

## General comments

The manuscript introduces a wealth of new and important observations over a significant European pollution hotspot, and critical in-depth analysis. The first two sections (intro and methodology) are well written. However section 3 (results and discussion) would benefit from a better structure, specifically:

Lines 230-266 (incl Table 1, Figures 4 and 5): deserve their own results section, possibly titled "3.1 Boundary layer meteorology during flights E-EU-03 and E-EU-06"

Arguably, Lines 268-282 are still describing methodology rather than presenting results, so should go in a new Section 2.3 possibly titled "2.3 Analysis approach for pollutant distribution and gradients within the BL during flight E-EU-06" .

The current sections 3.1.1, 3.1.2 and 3.1.3 provide the bulk of the observational data set analysis (11 pages), whereas subsequent sections 3.2, 3.3 and 3.4 are much shorter (7 pages in total).

For better clarity and better structure of paragraphs, I suggest renaming sections as follows:

3.1 Boundary layer meteorology during flights E-EU-03 and E-EU-06 [lines 230-266 incl Table 1, Figures 4 and 5 as suggested above]

3.2 Vertical distribution and advection of pollutants in the Gulf of Venice (GV) [line 290]

3.2.1 Shuttle BC along Croatian coast [line 302]

3.2.2 Shuttle FG in Gulf of Venice [line 320]

3.2.3 MBL transect BF across Adriatic Sea [line 404]

3.3 Distribution of pollutants in the BL across the central Po Plain (CPP) [line 430]

3.4 Vertical distribution and advection of pollutants in the Gulf of Genoa (GG) [line 508]

3.5 Comparison of ground and airborne observations over the Po Plain [line 530]

3.6 General features in the processing of the air masses over the Po Plain [Line 574]

3.7 Desert dust transport and secondary organic aerosol formation above the central Po Plain [Line 636]

Although a significant effort was put into calculating ratios and presenting them in Figures, the main text often refers to observational data not reported in either the supplementary material nor the main manuscript tables and figures. This also applies to backward trajectories. Some of the referencing and stated results do not match observational or computational evidence, or figures referencing is inconsistent, which I have highlighted below and will require correction or explanations.

Main manuscript:

Line 93: "...of the local meteorology and orography" [instead of "dynamic"; orography as study of mountains' topography effects]

Line 190 (caption of Fig3) AQM... stations are identified by their station number (tabulated in Supplementary Table S6.1)

Line 171 (section 2.1.3 Met soundings)

In Fig 3, San Pietro Capofiume is listed as a radiosonde station, but is not listed in the main text or in Table 1 of Section 3 Results and discussion.

Line 203 b) COSMO: high resolution wind fields [strengthens the need for this model]

"The COSMO-Model (...) offers a factor ten higher spatial resolution than ERA5, so is employed in this study..."

Line 218 Marengo et al and Birmili et al merely use HYSPLIT. Please cite Draxler, R. and Hess, G.: Description of the HYSPLIT4 modeling system, NOAA Technical Memorandum, ERL, ARL-224, revised April 2020, and "NOAA's HYSPLIT Atmospheric Transport and Dispersion Modeling System", Bulletin of the American Meteorological Society 96, 12 (2015): 2059-2077, accessed Oct 7, 2021, <https://doi.org/10.1175/BAMS-D-14-00110.1>.

Line 226 correct URL for EDGAR HTAP V2 is  
[https://edgar.jrc.ec.europa.eu/dataset\\_htap\\_v2](https://edgar.jrc.ec.europa.eu/dataset_htap_v2)

Line 228 If possible, could you provide a doi or GitHub reference for the DLR/IPA infrastructure?

Line 237 "JNO2 was used as a qualitative proxy metric for cloudiness..."

Line 249 "...Gulf of Genoa, which contrasted with speeds ranging -2 to +4 m s<sup>-1</sup>..." [I assume that this statement was meant to contrast low variability and speed over the sea versus the more turbulent winds over the CPP]

Line 254 "In Fig. 5, the wind fields calculated by COSMO for..."

Line 256 "Inside the BL (<1000 m altitude), sea breeze regimes are..."

Lines 257-258 "... with altitude over the Gulf of Genoa coastline (43.5-45° N; 8-10° E) and sea to land circulation up to approximately 600 m altitude over the Gulf of Venice coastline (44-46° N; 12-14° E)." [consistent geographical references as used in Fig 5 caption]

Line 260 "... following the dominant pattern previously observed over the ..."

Line 291 "Figure 6 shows the spatial variation of ..." [although the observations are presented as timeseries, their variability is spatial]

Line 300 "3)" refers to new section 3.2.3

line 306 "At 3230 m asl, mixing ratios are less than in the BL for all species". Could FT leg 6-6a averages be added in Supplementary Table S8 to support the HCHO/NO<sub>2</sub> ratios discussion on lines 312-314?

Line 307 "...of FT air masses (> 2000 m) at 3220 m..." The 12 UTC radiosonde sounding at Rivolto suggests a BLH of 1000 +/- 70 m according to Table 1, which may suggest that the 6b-6c leg at 1630 m altitude may be FT-influenced, possibly by BL/FT entrainment zone. The proximity of the Croatian coast to the "B-C shuttle" may have contributed to this entrainment, as hinted by the easterly veering of winds at 1000 and 1600 m shown in Figure 5.

Lines 315-318 for a better reference for emissions from north industrial area of Porto Marghera in Venetto Lagoon, especially SO<sub>2</sub> monitored at Station Enel Fusina, see [https://apice-project.eu/img\\_web/pagine/files/Results/Apice\\_WP3%20Report.pdf](https://apice-project.eu/img_web/pagine/files/Results/Apice_WP3%20Report.pdf)

Line 318 "... from the sea surface to 520 m, 10-16 hours before the measurements, as shown on the left-hand panel in Fig. 9."

Line 321 "Figure 6: Spatial variation of NO, ..."

Lines 329-328 comments on Fig 6 and its caption

The colour shading scheme complicates Fig 6 significantly and I would advise against it. Certainly the darker/lighter shading is unnecessary given that altitude is charted in the top plot of Fig 6. If shading must be kept to better highlight legs on individual time charts, I'd recommend a light neutral grey shading.

I also wonder whether the top chart would benefit from geolocations B, C, F, G and X to be added alongside waypoints 6-6l, so the reader can better identify the B-C, X-F and G-X legs discussed in the main text.

Line 326 "(see Figure 13)". Not sure this reference is correct; presumably should be Fig 3?

Lines 333-334 see above comment about shaded areas in Fig 6

Line 317-318 "Backward trajectories indicate that air masses were lifted up from the sea surface to 520 m, 10-16 hours before the measurements, as showed in Figure 9 left-hand panel."

Line 348 "... it is less water-soluble and its rate of removal by reaction with OH is much slower than that of SO<sub>2</sub>".

Line 372-373 HCHO/NO<sub>2</sub> values are not provided in Figure 8 nor in Table S8c. NO<sub>2</sub> data are not provided in Fig 8 either

Line 382-383 "... being on average a factor of ~3 to 4 higher than that in the BL (see Table S8c).

Line 383-386 No RH or H<sub>2</sub>O mole fractions are presented in any of the observed meteorology data shown so far, such as in the new Section 3.1 which focuses mainly on winds. Do radiosonde soundings support this statement?

Line 392 change "BB" to "biomass burning". A more definitive BB marker such as acetonitrile CH<sub>3</sub>CN was measured by HALO's PTR-MS (Förster et al 2023, <https://doi.org/10.5194/acp-23-1893-2023>) to substantially indicate fresh wildfires in the Mediterranean area. BC particles microphysics were also reported by Andrés Hernández et al 2022 to illustrate the complex mixing of BB and anthropogenic emission sources.

Line 396 Millán et al 2004 reference is missing. Similar land-sea breeze coastal shallow circulations were reported in southern West Africa (Flamant et al 2018, <https://doi.org/10.5194/acp-18-12363-2018>).

Line 412 "(see Section 3.3)" ensure correct section ref

Lines 410-413 The FLEXTRA backward trajectories on the RH panel in Figure 9 (10:12-10:27 UTC, 520 m, 6e-6f and part of 6f-6g) do not substantiate the statement "...of air masses circulating below 500 m agl over the CPP between approximately 45.2°N – 45.8°N, and 10.4°E – 11.6°E, an area including Brescia and Verona urban areas". Air masses appear to be advected south of 45°N, between 10°E – 12°E, encompassing Bologna-Modena-Parma from the Apennine Mountains, rather than as stated from NW Veneto.

Lines 421-422 "...A significant contribution to air pollution from shipping and industrial activities around the ports of Venice and Marghera is consistent with..." [Porto Marghera should be referred to as it is by far the biggest industrial emitter in the Venetian Lagoon]

Line 426 Figure 9 caption would benefit quoting back traj origin, eg 6d-6e (B-C) transect at 520 m (LHS), and 6e-6f (B-F) transect at 520 m (RHS)

Line 443 Figure 10 caption. These are twenty four FLEXTRA backward trajectories assuming the dots mark 6h time steps (same as Fig. 9)

Line 448 "... could not be safely qualified as NO<sub>x</sub>- nor VOC-limited."

Line 461-464 "(44.5°N-45.5°N, 10°E-11°E)" ["10°N" is a typo]

Figure 10 does not evidence air mass advection below 500 m during previous 24 hours. Between 10°-11°E, the cyan coloured trajectories indicate heights > 1000 m. However since the Milano Linate derived BLH is 1600±400 m (Table 1), one can argue that air masses remained in the BL during their slow advection

Line 486 "Figure 11: Spatial variation of NO<sub>x</sub>,...". Since CO is such an important tracer in this study, could the observed CO blue trace be overlaid on top of the HYSPLIT simulated deltaCO on the bottom time chart? The same comment applies to Figure 6.

Line 520-521 "This means that on 20 July 2017 the CPP area did not appear to be a source of pollution in the FT above 2500 m asl."

Line 529 Caption of Figure 12. "The delimiting times are marked in Fig. 11 as red lines in the bottom panel" [Fig. 10 incorrectly referred]

Line 525 : Arguably this extra LR transported CO could be from forest fires in south-eastern France which was experiencing an exceptionally hot and dry summer in 2017, which were later detected during HALO E-EU-07 and E-EU-09 flights downwind of Marseille, Nice and Saint Tropez on 24 and 28 July 2017 (Andrés Hernández et al 2022).

Line 531 PP is undefined in this main manuscript. Keep to previous used CPP acronym? [see suppl comment]

Line 530 Section 3.2 Comparison of ...

I feel that the comparison presented in this section is overly simplified and does not illustrate the Eulerian and Lagrangian nature of respectively ground-based and aircraft observations.

How were hourly concentrations at ground sites time selected, given that some of these sites are located up to 18 to 24 hours advection time from the HALO flight track according to the FLEXTRA backward trajectory simulations? These advection times are short enough for long-lived CO (~1 month), but much closer to the NO<sub>x</sub> and O<sub>3</sub> lifetimes (hours-day). Some ground sites considered in the comparison do fall outside the backward trajectories lat/long domain when inspecting Figures 10 and 13, for instance sites 8, 9, 10, 11, 17, 18, 19, 23.

For NO<sub>x</sub> and O<sub>3</sub>, you quote 11:30-12:00 UTC and 11:00-12:00 UTC for the 1h-mean mixing ratios at ground stations (lines 565 and 568), which suggest you did not consider advection times; I admit that day-to-day variability during the study period maybe be low, however this should be stated somehow.

O<sub>3</sub> mixing ratios measured by HALO over the CPP at 800 m being 8% higher than at ground level is explained by the possible result of O<sub>3</sub> photochemical production in convected air masses or poor mixing of NO<sub>x</sub> emissions on the ground (lines 571-573). Higher O<sub>3</sub> deposition velocities near the ground and associated O<sub>3</sub> losses would also affect net O<sub>3</sub> production efficiencies at ground level, and could also explain the observed discrepancy.

Line 549-551 "This might be explained by the large contribution of long-range transported and long-lived CO to the BL mixing ratios at 800 m above the ground. According to HYSPLIT simulations, emissions from the Po Valley actually accounted at the maximum for 15 % (~20 ppb) to the BL CO mixing ratios measured on-board the aircraft (~130 ppb). " [quoting max deltaCO and mean BL CO values] Your CO comparison conclusion sounds reasonable.

Line 552 30-60 ppbv NO<sub>x</sub> are not "extreme concentrations", they are fairly common for cities curbside monitoring stations...

Lines 560-564 "Based on the mean vertical... ..(e.g. Maclean et al., 2017; Helbig et al, 2021)". I'm afraid I do not understand the statement "the decrease in NO<sub>x</sub> mixing ratio between the ground and the aircraft altitude could be estimated to a factor of ~3 only." The two references provided ("Maclean et al., 2017; Helbig et al, 2021") do not support the statement "upper limit of the range for a convective BL between 20-30 min to a few hours".

Line 570 "...NO<sub>x</sub> and VOC have mixed upwind with biogenic VOC..." [rather than "upstream"]

Line 584 "...with respect to the GV." [full stop missing]

Line 604 "..., but also by an effective oxidation of NO<sub>x</sub>-rich emissions..." [rather than "processing"]

Line 610 "...measurements points at the western tip of the CPP..." [rather than "west"]

Line 615 "... and to a lesser extent O<sub>3</sub>."

Line 624-625 "However measured and simulated radiosondes vertical soundings in this study indicate that turbulence in the BL atmosphere over the CPP was much less than in the simulations of Wang et al. (2022)." [Wang's study in the vicinity of Hong Kong Island was subject to strong turbulent flow which was not the case for the CPP study]

Line 626 Hůnová et al. (2023) reference missing

Line 660 "In particular, elevated aerosol layers up to 5000 m altitude are visible in the ALC and lidar traces (Fig. 14-15)". [delete "over"]

Line 643 "... if they are entrained back inside the BL."

Supplement S3 : you introduce the acronym PP without defining it (Po Plain), and refer to PP in the supplementary info.

However in the main manuscript you refer to CPP (central Po Plain) in section 3.1.2, and reference S9. For consistency, could you use a single acronym?