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To cite this article: Paolo Cristofanelli et al 2021 Environ. Res. Lett. 16 074029

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RECEIVED 16 March 2021

REVISED 8 June 2021

ACCEPTED FOR PUBLICATION 15 June 2021

published 2 July 2021

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Negative ozone anomalies at a high mountain site in northern

Italy during 2020: a possible role of COVID-19 lockdowns?

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Keywords: COVID-19, ozone, air mass transport, mitigation, Europe, Po basin Supplementary material for this article is available online

Abstract

Several studies investigated the possible impacts of the restriction measures related to the containment of the spread of the COrona VIrus Disease (COVID-19) to atmospheric ozone (O₃) at global, regional, and local scales during 2020. O_3 is a secondary pollutant with adverse effects on population health and ecosystems and with negative impacts on climate, acting as greenhouse gas. Most of these studies focused on spring 2020 (i.e. March-May) and on observations in the planetary boundary layer (PBL), mostly in the vicinity of urban agglomerates. Here, we analyzed the variability of O₃ above the PBL of northern Italy in 2020 by using continuous observations carried out at a high mountain WMO/GAW global station in Italy (Mt. Cimone–CMN; 44°12' N, $10^{\circ}42'$ E, 2165 m a.s.l.). Low O₃ monthly anomalies were observed during spring (MAM) and summer (JJA), when periods of low O_3 intertwined with periods with higher O_3 , within climatological ranges. A similar variability was observed for O₃ precursors like NO₂ and 15 anthropogenic non-methane volatile organic carbons, but the systematic O₃ anomalies were not reflected in these variables. The analysis of meteorological variables and diel O₃ cycles did not suggest major changes in the vertical transport related to the thermal circulation system in the mountain area. The analysis of five days back-trajectories suggested that the observed O3 anomalies cannot be explained by differences in the synoptic-scale circulation with respect to the previous years alone. On the other hand, the characterization of two transport patterns (i.e. air masses from the regional PBL or from the free troposphere) and the analysis of back-trajectories suggested an important contribution of transport from the continental PBL during the periods with the lowest O_3 at CMN. When proxies of air mass transport from the regional PBL are considered, a lower NO_x content was pointed out with respect to the previous years, suggesting a lower O_3 production in a NO_x -limited atmosphere. Our study suggested for the first time that, during MAM and JJA 2020, the reduced anthropogenic emissions related to the COVID-19 restrictions lowered the amount of this short-lived climate forcer/pollutant at remote locations above the PBL over northern Italy. This work suggests the importance of limiting anthropogenic precursor emissions for decreasing the O₃ amount at remote locations and in upper atmospheric layers.

1. Introduction

Several studies investigated the possible impacts of the restriction measures related to the containment of the spread of the COrona VIrus Disease (COVID-19) to atmospheric composition at global, regional, and local scales (see, e.g. Gkatzelis *et al* 2021). A large fraction of these studies was focused on the analysis of evidence related to *in-situ* observations occurring at the Earth's surface (e.g. Chen *et al* 2020, Collivignarelli *et al* 2020, Lee *et al* 2020, Shi and Brasseur 2020, Sicard *et al* 2020, Siciliano *et al* 2020) or on satellite observations representative of the whole tropospheric column (e.g. Bauwens *et al* 2020, Elshorbany *et al* 2020, Le *et al* 2020). Other studies involved analyses of model outputs (e.g. Menut *et al* 2020, Weber *et al* 2020).

The emergence of the COVID-19 was first observed in late December 2019 in China, and the World Health Organization declared it as a pandemic disease on 11 March 2020 (Cucinotta and Vanelli 2020). Several countries have implemented stringent measures to isolate cases and limit the spread of the virus. The first country to adopt such strategies was China on 23 January 2020, while Italy was the first western country to enter a lockdown (i.e. closing of schools and non-essential activities, adopting transportation limitations) on 10 March. It was followed by Spain and France, and then several measures were also adopted in other European countries.

Globally, the sector most directly impacted by the measures in response to the COVID-19 outbreak was private transportation (Kroll et al 2020, le Quéré et al 2020). This would imply a strong reduction of a suite of air pollutants (e.g. nitrogen oxides (NO and NO₂), carbon monoxide (CO), non-methane volatile organic carbons (NM-VOCs)), which affect the variability of ozone (O₃). O₃ is a secondary pollutant with adverse effects on population health and ecosystems (Fleming et al 2018, Mills et al 2018), and with negative impacts on climate, acting as a short-lived climate forcer (UNEP and WMO 2011). Due to its absorbing properties on long-wave radiation, it is a powerful greenhouse gas in the troposphere, with substantial impacts on the Earth's climate. In the troposphere, the O₃ chemistry is strongly affected by NO_x (i.e. $NO + NO_2$), VOC and their ratio. At high VOC/NO_x ratios (typically occurring in background conditions), the O3 chemistry tends towards a NO_x -limited regime (i.e. NO_x reductions are more effective to reduce O₃). Under low VOC/NO_x ratios (typically in urban areas or near emission sources) a decrease in NO_x can lead to an increase in O₃ (VOC-limited conditions).

For many polluted regions in the world, studies reported increased near-surface O_3 as a consequence of COVID-19 lockdowns in spring 2020 with respect to the previous years (Collivignarelli *et al* 2020, Shi and Brasseur 2020, Sicard *et al* 2020, Siciliano *et al* 2020, Venter *et al* 2020). Reduced surface O_3 is also reported for some rural areas after COVID-19 lockdowns, e.g. in the US and western Europe (Chen et al 2020, Elshorbany et al 2020, Menut et al 2020, Ordóñez et al 2020, Shi and Brasseur 2020, Siciliano et al 2020). These impacts can be related to the above-mentioned different O₃ photochemical sensitivity (i.e. NO_x-limited vs VOC-limited regimes) as well as with meteorological conditions, which were more or less favorable to the production or removal of O₃ (Goldberg et al 2020, Ordóñez et al 2020, Keller et al 2021). Most of these studies, however, only focused on spring 2020 (March-May) and different strategies were used to quantify O3 anomalies in 2020 because of the COVID-19 restriction measures. Methodological differences exist, for instance, in the adopted O₃ metrics (considering seasonal, monthly, daily, or hourly averages, median, percentiles), and in the definition of the COVID-19 lockdown and base/reference periods.

As detailed above, many previous works on the possible impacts of anthropogenic emission reduction during COVID-19 containments on atmospheric O_3 were focused on observations from ground-based monitoring stations in the planetary boundary layer (PBL), mostly in the vicinity of urban or industrial agglomerates, or considered the tropospheric column of O_3 . A first attempt to quantify the lockdown impacts on free tropospheric (FT) O_3 was provided by Steinbrecht *et al* (2021) by using a global dataset of atmospheric vertical profiles, indicating a widespread O_3 decrease in the Northern Hemisphere FT.

In this study, we analyzed the variability of O_3 above the PBL of northern Italy. We took advantage of the continuous observations carried out at a high mountain WMO/GAW global station in Italy (Mt. Cimone–CMN; 44°12′ N, 10°42′ E, 2165 m a.s.l.). The high temporal resolution of CMN observations, allowed us to disentangle the high frequency variability affecting O₃ during 2020. The aim of this study is to investigate the possible links between the observed O₃ variability at CMN in spring-summer 2020 with changes in local thermal wind behaviors (by in-situ meteorological parameters), photochemistry (by analyzing co-located measurements of NO_x and NM-VOCs) and synoptic-scale atmospheric circulation (by air mass back-trajectories). Air quality data in northern Italy and Europe were explored to better assess the role of air mass transport from the regional PBL.

2. Methods

An overview of the dataset used in this work is provided in the supplementary material (see supplementary table S1 (available online at stacks.iop.org/ ERL/16/074029/mmedia)).

2.1. Atmospheric observations at CMN

CMN (see supplementary figure S1) is the highest peak of the northern Italian Apennines and overlooks the Po basin (towards NW-SE) and northern Tuscany (towards S-NW). Within several kilometers from the site, human activity is very limited.

As reported in previous studies, the atmospheric observations carried out at CMN can be considered representative of the FT conditions in the Mediterranean basin/southern Europe during the cold months (see, e.g. Bonasoni *et al* 2000), as well as during night-time in the warm season. However, especially from April to September, the measurement site can be affected by thermal wind circulation (slope and valley winds, diurnal PBL growth) and convective vertical transport of air masses. This favors the advection of polluted air masses from northern Italy where the Po basin, one of the most polluted areas in Europe, is located.

Near surface O_3 is measured by using an UVabsorption photometer Tei-49i (Thermo Scientific). The quality assurance program included daily checks and regular calibration (roughly every three months) with a laboratory transfer standard (Tei 49i-PS, Thermo Scientific). The total combined uncertainty of observations is usually below 1 ppb.

 NO_x are continuously observed by a chemiluminescence analyzer Tei42i-TL (Thermo Scientific) equipped with a photolytic converter (Blue Light Converter by Air Quality Design and Teledyne) for NO_2 . Every 48 h, zero and span checks are carried out according to ACTRIS-2 guidelines (Gilge *et al* 2014). A total combined uncertainty of 5% and 25% for NO and NO_2 was assessed by Cristofanelli *et al* (2021).

NM-VOCs are analyzed via thermal desorptiongas chromatography-mass spectrometry (TD-GC-MS): air samples are pre-concentrated on a focusing trap cooled to -30 °C every hour by an online sampler/thermal desorber Unity2-AirServer2, Markes; NM-VOCs are desorbed and analyzed by the GC-MS Agilent 6850-5975 operating in SIM mode; calibration occurred after every run by sampling the same volume from a real air working standard, calibrated periodically against a primary reference standard prepared by National Physical Laboratory (NPL, Teddington, UK) (Maione et al 2013). In total, 15 different anthropogenic NM-VOCs are observed at CMN (see supplementary table S2). We consider the total NM-VOC as obtained by summing the mixing ratio of each single NM-VOC weighted for their Photochemical Ozone Creation Potential (Jenkin et al 2017).

More details of the experimental set-up at CMN are presented in the supplementary material.

2.2. O₃ and NO₂ in the European PBL

To set the O_3 variability observed at CMN into context, observations of O_3 and NO_2 from four air quality stations managed by ARPAE Emilia-Romagna in the Po basin were considered. Febbio (FEB; 44.30° N, 10.43° E; 1121 m a.s.l.) is a rural background station located in a mountainous area 25 km northwest of CMN. Three urban background stations in the Po basin were further treated: Modena 'Ferrari' (MOF; 44.65° N, 10.90° E), Bologna 'Margherita' (BOM; 44.48° N, 11.35° E), and Reggio Emilia 'S. Lazzaro' (RSL; 44.68° N, 10.66° E).

To obtain information on the variability of near-surface O_3 over specific European regions, we considered the O_3 and NO_2 time series for 50 European cities produced by Copernicus-CAMS ('European air quality analyses'), available at https://atmosphere.copernicus.eu/european-air-quality-inf-ormation-support-covid-19-crisis/. These time series were aggregated over eight geographical regions (see supplementary figure S1). Data from 2015 to 2019 are obtained by the CAMS regional re-analysis, while data for 2020 are produced by the CAMS daily regional analysis (METEO-FRANCE *et al* 2020).

2.3. Air mass back-trajectories

To determine the synoptic origin of the air masses reaching the measurement site, five days 3D backtrajectories were calculated based on six-hourly meteorological data (00, 06, 12, and 18 UTC) with the Lagrangian analysis tool LAGRANTO (Wernli and Davies 1997, Sprenger and Wernli 2015). For each set, three back-trajectories were computed, with starting points shifted by a vertical range of ± 50 hPa with respect to the station location (i.e. at 840, 790, and 740 hPa). The trajectory calculations were based on the ERA5 reanalysis dataset of the European Centre for Medium-Range Weather Forecasts (see Hersbach *et al* 2020).

3. Results and discussion

Figure 1 shows the monthly mean values for nearsurface O₃ at CMN for 2020, compared to the 1996-2019 variability. It is evident that during specific months in 2020 (i.e. March and from May to July), lower values with respect to the previous 25 years were observed (ranging from -7.2 ppb in March to -11.5 ppb in July). These negative anomalies are still detected when detrended O3 values over 1996-2019 are considered (details about O₃ detrending are presented in the supplementary material), with values of the anomalies ranging from -4.8 ppb in March to -9.6 ppb in July. For completeness, supplementary figure S2 reports the same analysis, but focusing on the shorter period 2015-2020. The CMN observations fit nicely with the broader picture provided by Steinbrecht et al (2021), showing consistent and widespread O3 decreases in the FT in the Northern Hemisphere during 2020. This was mainly attributed to the global decrease in emission of anthropogenic O₃ precursors, as a consequence of COVID-19 restriction measures. The negative anomalies observed at CMN





in March and April are in evident opposition with the O_3 increases observed at the three urban background stations in the Po basin and in northern Italy during the same period (supplementary figure S3; Ordóñez *et al* 2020, Sicard *et al* 2020).

We analyzed the year-to-year variability of the percentiles of daily mean values of O3 and NO2 at CMN and at the air quality stations in the Po basin during 2015-2020 (supplementary figures S3 and S4, respectively). At CMN, March 2020 and May 2020 were characterized by the lowest values for all percentiles, compared to the previous years. The same was observed at FEB. At the urban sites (i.e. BOM, MOF, and RSL) higher (or similar) O3 percentiles were detected in 2020 compared to the previous years. In April 2020, the O3 percentile distribution did not differ much from the previous years for CMN, while they were lower at FEB and higher (or similar) compared to the previous years at the other stations. A different situation characterized summer (i.e. JJA) 2020: with respect to 2015–2019, O3 decreases were observed at the mountain stations of CMN and FEB in June and July, while urban stations reported percentiles well within the variability of the previous years, or even lower. In August, the range of O₃ percentiles in 2020 was comparable to the reference period for all the stations (including CMN). The same analysis for NO₂ did not show strong deviations at CMN and FEB in 2020 (except for July), while evident NO₂ decreases affected the urban sites. The NO₂ decrease at the urban stations was larger in MAM than in JJA.

To better understand the possible reason for the negative O_3 anomalies observed at CMN, we investigated the interannual variability of the monthly O_3 diel cycles over 2015–2020 for the March–August period (see supplementary figure S5). It is well assessed that O_3 diel variability at mountain sites is determined by the interaction of: (a) mountain thermal wind regimes (slope and valley winds), (b) vertical extension of the PBL, and (c) photochemistry (see, e.g.

Price et al 1963). In particular, during the daytime in the warm months, processes a-b can favor the direct transport of (polluted) air masses from the regional PBL up to mountain sites (and possibly to the FT). The relative importance of each process depends on different factors: the altitude of the site, the local topography, and the distance from pollution sources. At CMN, we did not observe clear changes in the shape of the diel cycle in 2020, thus suggesting only a limited impact of processes occurring at diurnal time scales (i.e. processes a-c). No major changes in the local wind speed were observed at CMN during 2020 (supplementary figure S6(a)): with respect to 2015– 2019, slightly higher values were only observed in April-May during night-time (00-06 UTC). The specific humidity (supplementary figure S6(b)), which is considered as a good tracer for PBL air masses at mountain sites, showed the lowest values in April and June 2020 with respect to the previous years (please note that no specific humidity data were recorded in March 2020). This is in agreement with Ordóñez et al (2020), who detected low specific humidity conditions in April 2020 over northern Italy.

To specifically assess how much changes in the synoptic-scale air mass transport pattern could explain O₃ variability at CMN, we analyzed the air masses arriving at the measurement site by means of back-trajectories. To spot any potential difference in circulation patterns for 2020 with respect to the last five years, we first aggregated the back-trajectory points over spatial grids $(1^{\circ} \times 1^{\circ})$ on the horizontal and 81 pressure levels), for MAM and JJA, and for each year. Then, we computed the anomalies of each year with respect to the 2015-2020 average. The results for 2020 are shown in figure 2, while the plots for all years are presented in the supplementary figure S8. In MAM 2020, transport to CMN from eastern Europe was enhanced, while transport from western Europe was diminished. The reversed pattern was observed for JJA 2020. However, by comparing 2020 with the last five years (supplementary figure S8), it





is evident that similar results were also obtained in the past (e.g. MAM 2018, JJA 2017). Therefore, it is difficult to robustly attribute the low O3 observed at CMN in MAM and JJA 2020 to an overall change of the seasonal synoptic-scale circulation. At CMN, NO2 and NM-VOCs did not stand out compared to 2015-2019 (supplementary figures S4 and S7). The highfrequency observations carried out at CMN allowed us to investigate the variability of O₃, NO₂ and NM-VOCs during MAM and JJA 2020 in more detail. The O₃ values were indeed not constantly below the variability observed in 2015–2019 (figure 3): periods with low O₃ values alternated with periods characterized by values comparable to the previous years. For NO₂ and, especially, NM-VOCs, no obvious systematic differences can be observed with respect to the previous years. Compared to NM-VOCs, NO2 was frequently low during 2020, but this did not impact the overall NM-VOC/NOx ratio (supplementary figures S9 and S10). Therefore, it is difficult to unambiguously assess the role of local photochemistry in determining the observed negative O3 anomalies. As for NO₂, the experimental set-up used at CMN is often at the limit of detection sensitivity (especially during warm months), thus we cannot exclude that a larger decrease of NO2 would have passed undetected.

For each week in supplementary table S3, we inspected air mass trajectories arriving at CMN. We were able to find a robust and consistent relationship with synoptic-scale circulation classes and the occurrence of O3 weekly anomalies at CMN in summer. For June and July 2020, low O₃ was typically related to air masses which travelled through or originated from the European continental PBL (mostly from the western sector). On the other hand, higher O₃ values were linked to air masses from the FT (i.e. above 700-600 hPa). A similar situation was observed in March 2020, while April 2020 (which reported O₃ values similar to 2015-2019 at CMN), was characterized by a frequent occurrence of transport from the FT, or from regions usually not considered as sources of anthropogenic pollution (i.e. the Mediterranean Sea or northern Africa). As deduced by the analysis of potential vorticity (PV) along the LAGRANTO back-trajectories, stratospheric air masses (i.e. with PV > 1.6 pvu) episodically affected CMN (on 2–4 April, 15 and 17 April, and 25 April 2020) possibly explaining a fraction of the relatively high O₃ values. They would contribute to the differences, observed in April 2020 at FEB, located at a lower altitude and less affected by transport from the FT and the stratosphere. We were not able to find a clear relationship between air mass circulation patterns and weekly O₃ for May, likely due to episodic variability.

To further investigate the possible role of air mass transport from the PBL, we clustered the CMN observations in periods representative for 'FT' and 'regional PBL' conditions (see the supplementary material for more details about the selection methodology). O₃ and NM-VOCs were detrended to take into account the O3 trend at CMN (Cristofanelli et al 2020) and the reduction of anthropogenic NM-VOCs in Europe due to air-quality policies (Lewis et al 2020). The trend calculations are detailed in the supplementary material. For O₃, we observed that the deviations from monthly mean values with respect to 2015-2019 were indeed more evident for the conditions representative of transport from the PBL (table 1): they ranged from -4.6 ppb (-7%) in May to -8.5 ppb (-13%) in July. For the observations in the FT group, these deviations ranged from +2.3 ppb in May (+4%) to -7.4 ppb (-11%) in June. For NO_x, we observed notable decreases in April and May 2020, more evident for the PBL air masses (up to -86%in May), while a tendency for NO_x decrease was also observed in PBL air masses for July and August. No robust deviation for NM-VOCs were observed in 2020 compared to 2015–2019: we observed decreases of anthropogenic NM-VOCs (with p > 0.10 when compared to 2015-2019) in April-May for both FT and PBL air masses (from +17% to -66%) as well as in June and July for PBL air masses (from -23% to -19%).

In summary, despite what was observed for O_3 , no robust deviations were observed for NM-VOCs in

Table 1. Average monthly deviations for 2020 with respect to 2015–2019 for the free troposphere (FT) and the PBL data selections. Bold character denotes values exceeding the 90% confidence level (p < 0.10). O₃ and NM-VOC data have been detrended over the common period 2010–2019 (see supplementary material).

	FT regime			PBL regime		
Month	O ₃ (ppb)	NO_x (ppb)	NM-VOC (ppb)	O ₃ (ppb)	NO_x (ppb)	NM-VOC (ppb)
April	-2.3	-0.12	-4.2	-7.6	-0.29	-1.4
	-4%	-74%	-30%	-12%	-72%	-66%
May	+2.3	-0.17	-2.9	-4.6	-0.15	+0.9
	+4%	-72%	-32%	-7%	-86%	+17%
June	-7.4	+0.01	+1.2	-8.5	-0.01	-1.4
	-11%	+4%	+7%	-13%	-4%	-23%
July	-3.9	-0.01	+1.3	-6.5	-0.08	-1.2
	-6%	-3%	+7%	-10%	-31%	-19%
August	+0.9	-0.01	-0.1	-1.8	-0.06	+0.3
	-1%	-1%	-1%	-3%	-24%	+4%



denotes the envelope of single years from 2015 to 2019. The black line indicates the average value over 2015–2019.

2020, while for NO_x robust deviations occurred in spring both for FT- and PBL-segregated observations, and in summer for PBL-segregated observations only. The higher reactivity of these chemical species could limit the possibility to fully detect lockdown-related emission decrease at a remote site like CMN. However, the detected NO_x reductions would suggest an impact of emissions.

Interestingly, as reported in figure 4, air quality stations in the Po basin (both urban and rural) were characterized by relatively low O_3 values in June–July 2020 with respect to 2015–2019. This is in opposition to what was observed in April–May (Sicard *et al* 2020). This negative anomaly was not homogeneous over the European continent, but was localized in the area we identified as 'North Italy' (NIT), mostly overlapping with the Po basin (see supplementary

figure S11). In March 2020, it was not possible to detect any shift of the daily O_3 values with respect to 2015–2019. In April–May 2020, in agreement with the previously cited studies (e.g. Ordóñez *et al* 2020), a shift towards higher values can be detected over almost all the regions excluding south-western (SWE) and eastern Europe (EEU and NEU). For August 2020, no deviations can be observed with respect to the previous four years. A more consistent view could be obtained for NO₂, which markedly decreased over near-surface Europe in 2020, for all months and regions (figure 4 and supplementary figure S12).

4. Conclusions

We showed that low O₃ monthly anomalies were observed at the high mountain station Mt. Cimone (CMN, 2165 m a.s.l.) during spring (MAM) and summer (JJA) 2020, in good agreement with observations in the FT (Steinbrecht et al 2021). The analysis of local wind speed behaviors, specific humidity and O₃ monthly diel cycles did not suggest major changes in the vertical transport related to the thermal circulation system in the area. The low O₃ values that characterized MAM and JJA 2020 cannot be explained by differences in the synoptic-scale circulation compared to the previous five years. The continuous CMN observations allowed us to analyze the high-frequency variability of O3 during MAM-JJA 2020. This variability was characterized by periods of low O₃ intertwined with periods with higher O₃, within climatological ranges. A similar variability also affected NO₂ and NM-VOCs that led, on average, not marked variations with respect to the previous years, when the whole dataset was considered. Together with the characterization of two transport patterns occurring at CMN (i.e. air masses from the regional PBL or from the FT), the analysis of the back-trajectories suggested an important contribution of air mass transport from the continental PBL for periods with lowest O₃ at CMN. The subset of the PBL-segregated observations reported robust NO_x decreases in respect to

the previous years. The same was also observed for FT-segregated observations, but only for spring. This would suggest a less efficient photochemical O3 production in a NO_x-limited atmosphere, which could contribute to explain part of the negative O3 anomalies. With respect to 2015–2019, background urban sites in the Po basin reported lower O₃ values in JJA, supporting the low O₃ content in PBL air masses at CMN. Our independent results support the finding by Steinbrecht et al (2021) that negative O₃ anomalies occurred above the PBL in MAM-JJA 2020 due to mobility restrictions and reduced emissions of anthropogenic O₃ precursors. Our results indicated that, once transported to CMN, PBL air masses are characterized by lower O₃ compared to previous years. In our opinion, this is consistent with the results by Steinbrecht et al (2021) for the following reasons: (a) the transport of PBL air masses depleted in O₃ to the FT can be one of the processes leading to the large-scale hemispheric anomalies in the FT; (b) O₃ decreases are also observed for FT-segregated observations for April, June and July 2020 (even if lower than for PBL-segregated data). In summary, during MAM-JJA 2020, the COVID-19 restrictions reduced the emissions of anthropogenic O₃ precursors. This was reflected in a decrease of the amount of this short-lived climate forcer/pollutant above the PBL and at remote locations over northern Italy, especially when PBL air masses were transported vertically. Nevertheless, definitively quantifying the relationship between CMN negative O₃ anomalies and decreased emissions in the European PBL remains elusive due to the complex mechanisms at play (see also Kroll et al 2020). The integration of high frequency observations carried out at high mountain sites together with chemistry and transport modeling, would allow a more accurate attribution of the impact of COVID-19 restrictions in atmospheric layers above the PBL.

Data availability statement

The data generated and/or analyzed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

Acknowledgments

CNR-ISAC strongly acknowledges the collaboration with Italian Air Force (CAMM Monte Cimone) for the management of the Mt. Cimone WMO/GAW global station. CMN observations of O_3 , NO_x and meteorological variables at the 'O Vittori' observatory were supported by the National Project of Interest NextData (funded by MIUR) in the years 2012–2018. Meteorological observations in 2019– 2020 were supported by JRU-ICOS.Italia (funded by MIUR/MUR) which also supported the open access pubblication costs. NOx and NM-VOC observations at Mt. Cimone were partially supported by ACTRIS-2 (H2020-EU.1.4.1.2) and are currently supported by MIUR/MUR through the ACTRIS-IT infrastructure project. The LAGRANTO back-trajectories were generated using Copernicus Climate Change Service ERA5 reanalysis (2021). Data of O₃ and NO₂ at the European cities were generated using the Copernicus Atmosphere Monitoring Service information (2021). The authors are grateful to ARPAE Emilia-Romagna for providing O3 and NO2 data at air-quality stations by the web site https://dati.arpae.it/dataset. Part of the analyses reported in this work have been generated by using the 'OpenAir' analysis package for R that was obtained from www.openair-project.org. Finally, the authors thank the three anonymous reviewers for their valuable work.

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