Answer to general comments RC2

(…) 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"*

Reply: Section 3.1 and 2.3 have been included in the manuscript as suggested by the referee.

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. 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]

Reply: The sections of the manuscript have been renamed and renumbered as suggested by the referee above. A new section has been included: "*3.2.3 Comparison of the two shuttles across the GV" and the following sections were renumbered accordingly:*

(..) 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].*

Reply: This has been changed as suggested by the referee.

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

Reply: This has been added in the figure caption as suggested by the referee.

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 3 text or in Table 1 of Section Results and discussion*.

Reply: San Pietro Capofiume is a radiosonde station but there were no data available for the period of study and therefore could not be considered in the discussion of results.

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..."

Reply: The term “high resolution” has been included in the title of b) as suggested by the referee and the following sentences in the manuscript have been rephrased to emphasise the added value of the COSMO simulations.

Line 218 *Marenco 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/BAMSD-14-00110.1.*

Reply: The suggested references have been included.

Line 226 *correct URL for EDGAR HTAP V2 is https://edgar.jrc.ec.europa.eu/dataset_htap_v2.*

Reply: The URL has been corrected

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

Reply: We agree that a Doi or GitHub reference would be helpful. Unfortunately, the colleague who did this work has retired and is no longer available.

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

Reply: The sentence has been modified as suggested by the referee.

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

Reply: This assumption is right and the corresponding sentence (in Line 271 in the revised version) has been extended as suggested by the referee.

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

Reply: The sentence has been modified as suggested by the referee.

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

Reply: The sentence has been modified as suggested by the referee.

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].*

Reply: The sentence has been corrected as suggested by the referee.

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

Reply: The sentence has been modified as suggested by the referee

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

Reply: The sentence has been corrected as suggested by the referee.

Line 300 *"3)" refers to new section 3.2.3. Could FT leg 6-6a averages be added in Supplementary Table S8 to support the HCHO/NO2 ratios discussion on lines 312-314?*

Reply: The reference has been updated and the Table S8 has been extended with the 6-6a averages as suggested by the referee.

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.*

Reply: Measured and reanalysed meteorological data profiles (Fig. S10.3 and S10.4) indicate that at 1630 m asl the aircraft flew in the FT indeed, and at the top of the entrainment zone. There is no evidence from transport of pollutants to the aircraft altitude from aloft. In contrast, backward trajectories suggest that the air masses intercepted at 1630 m asl were lifted up from the surface of the CPP during the afternoon the day before.

Lines 315-318 *for a better reference for emissions from north industrial area of Porto Marghera in Venetto Lagoon, especially SO2 monitored at Station Enel Fusina, see https://apice-project.eu/img_web/pagine/files/Results/Apice_WP3%20Report.pdf*

Reply: This report is no longer available but a similar adequate reference is the paper Toscano, D. The Impact of Shipping on Air Quality in the Port Cities of the Mediterranean Area: A Review. Atmosphere 2023, 14, 1180. https://doi.org/10.3390/atmos14071180, which has been included in the text and reference list.

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.".*

Reply: The sentence has been extended as suggested by the referee.

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

Reply: The figure caption has been extended as “temporal and spatial variation of…” since some of the places are overflown twice, as indicated by the shaded areas.

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 GX legs discussed in the main text*

Reply: The shading helps to emphasise the part of the leg directly flown on the reverse, i.e., the temporal closeness of the vertical profile over the same area, what is not always obvious. They are actually indicating the geolocations B, C, F, and G. There are areas flown at the same altitude, which do not belong to the spatial area covered

by the shuttle. This visualisation is not possible if the shading is all in grey or if the darker/lighter shading is not included. The plot has been slightly modified to improve clarity. The geolocations have been additionally included on the top as suggested by the referee.

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

Reply: Yes, this is indeed Fig.3 and it has been corrected.

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

Reply: Please see the answer above for the comment in Lines 329-328.

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."*.

Reply: The sentence has been extended as suggested by the referee in the comment for Line 318.

Line 348 *"... it is less water-soluble and its rate of removal by reaction with OH is much slower than that of SO2".*

Reply: The sentence has been corrected as suggested by the referee.

Line 372-373 *HCHO/NO2 values are not provided in Figure 8 nor in Table S8c. NO2 data are not provided in Fig 8 either. "... being on average a factor of ~3 to 4 higher than that in the BL (see Table S8)*.

Reply: The $HCHO/NO_2$ and SO_2/CO values have been included in the table and the sentence has been corrected according to the table**.**

Line 383-386 *No RH or H2O 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?*

Reply: RH and water vapor profiles from the radiosonde launched on 20 July 2017 at 12 UTC from Rivolto, as well as RH vertical profiles along both the B-C and F-G tracks above GV generated the EMEP-MSC-W model for 20 July 2017 at 9 UTC are provided in the Sect. S10 in the supplement. Both the measurement and model data show an increase in RH and water vapor mixing ratio around 1600 m above the GV surface.

Line 392 *change "BB" to "biomass burning". A more definitive BB marker such as acetonitrile CH3CN 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*.

Reply: We have revised the PTR-MS measurements of acetonitrile during the HALO flight and the observations do not support the statement above. The text has been modified to clarify this point:

“Interestingly, the HYSPLIT simulations do not capture the increase in CO observed at 1630 m between G and X, which may have a fresh anthropogenic origin given the increase in benzene and HCHO mixing ratios as measured by PTR-MS on board (Förster et al, 2023). In contrast, the biomass burning marker acetonitrile CH_3CN did

not show simultaneous enhancements despite the number of active wildfires at the time of the measurements.

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).*

Reply: The references and the sentence have been included as suggested by the referee.

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

Reply: The Section is now 3.5 and has been correctly re-numbered.

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*. Brescia and Verona, what I do not think is NW Veneto

Reply: The description of these back-trajectories was indeed erroneous and was corrected in the revised manuscript as “air masses originating from the surface in the CPP between approximately 44.0°N-44.6°N, and 10.0°N-12.5°E, a densely populated area (Figure S1) including Modena, Bologna, and one of the busiest highways in Italy”.

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]*.

Reply: The sentence has been extended as suggested by the referee.

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)*

Reply: The Figure 9 has been changed to emphasise the back-trajectories origin in the shuttles.

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

Reply: These are indeed 24h FLEXTRA trajectories and the figure caption has been corrected.

Line 448 *"... could not be safely qualified as NOx- nor VOC-limited."*

Reply: The sentence has been modified as suggested by the referee.

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

Reply: The typo has been corrected.

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*.

Reply: Mass advection below 500 m is evidenced at least for the first 2 backward trajectories (11:30-11:31h) corresponding to the period P1 described in this part of the text (Line 499 of the revised manuscript). The sentence has been modified for clarification: “Backward trajectories suggest that the air mass sampled during P1 originated from the south and traveled within the BL below 500 m in the prior 12 to 18 hours (Fig. 10).”

Line 486 *"Figure 11: Spatial variation of NO,...". 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*.

Reply: The Figures 6 and 11 have been modified as suggested by the referee.

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."*

Reply: The sentence has been included as suggested by the referee.

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]*

Reply: The figure caption has been corrected.

Line 525*: Arguably this extra LR transported CO could be from forest fires in southeastern 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).*

Reply: We thank the referee for the suggestion. The text has been accordingly extended.

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

Reply: This acronym has been replaced by “Po Plain” for clarity in the manuscript and supplement.

Line 530 Section 3.2 *Comparison of...I feel that the comparison presented in this section is overly simplified and does not illustrate the Eularian 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 NOx and O3 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 NOx and O3, 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. O3 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 O3 photochemical production in convected air masses or poor mixing of NOx emissions on the ground (lines 571-573). Higher O3 deposition velocities near the ground and associated O3 losses would also affect net O3 production efficiencies at ground level, and could also explain the observed discrepancy.

Reply: The HALO flight E-EU-06 was not intended to follow pollution plumes in a Lagrangian approach. The section comparing "ground and airborne observations over the Po Plain" was revised to better highlight that in the conditions of neutral thermal stability and low wind speed that are common in the Po Plain, and which were well documented for the 20 July 2017 (Section S10 in the supplement), the BL is not well mixed and strong negative gradients for primary pollutants emitted at the surface can occur. In particular, we modified the sentence in lines 611-615 as "The significantly lower NO and NO_2 mixing ratios measured on board HALO than at the ground around 11:30 – 12:00 UTC on 20 July 2017 (Figure 13) suggest a decoupling between the ground and the aircraft altitude (~800 m agl).".

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 delta CO and mean BL CO values] Your CO comparison conclusion sounds reasonable*.

Reply: The sentence has been extended for clarification according to the comments made by the referee.

Line 552 *30-60 ppbv NOx are not "extreme concentrations", they are fairly common for cities curbside monitoring stations...*

Reply: "extreme" has been replaced by "high".

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 NOx 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".*

Reply: The factor ~3 estimate was coming from a simple 1-D steady state transport calculation: 800/0.07/3600 = 3.2 hr, $[NOx]_{HALO}/[NOx]_{ground}$ = exp (-3.2/3) = 0.35, and 1/.35=2.9. The estimate 4-6 hr came from H/0.07, with H ranging from 1000 to 1500 m.

Maclean et al. (2017) quoted (Wallace and Hobbs, 2006) when stating that vertical mixing of air masses in the PBL is rapid, on the order of 30 min. Seibert et al., 2000 refers that it can take hours to get a full equilibration of the BL.

However, since this estimation was unclear to the referee, and not essential, it was substituted by "Indeed, a 1-D model simulating correctly the ground and aircraft level NO_x mixing ratios, as well as the HNO_3 mixing ratio at the aircraft altitude, leads to a BL mixing time of ~30 hrs, i.e. inconsistent with the order of magnitude (30 min) stated by Wallace and Hobbs (2006). Back-trajectories also suggest that the air probed at 830 asl over the CPP left the ground at least ~24 hrs before (Fig. 9)."

Line 570 *"...NOx and VOC have mixed upwind with biogenic VOC..." [rather than "upstream"]*

Reply: Upstream has been replaced by upwind as suggested by the referee

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

Reply: The full stop has been added.

Line 604 *"..., but also by an effective oxidation of NOx-rich emissions..." [rather than "processing"]*

Reply: Although oxidation is likely dominant in the processing of the airmass, getting nitrate ions needs something more than oxidation only of NH_4^+, or deliquescent particles. Therefore, the sentence has been modified as "... also by oxidation and subsequent processing of NOx rich emissions (...)"

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

Reply: The sentence has been modified as suggested by the referee.

Line 615 *"... and to a lesser extent O3*."

Reply: The sentence has been modified as suggested by the referee.

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]*

Reply: The sentence has been modified for clarification as suggested by the referee.

Line 626 *Hůnová et al. (2023) reference missing*.

Reply: The reference has been included.

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"]

Reply: The sentence has been modified as suggested by the referee.

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

Reply: The sentence has been modified as suggested by the referee.

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?*

Reply: The acronym has been deleted and replaced by "Po Plain" all over the supplement