line 82: There seems to be a typo in the coordinates for the Yangpu environment monitoring station ($31.53^\circ N$, $31.25^\circ E$). The longitude seems incorrect.

R: Thanks for your correction. The correct latitude and longitude information is $31.25^\circ N$, $121.53^\circ E$. We have made the correction. Please refer to **Line 90**.

Lines 107-111: The text is clear but might benefit from a brief explanation of why the stacking model is preferred over simple linear interpolation.

R: Thanks for your suggestion. Because if more than half of the hourly data is missing in a day, linear interpolation would obscure the true diurnal variation characteristics. The stacking model, however, can relatively accurately simulate the missing values.

Line 153: The methodology for classifying the 103 VOCs into six categories, including how each category specifically influences ozone formation, requires clarification. How does the classification relate to their respective roles in ozone formation? For example, the study notes a significant reduction in aromatics and a relative stability in OVOCs. What are the implications of these changes for ozone formation, considering their different sources and chemical behaviors?

R: Thanks for your comments. VOCs components are classified according to functional groups. We have modified this sentence to: “We classified the 103 VOCs into six categories based on functional groups, including alkanes, alkenes, alkynes, aromatics, oxygenated VOCs (OVOCs), and halohydrocarbons”. Please refer to [Line 162](#). We have added an analysis of the role of VOCs in ozone formation in the Supplement, as described in the following text and Figure R3. Please refer to [Text S4](#) and [Figure S11](#) in the supplement.

“Different VOC species display a range of reactivity and diverse potentials for O₃ formation, which can be assessed using the maximum incremental reactivity (Carter, 2009). The calculated ozone formation potential (OFP) for each VOC species illustrates the maximum contribution of the species to the formation of ozone. (Bufalini and Dodge, 1983). The OFP for each VOC species is calculated using the following equation (Ma et al., 2019; Zhu et al., 2020b):

$$OFP_i = MIR_i \times [VOC_i] \times \frac{M_i}{M_{ozone}} \quad R1$$

where OFP_i (ppbv) represents the ozone formation potential of VOC species i , $[VOC_i]$ (ppbv) denotes the atmospheric concentration of VOC species i , and MIR_i (g O₃/g VOC) is the ozone formation coefficient of VOC_i in the maximum increment reactions of ozone. M_{ozone} and M_i are the molar masses (g mol⁻¹) of O₃ and VOC species i , respectively.

In addition, another widely used indicator of atmospheric oxidative capacity is the OH reactivity, defined as the reaction rate coefficient multiplied by the concentration of OH reactants, depending on the abundance and composition of major pollutants. The OBM model can output the kOH for each VOCs, which reflects the reactivity of VOCs.

The comparison of the mean concentration of the six VOCs groups and their OFP in 2020, 2021, and 2022 is presented in Figure R3. It is obvious that the concentration of the VOC group was not proportional to its OFP. The average proportions of each VOCs component in 2020 and 2021 are 47.2%, 6.7%, 9.2%, 4.8%, 13.8% and 18.4% respectively, while the corresponding average proportions of OFP are 19.6%, 24.0%, 40.4%, 1.1%, 14.1% and 0.9%, respectively. In 2022, with minimal changes in the concentration proportions of alkenes, the OFP proportion increased by 11.3%. The proportion of aromatic hydrocarbons decreased by 4.2%, resulting in a 23.7% decrease in their OFP proportion. The proportion of OVOCs increased by 3.7%, leading to an 8.5% increase in their OFP proportion. In short, the primary contributors to OFP in 2020 and 2021 were aromatic hydrocarbons, followed by alkenes, while in 2022, the main contributors were alkenes, followed by OVOCs.

We combined two indicators, OFP and kOH, to identify key VOCs in photochemical processes. Figure R3b clearly shows a significant positive correlation between the OFP and kOH for each VOC after logarithmic transformation. Therefore, VOCs that rank high in both indicators are sufficient to indicate that these VOCs are key contributors in photochemical processes. In 2020 and 2021, m/p-xylene, toluene, ethylene, and propylene were the top contributors to both OFP and kOH. However, in 2022, propylene and ethylene took the lead in OFP, while propylene, isoprene, and ethylene topped the kOH.”

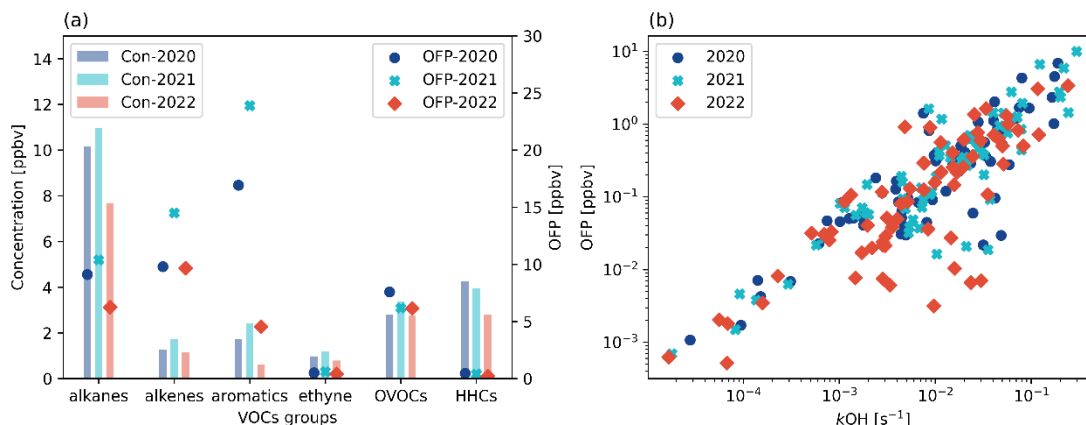


Figure R3. (a) The mean concentration and OFP of six VOC groups and (b) Scatter plots of the average OFP and OH reactivity for individual VOCs during daytime hours between 06:00 and 18:00 for the periods of April to May in 2020, 2021, and 2022.

Line 171: The observed delay in the peak time of VOCs in 2022 compared to 2020 and 2021 is attributed to reduced human activities. Can the study provide further evidence or analysis to support this correlation? For example, have VOC patterns changed again and peaked at around 6 am since recovering from the pandemic?

R: Thanks for your comments. The diurnal variation profiles of VOCs in June 2023 clearly illustrate a shift in the diurnal pattern of VOCs since the recovery from the pandemic, with peaks occurring around 06:00 (see Figure R4a). Additionally, a comparison between the weekday and weekend diurnal profiles in June 2023 confirms historical research, as Cai et al. (2010) suggested, that the diurnal variation of VOCs in the Shanghai area exhibits a distinct weekend effect (see Figure R4b).

We have included an analysis of this section in the Supplement, as referenced by [Figure S12](#). Additionally, the manuscript has been updated to respond to this analysis; please refer to [Lines 182-183](#).

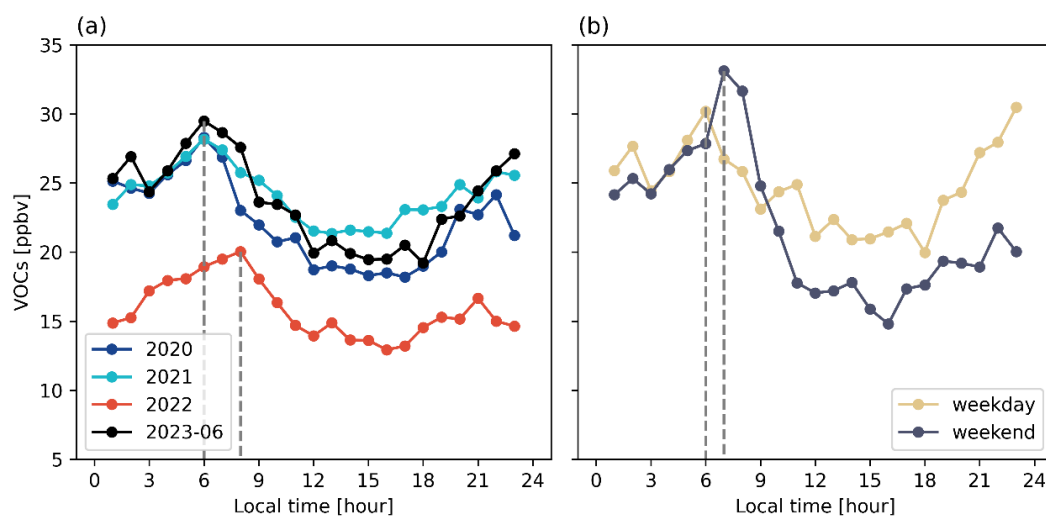


Figure R4. (a) The mean diurnal profiles of VOCs for the periods of April to May in 2020, 2021, and 2022, as well as June 2023. (b) The mean diurnal profiles of VOCs for weekdays and weekends in June 2023.

Line 200: The relationship between meteorological conditions, pollution environments, and different types of ozone profiles warrants further exploration. How do these factors interact to form the distinct ozone profile clusters? Recent references (e.g., <https://doi.org/10.5194/acp-18-1185-2018>) also suggest that night-time O₃ tends to increase for some cities, would this affect the results?

R: Thanks for your comments. In the response to Specific Comments 3, the characteristics of the four ozone profiles and how precursor species NO₂ and VOCs influence ozone profiles were summarized. For meteorological conditions, Cluster 2 and Cluster 4 were in environments typical for photochemical processes with high temperature, low RH, and high radiation. This aligns with their corresponding ozone profile features. Cluster 3 experienced low temperature and low RH conditions, while Cluster 1 is characterized by low temperature, low RH, and low radiation, representing conditions typically unfavorable for ozone formation.

You mentioned Yan et al. (2018)'s study, where nighttime ozone concentrations showed an increasing trend in some cities. However, in this study, we compared data for the same months over three consecutive years. The variations in meteorological conditions over these three years, as detailed in the Supplement (see [Figures S7-S10](#)), were not particularly pronounced. The primary influencing factor was the reduction in pollutant emissions.

Line 221: The phrase "Reviewing previously observational results" should be "Reviewing previous observational results."

R: Thanks for your suggestion. We have modified it according to your opinions. Please refer to [Line 241](#).

Line 248: The phrase "which has" would be more grammatically correct as "which had."

R: Thanks for your suggestion. We have modified it according to your opinions. Please refer to [Line 269](#).

Line 253: A typo here, "sources" should be corrected to "sources."

R: Thanks for your suggestion. We have modified it according to your opinions. Please refer to [Line 276](#).

Line 284: The word "taked" should be corrected to "took." The sentence provides a breakdown of sources in Cluster 4.

R: Thanks for your suggestion. We have modified it according to your opinions. Please refer to [Line 307](#).

Line 313: The phrase "It can be interfered" should be "It can be inferred."

R: Thanks for your suggestion. We have modified it according to your opinions. Please refer to [Line 342](#).

Line 322: The phrase "which provides a valuable opportunity" is correct but could be more concise. Suggested revision: "providing a valuable opportunity."

R: Thanks for your suggestion. We have modified it according to your opinions. Please refer to

Line 351.

Line 323: The verb "shows" should be "show" to agree with the plural subject "observations."
Remove the comma after "shows that."

R: Thanks for your suggestion. We have modified it according to your opinions. Please refer to **Line 352.**

Line 329: The phrase "resulted in the overall increase in the average ozone level" could be more concise. Suggested revision: "led to an overall increase in average ozone levels."

R: Thanks for your suggestion. We have modified it according to your opinions. Please refer to **Line 358.**

Line 336-337: Consider rephrasing for clarity: "The different proportions of NO₂ and VOC reduction during static management led to an increased OH radical propagation (OH+VOCs) to termination (OH+NO₂) ratio, reaching 2.10, higher than 1.03 in 2020 and 1.60 in 2021."

R: Thanks for your suggestion. We have modified it according to your opinions. Please refer to **Line 366.**

Line 339: Consider rephrasing for clarity: "The important lesson from the static management 'large-scale field experiment' is that Shanghai operates in a VOCs-limited regime."

R: Thanks for your suggestion. We have modified it according to your opinions. Please refer to **Lines 368-369.**

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