

Pollution transport and transformation over the Po Plain as revealed by airborne and ground-based measurements in July 2017 during EMeRGe

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Abstract. Airborne measurements provide valuable information about the vertical distribution of pollutants enabling the complex transport and dispersion pathways within and above the boundary layer (BL) to be investigated. In this study, the transport of pollution within the Po Plain, a major atmospheric pollution hotspot in Europe, was explored by exploiting airborne measurements made within the EMeRGe (Effect of Megacities on the transport and transformation of pollutants on the Regional to Global scales) project in combination with in situ and ground-based remote-sensing measurements over the whole Po basin. The analysis considers three areas where pollution emission and mixing are dominated by different processes: the Gulf of Venice to the east, the central part of the Po Plain, and the Gulf of Genoa to the west. Wind fields and backward trajectories during the days of the flights indicate the impact of the sea and mountain breezes on the BL distribution of pollutants, and of synoptic scale transport above it. Overall, the extensive data set of primary and secondary trace gases and aerosols at different altitudes provides insight into the effect of vertical and horizontal dynamical mixing on the chemical processing of pollutants within the BL. In this context, mixing of pollution plumes during stagnant conditions within the BL, stratification, venting and export of pollutants towards the Adriatic coast were observed. In addition, desert dust layers of Saharan origin at different altitudes confirm the mixing of naturally occurring dust and its impact on air quality of the lowermost atmosphere over the Po Plain.

36 1 Introduction

37 The Po Plain is the most densely populated area of Italy (Castaldini et al., 2019; Finardi et al., 2014) and its most important
38 industrial and agricultural region. It comprises the administrative districts of Piedmont, Lombardy, Emilia-Romagna, Veneto,
39 and Friuli Venezia Giulia, which comprise the urban agglomerations of Turin, Milan, Bologna, and Venice. With a population
40 of approximately 20 million people (ISTAT, Annuario statistico Italiano 2022) and an average population density of 450
41 inhabitants km⁻² (Castaldini et al., 2019; see also Sect. S1 in the supplement), the Po Plain is one of the European major
42 population centres (MPC) (see <https://ineris.hal.science/ineris-00973562v1>; Molina and Molina, 2004; Gurjar and Lelieveld,
43 2005; Butler et al., 2012). The Po Plain is located in the north of Italy, and borders France, Switzerland, Austria, and Slovenia.
44 It is bounded by the Alps to the north and west, by the Apennines to the south, which separates the plain from the Gulf of
45 Genoa and the Ligurian Sea, and by the Gulf of Venice and the Adriatic Sea to the east (see Fig. 1). The topography of the
46 area leads to a limited dispersion of air masses to the northern, western, and southern sides of the Po Plain, although regular
47 pollution transport from the valley to the pre-alpine and alpine areas via a daily mountain-breeze circulation has been
48 documented (Tampieri et al., 1980; Diémoz et al., 2019a, b). Overall, weak winds and intense solar radiation particularly in
49 summer dominate the meteorological conditions in the Po Plain (e.g., Finardi and Pellegrini, 2004; Raffaelli et al., 2020).
50 Frequent anticyclones cause subsidence of warm air in the mid-troposphere and the development of a stable temperature
51 inversion that traps air pollutants in the boundary layer (BL) (e.g., Finardi and Pellegrini, 2004), leading to pollution episodes
52 in both winter and summer months (Baklanov and Mahura, 2010; Finardi et al., 2014; EEA, 2019; Raffaelli et al., 2020). The
53 high emission rates of pollutants from human activities e.g., industry, transport, domestic heating, use of air conditioning and
54 agriculture (please note that the main emission sources are described in Sect. S2 of the supplement) combined with the
55 topography of the area make the Po Plain one of the most polluted regions in Europe (e.g., Folberth et al., 2012; Gonzalez
56 Ortiz et al., 2020, Targa et al, 2024).

57 Thermally- and pressure-driven circulation systems between mountains, plains, and the sea - such as mountain-valley
58 circulation, sea breeze, and topographic venting from the BL to the free troposphere (FT) - cause complex patterns of the
59 distribution of pollution (Henne et al., 2004). For example, pollutants emitted in the coastal areas (e.g., NO_x, i.e., the sum of
60 nitrogen monoxide NO and nitrogen dioxide NO₂) are transported inland by sea-land breezes with pollutants emitted in the
61 plain flowing towards the mountains, i.e., mountain venting (e.g., Diémoz et al., 2019a). Consequently, the oxidation of
62 primary pollutants leads to the production of ozone (O₃) and secondary aerosol along the mountain valleys (Henne et al., 2004;
63 De Wekker et al., 2018). The compensating return circulation aloft subsides when flowing towards the sea, creating a vertical
64 stratification in the upper coastal BL where O₃ and aerosols accumulate in the first 1-5 km altitude above the coast and offshore.
65 Reservoirs of pollutants aloft are then subject to transport along the coast or form a pool in the mountain valleys and may
66 partially be entrained into the surface level on the following day when the BL rises because of convection. This day-night
67 circulation pattern usually has a turnover time of 2-3 days, similar to that found on the northeastern coast of Spain (Millán et
68 al., 1997, 2000, 2002; Yus-Díez et al., 2021) and on the eastern and western coasts of Italy (Georgiadis et al., 1994; Nyeki et

al., 2002; Finardi et al., 2018). A vertical export of air from the BL to the FT also occurs during venting events (Rotach et al., 2004). As a consequence, NO_x-rich air mixes in the FT with the high background concentrations of methane (CH₄) and carbon monoxide (CO) which is expected to increase the tropospheric O₃ column (Henne et al., 2004, 2005). The meso- or synoptic-scale horizontal mixing of air masses dominates the FT, contributing to the export of locally produced pollutants from the Po Plain to the north and east directions and above the Mediterranean basin. In this manner, the Po Plain pollution can affect the air quality of distant regions when re-entrained inside the BL (Henne et al., 2004; Weissmann et al., 2005; Diémoz et al., 2019a, b).

The atmospheric composition and distribution of pollutants in the Po Plain is constantly and extensively monitored at the surface and aloft by in-situ and remote-sensing observations (e.g., Folberth et al., 2012; Putaud et al., 2014; Ferrero et al. 2019; Gonzalez Ortiz et al., 2020, Bellini et al. 2024). Several studies targeting different pollutants and transport patterns from/to the Po Plain (e.g., Ambrosetti et al., 1998; Wotawa et al., 2000; Stortini et al., 2007; Highwood et al., 2007; Gohm et al., 2009; Barnaba et al., 2007, 2010) have been published. The production and dispersion of pollutants from the Po Plain to the neighbouring regions have also been intensively investigated. Several projects and campaigns have shown the transport of pollution in the Italian Pre-Alps, Alps, the Adriatic Sea, and other Italian regions as well as transboundary transport into neighbouring countries (see Sect. S3 in the supplement).

However, the vertical distribution of pollutants within and above the BL is not sufficiently or adequately known, limiting our knowledge of the complex transport and dispersion pathways in the Po Plain. The information provided by airborne measurements, although snap shots and scarce, is very valuable (e.g., Kaiser et al., 2015). In this context, airborne measurements in the Po Plain were carried out within the project EMeRGe (Effect of Megacities on the Transport and Transformation of Pollutants on the Regional to Global Scales) in July 2017 (Andrés Hernández et al., 2022). The objective of the EMeRGe measurement campaigns was to improve the current understanding of the photochemical and heterogeneous processing of pollution outflows from MPCs by exploiting airborne measurements made on board the High Altitude and Long Range Research aircraft (HALO, <https://halo-research.de>).

The present study investigated the transport and transformation of pollutant emissions in the Po Plain by using aircraft-borne and ground-based instrumentation to extend our knowledge of summertime air pollution and the impact of the local meteorology and orography. A key focus was to identify the dominant transport and transformation patterns in the targeted region and to assess the impact of emissions from the diverse range of sources present. To achieve this goal, the EMeRGe airborne measurements of trace gases and aerosol particles in the lower troposphere and BL of the Po Plain were combined with those from relevant surface in situ and ground-based data from air quality measurement sites and research stations operating in July 2017 within the targeted area. Measurements of long-lived and reactive trace gases and particles were used to determine the time required for mixing and to assess boundary layer mixing dynamics.

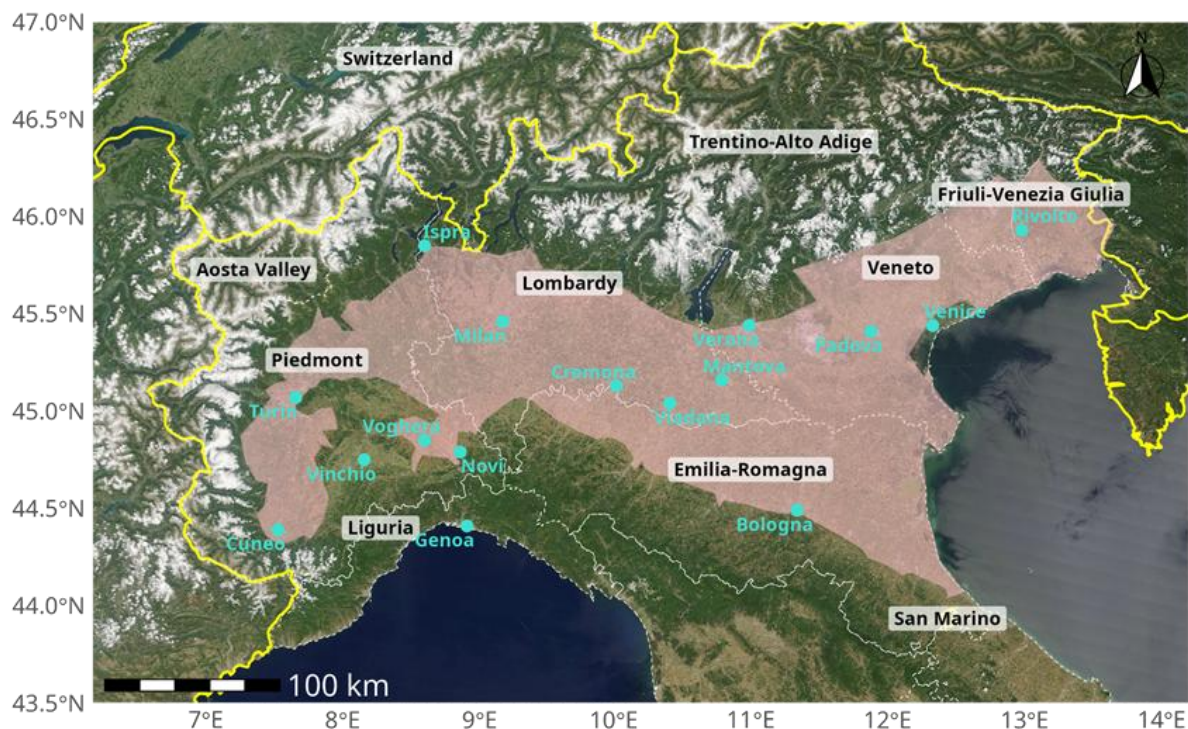


Figure 1: Northern Italy and relevant administrative regions (from west to east) of: Liguria, Piedmont, Lombardy, Emilia-Romagna, Veneto, and Friuli-Venezia Giulia. The Po Plain is highlighted in brown. The Alpine range surrounds the Po Plain on the north and west, and the Apennines in the southwest. Source: MODIS/Terra background from worldview.earthdata.nasa.gov (19 June 2017).

The investigation explored three key topics:

- The horizontal distributions of selected pollutants in the BL over such a complex terrain and the effect of mixing on the vertical distribution of pollutants. One focus was the assessment of the information provided by airborne observations with respect to the BL composition and on the distribution of emissions at the ground.
- The identification of trans-regional and trans-boundary transport to and from the Po Plain.
- The performance of dispersion models using CO as a tracer to identify the origin and transport pathways of pollution in a complex topography.

111 2 Materials and methodology

112 2.1 Observational data

113 The present investigation exploited a set of airborne and ground-based observations obtained in July 2017 from instrumentation
114 on different platforms having different temporal sampling and spatial resolutions.

115 2.1.1 Airborne measurements of trace gases, aerosol particles, and meteorological variables

116 The HALO research aircraft was purchased as a result of a joint initiative of scientists at German universities and environmental
117 and climate research institutions. It is owned and operated by the German Aerospace Centre (Deutsches Zentrum für Luft-und
118 Raumfahrt/ Institute of Atmospheric Physics of the German Aerospace Center, DLR). HALO is a Gulfstream G550 business
119 jet modified and specifically equipped for scientific research. During the EMERGE campaign in Europe, the HALO aircraft
120 performed seven flights for a total of 53 flight hours covering a set of targeted MPCs in western Europe. A list of the in situ
121 and remote-sensing instrumentation on board HALO used for the measurement of trace gases and aerosol particles as well as
122 the basic aircraft data and ancillary measurements with instrument details in the quoted literature is provided elsewhere (Andrés
123 Hernández et al., 2022). In the present study, only a subset of the trace gases measured by the HALO aircraft was selected to
124 identify the transport of pollution in the BL. These were carbon monoxide (CO), carbon dioxide (CO₂), sulphur dioxide (SO₂),
125 nitrogen monoxide (NO), total reactive nitrogen (NO_y), O₃, acetone (C₃H₆O), and the total sum of hydroperoxyl (HO₂) and the
126 organic peroxy (RO₂) radicals which form NO₂ in their reaction with NO (defined as RO₂*). Non-refractory nitrate (NO₃⁻),
127 sulphate (SO₄²⁻), ammonium (NH₄⁺), total organic aerosol (OA), m/z 44 as a marker for oxidized organic aerosol (OOAm),
128 and refractory black carbon (rBC) in the submicron aerosol fraction, as well as the particle number size distribution (from 10
129 nm to 2.5 µm) were additionally measured in situ. Nitrogen dioxide (NO₂) and formaldehyde (HCHO) were measured using
130 an airborne mini-DOAS (Differential Optical Absorption Spectrometer) with a temporal sampling of 1 min. For clear skies the
131 averaging volume of the NO₂ miniDOAS measurements is estimated in the perpendicular flight direction by the field of view
132 of the telescope and in the horizontal by the distance the aircraft travelled during integration (~7 km). The latter ranges between
133 10 km to 25 km near the ground with considerably shorter photon path lengths occurring in the aerosol loaded and cloudy
134 atmosphere. This inherent radiative transfer related averaging may smooth the actual mixing ratios over the observing kernel
135 depending on the location of the pollutant layers with respect to the aircraft (for details, see Hüneke et al., 2017 and Kluge et
136 al., 2020).

137 Two EMERGE flights, E-EU-03 and E-EU-06, were carried out over the same geographical region and targeted specifically
138 the Po Plain on 11 and 20 July 2017, respectively. Initially, HALO flew over the Alps, then along the Po Valley to the
139 Mediterranean coast of Italy crossing the Italian Peninsula from west to east over Rome and then north to the Alps along the
140 Adriatic coast back to the HALO base in Germany (Andrés Hernández et al., 2022). Only the flight tracks that overflew the
141 Po Plain were considered in this study, and are shown in Fig. 2. Letters and numbers are used to indicate the waypoints of the
142 flight tracks (i.e., 6a to 6o for E-EU-06, see Table S4 in the supplement for full details). The vertical and horizontal distribution

of pollutants were investigated by flying at lower altitudes and incorporating shuttles (i.e., descent or ascent flight patterns between holding altitudes) in the tracks.

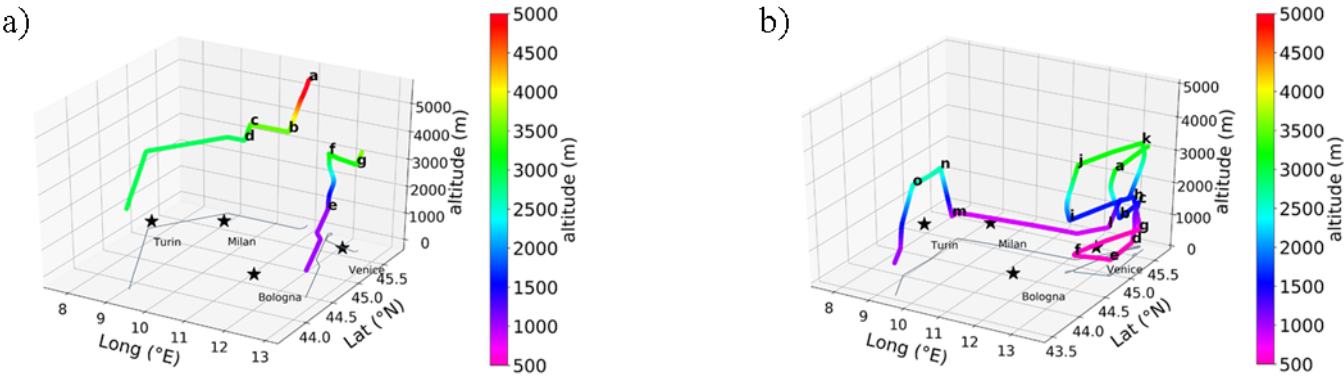


Figure 2: Flight tracks from the EMeRGe flights a) E-EU-03 on 11 July 2017, and b) E-EU-06 on 20 July. The colour-code refers to flight altitude during the flight tracks considered in this study and the letters indicate the waypoints as mentioned in the text. All altitudes are above sea level (asl). The 2D flight track is shown in grey on the xy plane, main cities in the area are also reported (black stars) to facilitate geo-reference and comparison with Fig.1.

2.1.2 In situ surface and ground-based remote sensing measurements

In Italy, air quality is monitored at the regional level by the local Environmental Protection Regional Agencies (ARPAs) measuring EU-legislated pollutants and meteorological variables in air quality networks (see Sect. S5 and S6 in the supplement). In this work, the hourly resolved data from ARPA traffic and background air quality monitoring network (AQMN) stations located in the proximity to the HALO flight tracks in the regions of Piedmont, Lombardy, Veneto, and Liguria were used (see Fig.3). In addition, trace gas measurements of high accuracy and 10-minute temporal sampling were provided by the regional background atmospheric observatory of the European Commission’s Joint Research Centre (EC-JRC) in Ispra (<https://abc-is.jrc.ec.europa.eu/>).

Aerosol profiles from selected ground-based active remote-sensing stations were used in support of the analysis (see S7 in the supplement). These were obtained by an aerosol LiDAR (Light Detection and Ranging) operating in Ispra in association with ACTRIS (Aerosol, Clouds and Trace gases Research Infrastructure, www.actris.eu), and by an automated LiDAR-ceilometer (ALC) operating in Milan as part of ALICENET (Italian Automated Lidar-CEliometer NETwork, www.alice-net.eu, Bellini et al., 2024). Both LiDAR and ALC profiles of the particle backscatter coefficient (β_p) provided information about the presence of different aerosol stratifications within the BL and in the FT (see Fig. 3 for instrument location). In Ispra, profiles of the particle depolarisation ratio (δ_p) at specific measurement times were used to identify the presence of desert dust (particles of non-spherical shapes) within some specific aerosol layers (Wandinger, 2005), while high temporal sampling and continuous ALC profiles enabled the diurnal variability of the aerosol structures to be identified and the relevant diurnal evolution of the

168 Mixed Aerosol Layer (MAL) to be inferred (in cloud-free conditions only) following the approach described in Bellini et al.,
169 (2024).

170 **2.1.3 Meteorological soundings**

171 The radiosonde stations selected for this study were Cuneo Levaldigi, Milano Linate, and Rivotto (see Fig. 3). For the
172 determination of the height of the BL, two different methods were applied to the radiosonde in situ measurements of
173 temperature (T), potential temperature (Θ) and relative humidity (RH) at 12 UTC on the days of flight. In the parcel method,
174 the BL height is either defined as the elevation at which an ascending air parcel becomes neutrally buoyant (Hennemuth and
175 Lammert, 2006) or to which an air parcel with surface temperature rises adiabatically from the ground by convection (Collaud
176 Coen et al., 2014). The height of the BL is calculated as the intersection between the temperature profile and the dry adiabatic
177 lapse rate starting at near-surface temperature (Seibert et al., 2000; Collaud Coen et al., 2014). In contrast, the gradient method
178 defines the BL height as the height where the gradient of Θ is maximum (T gradient method), corresponding to the top of the
179 capping inversion, or where the gradient of the RH is minimum or zero (RH gradient method), associated with a reduction in
180 water vapour content (Hennemuth and Lammert, 2006; Wang and Wang, 2014). Among the methods applied to the radiosonde
181 profiles to estimate the BL, the parcel method is considered the most reliable, but it has proven to fail when applied to a stable
182 BL over land or sea. A cloud-topped BL is also hardly identifiable because of the complex structure associated with cloud
183 layers (Seibert et al., 2000; Hannemuth and Lammert, 2006). Despite the limitations of single radiosonde profiles to describe
184 the changes in space and time of the vertical structure of the atmosphere and to identify the limits of the BL in the presence of
185 cloud layers (e.g., Seibert et al., 2000; Hennemuth and Lammert, 2006), both methods agreed reasonably well for
186 measurements made on the days studied.

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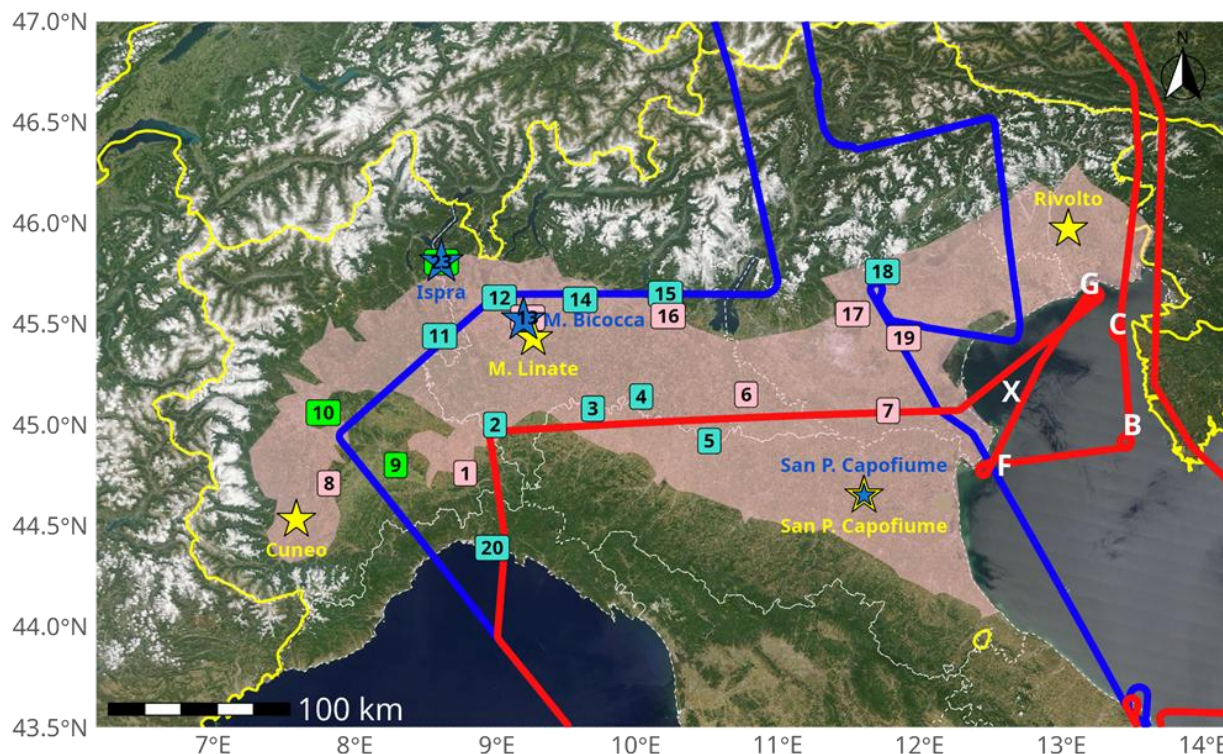


Figure 3: Data sources used in this study, covering the whole area of the Po Plain: E-EU-03 (blue) and E-EU-06 (red) HALO flight tracks; AQMN traffic (pink squares), urban background (turquoise squares) and regional background (green squares) stations are identified by the station number (tabulated in the supplement Table S6.1); radiosonde stations (yellow star) and LiDAR/ALC stations (blue star). Geographical points indicated by white capital letters are used in the discussion of the E-EU-06 track (see Sect.3).

2.2 Modelled estimation of transport patterns of pollution

The data interpretation and the estimation of pollution transport patterns during the E-EU-03 and E-EU-06 flights rely on the prevailing meteorological conditions before and during the measurements to determine the origin of the air masses probed. Following model-based tools were used:

a) FLEXTRA: backward trajectories

The FLEXTRA backward-trajectories provided for EMeRGe were calculated with the FLEXTRA 5.0 trajectory model (see Stohl et al., 1995; Stohl and Wotawa, 1995; <https://folk.nilu.no/~andreas/flextra.html>), using the European Centre for Medium-Range Weather Forecast (ECMWF, <https://www.ecmwf.int/>) operational data set ERA5 meteorological data (see Hersbach et al., 2020) at 0.25° horizontal resolution (around 27.8 km). Trajectories were initialised every minute of the flight time and cover the trajectory over the 10 days prior to the locations.

b) COSMO: high resolution wind fields

The COSMO-Model (Consortium for Small-scale Modeling, <http://www.cosmo-model.org>) which offers a factor 10 higher spatial resolution than ERA5, was additionally employed in this study to ensure an accurate analysis of transport dynamics on

the mesoscale, such as the valley-mountain breeze. COSMO is a non-hydrostatic, fully compressible, limited-area atmospheric prediction model. It is based on thermo-hydrodynamical equations for compressible flow in a moist atmosphere, formulated in rotated geographical coordinates and a generalized terrain following height coordinates. The data used by COSMO were provided for the period under investigation by the meteorological operational centre – air force meteorological service COMET. The present study considers the high-resolution version COSMO-I2 or COSMO-IT (2.8 km grid cells and 65 vertical levels) in its numerical weather prediction declination for the assessment of the wind field in the Po Plain area. Notably, as complete 3D fields (surface and vertical profiles) are released at 6-hour intervals, the wind fields simulated at 09 and 12 UTC on 11 and 20 July were used, with altitude steps of 200 m between ground level and 2000 m. The origin of air masses is assessed in combination with the Lagrangian tool LAGRANTO (Sprenger and Wernli, 2015) integrating the COSMO wind fields and tracing 3-D backward-trajectories for air masses. For this study, 12 hours backward-trajectories were computed with a time step of 15 minutes, starting from the aircraft coordinates.

c) HYSPLIT: CO enhancements during transport

The Lagrangian Particle Dispersion Model HYSPLIT (Draxler and Hess, 2014; Stein et al., 2016) calculates the atmospheric dispersion of local emissions of CO, accumulated over 6 days of transport. HYSPLIT forward dispersion simulations (Marenco et al., 2006; Birmili et al., 2010) were used to estimate the contribution of CO emissions within the Po Plain (44-46N, 7.5-13.5E) at the time and place of the CO measurements aboard HALO, as well as the ages of the emissions. The forecast assumes the Po Plain to be a continuous emission source. The HYSPLIT simulated CO concentrations do not include accumulated "background" values due to the much longer lifetime of CO and are therefore not to be compared with absolute concentrations but rather with CO enhancements (i.e., ΔCO) in local plumes. HYSPLIT was driven by meteorological data from the operational ECMWF forecast (0-11 hours forecast, 12-hourly update, interpolated at 0.1° horizontally, pressure levels, 1-hourly output). CO emission rates were taken from the EDGAR HTAP V2 emission inventory (http://edgar.jrc.ec.europa.eu/dataset_htap_v2). Neither chemical reactions nor convection are modelled. The computation (core-model) and the visualisation (post-processing) were controlled by a specific client-server infrastructure developed at the Institute of Atmospheric Physics of the DLR for campaign support as well as post-campaign analysis.

2.3 Analysis approach using pollutant distribution and gradients within the BL during E-EU_06

The airborne trace gas and aerosol particle concentrations were analysed in three selected areas of the Po Plain (see Fig.5) during the E-EU-06 flight to assess vertical gradients and the degree of mixing in the BL. Information about the vertical distribution of pollutants at the time of the flight was provided by measurements at different altitudes during the HALO shuttles.

Increases in the airborne mixing ratios of NO_y , O_3 , and CO as well as in rBC and particulate nitrate concentrations inside the BL were attributed to HALO flying through plumes of pollution. Short-term variations in the relative concentrations of trace gases provided additional information about the origin and chemical transformation of the plumes during transport. In particular, the HCHO to NO_2 ratio is an indicator of the sensitivity of O_3 photochemical formation to NO_x and VOC

concentrations in the atmosphere. HCHO is an intermediate formed in the oxidation of most VOC and is often used as a proxy for the total VOC reactivity (Sillman, 1995). The HO₂ formed by HCHO photolysis increases the rate of catalytic cycling of NO to NO₂. A HCHO / NO₂ <1 indicates a VOC-limited regime while a HCHO/NO₂ > 4 indicates a NO_x-limited regime (e.g., Souri et al., 2020; Hong et al., 2023, Vazquez Santiago et al., 2024). Ratios between secondary and primary pollutants (O₃/CO, NO_y/CO, NO₃⁻/rBC, OOA_m/rBC) were used as an indicator of pollution plume chemical processing. The effective mixing of freshly emitted and aged pollution was evaluated from HYSPLIT CO dispersion simulations. The CO enhancement provided by HYSPLIT (ΔCO) is used as an indicator of the contribution of the CO emissions within the Po Valley as well as of the age of the air masses mixed before the CO measurement point. This information was complemented by FLEXTRA back-trajectories and COSMO wind fields for identifying the origin and potential sources of pollution of the air masses probed on-board HALO. The comparability of FLEXTRA and LAGRANTO back-trajectories is discussed in Sect. 3.3.

3 Results and discussion

3.1. Boundary layer meteorology during flights E-EU-03 and E-EU-06

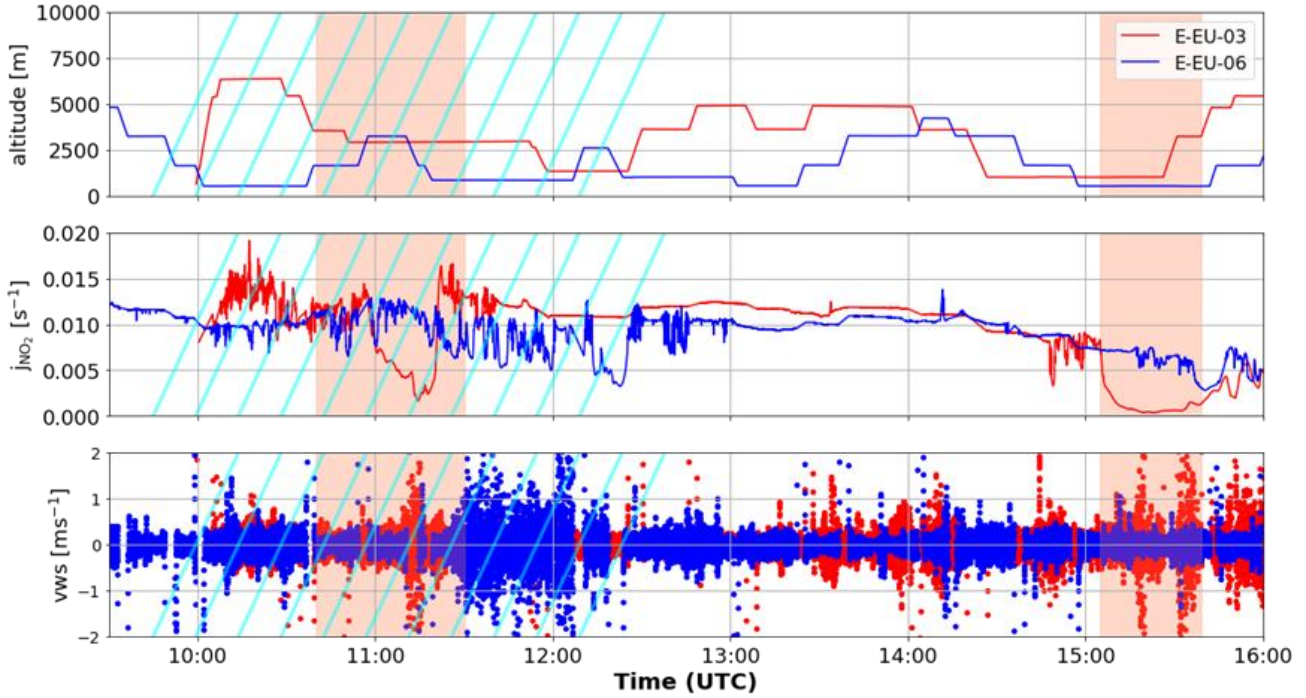
A main focus of the analysis is on the distribution of pollutants within the BL of the Po Plain. For this, the BL height was calculated from the air parcel and gradient methods applied to the radiosonde measurements in each station (see Table 1). Due to the presence of clouds, the RH gradient method underestimated the BL depth on 20 July and was thus not used for the BL estimate. The BL height values obtained in Table 1 are consistent with the available ground-based aerosol profile measurements. According to the weather reports provided by the corresponding ARPAs, the weather was unstable on 11 July because of the passage of a low-pressure system, which came from Great Britain in the NW. The on-board measured photolysis frequency j_{NO2} was used as a qualitative proxy metric for cloudiness during the flights while the vertical wind speed measured by HALO at the flight altitude was taken as an indicator of vertical transport at comparable altitudes within the BL (Fig.4).

Table 1: Average BL height at 12:00 UTC as estimated by using the parcel, the temperature gradient, and the relative humidity methods to the radiosonde measurements in Milano Linate, Cuneo Levaldigi, and Rivolto on the 11 and 20 of July. On 11 July the values are derived from the average of the three methods described in the Sect. 2.1 while the parcel and temperature gradient methods are used for the 20 July. The uncertainty on the values is the maximum error ((max value – min value)/2).

	11 July 2017	20 July 2017
Milano Linate	1450 ± 100 m	1600 ± 400 m
Cuneo Levaldigi	1340 ± 80 m	No measurement available
Rivolto	1710 ± 180 m	1000 ± 70 m

As expected, the measured j_{NO2} was lower when the E-EU-03 flight approached regions of unstable weather and turbulence in the surroundings of Cuneo (11-11:50 UTC) and Padova (from 15:15 UTC onward). This instability may have favoured the

268 vertical dilution of emitted pollution in comparison to the 20 July, when anticyclonic conditions stabilized the atmosphere.
 269 During the E-EU-06, a pronounced j_{NO_2} variability was observed during passage through a cloud-covered sky south of Milan
 270 (around 12 UTC). In that case, in the lowermost levels sounded HALO (830-840 m approximately), the vertical wind speed
 271 (vws) and its variability were higher over the central Po Plain (-2 to $+4$ m s^{-1} , 1 s values, time range 11:25-12:07 UTC) with
 272 respect to that observed above the sea over both the Gulf of Venice and the Gulf of Genoa ($\text{vws} < 1$ m s^{-1}).
 273



274
 275 **Figure 4: Photolysis frequency (j_{NO_2}), flight altitude and vertical wind speed (vws) measured during the E-EU-03 flights (red) and**
 276 **the E-EU-06 flight (blue). The periods of the two flights above the Po Plain are shaded in coral and striped in cyan, respectively.**

277 In Fig. 5, the wind fields calculated by COSMO for the 20 July at 9 and 12 UTC provides evidence for the complex thermally
 278 and orographically driven air transport patterns over the Po Plain (see Sect. S10, Fig. S10.1 in the supplement for the 11 July
 279 E-EU-03 flight). Inside the BL (< 1000 m altitude), sea breeze regimes are observed, with stronger winds increasing with
 280 altitude over the Gulf of Genoa coastline ($43.5\text{--}45^\circ$ N; $8\text{--}10^\circ$ E) and sea to land circulation up to approximately 600 m altitude
 281 over the Gulf of Venice coastline at the east ($44\text{--}46^\circ$ N; $12\text{--}14^\circ$ E). In the upper layers of the BL (ca 800-1000 m), an inland-
 282 bound breeze flows from the west coast to the mountains ($8\text{--}10^\circ$ E, 46° N) at 9:00 UTC and is still visible with slight changes
 283 in intensity and wind direction at 12 UTC. In the FT, the model computed eastwards to north-eastwards air transport, following
 284 the dominant pattern previously observed over the Po Plain (Finardi et al., 2004 and Diémoz et al., 2019a, b), revealing a
 285 strong wind shear between ~ 1000 and 1600 m above sea level (asl).

286 As HALO remained during the E-EU-03 above the BL except for the last flight tracks late in the afternoon, further data analysis
287 will focus on E-EU-06, which remained mostly in the BL between 10:00 and 12:10 UTC . The investigated region was divided
288 into three geographical partly overlapping areas (see Fig.5 top left) marked by different mixing regimes: the two coastal areas
289 of the Gulf of Venice (44.5-46° N; 11.5-13.5° E) and the Gulf of Genoa (43.5-45.5° N; 7.5-10° E), and the central part of the
290 Po Plain (44.5-46.5° N; 8-13° E). These areas of study will hereafter be referred to as GV, GG, and CPP, respectively.

291 **3.2. Vertical distribution and advection of pollutants in the Gulf of Venice (GV)**

292 Figure 6 shows the spatial variation of NO, NO_y, NO₂, O₃, CO, HCHO, C₃H₆O, SO₂, RO₂^{*}, CO₂ mixing ratios, and rBC, OA,
293 NO₃⁻, NH₄⁺, and SO₄²⁻ mass concentrations measured on board HALO over the GV during the EMeRGe E-EU-06 flight.
294 Measurements made over the same GV area at different heights are shaded with the same colour (darker shades at lower
295 altitudes). Two shuttles were carried out over the GV (see Fig. 3):

- 296 1) from 09:42 to 10:10 UTC between **B** (45.0°N, 13.4°E) and **C** (45.4°N, 13.5°E) about 100 km off the Italian coast and
297 along the Croatian west coast at 3230 m (6 to 6a), 1630 m (6b to 6c) and 520 m (6d to 6e);
- 298 2) from 10:21 to 11:10 UTC between **F** (44.9°N, 12.6°E) and **G** (45.6°N, 13.1°E) less than 35 km off the Italian coast at
299 520 m (6f to 6g), 1630 m (6h to 6i), and 3230 m (6j to 6k).

300 **3.2.1 Shuttle B-C along the Croatian coast**

301 In Fig. 7, the 3D distributions of CO, O₃ and NO are plotted for shuttles 1 (waypoints 6 to 6e) and 2 (waypoints 6f to 6k). The
302 transect between both shuttles in the marine BL across the Adriatic (6e to 6f) is analysed separately in Section 3.2.4.
303 During the first shuttle (between points **B-C** in Fig. 3), the concentrations of gaseous and particulate species were deemed
304 constant enough during the slots selected for each of the legs 6-6a, 6b-6c and 6d-6e to be averaged. The averages calculated
305 for several species including CO, O₃, C₃H₆O, particulate OA, NO_y and particulate NO₃⁻ were higher at 1630 m in the FT (6b-
306 6c) than at 530 m (6d-6e) in the BL. This was not the case for NO, NO₂, SO₂, HCHO, particulate SO₄²⁻ and rBC (Fig. 6).

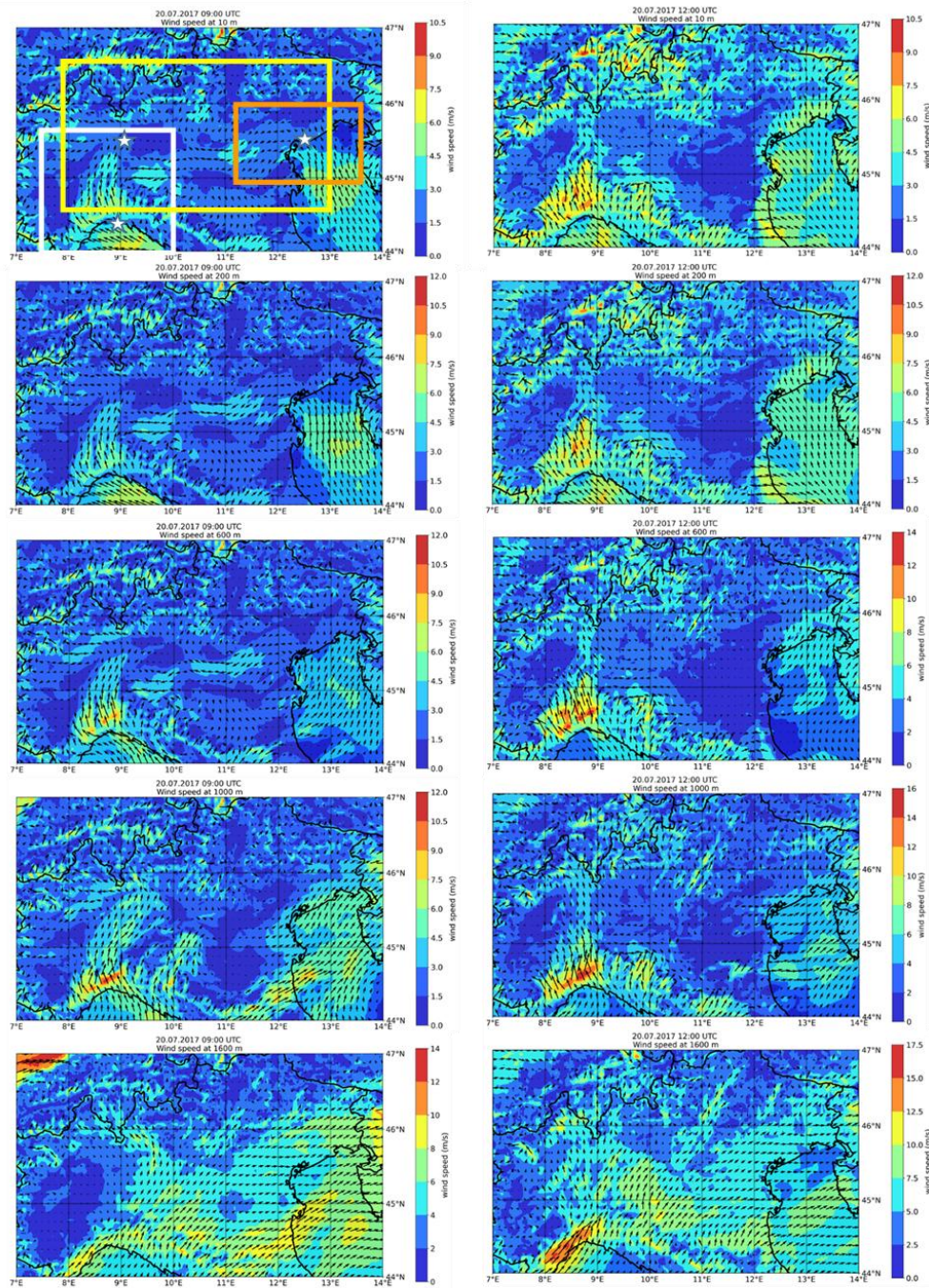


Figure 5: Wind speed and direction from 10 m (top) to 1600 m (bottom) altitude above ground level (agl) simulated by COSMO on 20 July 2017 at 9:00 UTC (left) and 12:00 UTC (right) in Northern Italy. Boxes in the top left panel indicate the three geographical areas selected for this study: the Gulf of Venice (GV, red), the Gulf of Genoa (GG, white) and the central Po Plain (CPP, yellow). Sea-land circulation dominates on the ground in the coastal areas and reverses in the GV from about 600 m. Please note the changes in the scale of the wind speed (ws). White stars indicate the position of Genoa, Milan and Venice (from left to right).

As a consequence, NO_y/NO_2 (Table S8), O_3/CO , $\text{C}_3\text{H}_6\text{O}/\text{CO}$, NO_y/CO , NO_3^-/rBC , OOAm/rBC and OA/rBC ratios (Fig. 8) were high at the 1630 m level (6b-6c). At 3230 m asl, mixing ratios are less than in the BL for all species. HCHO/NO_2 ratios (Table S8) increased from 4 at 520 m, to 6 at 1630 m, and 8 at 3230 m, indicating that O_3 photochemical production becomes increasingly NO_x limited with altitude during this shuttle along the Croatian coast. The highest SO_2 mixing ratios were observed when approaching waypoint 6e (B, 530 m) close to the Croatian coast at ~10:10 UTC, suggesting a significant contribution from shipping (cargo ships and cruise ferry traffic), which has been attributed to be the main source of gaseous pollutants emissions in the GV (see <https://www.port.venice.it/en/projects-and-sustainability/> and Toscano, D., 2023). The NO and NO_y data are not available for this period due to instrumental zero calibration. Backward trajectories and wind maps indicate that air masses were lifted up from the sea surface to 520 m about 10-16 hours before the measurements (left hand panel in Fig. 9), advected from the west in the FT (> 2000 m) at 3230 m, lifted from the surface of the CPP at 1630 m. At this level, larger O_3/CO , $\text{C}_3\text{H}_6\text{O}/\text{CO}$, NO_y/CO , NO_y/NO_2 , particulate NO_3^-/rBC and OOAm/rBC ratios (see Fig. 8 and Table S8 in the supplement) indicate enrichments in secondary pollutants, characteristic of photochemically processed air masses, across this leg. Furthermore, the HYSPLIT calculation of the CO enhancement also implies a significant contribution (10 ppbv) of emissions from the Po Valley, primarily from the previous 12-48 hours for this leg (Fig. 6). In line with these observations, FLEXPART back-trajectories suggest that this polluted air mass probed at 1630 m originated from the surface in the CPP 12-24 hours earlier, and travelled westwards before returning to GV above the Croatian coast. HYSPLIT 72-hr forward trajectories show that it was exported westwards across borders without reaching the ground (Fig. S12.1).

3.2.2. Shuttle F-G along the Italian coast

During the second shuttle across GV, near the Italian coast (between points **F-G** in Fig. 3), the concentrations of the gaseous and particulate species changed significantly between waypoints 6h and 6i at 1630 m asl. Each leg of the shuttle is covering the same spatial area but in the opposite temporal order, so that the area at the end of the leg at 520 m is overflowed at the beginning of the leg at 1630 m and again at the end of the leg at 3230 m (see also HALO tracks in Fig. 2b). To clarify this, observations over the same GV area at different heights are shaded with the same colour (darker shade at lower altitudes) in Fig. 6. Further analysis was undertaken by splitting in two the legs between **F** and **G** at point **X** (Fig. 3), thus north and south of 45.13°N.

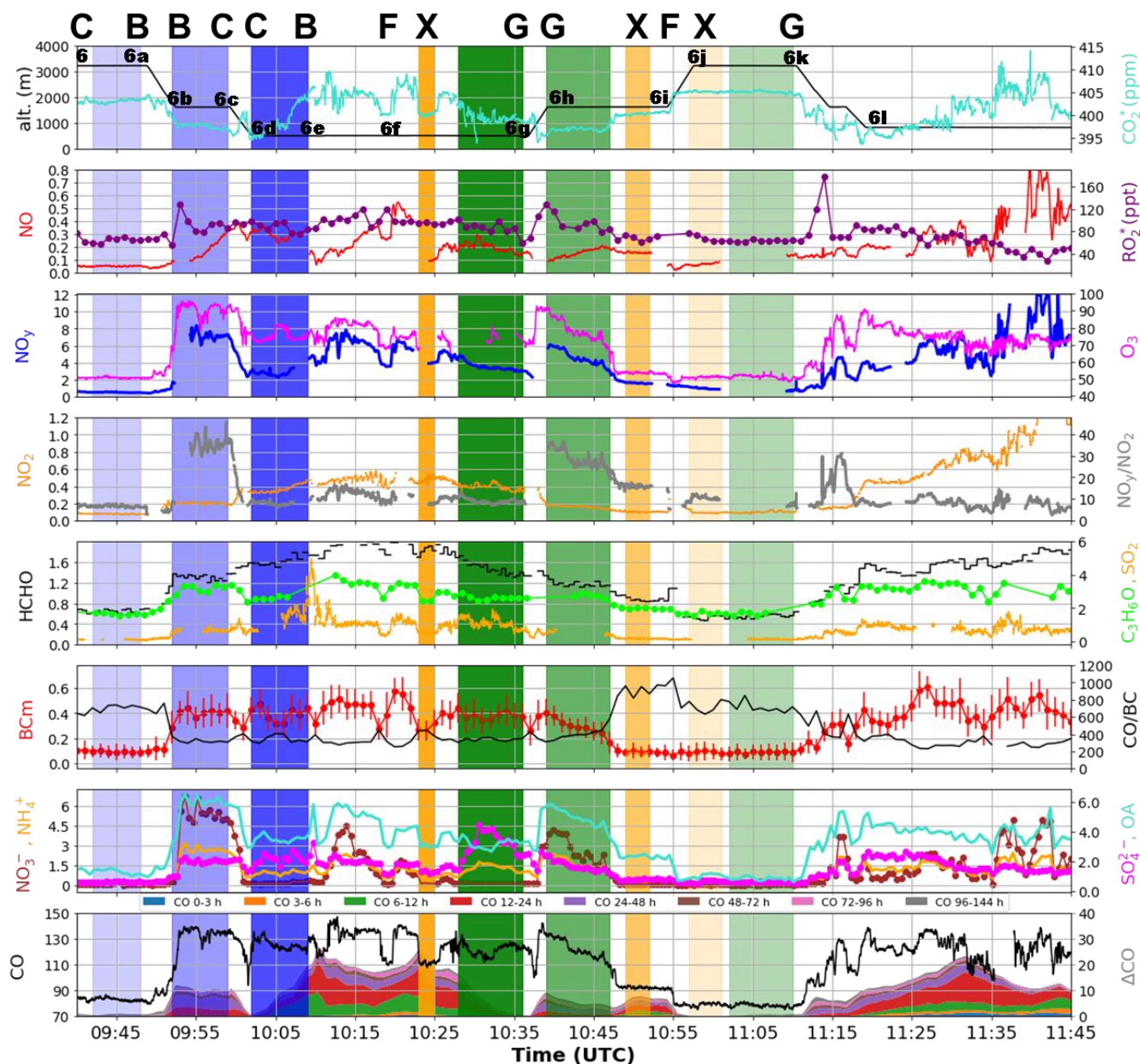


Figure 6: Temporal and spatial variation of NO, NO_y, NO₂, O₃, CO, HCHO, C₃H₆O, SO₂ (all in ppbv, units not written in the axis for clarity), RO₂^{*} (in pptv), CO₂ (in ppm) mixing ratios, and rBC, NO₃⁻, NH₄⁺, SO₄²⁻ and OA mass concentrations (in μg m⁻³ STP) measured on board HALO over the Gulf of Venice (GV) during the EMerGe E-EU-06 flight. HCHO and NO₂ values are retrieved from miniDOAS measurements. BC_m are 1 min averages of rBC with 1σ error bars. The flight altitude and the changes in course and altitude (waypoints 6-6l) are marked in the top panel. Blue, orange and green shaded coloured time windows highlight air masses each captured over the same geographical area (see Figure 3) but at different heights (darker at lower altitudes). HYSPLIT simulations of the contribution of Po Valley emissions to the observed (ΔCO) coloured according to the estimated age are shown in the bottom panel. The geolocations B, C, F, X, and G as in Fig. 3 are shown in the top panel for clarity.

348 North of point **X** (X-G), the mixing ratios or accordingly the mass concentrations in the BL (520 m) and the FT (1630 m) were
 349 similar for CO, NO, O₃, C₃H₆O, and rBC, whereas they were significantly lower at 1630 m for NO₂, HCHO, and SO₄²⁻ (Fig.
 350 6). At 3230 m the concentrations or mixing ratios of all species were lower. Similarly to the first shuttle, particularly high
 351 NO_y/CO, NO_y/NO₂, NO₃⁻/rBC, OA/rBC and OOAm/rBC ratios north of between **X** and **G** at 1630 m indicated a highly
 352 processed pollution plume. In contrast with carbon and nitrogen compounds, sulphur compounds (SO₂ and SO₄²⁻) were not
 353 enhanced in this plume probed at 1630 m. In particular, SO₂ mixing ratios and SO₂/CO were a factor of ~2 lower at 1630 m
 354 compared to 520 m asl, which is consistent with sulphur-poor emissions and/or SO₂ sinks such as oxidation by OH or uptake
 355 by dust or cloud droplets inside the BL. However, the lack of enrichment in SO₄²⁻ suggests that SO₂ oxidation followed by
 356 gas-to-particle conversion did not play a major role. The HYSPLIT simulations indicate a predominant contribution of
 357 emissions older than 24 h to a moderate (5 ppb) CO enhancement, characteristic of an aged pollution plume. This could be due
 358 to the fact that exceptional sources (i.e., not being part of the emission inventories) contributed to the observed CO mixing
 359 ratio. The observations were consistent with FLEXPART 96-hr back-trajectories suggesting that the probed air mass was
 360 impacted by wildfire emissions in southern France 3-4 days earlier. In contrast, particularly high SO₂ mixing ratios (Figure 6)
 361 and SO₂/CO ratios (Figure 8) were observed in the BL (520 m) during this leg, being on average a factor of 2 higher than that
 362 in the FT (1630 m) (see Table S8c). Back-ward trajectories (Fig.9, bottom of the right panel) indicate that air masses travelled
 363 in the BL below 520 m asl during the previous 24 hours, pointing at shipping as a major source of SO₂. Port traffic and activities
 364 around the port of Venice have been found to impact negatively on the local air quality, especially in summer months when
 365 the meteorological conditions in the Mediterranean contribute to the formation of photochemically generated secondary
 366 pollutants and their accumulation in the lower tropospheric layers (Marmer and Langmann, 2005; Contini et al., 2011; Merico
 367 et al., 2021). Ship diesel engines are strong emitters of both primary and secondary PM. Primary PM in diesel are mostly
 368 emitted as ultra-fine particles and include soot, ash and a variety of organics as polycyclic aromatic hydrocarbons. Shipping
 369 secondary PM emissions include SO₄²⁻, NO₃⁻ and organics (Gobbi et al, 2020). From previous studies using high temporal
 370 resolution particle measurements at three sites on the coast of Venice, the mixing time of typical pollution plumes from ships
 371 with the surrounding air is between 20 minutes and one hour (Contini et al., 2011; Merico et al., 2021). This transport is
 372 confirmed by the COSMO wind direction and speed (see Fig. 5 and Fig. S10.2 in the supplement) at 12:00 UTC on 20 July
 373 2017, that indicates SE (sea-land breeze) prevailing winds up to an altitude of 200 m, whereas SW winds were found to
 374 predominate between 500 m and 2000 m.

375

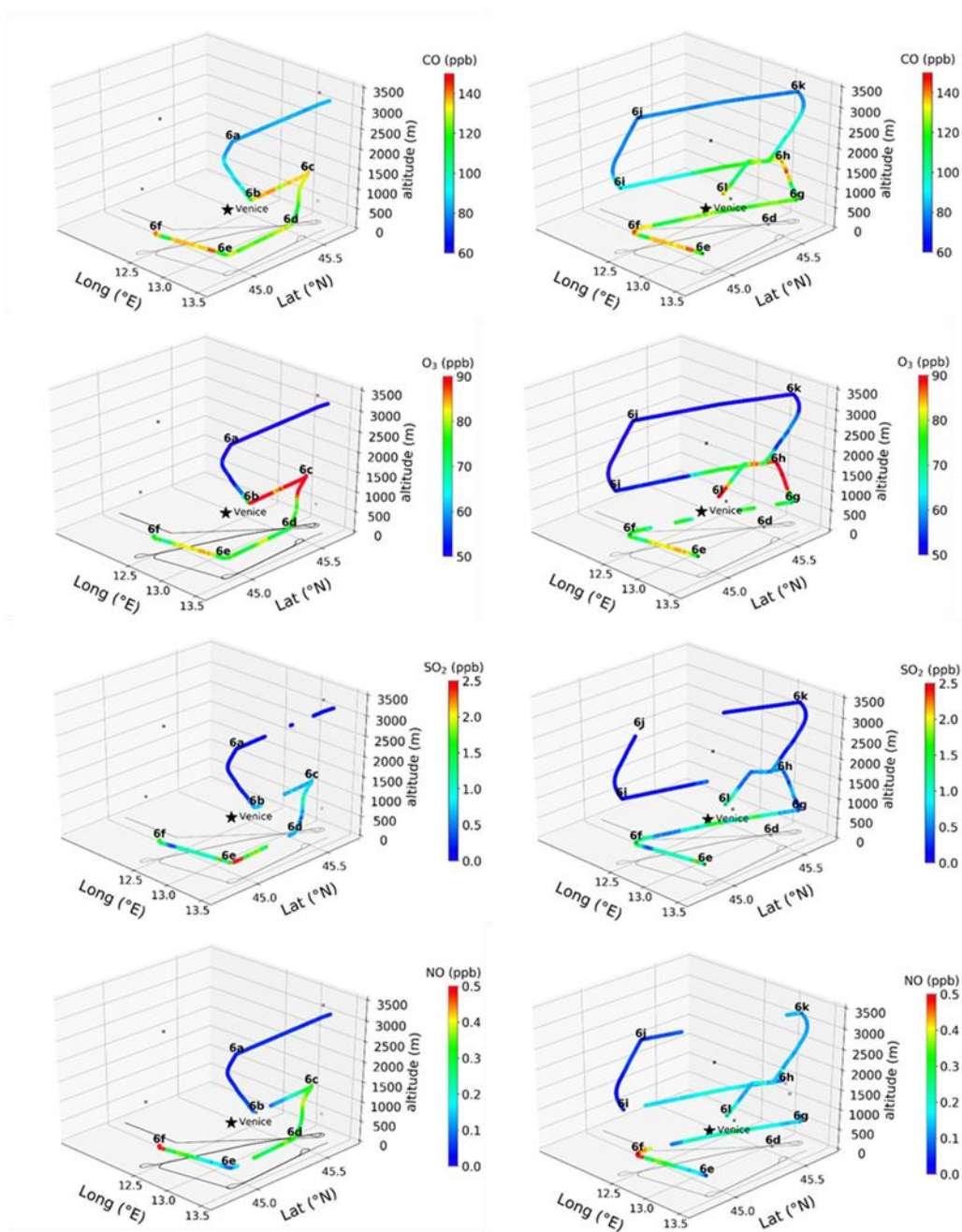


Figure 7: Vertical distribution of CO, O₃, SO₂ and NO observed during the first (left; waypoints 6a to 6e) and second (right; waypoints 6f to 6k) shuttles during E-EU-06 on the 20 July 2017.

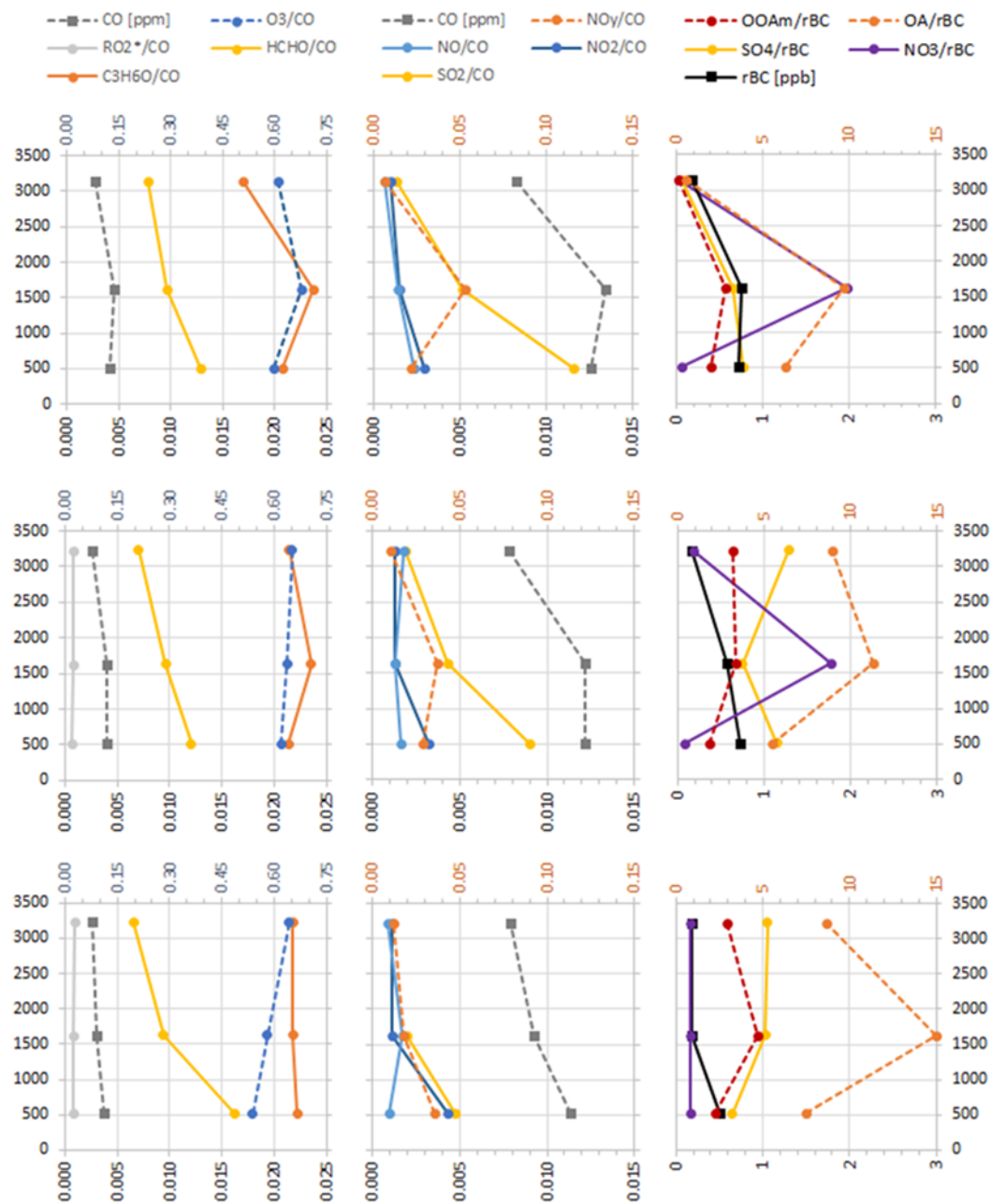


Figure 8: Profiles of CO (ppm) and rBC (ppb), and molar ratios between selected species between B and C (top), G and X (middle) and X and F (bottom) in the GV. See Fig. 3 for the position of B, C, F, G and X. Dashed lines refer to the top x-axis.

As anticipated, the average values of CO, SO₂, NO₂, NO_y, HCHO, C₃H₆O, O₃, rBC, NO₃⁻, SO₄²⁻, and OA mixing ratios or accordingly mass concentrations were all significantly smaller during the southern part (X–F) of the leg at 1630 m asl compared to the northern part (G–X). In contrast, concentrations at 520 m asl were all similar (or significantly greater for HCHO) in the south (X–F) compared to the north (G–X) part of the leg. Particularly high HCHO/NO₂ ratios (ranging from ~9 to 10) resulting

from rather low NO_2 concentrations were observed between X and F at 1630 m, indicative of an aged pollutant plume. Backward trajectories indicate similar air mass origin to those observed further north (G-X) in the same leg, albeit not passing lower than ~1200 m asl, whereas at 520 m asl they indicate a slow motion of air masses from ground level around 45.0 °N, 12.0 °E during the previous 12 hours. The air motion was therefore noticeably different between the BL at 520 m and the FT at 1620 m asl. The HYSPLIT calculations indicate that the contribution of CO emissions from the Po Valley to the CO enhancement at 520 m asl (~8 ppb) was primarily due to emissions within the last 6-24 hours, with no significant contribution from more recent emissions, i.e., different again from what was computed for 1630 m asl.

3.2.3. Comparison of the two shuttles across the GV

Similar mixing ratios were observed for each species at 3150 m above the GV during the two shuttles. The probed air masses were transported in the FT from ~ SW at about 11 m s^{-1} (almost 1000 km per day). Mixing ratios were much more variable at 1630 m where plumes of pollutants originating within the BL in the CPP (6b-6c along the Croatian coast) or transported in the FT from ~ WSW (6h-6i, along the Italian coast), and traveling eastward were probed. In the BL (520m), mixing ratios were again similar during the two shuttles, except for SO_4^{2-} , whose concentration was on average twice as much along the Italian coast. The air masses probed in the BL had the same origin, traveling along the Italian east coast in the BL.

The pollution layers probed at 1630 m along segments B-C (6b-6c) and G-X resulted from significant chemical processing, as indicated by enhanced OOA_m/rBC , NO_3^-/rBC , NO_y/CO and NO_y/NO_2 ratios compared to that in the BL (Figure 8, Table S9). The enrichments in O_3 , NO_y , and NO_3^- were slightly higher along B-C than along G-X, although air mass origins were quite different. There were no such enrichments in the FT (1630 m) compared to the BL (520 m) along X-F, except for O_3 , OA and OOA_m .

The chemical processing of emissions during mixing is affected by the ambient air conditions. In the lower FT (1600 – 2000 m), the relative humidity was higher than at the ground, and H_2O mixing ratio increased with altitude (Fig. S10.4 in the supplement). Under high humidity conditions, transformation of NO_x compounds to HNO_3 and subsequent transfer to aerosol phase is favoured (e.g., Guimbaud, 2002). Nitrate production in the entrainment zone of the BL has been previously documented in the area of Milan in summer (Curci et al., 2015). Based on WRF-Chem simulations at the regional scale, Curci et al. (2015) showed that coupling of chemistry and dynamics leads to a large NO_3^- spatial variability and positive vertical gradients over the whole Po Valley and Northern Adriatic in July. In particular, the rate of nitrate production is higher in the upper BL, where RH is above the ammonium nitrate deliquescence point (~ 60 % RH, Talbot et al, 2016), which occurred in the plumes where NO_y and NO_3^- enrichments were observed by HALO (Figures S10.3 and S10.4). 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 increases 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. The polluted layer observed at this altitude may be a returning layer of pollution transported from inland to the coast as the result of combined breezes reinforced by upslope winds. This behaviour

has been observed in other coastal areas (McKendrey and Lundgren, 2000; De Wekker and Kossman, 2015). The air masses in the sea breeze travel inland during the morning and early afternoon by incorporating weaker up-slope circulatory cells (e.g., Millán et al., 2004). The mountain slopes act as convective–orographic chimneys that link the surface flows directly with their return flows aloft and lead to vertical recirculations of differently aged pollutants emitted along the coasts for several days. Similar land-sea breeze coastal shallow circulations were reported in southern West Africa (Flamant et al 2018). The return layer is illustrated by 96h back trajectories (Fig. S11 in the supplement) for B-C (waypoints 6b-6c) but not for F-G (6h-6i) where a general decrease in mixing ratios is observed around 10:50 UTC.

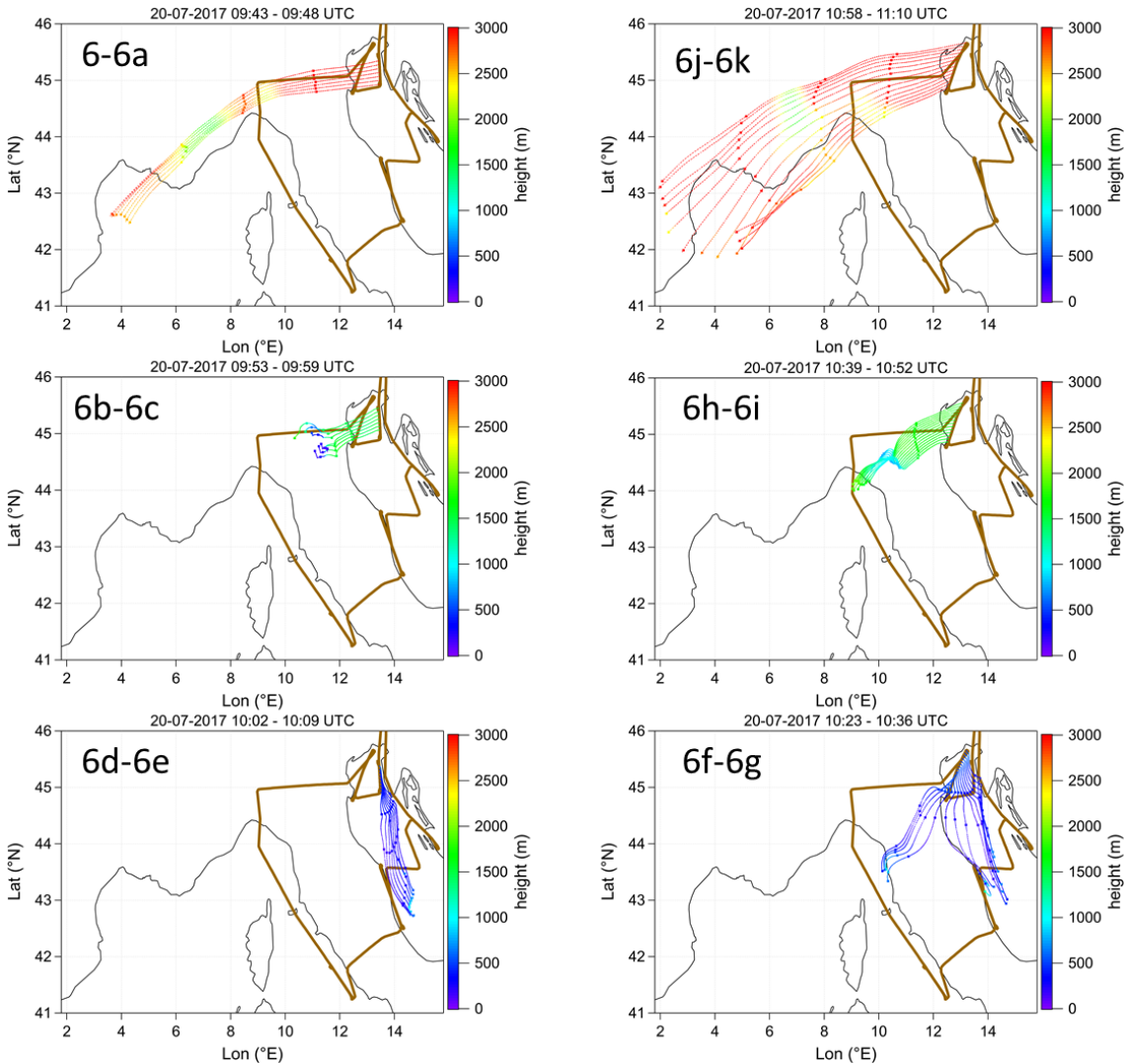


Figure 9: Twenty four hours FLEXTRA backward trajectories for the first (left panel) and second (right panel) shuttles during the E-EU-06 flight. The waypoints for each level of the shuttle are indicated in each graph. The trajectories are started every two minutes at the HALO altitude within the time intervals indicated on the top of each graph. Dots mark the 6h time steps along each trajectory. The flight track is indicated in brown.

3.2.4 MBL transect B-F across the Adriatic Sea

During the westwards transect at 520 m asl from **B** to **F** (6e to 6f), a pollution plume was probed between 10:12 and 10:18 UTC with CO mixing ratios greater than 130 ppb. This plume was characterised by significant increases in CO, HCHO, C₃H₆O, O₃, NO₂, NO_y, NO₃⁻, and OA compared to the previous transect along the Adriatic coast at 520 m asl (6d-6e). Increases in NO_y/CO, C₃H₆O /CO, NO_y/NO₂ ratios were also significant, pointing to a photochemically processed air mass. Notably, the HCHO/NO₂ ratio being 4.1 indicates that O₃ photochemical production was NO_x-limited at the time and location of the measurements (Table S8). HYSPLIT simulations suggest a 20 ppbv enhancement in CO due to emissions from the Po Valley primarily during 6 to 48 hours prior to the measurements. FLEXPART 24-hr backward trajectories (Fig.10) confirm a slow motion to the sampling point of air masses originating from the surface in the CPP between approximately 44.0°N – 44.6°N, and 10.0°E – 12.5°E, a densely populated area (Figure S1) including Modena, Bologna, and one of the busiest highways in Italy.

A second pollution peak (CO = 135±6 ppbv) was probed at the end of this transect around waypoint 6f. Mixing ratios and ratios of the mixing ratio of different species were not significantly different from those in the previous plume, except for the NO mixing ratio and NO/CO ratio, which were about twice as high, indicating a larger contribution of fresh emissions. This was confirmed by HYSPLIT simulations showing a significant contribution of 3-6 hr old emissions from the Po Valley to ΔCO. In contrast with the previous plume, backward trajectories indicate stagnant air masses for the previous 6 hours, and contact with the surface at ~45.0°N, 12.1°E (i.e., near Venice) about 12 hr before the measurements. NO and SO₂ peaks at 6f (520 m asl) could be associated with fresh local surface emissions. A significant contribution to air pollution of shipping and industrial activities around the ports of Venice and Marghera is consistent with the significant contribution of recently emitted air masses (3-6 hr age) to the 20 ppb CO enhancement of Po Valley origin computed by HYSPLIT (see e.g., waypoint 6f in contrast to 6e).

Forward trajectories (Sect. 13 in the supplement) indicate that the two pollution plumes probed at 520 m above in GV and originating from the Po Valley would be transported back to the Po Valley in the BL within 12 to 18 hours, before being exported to the Alps after 36 to 50 hours.

3.3. Distribution of pollutants in the BL across the central Po Plain (CPP)

HALO flew within the BL at 840 m between 11:25 and 12:07 UTC (waypoints 6l-6m). The wind field simulations at the HALO flight altitude of 840 m ± 200 m evidence the difficulties in exactly assigning the origin of the air masses in this flight transect. According to COSMO simulations (Fig. 5 and Sect. 10 in the supplement), there was a light breeze (wind speed < 2 ms⁻¹) with a SW component above 1200 m within the BL during the E-EU-06. The FLEXTRA trajectories indicate that the probed air masses mostly travelled across the CPP (see Fig. 10). However, the accuracy of the trajectories is limited by the prevailing low wind conditions during the E-EU-06 flight. The comparison between 12-hour backward trajectories calculated with LAGRANTO and FLEXTRA, initialized from the aircraft coordinates over the CPP (Fig. S12.1 in the supplement), shows

reasonable agreement. However, the agreement deteriorates in the BL between 11-13°E, particularly with respect to the geographical extent of the trajectories. The observed differences may be related to slight discrepancies in the parameterisation of the vertical wind velocity considered by the models and the specific aircraft altitude. Indeed, in the regions where the discrepancies between the models are largest, the aircraft was flying close to the upper limit of the BL, where the strongest vertical gradients in horizontal wind velocity are expected (low wind velocities at lower altitudes, high wind velocities higher up). A sensitivity study of the COSMO wind field was carried out by perturbing the starting point of the COSMO-LAGRANTO backward trajectories on 20 July 2017 horizontally within a radius of 2000 m and vertically by ± 200 m around the actual location and altitude of HALO, respectively (see Fig. S12.2 in the Supplement).

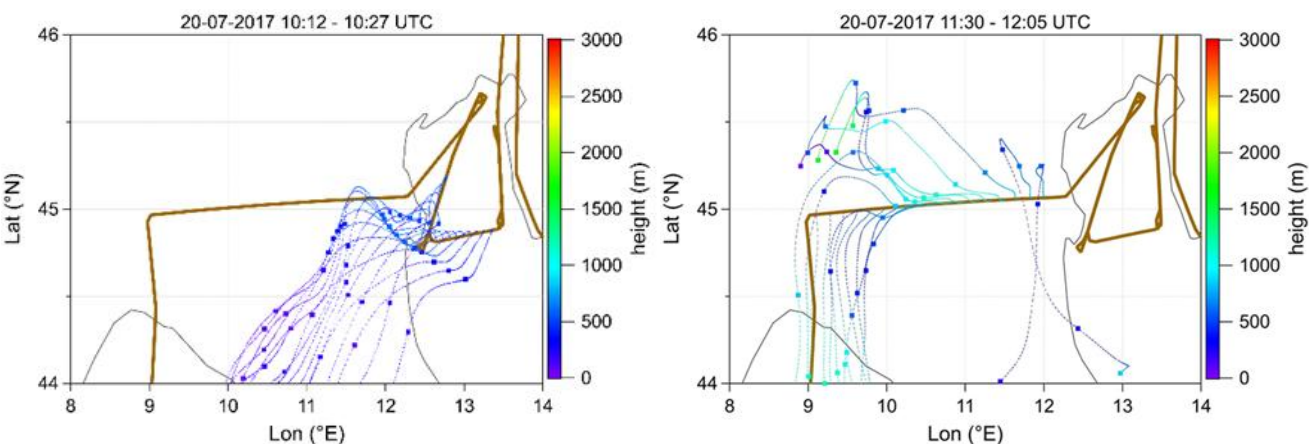


Figure 10: Twenty-four hours FLEXTRA backward trajectories calculated for E-EU-06 on 20 July 2017 for the transect B-F (left) and when overpassing the CPP (right). The trajectories are started each minute at the HALO altitude within the time intervals indicated on the top of each graph. Dots mark the 6h time steps along each trajectory. The flight track is shown in brown.

Both COSMO and LAGRANTO SW flows at the top and above the BL are compatible with a SW synoptic scale circulation also transporting some desert dust (see Sect. 3.7 and Fig. S14). Furthermore, the results indicate that slow horizontal and vertical mixing resulted in a poorly or slowly mixed BL. This is further discussed in Sect. 3.6.

Selected mixing ratios of different species and ratios of mixing ratios obtained from airborne measurements during this east to west transect above the CPP are shown in Fig. 11. HCHO/NO₂ ratios (Table S9) ranging from 1 to 4 were the lowest observed during the whole E-EU-6 flight, and indicate that the O₃ photochemical production regime could not be safely qualified as NO_x- nor VOC-limited.

Pollution plumes were highlighted by averaging measurement data over 8 different periods (P) lasting ~2 to 11 minutes (i.e., 16 to 80 km), primarily defined on the basis of CO variations, which were used as an indicator of ground-based pollution source emissions (see vertical red lines in Fig.11 and Table S9 in the supplement). Three of these periods: P2 (11:32-11:35 UTC), P5 (11:43-11:52 UTC) and P8 (12:03-12:07 UTC) with CO mixing ratios ≤ 115 ppbv were defined as local and temporary background. In these 3 periods, comparatively lower SO₂, NO, NO₂, NO_y mixing ratios and NO₃⁻, OA, and rBC

mass concentrations were observed (Fig.11). The HYSPLIT computed contributions of emissions from the Po Valley to the measured CO mixing ratios dropping from 20 ppbv during period P2, to 5 ppbv and 2 ppbv during periods P5 and P8, respectively, suggest that the causes for the relatively low CO mixing ratios observed during these 3 periods were probably different.

During period P1 between 11:26 and 11:32 UTC (from 12.33°E to 11.83°E), CO mixing ratios >115 ppbv (average = 128 ± 7 ppbv) were measured quasi continuously. However, no significant enhancements in gaseous or particulate species with respect to CO and rBC, respectively, were observed during this period (see histogram in Fig.12). NO/CO and NO₂/CO ratios were even significantly lower than in the periods defined as background. 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). HYSPLIT simulations also indicate a large contribution (~ 20 ppbv) of local emissions primarily during the past 6 to 48 hours to the measured CO mixing ratios. The composition of the air sampled during P1 is probably representative for the mid-day CPP regional pollutant mix. Low NO_y/CO, NO₃⁻/rBC and OOAm/rBC ratios suggest that this air mass was not much chemically processed.

Period P3 between 11:36 and 11:39 UTC (from 11.50°E to 11.26°E) was characterised by increases in SO₂, NO, NO_y, and particulate species (except SO₄²⁻), but cannot be further analysed due to the lack of simultaneous measurements of CO and nitrogen oxides during most of the period.

During period P4 (11:40 – 11:43 UTC) from 11.14°E to 10.94°E, CO mixing ratios averaged 126 ± 9 ppbv. Increases in NO, NO₂, NO_y, NO₃⁻, SO₄²⁻, OA and rBC were observed. However, only NO_y/CO and NO₃⁻/rBC were significantly larger while HCHO/NO₂ ratios were lower than in the so-called background periods. FLEXTRA backward trajectories (Figure 10) indicate air masses coming from the BL in the CPP (around 45.5°N, 9.5°E) about 18 hours before. These observations indicate that the probed air masses resulted from the processing of originally NO_x rich emissions (e.g., from traffic). However, HYSPLIT calculates only a 10 ppbv CO increment coming from emissions in the Po Valley, primarily emitted 6-24 hours prior to the measurements.

In contrast, the period P6 (11:53 – 11:57 UTC) between 10.03°E and 9.72°E (CO = 119 ± 2 ppbv) is primarily characterised by increases in NO₂ and SO₂ mixing ratios. While NO₂/CO ratios were on average not significantly larger than during the background P5 period, SO₂/CO ratios reached the maximum mean value (0.017) observed over the CPP. Backward trajectories (Fig. 10) indicate that air masses travelled in the BL around Genoa (approx. 44.5°N, 9°E) about 12 hours prior to the measurements, i.e., a drastic shift in air mass origin compared to P4 is observed. According to HYSPLIT, the Δ CO contribution of emissions from the Po Valley to the CO observed is less than 3 ppbv, and about half of this increase occurred during the last 6 hours before the measurements.

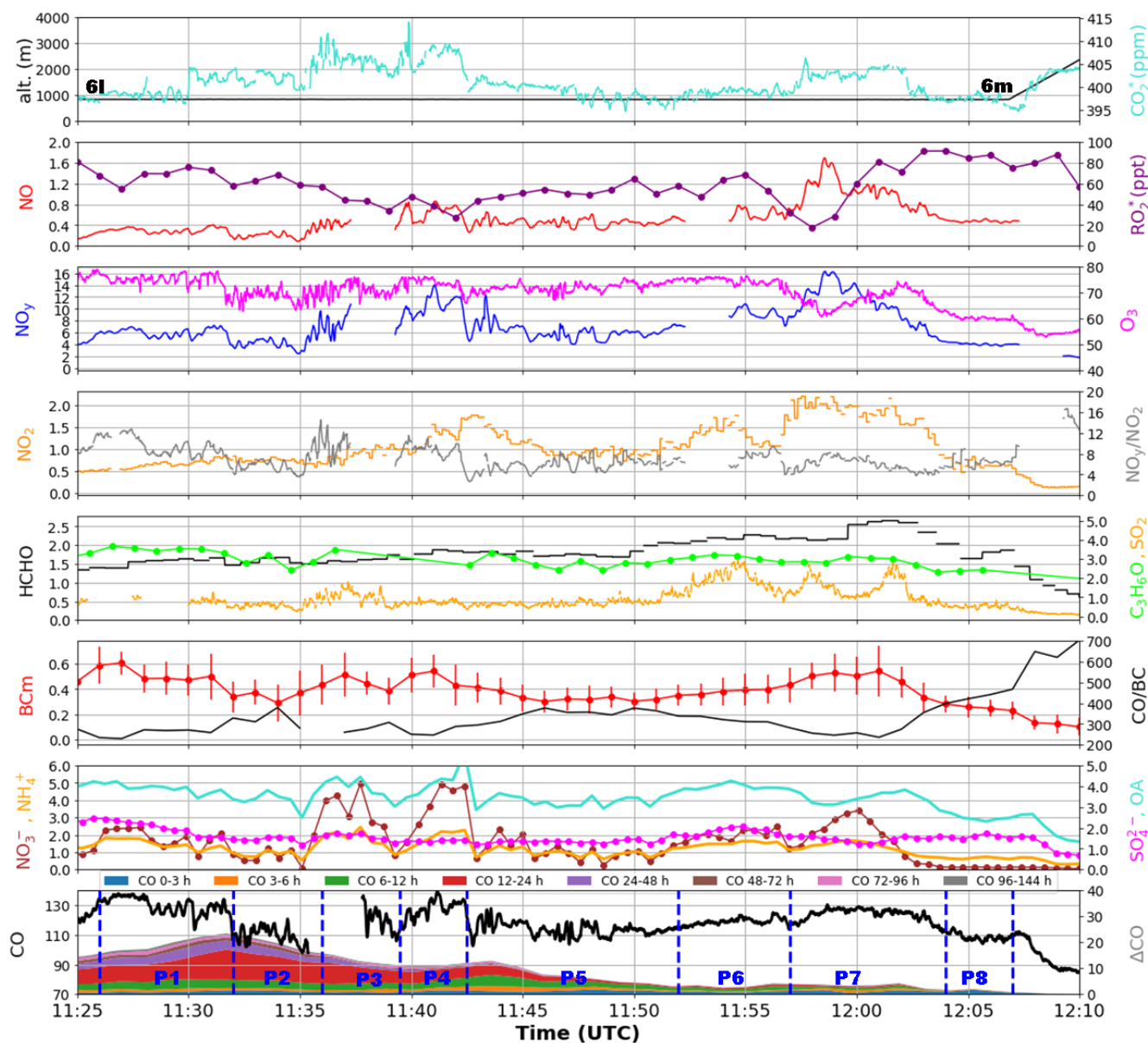


Figure 11: Spatial and temporal variation of NO, NO₂, NO_y, O₃, CO, HCHO, C₃H₆O, SO₂, RO₂^{*}, and rBC, NO₃⁻, NH₄⁺, SO₄²⁻, and OA (in μg m⁻³ STP) observed on board HALO over the CPP during EMerge E-EU-06. The mixing ratios are in ppb if not indicated otherwise. HCHO and NO₂ values are retrieved from miniDOAS measurements. The flight altitude and the changes in course and altitude (waypoints 6m-6n) are marked in the top panel. The NO_y/NO₂ ratio is also shown. In the bottom panel HYSPLIT simulations of the contribution of Po Valley emissions (ΔCO) in different aged air masses to the observed CO (in black) are shown. Vertical blue lines mark the time intervals selected for the analysis (P1-P8, see text).

High SO₂/CO emission factors are characteristic of emissions from ships and refineries, which use higher sulphur-content fuels compared to e.g. road transport. Potential emission sources in the GG are the port of Genoa, a large European port involved in

sea freight import-exports having a substantial amount of maritime traffic (APICE, 2009; Marmer and Langmann, 2005), its surroundings, and the refinery IPLM in Busalla (<https://iplom.it/>, 44°34'54"N, 8°56'29"E). During P7 (11:58-12:02 UTC, CO = 126 ± 2 ppbv) from 9.62°E to 9.25°E, the highest NO, NO₂, NO_y, and HCHO mixing ratios of all transects in the BL over the CPP were measured. Two SO₂ peaks were also observed at the beginning and the end of the period. In contrast, peaks in particulate species such as rBC and NO₃⁻ were similar to or lower than in the other pollution plumes. NO/CO, NO₂/CO and NO_y/CO ratios were significantly higher than during the background periods, pointing to a mixture of fresh and aged emissions from combustion sources. HCHO/NO₂ ratios were significantly lower, and the lowest observed over the CCP (1.3), getting close to the threshold indicating a VOC-limited O₃ production regime. The O₃/CO was significantly lower than in background conditions, and also the lowest observed over the CPP, suggesting the titration of O₃ by NO as additionally indicated by the NO, O₃, and RO₂^{*} observations. The two peaks in SO₂/CO suggest that ship or refinery emissions were partially sampled. The advection of coastal emissions inland is confirmed by backward trajectories passing in the MBL over the GG within 12 hours before the measurements, and by the HYSPLIT estimate of ~50% contribution of fresh emissions (< 6hrs) to the ΔCO from the Po Valley. HYSPLIT forward trajectories suggest that the pollution plumes intercepted during the 840 m asl transect over the CPP were transported in different directions (Fig. S13). The plume probed over the east of the CPP during P1, originating from further south, was transported over the Adriatic Sea, and turned back due to the daytime sea breeze to reach the surface level in the CPP about 36 hours later. In contrast, chemically processed emissions from the CPP itself and more primary emissions from the GG port areas travelled in the CPP for 12-18 hours in the BL before being exported to Switzerland and Austria across the Alps, probably due to the combined effect of daytime upslope winds and synoptic winds.

3.4. Vertical distribution and advection of pollutants in the Gulf of Genoa (GG)

HALO flew southwards from waypoint 6m (44.86°N, 8.97°E, 840 m asl) to waypoint 6n (44.63°N, 9.04°E, 2590 m asl) between 12:06 and 12:10 UTC. CO, SO₂, NO₂, NO_y, RO₂^{*}, O₃, rBC, OA, OOAm, and SO₄²⁻ values significantly decreased during the ascent, while the NO₃⁻ concentration did not significantly change and remained around 0.06 μgm⁻³ STP. Across the southward transect at 2590 asl between waypoints 6n and 6o (44.14°N, 9.05°E, 2590 m asl), mixing ratios of all species remained low and little variable. RO₂^{*} remained around 45±13 pptv (Table S8 in the supplement). HCHO/NO₂ ratios were constantly greater than 4, characterising a NO_x-limited photochemical O₃ production regime. According to HYSPLIT simulations, the contribution of sources located in the Po Valley to ΔCO was negligible. There is no evidence that the air probed across this transect had recent contact with land for the previous 96 hours, air masses travelling above 2000 m asl parallel to the French south coast coming from the Iberian Peninsula via the Balears. During this transect above GG (upwind of the CPP) at 2580 m asl, NO₂, NO_y, and O₃ mixing ratios were higher than above GV (downwind of the CPP) at 3200 m asl, while the values of CO, NO, SO₂, HCHO, C₃H₆O, and the particulate species (NO₃⁻, SO₄²⁻, rBC, OA, OOAm) were not

significantly different. 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. The NO_y/CO ratio computed from E-EU-06 measurements remains between 0.03 and 0.12 within the BL. Above the BL, the concentration of both species decreases and their ratio remains around 0.01 at 2500 m in E-EU-06 and at 3000 m in E-EU-03. Apart from reflecting the shorter lifetime of NO_y , this indicates the significance of additional long-range transport of CO in the upper levels eastwards from the south of France during both HALO flights. This long-range transported CO may be from forest fires in southeastern France, which was experiencing an exceptionally hot and dry summer in 2017, as 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).

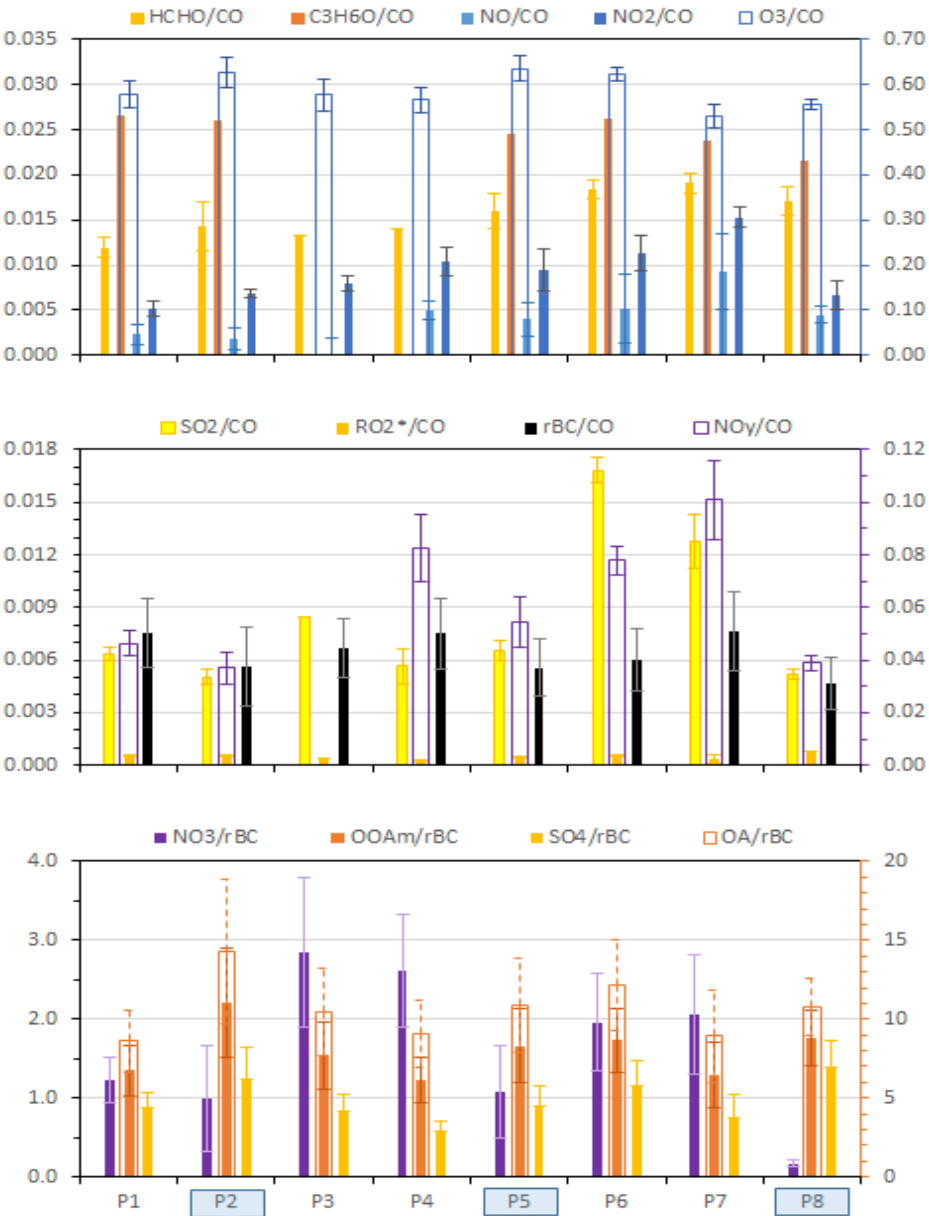
3.5. Comparison of ground and airborne observations over the Po Plain

Vertical and horizontal gradients of pollutants are expected to depend on the efficiency of the mixing within the BL. If the time scales are shorter for the horizontal than for the vertical mixing within the BL, the distribution of trace gases above the surface may not reflect the allocation of the emissions at the ground but be more homogeneous over larger areas in the upper layers. Short-lived species may react completely before mixing by small-scale turbulent motions that consequently affect the production of secondary pollutants such as O_3 .

The mixing ratios of the primary pollutants (CO , NO_x , rBC) investigated during the HALO flights were mostly higher in the BL than in the lower FT (Table S9). This is expected as emission sources are predominantly at the ground, and convective and advective mixing within the BL were slow over the Po Plain on 20 July 2017, as illustrated by a neutral thermal stability and no strong wind shear, at least between 10.25 and 12.25 E (S10 in the supplement). The weakness of the pollution vertical transport in the BL along the Po Plain was further highlighted by comparing measurement values at the surface with the airborne observations performed at 840 m asl. NO_x , CO , and O_3 measured with 1hr resolution at the ARPA AQMN stations at altitudes between 10 m and 250 m asl. (see Table S6.1 in the supplement) in the proximity of the aircraft track were used for this purpose.

Looking at the Po Plain as a whole, it appears that the largest CO mixing ratios (300 – 500 ppbv) were observed at traffic sites (7, 13, 16, 17), with the exception of the traffic site 6, while the lowest (100 – 200 ppbv) were generally observed at rural and urban background sites (2, 3, 4, 15, 19, 23), with the exception of rural background site 10 (Fig.13). Note that according to Figure 5, the station 10 at 250 m asl is potentially under the influence of the transport of pollution of coastal origin. The observed CO distribution roughly reflects the distance of each site to major combustion sources, i.e., predominantly road traffic in summer. CO mixing ratios measured at ~800 m above the CPP (120 ± 8 ppbv) were not significantly different from those measured at 520 m asl in GV (126 ± 15 ppbv), and were independent from the CO mixing ratios measured at the overflowed ground stations (100 – 400 ppbv). 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

591 actually accounted at the maximum for 15 % (20 ppb approximately) to the BL CO mixing ratios measured on-board the
 592 aircraft.
 593



594
 595 **Figure 12: Molar ratios between selected species measured along the transect over the CPP at 830-840 m asl. Open bars refer to the**
 596 **right-hand y-axes. Periods defined as background are highlighted in blue in the x axis. The delimiting times are marked in Fig.11 as**
 597 **red lines in the bottom panel**

Regarding NO_x, high levels (30 – 60 ppbv) were observed at traffic sites 13 and 16, while moderate mixing ratios (10-12 ppbv) were measured at traffic sites 6 and 8. Lower values (5-10 ppbv) were observed at regional background sites. Unlike CO, mean NO_x mixing ratios were significantly greater at ~800 m above the CPP (1.4 ± 0.5 ppbv) compared to 520 m asl in GV (0.7 ± 0.1 ppbv), but 4 to 10 times less than at the air quality monitoring stations (5 – 15 ppbv), which were flown over, with no significant correlation between the ground level and aircraft altitude mixing ratios.

The lower horizontal variability in NO₂ measured in the BL at ~800 m agl compared to ground-level stations suggest again road traffic as the major NO_x source in the CPP in summer. The significantly lower NO and NO₂ 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). Indeed, a 1-D model simulating correctly the ground and aircraft level NO_x mixing ratios, as well as the HNO₃ mixing ratio at the aircraft altitude, indicates 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).

The range of the 1h-mean O₃ mixing ratios at ground stations between 11:00 and 12:00 UTC is smaller (45 – 72 ppbv) than for CO and NO_x. As expected, the highest mixing ratio was observed at the regional background station 23, where anthropogenic NO_x and VOC have mixed upwind with biogenic VOCs (primarily isoprene). However, there is no correlation between the type of site and O₃ concentrations across the whole Po Plain. O₃ mixing ratios in the CPP at ~800 m agl were significantly higher than at ground level (+ 8%). This may imply incomplete mixing with the NO_x ground emissions at the time of the flight and/or O₃ photochemical production in O₃ precursor rich air rising up by convection, and/or larger O₃ sinks at the ground (titration by NO, dry deposition).

3.6. General features in the processing of the air masses over the Po Plain

Based on the ground-based and airborne observations described in the previous sections, some general features were identified in the transport and processing of pollution within the complex Po Plain. Besides information about the O₃ and secondary aerosol formation potential of the air masses, the obtained data give some insights into the suitability of HYSPLIT and dispersion models to reproduce the observed pathways.

Considering the BL only, the air probed in GV was the most photochemically active as indicated by the radical observations. This resulted from the mixing of fresh emissions of primary pollutants with processed air masses, leading to the highest O₃ formation potential. The HCHO to NO₂ ratios were generally higher than in GG and CPP, and indicated a NO_x limited production of O₃. The difference in HCHO/NO₂ ratios in the BL between GV and CPP is consistent with RO₂* mixing ratios being about 20-50% higher in the former. The lower HCHO to NO₂ ratios detected anywhere else indicate a transition regime between NO_x and VOC limited production of O₃ in the probed air masses with respect to the GV. However, the increase in NO to NO₂ ratios in the GV transect with respect to the CPP was consistent with the increasing importance of fresh emissions in the transported air masses.

630 The higher ratio between NO and SO₂ additionally indicated the mix of combustion processes responsible for pollution,
 631 primarily the sulphur content of the fuel burnt. Concerning the origin of sulphur compounds in the BL, port traffic and activities
 632 were identified as the major source of SO₂ across the Po Plain. The highest SO₂/CO ratios were observed during 3 transects at
 633 520 m asl over GV (range = 0.008 – 0.012) and in the west of the CPP at 830-840 m asl (0.013). In the first case, the air masses
 634 had been transported in the BL above the Adriatic Sea during the previous 24 hours. In the western part of the HALO transect
 635 in the BL at ~800 agl above the CPP, the backward trajectories passed in the MBL over the port of Genoa in the GG within 12
 636 hours before the measurements. SO₂ enrichments were not systematically accompanied by similar enrichments in SO₄²⁻ as
 637 revealed by similar SO₄²⁻/rBC ratios in the GV and the CPP (ca. 0.95), probably due to the slow homogeneous oxidation of
 638 SO₂ to SO₄²⁻ (**characteristic time during day in summer ≈ a couple of days**). High SO₄²⁻/rBC ratios
 639 were also observed during this measurement campaign in “background” conditions in the BL (up to 1.4, see sect. 3.1.2) and in
 640 the FT between 2600 and 3230 m asl (up to 2.3), which could also mask local photochemical SO₄²⁻ production.
 641 The mean NO_y mixing ratio measured in the BL over the CPP was on average ~50% larger than over the coastal areas. This is
 642 explained not only by less BL venting and dilution in the CPP, but also by oxidation and subsequent processing of NO_x-rich
 643 emissions leading to e.g., HNO₃ and NO₃⁻ production. This resulted in higher mean NO_y/CO and NO₃⁻/rBC ratio in the CPP,
 644 albeit larger ratio punctually observed in the BL above GV. Similarly, increases in the NO₂/NO and NO₃⁻/NO₂ ratios were
 645 generally concurrent.
 646 With regard to horizontal transport pathways, the observations indicate the contribution of fresh pollution advected from GG
 647 in the CPP. This was in agreement with model-based wind fields and thus with the HYSPLIT simulations showing a ~50%
 648 contribution of the Po Valley emissions to CO emitted recently (<6hr age). However, the CO emissions from the Po Valley
 649 advected to the measurement points at the western tip of the CPP were estimated by HYSPLIT to be less than 5 ppb, i.e., 4%
 650 enhancement with respect to the total CO measured. This contribution is much lower than the 20% maximum CO enhancement
 651 observed over the background periods in the CPP (see detailed analysis in Sect. 3.3).
 652 Regarding vertical transport, the comparison between HALO measurements performed at the lowest flight altitudes (about 800
 653 m asl) over the CPP and at ground stations showed inhomogeneities in the vertical distribution of several species mixing ratios,
 654 especially for CO and NO_x, and to a lesser extent O₃. Such inhomogeneities within the BL in urban areas with a complex
 655 distribution of emissions at the surface have already been addressed (Wang et al., 2021). Large eddy simulations suggest that
 656 the inefficient mixing of reactants such as e.g., NO and peroxy radicals can affect the production of secondary pollutants such
 657 as e.g., O₃, especially when the location of anthropogenic NO emissions and biogenic VOC emissions are separated.
 658 Simulations by Wang et al. (2022) showed that O₃ significantly increased with altitude (20 ppbv) between 100 and 800 m agl
 659 above Hong Kong in the polluted case (surface NO and NO₂ of ~30 ppbv), but not in the “clean” case (+ 1 ppb between 100
 660 and 800 m agl), where NO and NO₂ mixing ratios at the ground were 0.5 and 3 ppb, respectively. In polluted conditions, they
 661 computed a decrease in the O₃ photochemical production rate due to radical species segregation ranging from 50% at about
 662 150 m to less than 20% above 500 m over the urban area of Hong Kong. The NO_x mixing ratios measured across the CPP on
 663 20 July between 12:00 and 13:00 UTC ranged between the extremes of their simulations. However, measured and simulated

radiosondes indicate that turbulence in the BL atmosphere over the CPP was well below the strong turbulent flow in the simulations of Wang et al. (2022). This may explain the small increase of O_3 between the ground and 800 m agl over the CPP. Hůnová et al. (2023) showed non-uniform O_3 concentration gradients and temporal changes in air columns of 2-8 m, 8-50 m and 50-230 m from seven-year O_3 measurements taken at four heights up to 230 m above the ground in a rural area in the Czech-Moravian Highlands.

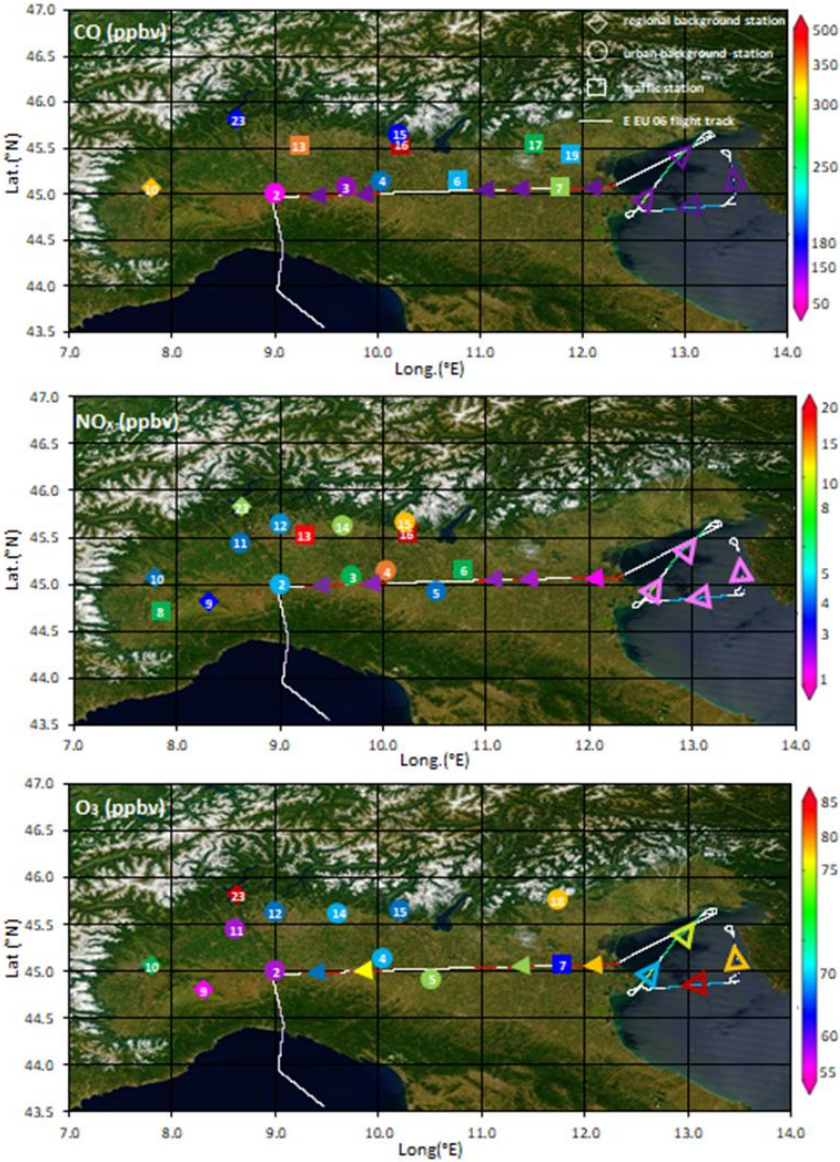


Figure 13: Ground-based CO, NO_x, and O₃ mixing ratios (colour scales) at traffic (square), urban background (circle), and regional background (diamond) stations of the ARPA and ACTRIS networks at the time of the E-EU-06 overpass. Station numbers refer to Table S6.1 in the supplement. Also shown are the mixing ratios measured along the aircraft E-EU-06 track (line) at 520 m asl over the GV (open triangles) and 830-840 m asl above the CPP (solid triangles)

674 In the FT, aged polluted layers were observed ca. 600 m above the top of the BL in GV. The HYSPLIT simulations did not
675 capture the increases in CO observed, which suggests that a large source of CO was not part of the emission inventory, but
676 assigned a higher relative contribution of emissions being > 24-48 hours older than in the air within the BL below, which
677 confirms the long-range transport of the air masses. HCHO/NO₂ ratios were on average particularly high in these layers (~6 to
678 8), as compared to the BL underneath (~4 at 520 asl) and above the CPP (~2 at 830-840 asl), and well above the threshold (~4)
679 above which O₃ photochemical production is considered to be NO_x-limited. In line with these observations, FLEXPART 96 h
680 backward trajectories suggest that a returning pollution layer originating from the surface in the CPP was earlier probed along
681 the Croatian coast, while a polluted air mass coming from areas affected by wildfires in southern France 3-4 days before was
682 intercepted along the Italian Adriatic coast.

683 **3.7 Desert dust transport and secondary organic aerosol formation above the central Po Plain**

684 Transport of desert dust to the Central Mediterranean and the Italian Peninsula is a frequent phenomenon, particularly in
685 summer (Barnaba and Gobbi, 2004), when it is mainly associated with anticyclonic conditions (e.g., Gaetani et al., 2016). It
686 also has important impacts on PM-air quality metrics (Pederzoli et al., 2010, Barnaba et al., 2022), as well as on the chemistry
687 of the atmosphere, such as providing surface for heterogeneous reactions including O₃ removal mechanisms from the gas phase
688 (e.g., Zhu et al., 2010; Wang et al., 2017). Desert dust may also influence nitrate partitioning between gas and aerosol phase
689 (e.g., Karydis et al., 2016), the heterogeneous formation of sulphate catalysed by iron (Itahashi et al., 2022) and the
690 neutralization of acids such as HNO₃ and H₂SO₄ (e.g., Athanasopoulou et al., 2016).
691 Elevated desert dust layers were observed by ground based remote sensing over the central Po Valley during the EMeRGe
692 HALO flights (Andrés Hernández et al., 2022). In particular, Figure 14 shows the complex aerosol stratification as observed
693 on July 20 during the E-EU-06 HALO flight by the ALICENET ALC operating in Milan-Bicocca. Aerosol profiles from the
694 LiDAR operating in Ispra at the time of the HALO overpass are reported in Fig. 15. The arrival of elevated, desert-dust layers
695 over the CPP is documented to occur already the day before by the Milan ALC (see Figure S14.1 in the Supplement showing
696 the continuous evolution of the aerosol vertical profiles during the whole EMeRGe campaign in Europe: 11-20.07.2017). This
697 is also in agreement to predictions by the multi-model desert dust forecasts (Basart et al., 2019) made available by the Dust
698 Regional Center (<https://dust.aemet.es/products/daily-dust-products>) and reported in Fig S15 in the supplement.

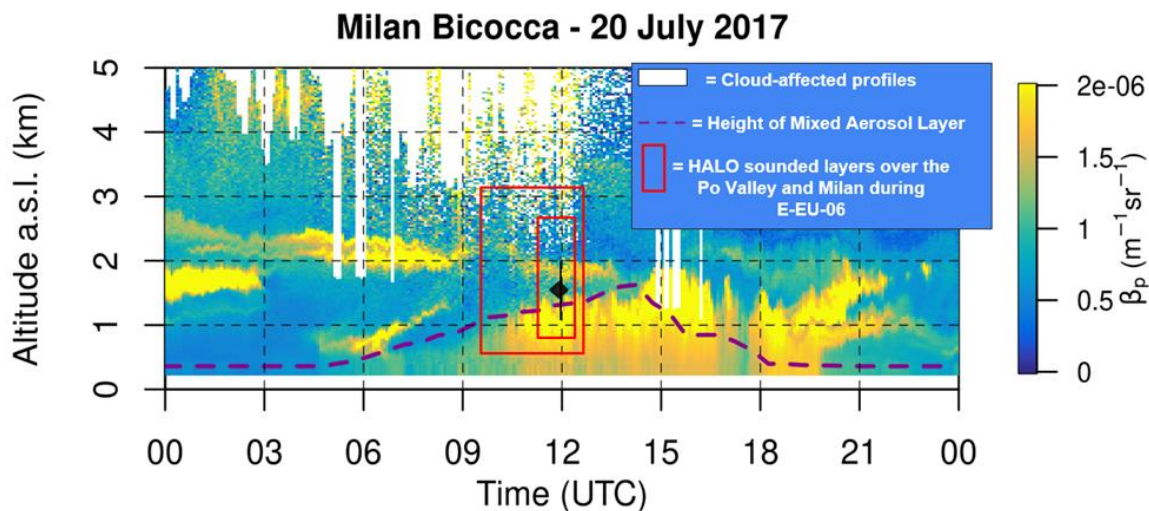


Figure 14: Continuous (0-24 UTC, x-axis) vertical profiles (0-5 km asl, y-axis) of aerosol backscatter at 1064 nm as observed by the ALICENET ALC system operating in Milan-Bicocca on July 20, 2017. Cloud-affected profiles are filtered out from the cloud base upwards (white areas). The height of the Mixed Aerosol Layer (MAL, dashed purple line), proxy of BLH, is derived from the ALICENET data processing (Bellini et al., 2024). BLH value derived at 12 UTC from radiosonde measurements in Milan is also reported (black diamond, see Table 1). Red boxes identify time-altitude windows sounded by HALO over the wider Po Valley (outer box) and Milan (inner box) areas.

In particular, elevated aerosol layers up to 5000 m altitude are visible in the ALC and LiDAR traces (Fig. 14-15). The mineral dust nature of the particles is confirmed by the aerosol depolarization trace of the Ispra LiDAR, markedly increasing above 2500 m. In the morning, clouds are observed to form above 3000 m within the dust layer. During E-EU-06, HALO actually flew 60 km south of Milan and 90 km south of Ispra around 12 UTC at 830-840 m asl. Particle number size distributions measured on board HALO when closer to Ispra and Milan showed a distinct coarse mode at $1.5 \mu\text{m}$, similarly to what has been previously observed during the MINATROC campaign in a desert dust outbreak at Monte Cimone (Italy) in June-July 2000 (Van Dingenen et al., 2005). However, the contribution of coarse particles to the total particle number was limited ($\sim 1/10000$) compared to what was previously measured ($\sim 2/1000$).

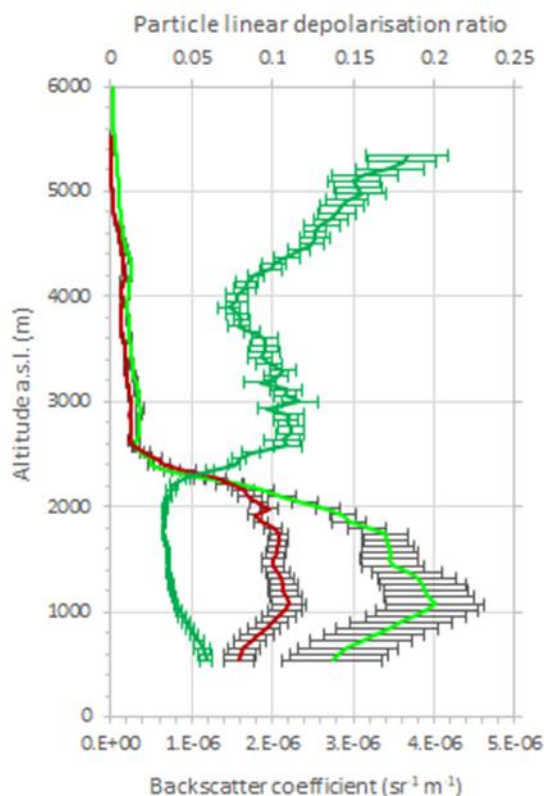


Figure 15: Vertical profiles of the particle light backscatter coefficient at 1064 (red) and 532 (light green) nm (bottom x-axis), and the linear depolarization ratio (dark green, top x axis) at 532 nm measured by the aerosol LiDAR in Ispra on the 20 July between 11:01 and 13:01 UTC.

The number concentration of particles with diameters greater than 500 nm ($N_{d>500\text{nm}}$) in the free troposphere is used as a proxy for the dust number concentration (DeMott et al., 2010; Weger et al., 2018; Zhang et al., 2019). For heterogeneous reactions, the surface area concentration is the decisive quantity and will be denoted here as $dS_{d>500\text{nm}}$. The HALO observations (Fig. 16) indicate a larger amount of dust in the upper levels: $dS_{d>500\text{nm}}$ was $\sim 30 \mu\text{m}^2 \text{cm}^{-3}$ at 1630 m above GV asl, and $\sim 20 \mu\text{m}^2 \text{cm}^{-3}$ at 2600 m asl above GG while it was $\sim 10 \mu\text{m}^2 \text{cm}^{-3}$ at 830-840 m asl above the CPP, where air masses coming from GG were advected. For comparison, the surface area due to the coarse mode desert dust observed in Monte Cimone (at 2165 m asl) in June-July 2000 was $44 \mu\text{m}^2 \text{cm}^{-3}$ (Van Dingenen et al., 2005), but in that case the dust plume was more intense and vertically thick (reaching up to 8 km altitude, Gobbi et al., 2003) than the one sounded during EMeRGe. In fact, on July 20, 2017, vertical mixing was not favoured by the high-pressure field extending from North Africa to northern Italy. Model-based data indeed show the gradient of the potential temperature to be neutral below 1000-1500 m during the HALO overpass above the CPP, whereas it was positive above 1500 m (Figure S10.5 in the supplement). Thus, the atmospheric layering was very stable in the FT, likely inducing minor or no mixing of dust within the boundary layer air.

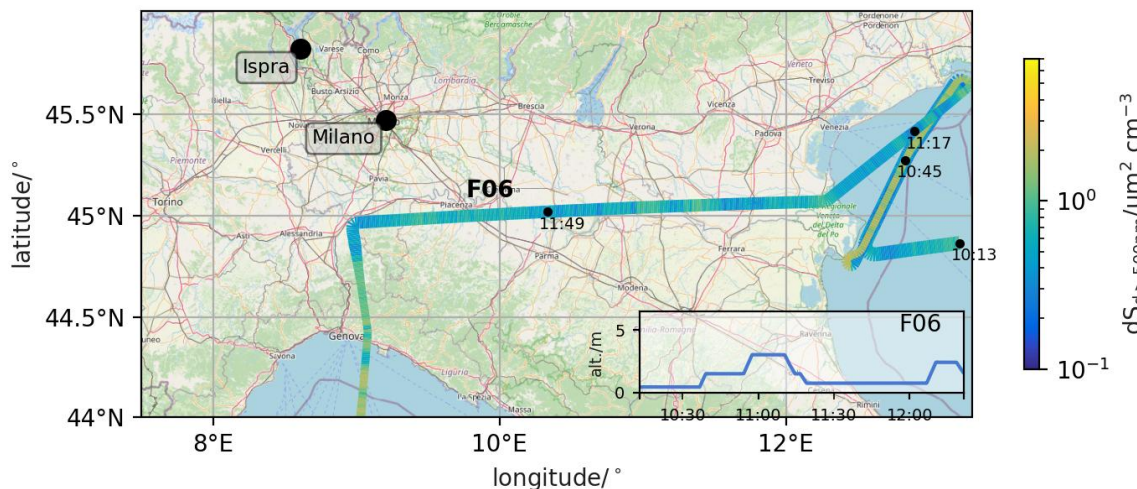
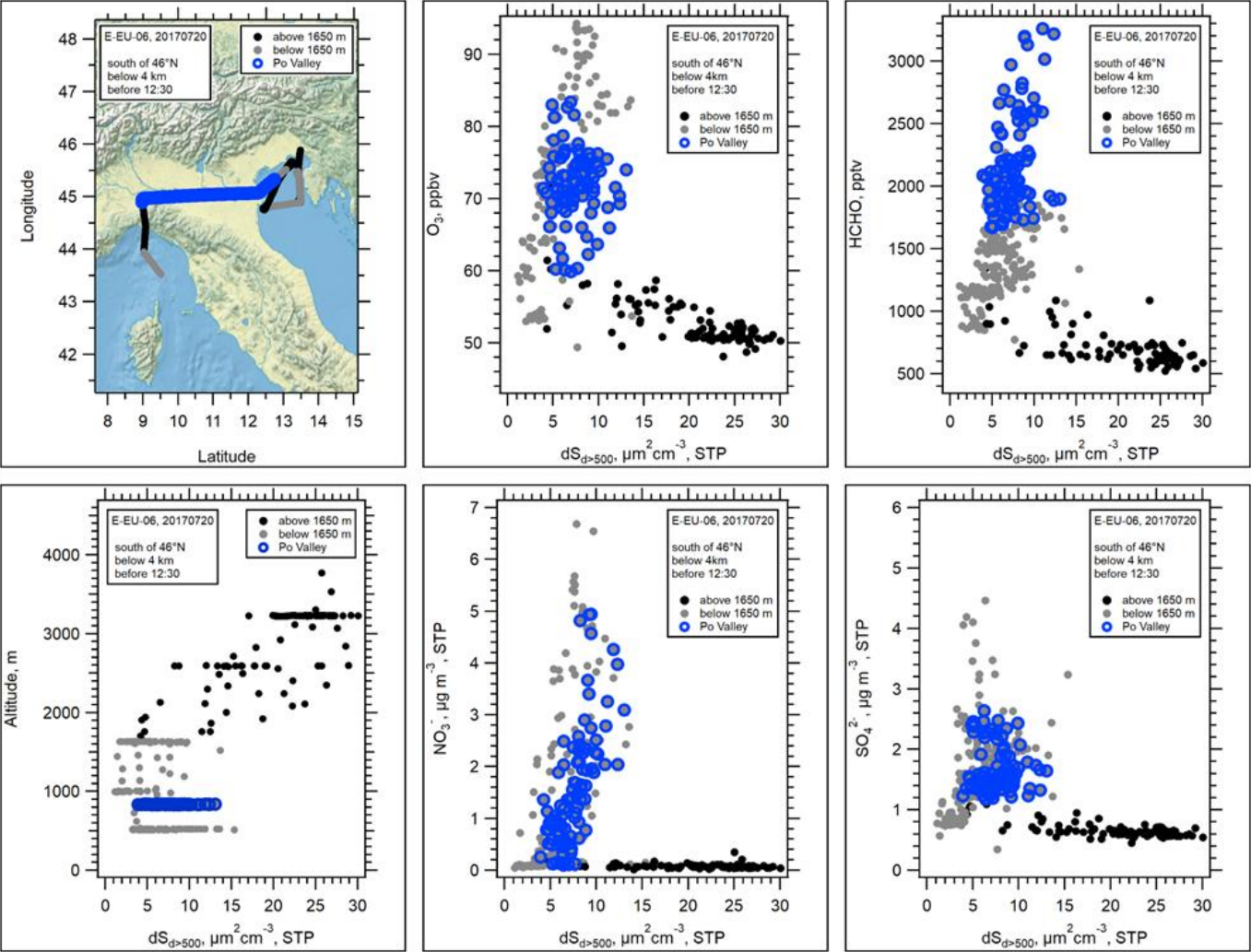


Figure 16: Surface area concentration of particles with diameter larger than 500 nm measured by the optical particle counter on-board HALO along the flight track. Map data from OpenStreetMap, <https://www.openstreetmap.org/copyright>.

Although the aerosol optical depth of the dust layer was low, correlations between the amount of selected species and $dS_{d>500nm}$ were further investigated in an attempt to find some indications of the effect of dust in heterogeneous processes. For this, HALO data across the Po Plain at 830-840 m altitude were selected when additional vertical information near the CPP was available. Figure 17 illustrates the measurement location and altitude as well as the vertical profile of $dS_{d>500nm}$ (left column). The vertical profile shows that the main dust layer was above about 1650 m, in agreement with ALC data (Figure 14) and the BL height of about 1600 m (Table 1), but HALO encountered air masses with significant amounts of particles with $d > 500$ nm also below that height. The plots in the upper row of Fig. 17 show the gas-phase substances O_3 and HCHO which both undergo heterogeneous reactions on dust (e.g., Wang et al., 2017) and should therefore decrease with increasing dust load. This behaviour is indeed observed above 1650 m (black dots), but not in the BL below 1600 m, where both species show a slightly positive correlation with $dS_{d>500nm}$. This may indicate that the BL source of both the particles with $d > 500$ nm and the two gas-phase species was local pollution from the Po Plain, while above the boundary layer, heterogeneous removal of O_3 and HCHO occurred.

In contrast, NO_3^- and SO_4^{2-} (lower row) show a positive correlation with $dS_{d>500nm}$ in the BL over the Po Plain and the surrounding regions. Above the BL, where the particle surface area increased due to an increasing amount of dust particles (see LiDAR and ALC profiles in Fig. 14), both particulate species show no correlation with $dS_{d>500nm}$ but remain constant at low concentration. Also, the mixing ratio of SO_2 , which is the precursor gas for sulphate production, does not show a negative correlation with $dS_{d>500nm}$ above 1650 m (not shown). Whether the positive correlations in the BL are due to heterogeneous production or to common local sources cannot be answered from the current data set.

For all four species shown in Figure 17, the slope of the correlation with $dS_{d>500nm}$ changes clearly between the BL and the FT. These observations are of interest for the validation of surface loss processes on aerosol models.



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Figure 17: Relation between mixing ratios or mass concentrations of selected species (O₃, HCHO, NO₃⁻, SO₄²⁻) and the surface area concentration of particles with diameter larger than 500 nm (dS_{d>500nm}) measured during E-EU-06 on July 20, 2017. On the left side, the flight location and the observed vertical distribution of particles are shown. Dots for flight altitudes below and above 1650 m are shown in grey and black respectively while the blue colour indicates the CPP crossing at 830-840 m. Public domain GIS data available in Wavemetrics IgorPro.

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4 Summary and conclusions

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Understanding the transport and transformation of pollutants is crucial for an adequate assessment of air quality and for the development of effective mitigation strategies for urban agglomerations. This is particularly important in the BL of highly polluted environments with complex topography.

765 The objective of this investigation was to undertake a case and investigate and characterise key primary and secondary
766 pollutants in the Po Valley, which hosts large urban agglomerations, an effective megacity, and both industrial and intense
767 agricultural activities. The study exploits the airborne observations of selected trace gases and particulate matter components
768 during two EMERGe flights carried out in the Po Plain from the Gulf of Venice to the Gulf of Genoa, and ground-based data
769 from air quality and LiDAR networks in July 2017. The differences in mixing ratios and variability of the targeted species as
770 well as the processing during the aging of the observed pollution plumes, as estimated by HYSPLIT dispersion simulations,
771 provide valuable information about the degree of mixing of the emissions within the BL and their photochemical
772 transformation during transport.

773 The observations of major air pollutants and short-lived climate forcer precursors such as NO, NO₂, CO and SO₂ at ground
774 level indicated that the south of Lombardy and the surroundings of Milan are the most polluted areas in the central section of
775 the Po Plain, CPP, which has a predominance of urban and traffic emission sources. The coastal areas of Genoa and Venice
776 have in comparison significant emissions from shipping, as well as tourism and industrial activities near their ports.

777 Overall, stagnant conditions dominated in the CPP at the time of the investigated flights and advection of pollutants from the
778 coastal areas into the CPP was favoured. Backward-trajectories indicated inland transport of emissions from the port of Genoa
779 in agreement with the ground-based observations of pollutants and the SO₂, CO and NO_y plumes probed during the flights. In
780 contrast, an apparent accumulation of local emissions was observed in the lower BL in the eastern part of the CPP, close to the
781 Gulf of Venice. The stagnant conditions resulted in a decoupling between the lower and the upper part of the BL causing
782 concentration negative gradients. Thus, the content of reactive primary pollutants such as NO, NO₂ and SO₂ in the air masses
783 probed onboard HALO in the upper BL was above the levels measured at ground-based background stations but lower than
784 elsewhere along the flight tracks. These gradients are interpreted as examples of the transformation of the primary pollutants
785 having a lower time constant than that of the vertical mixing within the BL, which is generally estimated to be about 20 to 30
786 minutes. The distribution of secondary products and long-lived species such as O₃ and CO provide additional information
787 about the transport and transformation of the probed air masses. The O₃ enhancements relative to the background in the lower
788 and upper parts of the BL indicate that the photochemical processing of the emissions in the polluted plumes during the
789 horizontal transport towards the Alps is similar to that during convective mixing in the BL of the Po Plain. Then again, vertical
790 and horizontal gradients of long-lived species depend on the efficiency of the mixing within the BL.

791 Furthermore, the combined effect of Alpine venting and thermally driven advection to the coast resulted in a returning layer
792 of pollution in the upper BL at 1600 m approximately. Another pollution layer coming from areas affected by wildfires in
793 southern France was detected at 1600 m. These layers were identified by residual plumes of long-lived trace gases and O₃
794 during the measurement period. These aged air masses are expected to be transported eastward by the synoptic-scale circulation
795 over the Po Plain above 2000 m and to affect air quality in Eastern Europe if they are entrained back inside the BL.

796 The results show that HYSPLIT dispersion simulations using CO as a tracer provide a consistent picture with the regional
797 transport and the degree of ageing of the observed pollution plumes but, importantly, are not able to simulate return layers
798 close to the upper BL or exceptional events such as wildfires which are not part of the emission inventory.

799 In this context of transboundary transport above the BL, the free troposphere over the Po Plain was additionally affected by
800 transport of dust from the Saharan desert. The results indicate that the synoptic conditions favoured dust transport and led to a
801 stable layering, such that mixing of the dust layer with the Po Plain urban pollution was not favoured. Therefore, direct
802 evidence of heterogeneous production of nitrate and sulphate on the dust surface in the dust layer above the BL was not
803 observed.

804 Overall, the results obtained show the complexity of the transformation and transport of emissions from the Po Plain into the
805 BL and the FT, which affects the primary and secondary air pollutants. The study reinforces the necessity and relevance of
806 airborne measurements of trace gases and aerosol constituents at different altitudes in combination with multiple radio
807 soundings as well as with remote sensing profiling of pollutants and meteorological variables to complement the observations
808 at the ground in the assessment of air pollution build-up and its effects on health, ecosystem services and agriculture. In
809 addition, this study shows how local circulation patterns strongly influence these processes in the Po Valley in summer. While
810 atmospheric chemistry models have improved greatly, continued model development and experimental studies are still needed
811 to better understand and predict pollution behaviour in complex terrain.

812 **Code, data, or code and data availability**

813 The EMERGe data are available at the HALO database (<https://doi.org/10.17616/R39Q0T> last accessed: 2025-12-22) and can
814 be accessed upon registration. Further data can be made available upon request to the corresponding author.

815 **Supplement link**

816 The supplement is provided as a separate document. The link to the supplement will be included by Copernicus.

817 **Author contributions**

818 CC prepared the manuscript with contributions from all co-authors, MDAH, JPP, FB and JPB supervised the findings of this
819 study and contributed significantly to manuscript revisions. HD provided COSMO-LAGRANTO and RB the HYSPLIT CO-
820 enhancement calculations. JS, HZ, KK, JS, OOK, BH, BW, EF, MG, YL, DS, JW, AB, BB, KP provided data used in the
821 study. All authors have contributed to the manuscript, corrections, post-writing formatting, and revisions in reviewing and
822 interpreting the results presented.

823 **Competing interests**

824 At least one of the (co-)authors is a member of the editorial board of Atmospheric Chemistry and Physics.

825 The peer-review process was guided by an independent editor, and the authors also have no other competing interests to
826 declare.

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830 appropriate place names, the final responsibility lies with the authors. Views expressed in the text are those of the authors and
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832 **Special issue statement.**

833 This article is intended to be part of the special issue “Effect of Megacities on the Transport and Transformation of Pollutants
834 at Regional and Global Scales (EMeRGe) (ACP/AMT interjournal SI)”. It is not associated with a conference

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