Interactive comment on "Continental pollution in the Western Mediterranean Basin: vertical profiles of aerosol and trace gases measured over the sea during TRAQA 2012 and SAFMED 2013" by C. Di Biagio et al.

At first, we would like to thank the reviewer for having carefully read the revised paper and provided valuable comments which helped to improve the quality of the manuscript. We have taken into consideration all the questions raised by the reviewer, and changed the paper accordingly. The details of our changes are highlighted in the text. The point by point answers to Reviewer #1 are provided in the following.

Anonymous Referee #1

Review of the manuscript "Continental pollution in the Western Mediterranean Basin: … by Di Biagio et al. Revised version

The manuscript improved compared to the previous version and several errors were removed.
However the current version still has a few deficiencies that should be corrected prior to publication. My comments refer to the version of the manuscript with 'track changes' option.

Specific comments:

Page15, line 83/84. Introduction. The statement that a large set of observations in the last decades permits to characterize a detailed view of pollution aerosols in the surroundings of the Western basin is in contradiction to the answer to my question of 'typical' for pollution aerosols section 5.3. These numbers are obviously not as well-known as stated in the Introduction. However, a few recent measurement campaigns could shed some more light on this issue.

As stated in lines 59-62 of the Introduction "A number of studies have investigated the dynamics of pollution export over the Western basin with the aim of characterizing the impact of anthropogenic emissions over this region. Most of these studies have been conducted in continental coastal areas and provide information on the vertical distribution of aerosols and their properties mainly close to local pollution sources.". So, mostly, the characterization available in the literature focusses on dynamical and seasonal processes controlling the export of pollution in the Western basin. Even if some information are available on the particle size distribution and optical properties of these aerosols (e.g., Mallet et al., 2003 and 2005; Perez et al., 2004), a lack of knowledge exists. With the aim of putting this more in evidence in the paper, the Introduction has been modified as:

"The large set of observations conducted in the last decades in the Western Mediterranean has permitted mostly to characterise the dynamics and processes of pollution export in the surroundings of the basin. However, at the present time we miss an extensive representation of the mean load, distribution, and physico-chemical and optical properties of the atmospheric aerosols, as well as trace gases distribution, in the whole region, in particular over the remote sea. In addition, there is a significant lack of observations over some key areas, as for example the Gulf of Genoa, directly under the influence of the outflow from the highly polluted Po Valley (Velchev et al., 2011)."

Section 3. Measurements and methods, page 18, lines 152 to 158. Both instruments, the GRIMM and the PCASP are optical particle spectrometers OPS's, to OPC's.
The terminology has been corrected as suggested by the reviewer.

Section aerosol scattering coefficient, line 173. Instrument was calibrated prior to each campaign.
The correction has been made.

Section 3.2 Aerosol number concentration. The PCASP seems to have a problem either with calibration or inlet losses. Even when the authors have the impression that the subsequent analysis is not affected, they should have an idea what could be the reason. The different options have consequences for the size distribution measurements with this instrument.
It is not clear based on the data and the information that we have if the PCASP problem between 0.4 and 1.0 µm comes from a calibration issue or others, like for example a reduced sensitivity of this instrument in this size range. An inlet losses problem has to be excluded since the PCASP is installed outdoor, on the left side of the aircraft fuselage.
What we observe from the data is a very good agreement with the GRIMM below 0.4 and above 1.0 µm, which indicates that in these ranges the PCASP data are accurate. So, excluded the problem between 0.4 and 1.0 µm, which is discussed in the text, as well as taken into account for the possible uncertainty on the calculated dN_{Acc}, the measurements of the PCASP can be assumed to be correct.

Section 4. Meteorological conditions, aerosol load, and pollution export regimes, page 24, line 297: The authors mention a profile V18, which is included in Table 1, but neither in Figure 1 nor in any of the other figures.
V18 was a high-altitude flight used to perform exclusively lidar measurements over the region; no profiles are available during this flight. We have eliminated V18 from line 292. For the reader's sake we have also specified in Table 1 the flights for which vertical profiles were not performed.

Line 305, Flights V24-V25-V26 were flown within two days of a certain meteorological situation, profile V31 one week later, still in the same meteorological situation?
This part has been rewritten as "Additionally, flight V31 sounded the atmospheric structure close to the Spanish coasts reaching the southern urban area of Valencia. The flight was performed one week later (10 July) under a similar meteorological condition characterized by south-westerly winds favouring the export from the Iberian Peninsula towards the basin"

Section 5.1, Vertical profiles of aerosol concentration, page 26, line 354 and also in the Abstract. The numbers given for the coarse aerosol mode are way too high. 4000 scm-3 would be probably possible directly in a heavy pollution plume, but even Saharan Dust layers are about one order of magnitude lower in concentration.
The reviewer is correct and by looking at Figure 6 the dN_{Coarse} is multiplied by 100 to let the plot more easily readable. So, the concentrations are a factor 2 lower than shown in the plot and stated in the text. I have corrected the numbers in the text.
Also, in the caption of Figure 6 I have added a note on this.

Page 28, line 393. ‘This suggests that the export towards the basin favours the redistribution of the pollution plumes along the vertical.’ This statement needs a further description of a possible process.

The description of all the possible processes, as observed in the Western basin, is already reported in the lines 393-419:

“Because of mixing in the BL, measured concentrations within the BL can be as high as those observed close to the surface over the continents. Values of dN as high as in the BL are observed in the FT because of transport in specific conditions, as discussed below.

The observations of aerosol profiles obtained during TRAQA and SAFMED are representative of the complex transport regimes which characterizes the export towards the Western basin and that is mostly determined by the interaction between regional meteorology and local dynamics (e.g., Gangoiti et al., 2001). A first example is associated to the measurements in the area of Barcelona. As discussed in Pérez et al. (2004) the presence of mountains up to ~500-3000 m altitude a few kilometres inland favours, during summertime, the recirculation of pollutants along the coasts of Spain. In these cases, the aerosols emitted at the surface in coastal areas are transported inland and uplifted by sea breezes and mountain winds then the plumes are re-injected at different altitudes and distances from the coast. During the TRAQA flights V24, V25, and V26, under the influence of pollution outflow from the Barcelona area, we detected the presence of aerosol layers with elevated concentrations (dN_{Acc}~2000-3000 scm^{-3}) up to 3500 m altitude at a distance of ~30 to 250 km from the coast of Spain. Another example of complex dynamics linked to coastal orography is that associated to the export from northern Italy and the Po Valley towards the Gulf of Genoa. The presence of the Apennine Mountains close to the Ligurian coasts (max elevation ~1500-2000 m) causes the uplift of continental air masses so determining the injection of aerosol plumes at different altitudes both inside and outside the BL. Examples are given by flights V19, V21 and V52 for which pollution aerosols from northern Italy are measured up to ~2000-3000 m altitude throughout the Gulf of Genoa. Finally, another meteorological condition which largely influences the aerosol export and distribution over the Western Mediterranean is the Mistral/Tramontane wind regime. Under the influence of the Mistral flow, atmospheric aerosols can be dispersed as far as hundreds of kilometres over the open sea, as discussed by Salameh et al. (2007). Examples are given in profiles V20 and V28, performed at more than 100 km from the French coasts, for which pollution layers associated to a Mistral flow are measured up to 2000-3000 m altitude.”

Section 5.3, O3/CO ratios and variability: In my first review I asked for a more details on the time resolution of the instruments and a possible mismatch within the data. This is especially important in vertical profile measurements when concentrations change more rapidly than in horizontal flights. In fact the Nedelec et al paper gives a 30 second time delay for the measurements of CO, the ozone instrument is not described, but a 4 second time resolution is given. In the profile this faster response can be seen in an earlier change of the ozone compared to the CO and especially the ratio of ozone to CO could be less noisy after correction.

As discussed in the first round of the revisions, we have checked and there is not a mismatch between the CO and the O_3 data. Concerning instead the reviewer comment on the different time resolution of CO and O_3 measurements, unfortunately we do not have enough information on the

instrument to correct the noise possibly arising from this effect. However, to evidence this possible factor of uncertainty, we have added a comment on this in the text (lines 456-458):
"The $\Delta O_3/\Delta CO$ ratio is highly noisy and this is due in part to the noise in the CO data, and in part also possibly associated to the slight mismatch between CO and O_3 caused by their different time resolution (30 s for CO and 4 s for O_3)."

Section 5.4, Layers with enhanced Aitken mode particle numbers, page 35, line 565 to 575
Investigations of new particle formation require a details size distribution measurement in the size range below 30 nm. An SMPS system would be necessary. As the authors do not have this instrument on board this section is highly speculative and should be omitted.
The whole text in lines 565-575 is not intended to be speculative. We observe the presence of enriched dN_{Aitken} layers in some cases and we propose some explanations based on the information we have available during the flights. We explicitly state in the text that we do not have the adapted resolution in size measurements to clearly discriminate NPF events. Moreover, we claim that the discussion is only intended to provide a qualitative indication of the possible occurrence of NPF.
Given the importance of NPF and ultrafine particles in several processes, as well as the lack of aerosol characterization in the Western Mediterranean basin, we consider very useful to maintain this part of the discussion in the text. Then, at the same time, we also assume that all the necessary information to completely evaluate our discussion/conclusions have been given to the reader.

New table 2, Page 47, line 917 to 927. In the citation Junkermann et al, line 925 correct the word September.
The correction has been made.

Editor comments

Following review of your revised manuscript, I would like to invite you to submit a further revised manuscript, taking onto account the reviewer's comments (attached in the pdf). The revisions requested are now minor, so thank you for the changes you have made so far.

By way of further clarification to the changes requested I have a few comments:

1. Please adjust the Introduction to better reflect the lack of detailed information on the character of aerosols in the Western Basin.
This part of the Introduction has been modified as suggested by the Reviewer.

2. I think the reviewer's second comment is meant to say that you should use the terms optical particle spectrometer for the GRIMM and PCASP instruments rather than optical particle counters.
The terminology has been corrected as suggested by the reviewer.

3. Whilst the possible mismatch between CO and Ozone instrument time resolution may lead to a large uncertainty and probably high noise in the O3/CO ratios, it is recognised that this is not really

important for the general results of the manuscript. However, please at least comment on this source of error in these ratios.
A comment on this has been added in lines 456-458.

Please also correct the caption to Figure 7 “Carbone” should be “Carbon”.
The correction has been made.

Continental pollution in the Western Mediterranean basin: vertical profiles of aerosol and trace gases measured over the sea during TRAQA 2012 and SAFMED 2013

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Abstract

In this study we present airborne observations of aerosol and trace gases obtained over the sea in the Western Mediterranean basin during the TRAQA (TRansport and Air QuAlity) and SAFMED (Secondary Aerosol Formation in the MEDiterranean) campaigns in summers 2012 and 2013. A total of 23 vertical profiles were measured up to 5000 m above sea level over an extended area

(40°-45°N latitude and 2°W-12°E longitude) including the Gulf of Genoa, Southern France, the Gulf of Lion, and the Spanish coast. During TRAQA and SAFMED the study area experienced a wide range of meteorological conditions which favoured the pollution export from different sources located around the basin. Also, several events of dust outflows were measured during the campaigns. Observations from the present study show that continental pollution largely affects the Western Mediterranean both close to coastal regions and in the open sea as far as ~250 km from the coastline. The measured aerosol scattering coefficient varies between ~20 and 120 Mm^{-1}, while carbon monoxide (CO) and ozone (O_3) mixing ratios are in the range of 60-165 ppbv and 30-85 ppbv, respectively. Pollution reaches 3000-4000 m in altitude and presents a very complex and highly stratified structure characterized by fresh and aged layers both in the boundary layer and in the free troposphere. Within pollution plumes the measured particle concentration in the Aitken (0.004-0.1 μm) and accumulation (0.1-1.0 μm) modes is between ~3~~1~~00 and 5000-6000 scm^{-3} (standard cm^{-3}), which is comparable to the aerosol concentration measured in continental areas under pollution conditions. Additionally, our measurements indicate the presence of highly concentrated Aitken layers (10000-15000 scm^{-3}) observed both close to the surface and in the free troposphere, possibly linked to the influence of new particle formation (NPF) episodes over the basin.

1. Introduction

Atmospheric aerosols play an important role on climate through their participation to several chemical, dynamical, and radiative processes. At present, still large uncertainties persist in the estimation of the aerosol direct and indirect effects mainly due to the difficulty of fully characterizing their spatial and vertical distribution and properties (Boucher et al., 2013).

The Mediterranean region is a complex area where atmospheric aerosols of different origins and types may be found (Pace et al., 2006; Kallos et al., 2007; Gkikas et al., 2012). High levels of

anthropogenic aerosol particles and pollutants are measured in the Mediterranean (Lelieveld et al., 2002), which is also indicated as one of the main hot spots for air quality issues (Monks et al., 2009).

The North-Western part of the Mediterranean basin, due to its proximity to highly polluted industrialized areas (such as the Po Valley in northern Italy and the Fos/Berre in southern France) and large coastal cities (Barcelona, Genoa, Marseilles, Nice, or Valencia), is frequently affected by continental outflows and severe pollution episodes (Mallet et al., 2005; Pérez et al., 2008; Pey et al., 2010). The strength of these episodes is particularly intense during summer when stable meteorological conditions and the high level of insolation promote photochemical reactions and the build-up of ozone and other pollutants (e.g. Millán et al., 2000).

A number of studies have investigated the dynamics of pollution export over the Western basin with the aim of characterizing the impact of anthropogenic emissions over this region. Most of these studies have been conducted in continental coastal areas and provide information on the vertical distribution of aerosols and their properties mainly close to local pollution sources. They include ground-based observations with lidars (Soriano et al., 2001; Pérez et al., 2004; Ancellet and Ravetta, 2005), and airborne campaigns, such as MECAPIP (MEso-meteorological Cycles of Air Pollution in the Iberian Peninsula) and RACAPMA (RegionAl Cycles of Air Pollution in the west central Mediterranean Area) in coastal Spain (Millán et al., 1996 and 1997), and ESCOMPTE (Experience sur Site pour Contraindre les Modeles de Pollution atmospherique et de Transport d'Emissions) in Southern France (Drobinski et al., 2007). The results of these studies have highlighted the important role of pollution in modulating the atmospheric composition in this part of the basin, as well as the high variability of the aerosol distribution and properties in link to different export conditions (Flamant and Pelon, 1996; Soriano et al., 2001; Mallet et al., 2005). In particular, the interaction between synoptic circulation and local dynamics, such as orography and sea breezes, has been shown to strongly impact the vertical distribution, layering, and aging of

particles along coastal regions (e.g. Millan et al., 1997; Gangoiti et al., 2001; Pérez et al., 2004; Velchev et al., 2011).

The capability of reproducing this complexity by air quality models represents a real challenge (Jimenez et al., 2006; Jiménez-Guerrero et al., 2008), and experimental observations gives a fundamental support to test the performances of the model outputs over the Western Mediterranean environment.

The large set of observations conducted in the last decades in the Western Mediterranean has permitted mostly to ~~acquire a detailed characterisation~~ characterise the dynamics and processes of pollution export~~aerosols~~ in the surroundings of the ~~Western~~ basin. However, at the present time we miss an extensive~~-~~ representation of the mean ~~aerosol~~ load, distribution, and physico-chemical and optical properties of the atmospheric aerosols, as well as trace gases distribution, in the whole region, in particular over the remote sea. In addition, there is a significant lack of observations over some key areas, as for example the Gulf of Genoa, directly under the influence of the outflow from the highly polluted Po Valley (Velchev et al., 2011).

In this study we present ~~-~~measurements of aerosols and trace gas vertical profiles acquired during 24 scientific flights performed with the ATR-42 French research aircraft during the TRAQA (TRansport and Air QuAlity) and SAFMED (Secondary Aerosol Formation in the MEDiterranean) campaigns in summers 2012 and 2013 in the framework of the Chemistry-Aerosol Mediterranean Experiment (CHARMEX, https://charmex.lsce.ipsl.fr/). The TRAQA and SAFMED flights explored an extended region of the Western Mediterranean basin between 40°-45°N latitude and 2°W-12°E longitude including the Gulf of Genoa, Southern France, the Gulf of Lion, and the Spanish coasts. Measurements were performed over the sea at various distances from the coastline with lidar and in situ instruments. During TRAQA and SAFMED the Western basin was under diverse synoptic conditions which led to the occurrence of different pollution export regimes

(Mistral/Tramontane events, outflow from the Po Valley and the Iberian Peninsula) and allowed sampling atmospheric aerosols of different origin and types.

The main objective of the present work is to provide observations of the vertical distribution of aerosols and trace gases related to the export of anthropogenic pollution at the regional scale of the Western Mediterranean basin. The detailed knowledge of the vertical structure of the atmosphere is very important to understand the impact of continental pollution over the basin.

The paper is organized as follows: in Sections 2, 3, and 4 we describe the flight trajectories and strategy during TRAQA and SAFMED, the in situ measurements carried out on board the ATR-42 aircraft, and the meteorological conditions observed during the campaigns. In Sect. 5 we present the results. The aerosol~~s~~ and trace gases vertical profiles are shown in Sections 5.1 and 5.2. Section 5.3 is dedicated to analyse the variability of the pollution plume composition and atmospheric structure also in link with the different outflow conditions. Airborne measurements in presence of layers with high concentrations of fine particles are discussed in Section 5.4. The main conclusions are reported in Section 6.

2. Overview over flights

Figure 1 shows the trajectories of the flights performed during the TRAQA (20 June-13 July 2012) and the SAFMED (24 July-1 August 2013) campaigns. Research flights were performed with the SAFIRE (Service des Avions Français Instruments pour la Recherche en Environnement, http://www.safire.fr/) tropospheric aircraft ATR-42. The aircraft has a maximum endurance of 4 h. The flight altitude ranges between a minimum of ~60 m over the sea, to a maximum of ~5000 m above sea level (a.s.l.). The aircraft was based in Toulouse (43°36'N, 1°26'E, France) during TRAQA and in Genoa (44°24'N, 8°55'E, Italy) during SAFMED. Twenty-four flights for a total of ~75 hours of data have been collected. Seventeen of the twenty-four flights presented in the paper were performed during TRAQA (flight numbers V16 to V32) and 7 during SAFMED (V46 to

V52). All flights were carried out during daytime, when light-induced chemistry favours the pollution levels. Frequently, two flights per day, with intermediate stops in different airports in Southern France, Corsica, and Sardinia, were performed. The majority of flights were over the sea, with some exceptions investigating inland areas in Southern France and central Italy. Main information concerning the TRAQA and SAFMED flights is summarized in Table 1.

The general flight strategy consisted in plane flights with lidar observations and vertical ascents/descents to sound the vertical atmospheric column (from ~60-100 m to 3000-5000 m a.s.l.) and identify main meteorological and aerosol features, followed by straight levelled runs (SLRs) within the detected aerosol layers. In this study we focus on vertical profiles data. A total of 23 profiles were acquired in 20-30 minutes each by performing a spiral trajectory ~10-20 km wide. Fig. 1 also identifies the geographical position of each sounding. As shown in Fig. 1 the profiles were performed at different distances from the coastline, from a minimum of ~5-10 km for V31 and V32 to more than ~250 km for V20 and V25, and covered almost all the different sectors of the Western basin.

3. Measurements and methods

The basic equipment of the ATR-42 aircraft includes sensors for the measurements of meteorological parameters (pressure, temperature, relative humidity, wind components), radiative fluxes (down- and up-welling shortwave and longwave radiation), and carbon monoxide (CO) and ozone (O_3) mixing ratios.

Aerosol sampling was performed using the AVIRAD system (Formenti et al., 2011). AVIRAD is an iso-axial and iso-kinetic inlet which, at the normal cruise speed of the ATR-42 (~93 m s^{-1}), samples air at a volumetric flow of ~350 l min^{-1}. The 50% passing efficiency of the inlet was tested to be 12 μm diameter. Various sampling lines depart from AVIRAD to connect to different instruments mounted inside the aircraft cabin: (i) a 3-wavelength nephelometer (TSI Inc., model 3563) for the

measurement of the dry particle volume total scattering (σ_s) and hemispherical backscattering (σ_{bs}) coefficients at 450, 550, and 700 nm; (ii) a 7-wavelengths aethalometer (Magee Sci., model AE31) for the measurement of the particle absorption coefficient (σ_a) at 370, 470, 520, 590, 660, 880, and 950 nm; (iii) an optical particle ~~counter~~ spectrometer (GRIMM Inc., model 1.129) for the measurement of the particle number concentration over 32 size classes between 0.3 and 32 μm in diameter; (iv) a Condensation Particle Counter (CPC, TSI Inc., model 3775) for the measurement of the total particle number concentration in the diameter range 0.004-3.0 μm; and (v) 3 lines for aerosol sampling on filter membranes and a 4-stage cascade impactor (Dekati Inc) to measure the bulk and size-segregated particle composition. In addition, the ATR-42 was equipped with a Passive Cavity Aerosol Spectrometer Probe (PCASP, model 100X) optical particle ~~counter~~ spectrometer for the measurement of the aerosol number concentration over 31 size classes between 0.1–3.0 μm. The PCASP was installed outside the cabin on the left side of the aircraft fuselage.

In this study we consider measurements of the (i) aerosol scattering coefficient from the nephelometer, (ii) particle concentration from the CPC and PCASP instruments (GRIMM data are not considered since they are available only below ~350 m during TRAQA), (iii) CO and O_3 trace gases from the MOZART analyser, and (iv) meteorological parameters from the ATR-42 sensors. A more detailed description of the nephelometer, CPC, PCASP, and MOZART measurements and their data analysis is provided in the following sections.

The present analysis is based only on measurements obtained in cloud free conditions.

3.1 Aerosol scattering coefficient

A three-wavelength integrating nephelometer has been used to measure the dry particle volume total scattering (σ_s) coefficient at 450, 550, and 700 nm. The sampling flow rate was 30 l min^{-1}. Data were acquired at 6 s resolution during TRAQA and 1 s resolution during SAFMED. The instrument was calibrated prior to each campaign with free-particle air and CO_2 as gases of low and

high known scattering coefficient. Nephelometer measurements have been corrected for angular truncation and Lambertian non-idealities by applying the formulae by Anderson and Ogren (1998). The measurement uncertainty on σ_s is calculated taking into account for the photon counting, gas calibration, and angular corrections uncertainties (Anderson et al., 1996; Anderson and Ogreen, 1998). The total uncertainty on σ_s is estimated to be lower than 10% at the three wavelengths.

The nephelometer measured the scattering coefficient in dry air conditions. This is due to the heating of the airflow while entering the aircraft cabin and the temperature in the cavity of the instrument. The relative humidity measured during the flights inside the nephelometer was <25% in more than ninety percent of cases, with values up to ~40% occasionally observed at very low altitudes (<200 m) over the sea surface. A possible underestimation of the scattering coefficient may thus occur in case of hygroscopic aerosols, especially under high relative humidity conditions in the atmosphere.

The particle scattering Ángström exponent (α_s) has been calculated from spectral nephelometer measurements with a power-law fit of the measured scattering coefficients versus wavelength.

3.2 Aerosol particle number concentration

The vertical profiles of the total particle number concentration in the Aitken (dN_{Aitken}, 0.004-0.1 µm), accumulation (dN_{Acc}, 0.1-1.0 µm) and coarse (dN_{Coarse}, >1.0 µm) modes have been obtained by combining CPC and PCASP data. The CPC and the PCASP measured at a sample flow of 1.5 and 0.06 l min^{-1}, respectively, and with a time resolution of 1 s for the PCASP and 5 s and 1 s for the CPC during TRAQA and SAFMED, respectively.

The PCASP was factory calibrated with monodisperse polystyrene sphere latex (PSL) whose complex refractive index at the instrument operating wavelengths (632.8 nm) is 1.59-0i. The measured sphere-equivalent optical diameter has been converted to a sphere-equivalent geometrical

diameter (D_g) by taking into account the complex refractive index of the sampled aerosol (Liu and Daum, 2000). Given that in the very large majority of cases the aerosol sampling during TRAQA and SAFMED was associated to the export of pollution plumes, only pollution aerosols have been considered for PCASP correction. Note that these data are not optimized for dust or marine aerosol observations. A large interval of values (n~1.50-1.72, k~0.001-0.1 for UV-visible wavelengths) are reported in the literature for the real and the imaginary parts of the refractive index for anthropogenic aerosols over Europe (e.g., Ebert et al., 2002 and 2004; Müller et al., 2002; Mallet et al., 2003 and 2011; Chazette et al., 2005; Raut and Chazette, 2008). For our calculations at 632.8 nm we have fixed the imaginary part of the refractive index to 0.01, thus representing a mean absorbing aerosol, and then we have varied the real part between its minimum (1.50) and maximum (1.72) reported value. D_g is then set at the mean ± one standard deviation of the values obtained for the different values of n. We assume in these calculations that the refractive index does not vary with height. After refractive index correction the D_g range for the PCASP becomes 0.10-4.47 µm, with an uncertainty between 1 and 25%. The smallest and the largest size bins of the PCASP, for which the minimum and maximum edges respectively are not defined, have been excluded from the datasets, thus reducing the PCASP D_g range to 0.11-4.17 µm.

Once corrected for the refractive index, PCASP data have been combined with those from the CPC to calculate dN_{Aitken}, dN_{Acc}, and dN_{Coarse}. Values for dN_{Acc} and dN_{Coarse} are obtained by integrating the PCASP number concentrations in the 0.1-1.0 µm and 1.0-4.17 µm ranges, while dN_{Aitken} is estimated as the difference between CPC concentration and the integral of PCASP data between 0.1 and 3.0 µm. The comparison between the PCASP and the GRIMM below 350 m altitude indicates that the former underestimates by about 50% the aerosol concentration in the range 0.4-1.0 µm (the accuracy of the GRIMM has been verified by optical closure study against simultaneous aircraft nephelometer measurements). This is estimated to induce a ~20% underestimation of the dN_{Acc}

calculated here. Conversely, the PCASP underestimation in the 0.4-1.0 µm range has almost a negligible impact on dN_{Aitken}.

CPC measurements, and so dN_{Aitken} data, were not available during SAFMED flights V49, V50, and part of V51.

3.3 Trace gases

Carbon monoxide (CO) and ozone (O_3) mixing ratios were measured by the MOZART instrument described in detail by Nedélec et al. (2003). CO is a long-lived tracer for air masses influenced by combustion processes, whereas O_3 in the troposphere is a photochemical product of the oxidation of CO and volatile organic compounds (VOCs) in the presence of nitrogen oxides (NO_x). CO and O_3 are measured at a resolution of 30 s and 4 s, respectively. The nominal uncertainty is ±5% for CO and ±2% for O_3 (Nedélec et al., 2003). However, a recent airborne intercomparison in May 2014 in the framework of the French ChemCalInt project and the TGOE European Joint Research Activity has suggested a greater uncertainty (up to 30%) on CO measurement by MOZART on-board the ATR-42 (A. Borbon, personal communication, 2015). Trace gas analysis will focus mostly on the vertical distribution of the $\Delta O_3/\Delta CO$ ratio rather than absolute concentrations (see section 5.3) and the uncertainty on CO should not affect data interpretation.

3.4 STP conversion

In order to compare measurements obtained at different altitudes the data presented here are reported at standard temperature and pressure (STP) using T=293.15 K and p=1013.25 hPa (NIST, National Institute of Standards and Technology, values). Hence, the scattering coefficient is scaled to STP conditions and the particle concentrations are given as particles per standard cm^{-3} (scm^{-3}).

For a generic parameter x measured at the temperature T and pressure p, the conversion at STP is calculated with the formula:

$$x(STP) = x(T,p)\frac{T}{293.15}\frac{1013.25}{p} \qquad (1).$$

CO and O_3 do not need to be corrected for STP since the mixing ratio does not depend on temperature and pressure.

3.5 Meteorological parameters

The vertical profiles of the pressure (p), the temperature (T), the relative humidity (RH) and the wind components towards the east and the north (U, V) measured on board the ATR-42 have been used to analyse the atmospheric structure during flights. Starting from the measured parameters the potential temperature (θ) has been also calculated as $\theta = T(p_0/p)^{0.286}$ with p_0=1013.2 mbar. For each profile the height of the marine aerosol boundary layer (MABL) and planetary boundary layer (BL) has been estimated visually by looking at the vertical gradients of T, θ, and RH. Meteorological parameters have been also used to calculate the vertical profiles of the gradient Richardson number (Ri):

$$Ri = \frac{g}{\theta}\frac{\partial\theta}{\partial z}\Bigg/\left(\left(\frac{\partial U}{\partial z}\right)^2 + \left(\frac{\partial V}{\partial z}\right)^2\right) \qquad (2).$$

In Eq. (2) g is the gravitational acceleration and z is the height. The Ri number is the ratio between the buoyancy force and the wind shear and it is used to indicate dynamic stability and the formation of clear air turbulence. Turbulence can develop when Ri is below the critical threshold Ri_{crit}=0.25, while it is inhibited for Ri>1 (e.g., Wallace and Hobbs, 2006). In this study the profiles of Ri are

used to provide indications of favorable/unfavorable conditions for the development of turbulent conditions within the atmosphere.

3.6 Tracking the air mass back-trajectories

The Lagrangian trajectory model FLEXTRA (FLEXible TRAjectories, Stohl et al., 1995) has been used in selected cases to track the origin of sampled air masses. Five days three-dimensional back-trajectories have been calculated using the ECMWF (European Centre for Medium-Range Weather Forecast) operational analysis with a 0.5° by 0.5° horizontal resolution and up to 30 vertical model levels below 4000 m. The model specific humidity and potential vorticity is also interpolated along the trajectory path.

4. Meteorological conditions, aerosol load, and pollution export regimes

In order to characterize the general aerosol conditions encountered over the Western Mediterranean basin during the TRAQA and the SAFMED campaigns we have plotted the time-series of the aerosol optical depth (τ, ±0.02) at 440 nm and the 440-870 nm Ångström exponent (α) measured with a Cimel sunphotometer (Holben et al., 1998) at the three AERONET stations of Barcelona, Frioul, and Ersa located along the coast around the Western basin (see Fig. 1). Level 1.5 cloud-screened data are used in this study. Data are shown in Fig. 2 and correspond to the period of the campaign of measurements plus 10 days before and after. Table 1 reports the date, location, and main meteorological and export conditions encountered during TRAQA and SAFMED flights.

Over the analysed AERONET sites the aerosol optical depth was below 0.2 before the beginning of the TRAQA campaign and increased, especially at Barcelona and Ersa, to ~0.3-0.5 (with $1<\alpha<2$) in the periods 23-26 June and 3-13 July 2012. Isolated peaks of τ were measured in correspondence of two Saharan dust intrusion events which occurred on the 17-23 June (τ~0.6) and 29 June 2012

(τ~1.4). Different wind regimes occurred during TRAQA and favoured the continental outflow from different regions located around the basin. Two examples of wind maps derived from WRF-Chem model (Grell et al., 2005) at 925 mbar are shown in Fig. 3 for 26 June and 3 July 2012. Main observed meteorological/export conditions can be summarized as follows: (i) on 26-27 June north/north-westerly winds blew across northern Italy determining an air mass outflow towards the Gulf of Genoa (measurements on flights ~~V18~~ V19-V21); (ii) on the same days a strong Mistral-Tramontane episode (i.e., strong northerly winds developing along the Rhône and Aude valley which bring a northerly/north-westerly flow over the Western Mediterranean, see Fig 3a) favoured the dispersion of pollutants towards the central part of the Western basin. Measurements during the event were performed during flight V20; (iii) on 3-4 July the wind regime was dominated by weasterly/south-weasterly winds mostly blowing at the surface across the Iberian Peninsula and southwestern France (see Fig. 3b). This condition allowed measuring the export of pollution from the Spanish coasts, in particular close to the area of Barcelona (flights V24-V25-V26, see Fig. 1). Additionally, flight V31 sounded the atmospheric structure close to the Spanish coasts reaching the southern urban area of Valencia. The flight was performed one week later (10 July) under a similar meteorological condition characterized by~~the influence of~~ south-westerly winds favouring the export from the Iberian Peninsula towards the basin; (iv) Mistral episodes occurred on the 6-7 and 11 July 2012. In those cases the Mistral wind combined with a persistent westerly flow thus yielding pollution export towards the central and central-eastern part of the Western basin, as measured during flights V27-V28-V30-V32; (v) finally, Saharan dust aerosols were sampled during flights V16 and V20 (episode of the 17-23 June) and flights V22 and V23 (episode of the 29 June).

During SAFMED the meteorological conditions were more stable and two distinct phases were observed: (i) a stable anticyclone affected the whole Western Mediterranean area during the first half of July until the 26th, thus possibly favouring a more pronounced accumulation of photochemical pollution in this part of the basin. Relatively high values of both τ (~0.2-0.8) and α

(~1-2.5) were measured at the three sites of Barcelona, Frioul, and Ersa in this period; (ii) a cyclonic system moving from the Atlantic region towards Europe then affected the Western basin on 28-29 July 2013. Very clean conditions (τ<0.1-0.2) were measured afterwards over the entire region until the end of the SAFMED campaign. Winds were mostly westerly/south-westerly in the first period of the campaign (24-29 July 2013, flights V46, V47, V48, V49, V50), which means that the sampled air flow came mostly from the sea. Then, from 30 July to 1 August 2013 a north-easterly flow affected the SAFMED investigated area thus promoting the export of pollution from Northern Italy towards the Gulf of Genoa (flights V51, V52). A strong Mistral event (29 July-1 August) and two Saharan dust outbreaks (27-28 July and 1 August) affected the Western basin, however not influencing the vertical profile observations during SAFMED.

In order to identify the distribution of observations during TRAQA and SAFMED as a function of the aerosol type we have plotted in Figure 4 the distribution of the measured scattering coefficient σ_s at 450, 550, and 700 nm as a function of the calculated scattering Ångström exponent α_s for all vertical profiles. The plot shows a similar scattering intensity between cases dominated by coarse particles (α_s<0.5-1.0), such as desert dust, and those dominated by fine particles (α_s> 1.0-1.5), such as pollution aerosols. For both dust and pollution σ_s peaks at about 100-120 Mm^{-1}. The frequency of occurrence of α_s shows that pollution plumes represent the large majority of the cases observed, with more than 70% of measurements with α_s> 1.0.

5. Results

Figure 5 shows the box and whisker plots of the aerosol scattering coefficient σ_s at 450, 550, and 700 nm, particle number concentration in the Aitken (dN_{Aitken}) and accumulation (dN_{Acc}) diameter ranges, and CO and O_3 measured in the boundary layer (BL) and in the free troposphere (FT) within pollution plumes for all the different vertical soundings analysed in this study. This plot summarizes the range of values observed during TRAQA and SAFMED. On average, the scattering coefficient

and CO are larger in the BL compared to the FT, whilst similar ranges of values are measured in the two regions for dN_{Aitken}, dN_{Acc}, and O_3. Even within the single BL and FT the different parameters show a large variability that will be explored in the following paragraphs.

5.1 Vertical profiles of aerosol concentration and scattering coefficient

Figure 6 shows the vertical profiles of σ_s, dN_{Acc}, and dN_{Coarse} during TRAQA and SAFMED flights. The date, time and coordinates of each profile, as well as the heights of the top of the marine and planetary boundary layer (MABL and BL) estimated from meteorological data are also indicated in the plot.

For the different vertical soundings the particle concentrations dN_{Acc} and dN_{Coarse} vary in the range ~30-3200 scm^{-3} and ~0.05-4000 scm^{-3}, respectively, for plumes with σ_s between 10 and 120 Mm^{-1}. The structure in the scattering profile is generally mirrored in dN_{Acc} profile, and this also reflects the pronounced spectral variability (i.e., decrease for increasing wavelength) of the scattering coefficient, typical of pollution/anthropogenic particles. dN_{Coarse} also contributes to the scattering signal in some cases especially at high altitudes (see V16, V20, V21, V22, and V23 above ~2000 m), and this reflects the low spectral variability of the scattering coefficient. These observations are associated to the dust intrusion episodes which occurred in the Western Mediterranean basin during TRAQA, which however will not be analysed in detail here. Aerosol layers affected by dust have been labelled with a “D” in Fig. 6.

Maxima of the scattering coefficient have been measured for TRAQA flights V21 and V23 (~120 Mm^{-1} for pollution in the BL and ~100 Mm^{-1} in the dust layer), whereas flights V46-V48-V49, during the first and more polluted phase of SAFMED, are the richest in dN_{Acc} (1500-3000 scm^{-3} over the whole column). Minima of σ_s and dN_{Acc} are obtained for flight V51 at the beginning of the second SAFMED phase when clean conditions were observed in the Western Mediterranean.

Pollution plumes observed in the different flights extend from the boundary layer to the free troposphere up to 3000-4000 m altitude. The vertical structure of the aerosol scattering coefficient/particle concentration is linked to the variability of the atmospheric thermodynamic structure and is generally characterized by a first layer confined in the MABL (<400 m, profiles V16, V20, V22, V25, V48, V51), followed by one or more layers within the BL. In the FT pollution particles occur both as single isolated plumes each about 500-1000 m deep (V21, V24, V25, V30, V46, V49), or as a more uniform layer extending from the top of the BL up to 2500-4000 m altitude (V26, V27, V28, V32, V48). The highest values of both the scattering coefficient and dN_{Acc} for pollution are found within the MABL or BL in most cases, while a local minimum of σ_s and dN_{Acc} is generally identified at the top of the BL. The scattering coefficient and the particle concentration measured in the FT are comparable with the values observed in the BL, and in few cases even larger (V25, V26, V30). Only in one case (profile V31) σ_s and dN_{Acc} decrease monotonically with height. The aerosol vertical distribution, both in the BL and in the FT, often presents a strongly stratified structure characterized by the presence of several thin sub-layers within one main identified aerosol plume, as it can be seen in particular in the dN_{Acc} profiles (V20, V21, V22, V25, V46, V49).

The particle concentration in the Aitken mode (0.004-0.1 μm; dN_{Aitken}, not shown in Fig. 6) is generally below 5000-6000 scm^{-3} at all altitudes up to 4000 m within pollution plumes. dN_{Aitken} is correlated with dN_{Acc} in most of the observed cases, which indicates the common source of particles in these two size ranges. Few layers exceeding ~10000-15000 scm^{-3} are observed occasionally both in the BL and in the FT. These will be discussed in more detail in Sect. 5.4.

The dN_{Acc} and dN_{Aitken} measurements within the BL and in the FT over the sea are comparable with the values measured close to the surface at continental sites under pollution conditions (see Table 2) (Petzold et al., 2002; Mallet et al., 2003 and 2005; Wiegner et al., 2006; Junkermann, 2009; Hamburger et al., 2012; Highwood et al., 2012). This suggests that the export towards the basin favours the redistribution of the pollution plumes along the vertical. Because of mixing in the BL,

387 measured concentrations within the BL can be as high as those observed close to the surface over
388 the continents. Values of dN as high as in the BL are observed in the FT because of transport in
389 specific conditions, as discussed below.

390 The observations of aerosol profiles obtained during TRAQA and SAFMED are representative of
391 the complex transport regimes which characterizes the export towards the Western basin and that is
392 mostly determined by the interaction between regional meteorology and local dynamics (e.g.,
393 Gangoiti et al., 2001). A first example is associated to the measurements in the area of Barcelona.
394 As discussed in Pérez et al. (2004) the presence of mountains up to ~500-3000 m altitude a few
395 kilometres inland favours, during summertime, the recirculation of pollutants along the coasts of
396 Spain. In these cases, the aerosols emitted at the surface in coastal areas are transported inland and
397 uplifted by sea breezes and mountain winds then the plumes are re-injected at different altitudes and
398 distances from the coast. During the TRAQA flights V24, V25, and V26, under the influence of
399 pollution outflow from the Barcelona area, we detected the presence of aerosol layers with elevated
400 concentrations (dN_{Acc}~2000-3000 scm^{-3}) up to 3500 m altitude at a distance of ~30 to 250 km from
401 the coast of Spain. Another example of complex dynamics linked to coastal orography is that
402 associated to the export from northern Italy and the Po Valley towards the Gulf of Genoa. The
403 presence of the Apennine Mountains close to the Ligurian coasts (max elevation ~1500-2000 m)
404 causes the uplift of continental air masses so determining the injection of aerosol plumes at different
405 altitudes both inside and outside the BL. Examples are given by flights V19, V21 and V52 for
406 which pollution aerosols from northern Italy are measured up to ~2000-3000 m altitude throughout
407 the Gulf of Genoa. Finally, another meteorological condition which largely influences the aerosol
408 export and distribution over the Western Mediterranean is the Mistral/Tramontane wind regime.
409 Under the influence of the Mistral flow, atmospheric aerosols can be dispersed as far as hundreds of
410 kilometres over the open sea, as discussed by Salameh et al. (2007). Examples are given in profiles

411 V20 and V28, performed at more than 100 km from the French coasts, for which pollution layers
412 associated to a Mistral flow are measured up to 2000-3000 m altitude.

413

414 **5.2 Trace gases vertical profiles**

415 Figure 7 shows O_3 versus CO for all TRAQA and SAFMED flights, while examples of CO and O_3
416 profiles representatives of different conditions are reported in Fig. 8 and 10.

417 CO and O_3 vary in the range 60-165 ppbv and 30-85 ppbv, respectively. The 25^{th} and 75^{th}
418 percentiles are 87 and 105 ppbv for CO and 49 and 62 ppbv for O_3, representative of moderate
419 pollution conditions (i.e., Parrish et al., 1998). By comparison, the values measured over land in
420 central Italy during flight V49 are in the range 80-180 ppbv for carbone monoxide and 40-85 ppbv
421 for ozone. CO and O_3 are generally correlated (correlation coefficient R^2~0.5-0.8) within measured
422 pollution plumes, and also correlated with σ_s and N_{Acc} both in the BL and in the FT, which indicates
423 photochemically active plumes. CO is generally higher in the BL, and shows absolute maxima in
424 the lowest levels (V20, V21, V24, V28, V46), then it decreases in the FT. Ozone presents a more
425 complicated vertical structure due to the different photochemical and dynamical processes which
426 control its formation and distribution. At first, local peaks of O_3 correlated with CO are observed in
427 correspondence of pollution plumes both in the BL and in the FT. An absolute maximum of O_3 is
428 sometimes found near the top of the BL (V24, V25, V30) possibly due to aged air masses trapped in
429 the boundary layer. Isolated peaks of O_3 (~75-80 ppbv) not correlated with aerosols and CO are also
430 measured in few cases above 3000-3500 m (V21, V25, V27, V28, V52). The analysis of back-
431 trajectories indicates that these high-altitude ozone layers are associated to the descent of air masses
432 travelling at about 7-8 km, which thus may suggest a downward transport from the upper
433 troposphere or the tropopause region due to a stratosphere-troposphere exchange (Ancellet and
434 Ravetta, 2005). Finally, absolute minima of O_3 (~15-30 ppbv) are measured within the dust layers

during flights V20 and V21, maybe related to the dust/ozone heterogeneous reactions which leads to O_3 destruction, as documented in several studies (Bonasoni et al., 2004; Haywood et al., 2011).

5.3 $\Delta O_3/\Delta CO$ and dN_{Aitken}/dN_{Acc} ratios and variability of pollution plume composition

Using the O_3, CO, dN_{Aitken} and dN_{Acc} measurements we have estimated:

- the O_3-CO enhancement ratio ($\Delta O_3/\Delta CO$), i.e. the ratio of the ozone to carbon monoxide variations compared to their baseline values. The $\Delta O_3/\Delta CO$ enhancement ratio is frequently used to estimate the efficiency of O_3 formation and its export (Parrish et al., 1993; Zhang et al., 2006). From our observations (Fig. 7) we have estimated a background value of ~70 ppbv in the BL and 60 ppbv in the FT for CO and ~30 ppbv for O_3 both in the BL and in the FT.

- The Aitken to accumulation number ratio (dN_{Aitken}/dN_{Acc}), which defines the relative importance of particles in the Aitken and accumulation modes. dN_{Aitken} is generally associated to gas-to-particle conversion and nucleation events and is higher in fresh plumes, while it decreases with the increasing of the plume lifetime due to coagulation or condensation of water-soluble chemical species on the particle surface (Kulmala et al., 2004).

The combination of $\Delta O_3/\Delta CO$ and dN_{Aitken}/dN_{Acc} has been used to retrieve additional information on the atmospheric vertical structure, layering, and particle aging.

Within detected pollution plumes the ΔCO and ΔO_3 reach up to 100-120 ppbv and 45-55 ppbv, respectively, with a corresponding $\Delta O_3/\Delta CO$ ratio which varies in the range ~0.10-2.0 for all cases. The $\Delta O_3/\Delta CO$ ratio is highly noisy and this is due in part to the noise in the CO data, and in part also possibly associated to the slight mismatch between CO and O_3 caused by their different time resolution (30 s for CO and 4 s for O_3). These values of $\Delta O_3/\Delta CO$ obtained in this study are

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459 comparable with the range of observations available in the literature for fresh and moderately aged
460 pollution plumes in the BL and in the lower FT (~0.2-1.0) (Chin et al., 1994; Parrish et al., 1998;
461 Zhang et al., 2006; Cristofanelli et al., 2013). dN_{Aitken}/dN_{Acc} is between about 1 and 20 in most of
462 pollution cases, which indicates the presence of both fresh layers rich in Aitken particles and aged
463 plumes poor in Aitken particles. Extremely high values of dN_{Aitken}/dN_{Acc} (~50-200) are measured in
464 few cases in layers with very low dN_{Acc} concentrations.

465 The large variability in $\Delta O_3/\Delta CO$ and dN_{Aitken}/dN_{Acc} indicates a strong heterogeneity in terms of
466 composition and lifetime for the different observed plumes. This heterogeneity reflects the
467 complexity in terms of sources, production processes, and transport mechanisms which
468 characterizes the Western basin. In order to illustrate this point, we have selected three examples
469 representative of different conditions observed in different areas of the basin: (i) V19, performed in
470 the Gulf of Genoa in correspondence of continental outflow events from Northern Italy/Po Valley;
471 (ii) V20, performed in Southern France during a Mistral event; (iii) V24, which measured the export
472 of pollution from the area of Barcelona. The vertical profiles of the spectral scattering coefficient σ_s,
473 temperature T, relative humidity RH, dN_{Acc}, dN_{Aitken}, CO, O_3, $\Delta O_3/\Delta CO$, dN_{Aitken}/dN_{Acc} and wind
474 are reported in Fig. 8 for these cases.

475 *1. V19: export from northern Italy/Po Valley*. The profile shown for flight V19 (Fig. 8a) is
476 characterized by the presence of three different aerosol structures: the first one below 800 m,
477 characterized by a lower dN_{Aitken}/dN_{Acc} (~1-5) and relatively high $\Delta O_3/\Delta CO$ (~0.4-1.5), possibly
478 associated to moderately aged pollution; the second one between 800 and 2600 m, richer in fine
479 particles (dN_{Aitken}/dN_{Acc}~5-15), so possibly linked to fresher emissions; and the third one above
480 2600 m, where the ratio dN_{Aitken}/dN_{Acc} rises rapidly, as will be further discussed in Sect. 5.4. The
481 export of fresh pollution at 800-2600 m from northern Italy as observed in V19 may be related to
482 the peculiar orography of this region and the uplift of continental air masses. This is confirmed by
483 the analysis of the back-trajectories (Fig. 9) which indicates that the air masses arriving at 1000 and

2000 m passed over the western Po Valley at an altitude of about 400-1200 m and were then uplifted near the Ligurian coast to enter the basin above the BL. Junkermann (2009) measured high levels of fine particles up to about 2000 m in the western Po Valley, which means that the altitudes of 400-1200 m reached by our investigated air masses could have been sufficient for them to collect fresh emitted particles along their path. Conversely, below 800 m the air mass trajectory shows a longer subsidence over the sea surface in the troposphere which has possibly favoured the advection of more aged plumes, or the mixing with sea salts thus inducing the decrease of the dN_{Aitken}/dN_{Acc} ratio. It should be noted that the aerosol layer in the FT also shows relatively higher values of the $\Delta O_3/\Delta CO$ ratio (~0.6-1.0) compared to the more aged plume in the BL. The enhanced amount of O_3 in this air mass can be linked to a high concentration of volatile precursors which may have favoured the build-up of ozone during the plume evolution. In a recent work, Kaiser et al. (2014) suggest that in the Po Valley the high content of formaldehyde, also observed by Junkermann et al. (2009), may be responsible for the excess of O_3 production. Fresh layers in the FT up to ~2000-3000 m possibly associated to pollution export from northern Italy have been also observed during flights V21 and V52 (not shown).

2. V20: export during a Mistral/Tramontane event. V20 provides an example of export during a Mistral/Tramontane event. As shown in Fig. 8b, winds from the northwest direction are measured at all altitudes during flight V20. The aerosol profile in the BL is characterized in the first ~400 m by the presence of a layer richer in dN_{Aitken} ($dN_{Aitken}/dN_{Acc}>20$) and CO (100 ppbv close to the surface; CO data not available between 150 and 650 m) possibly linked to fresh pollution, followed by the alternation of several layers characterized by a variable dN_{Aitken} (1000-6000 scm^{-3}) and lower CO (~70 ppbv). A local minimum of dN_{Aitken} and σ_s is found at ~400 m. For all these layers the O_3 is very low (~30-40 ppbv) and the $\Delta O_3/\Delta CO$ ratio is <0.6-0.8. At higher altitudes, between 1400 and 2000 m, we observe a layer enriched in O_3 ($\Delta O_3/\Delta CO$~1-2) in correspondence of an almost aerosol-free region. This enriched ozone layer might be possibly associated to a downward transport from

509 higher tropospheric layers, as also suggested by the back-trajectories (Fig. 9), as well as to the
510 mixing with ozone rich layers along the air mass trajectory. Larger particles, from long-range
511 transport of Saharan dust at latitudes below 30° N, are measured between 2000 and 3000 m, with a
512 minimum of O_3 (~15-20 ppbv) registered within the layer. Several other flights were performed
513 during Mistral/Tramontane episodes (V27, V28, V30, V32) and show, similarly to V20, the
514 presence of several layers both in the BL and the FT.

515 *3. V24: export from the Barcelona area.* Measurements during V24 may be taken as representative
516 of local recirculation (Pérez et al., 2004). In the V24 profile in Fig. 8c we may recognize up to 5
517 different aerosol layers. A first layer at <200 m within the MABL, coming from the southwest and
518 directly exported from the area of Barcelona. The layer is characterized by high CO (90-120 ppbv),
519 and relatively low values of dN_{Aitken} (~4000 scm^{-3}) and O_3 (~50 ppbv), which possibly suggest the
520 mixing of pollution with marine particles close to the sea surface. A second layer of fresher
521 particles, always coming from the southwestern direction, is observed above the MABL between
522 200 and 600 m (dN_{Aitken}~6000-8000 scm^{-3}, O_3~70 ppb, with dN_{Aitken}/dN_{Acc}~5-15, and
523 $\Delta O_3/\Delta CO$~0.8-1.5). A third, more aged, sublayer (dN_{Aitken}/dN_{Acc}~2-5, $\Delta O_3/\Delta CO$~0.8-1.0) is
524 observed within the BL between 600 and 1000 m. The FT is characterized by the presence of
525 moderately aged plumes from ~1000 to 2800 m (dN_{Aitken}/dN_{Acc}~2-10, $\Delta O_3/\Delta CO$~0.2-0.8), and a
526 very aged plume at 2800-3800 m almost deprived in Aitken particles and richer in O_3
527 (dN_{Aitken}/dN_{Acc}<1, $\Delta O_3/\Delta CO$~0.6-1.5). A marked local minimum is observed at the top of the BL
528 for σ_s, dN_{Acc}, dN_{Aitken}, CO, and O_3, suggesting the presence of air masses with different origin
529 between the BL and the FT. This is also confirmed by the analysis of the back-trajectories (Fig. 9)
530 which indicates a low level air masses coming from the Spanish coasts in the BL, and air masses
531 travelling at higher altitudes in the FT. In particular, the layer at 2800-3800 m is possibly associated
532 to an intercontinental transport from Northern America, as shown in the trajectory ending at 3500

m. A similar structure characterized by the alternation of fresher and more aged plumes in the BL and FT is also observed in V25 for which aerosol layers are detected up to 4000 m altitude.

The detailed analysis of these three events evidences the complexity of the atmospheric structure over the Western Mediterranean basin in link with the different dynamical processes involved.

5.4 Layers with enhanced Aitken mode particle numbers

Isolated layers with dN_{Aitken}~10000-15000 scm^{-3} have been observed occasionally both in the BL and in the FT. The vertical profiles of dN_{Aitken} for some selected cases are shown in Fig. 10.

For about half of the observed events the dN_{Aitken} layer appears related to a simultaneous increase in dN_{Acc}, CO, and O_3, which suggests that the layer has been transported from a region directly emitting in this size range. These cases are: V16 at ~200-400 m, V21 at ~400-800 m, V28 at ~250 m, and V31 at ~1000-3000 m (only V28 and V31 are shown in Fig. 10). The most remarkable example is V31 (Fig. 10a), performed close to the coasts of Spain near Valencia, for which the high dN_{Aitken} layer extends from the top of the BL to ~3000 m altitude. The wind vector and the back-trajectories (not shown) indicates that the air mass comes from the western-southwestern direction above 1000 m, so the dN_{Aitken} layer can be directly related to pollution export from the urban region of Valencia.

In all the other cases the high dN_{Aitken} layer is generally not related to simultaneous dN_{Acc} and O_3 increase. Two of these cases (V16 at ~800-1000 m and V28 at ~100 m) occur in the BL.

For the V28 layer (Fig. 10b) the dN_{Aitken} is correlated with CO which might indicate the influence of local emissions close to the surface level (i.e., ship emissions). CO values are relatively high (140-160 ppbv) within the layer. It has been often assumed that new particle formation events (NPF) only occur in almost clean environments (e.g., O'Dowd et al., 2010; Sellegri et al., 2010), and that they are suppressed under polluted conditions. In a recent study, Brines et al. (2014) show the occurrence

of NPF events also in urban areas with high level of pollution in the Mediterranean region. So, we explore the possibility of NPF in our observations. Given the size ranges of the CPC and PCASP, however, we cannot discriminate within dN_{Aitken} the particle concentration in the sole 4-20 nm range, i.e. the size range involved in nucleation. So it is not possible to directly associate the V28 observations to NPF. In order to obtain a qualitative indication of the possible occurrence of NPF, we have looked at the air mass dynamics within the layer. Several studies suggest, in fact, that NPF might be favoured by turbulence and air mass mixing (e.g., Nilsson et al., 2001; Wehner et al., 2010). We have thus looked at the gradient Richardson number (Ri) which gives information on the atmospheric dynamical stability. Vertical profiles of Ri are also shown in Fig. 10. For V28 the vertical profile of Ri indicates that below 200 m the Ri number is consistently below zero, which suggests well established turbulent conditions possibly favouring NPF in this layer.

In other two cases (V19, Fig. 10c, and V26, Fig. 10d), under lower pollution conditions (CO < 100), we measured high dN_{Aitken} concentration in correspondence of low dN_{Acc} layers in the FT at ~2800-3000 m for V19 and 3500-4500 m for V26. For V19 and V26 layers, dN_{Aitken} seems anticorrelated to CO. Also in this case the Richardson number is below Ri_{crit} in correspondence of the Aitken peak meaning that conditions are favorable for turbulence within the layer, and this may indicate also in this case the possible role of NPF.

Finally, a case of high dN_{Aitken} concentration has been also observed in correspondence of dust particles between ~3000 and 4000 m (V23b, Fig. 10e). This layer can be possibly linked to the photochemically-induced nucleation which may occur in presence of dust and SO_2 as hypothesised in a recent study by Dupart et al. (2012) and observed by Nie et al. (2014).

6. Conclusions

The data presented in this paper gives an overview of the distribution of aerosols and trace gases within the tropospheric column up to 5000 m above the Western Mediterranean basin.

These data add to the very few available measurements of aerosol and trace gases vertical profiles over the sea surface in the Central (e.g., Junkermann, 2001; Meloni et al., 2003; Di Iorio et al., 2003; Pace et al., 2014) and Eastern (e.g., Formenti et al., 2002; Dulac and Chazette, 2003) parts of the basin thus contributing to improve the description of the atmospheric composition and structure over the whole Mediterranean area.

Observations from the present study indicate that continental pollution strongly affects the composition and structure of the Western Mediterranean basin both close to coastal regions and in the open sea. Pollution layers extend up to 250 km far from the coasts and reach up to 3000-4000 m altitude, presenting a complex and highly stratified structure. The measured particle concentration is comparable with the values reported for continental Europe (Petzold et al., 2002; Junkermann, 2009; Hamburger et al., 2012).

Pollution plumes with different compositions, origins, and lifetimes are observed in link with the different observed dynamical export conditions and meteorological regimes. The aerosol and trace gas observations during TRAQA and SAFMED are consistent with the results of former campaigns and with the interpretation of observed or well known air-masses dynamics and meteorological phenomena that can occur in the Western basin (Flamant and Pelon, 1996; Millan et al., 1997; Gangoiti et al., 2001; Pérez et al., 2004; Mallet et al., 2005).

The large heterogeneity in aerosol compositions, origins, and lifetimes as documented in this study can reflect in a large heterogeneity of aerosol optical properties, with consequences for their direct radiative effect in this part of the basin. This aspect will be investigated in a companion paper analysing the TRAQA and SAFMED in situ measurements of the aerosol absorption and scattering properties and their variability.

From the present observations, it is also interesting to note the relatively high values of dN_{Aitken} measured both in the BL and the FT, which evidences the important contribution of ultrafine particles at all altitudes over the basin. These can be linked to the different export mechanisms

607 previously discussed, as well as the possible occurrence of NPF events. Aitken particle profiles are
608 very rare over the sea surface in the Mediterranean (e.g., Junkermann et al. 2001; Pace et al., 2015)
609 and data comparison is quite difficult. Few studies have observed NPF in the FT in continental
610 areas (Boulon et al., 2010; Rose et al., 2014) and suggest that the export of pollution into the upper
611 troposphere, as it is common in the Western basin, might promote the occurrence of these events.
612 The observations of the present study may thus also have very large implications due to the crucial
613 role of NPF in controlling the atmospheric cloud condensation nuclei concentration (Spracklen et
614 al., 2008) and the associated aerosol indirect effect on climate.

615

616 **Author contributions**

617 J.-L.A., F.R., G.A., M.B., A.B., P.F. and K.S. designed the TRAQA and SAFMED experiments and
618 coordinated the campaigns. C.G., N.G., and C.D.B operated the instruments on board the ATR-42
619 during the flights. C.D.B. performed the data analysis with contributions from L.D., P.F., F.R.,
620 A.B., G.A., J.-C.R., and M.B.. G.A. performed the FLEXTRA simulations. J.-C.R. performed the
621 WRF-Chem simulations. C.D.B. wrote the manuscript.

622

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Tables

Table 1. Summary of information on the TRAQA and SAFMED flights.

Measurement campaign	Flight number	Date	Take off-landing time (UTC)	Departure-arrival	Geographic area investigated	Description
TRAQA 2012	V16	20/06/2012	13:12 – 16:34	Toulouse-Toulouse	Gulf of Lion	Test flight
	V17*	22/06/2012	09:01 – 12:54	Toulouse-Toulouse	South-western France (over land) and the Atlantic Ocean	Test flight, biogenic emissions.
	V18*	26/06/2012	07:13 – 09:18	Toulouse-Bastia	Gulf of Genoa	Export of pollution from Northern Italy/Pô Valley, north-westerly winds
	V19	26/06/2012	10:42 – 13:46	Bastia-Toulouse	Gulf of Genoa	Export of pollution from Northern Italy/Pô Valley, north-westerly winds
	V20	27/06/2012	04:07 – 08:00	Toulouse-Nimes	Sea area south of Marseille/Toulon	Export of pollution during a Mistral-Tramontane event
	V21	27/06/2012	09:39 – 13:16	Nimes-Toulouse	Western coast of Corsica	Export of pollution from Northern Italy/Pô Valley, north-westerly winds
	V22	29/06/2012	05:13 – 08:50	Toulouse-Bastia	Eastern coast of Corsica	Dust outbreak
	V23	29/06/2012	10:13 – 14:12	Bastia-Toulouse	Eastern and western coasts of Corsica	Dust outbreak
	V24	03/07/2012	13:19 – 17:12	Toulouse-Toulouse	Sea area north-east of Barcelona	Export of pollution from Barcelona, westerly/south-westerly winds
	V25	04/07/2012	07:18 – 10:54	Toulouse-Toulouse	Sea area south of Marseille/Toulon	Follow of Barcelona pollution plumes
	V26	04/07/2012	15:25 – 18:36	Toulouse-Toulouse	Gulf of Lion	Follow of Barcelona pollution plumes
	V27	06/07/2012	08:00 – 11.55	Toulouse-Toulouse	Sea area south of Marseille	Export of pollution during a moderate Mistral-Tramontane event
	V28	06/07/2012	14:01 – 17:45	Toulouse-Toulouse	Sea area south of Nice/Toulon	Export of pollution during a moderate Mistral-Tramontane event
	V29*	07/07/2012	08:19 – 10:59	Toulouse-Nimes	Southern France (over land)	Biogenic emissions
	V30	07/07/2012	13:03 – 17:10	Nimes-Toulouse	Gulf of Genoa	Export of pollution during a moderate Mistral-Tramontane event
	V31	10/07/2012	13:41 – 17:21	Toulouse-Toulouse	Eastern coast of Spain	Characterization of pollution near coastal

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						sources
	V32	11/07/2012	11:23 – 14:48	Toulouse-Toulouse	Southeastern coast of France and Gulf of Genoa	Characterization of pollution near coastal sources
SAFMED 2013	V46	24/07/2013	10:34 – 13:06	Genoa-Cagliari	Gulf of Genoa and eastern coast of Corsica and Sardinia	Characterization of pollution plumes in the Gulf of Genoa, Corsica, and Sardinia; westerly/south-westerly winds
	V47*	24/07/2013	14:21 – 16:29	Cagliari-Genoa	Eastern coast of Corsica and Sardinia and Gulf of Genoa	Characterization of pollution plumes in the Gulf of Genoa, Corsica, and Sardinia; westerly/south-westerly winds
	V48	25/07/2013	13:12 – 16:02	Genoa-Ersa	Gulf of Genoa	Characterization of pollution in the Gulf of Genoa; westerly/south-westerly winds
	V49	27/07/2013	11:08 – 13:07	Genoa-Alghero	Central Italy (over land)	Characterization of pollution in central Italy
	V50*	27/07/2013	15:33 – 16:48	Alghero-Genoa	Eastern coast of Corsica and Gulf of Genoa	Characterization of pollution plumes in the Gulf of Genoa, Corsica, and Sardinia; westerly/south-westerly winds + dust outbreak
	V51	30/07/2013	13:05 – 15:50	Genoa-Ersa	Gulf of Genoa	Characterization of pollution in the Gulf of Genoa; very low north/north-westerly winds
	V52	01/08/2013	12:03 – 15:24	Genoa-Alghero	Western coast of Corsica	Characterization of pollution in western Corsica; export of pollution from Northern Italy/Pô Valley; north-easterly winds

* = No vertical profiles performed during these flights.

Table 2. Comparison of the number concentrations dN_{Aitken} (0.004-0.1 µm) and dN_{Acc} (0.1-1.0 µm) observed during the TRAQA/SAFMED field campaigns with those reported in literature for continental Europe. All literature data refer to airborne measurements.

Atmospheric layer	Parameter	TRAQA/SAFMED	Literature over continental Europe
Free troposphere (FT)	dN_{Aitken} (scm^{-3})	0-19250	812-9149[b]; 0-980[e]
	dN_{Acc} (scm^{-3})	34-3233	20-80[a]; 25-85[e]; 0-500[f]
Boundary layer (BL)	dN_{Aitken} (scm^{-3})	4-22471	1037-31370[b]; 1000-20000[c]; 0-30000[d]; 0-19000[e]
	dN_{Acc} (scm^{-3})	90-3215	70-560[a]; 10-50[c]; 400-1200[e]; 0-2000[f]

[a] Petzold et al. (2002), Central Europe, July-August 1998; size range dN_{Acc} (>0.15 µm)

[b] Mallet et al. (2005), Southeastern France, June 2001; size range dN_{Aitken} (0.006-0.6 µm)

[c] Wiegner et al. (2006), Germany, May 2003; ; size range dN_{Aitken} (>0.01 µm), dN_{Acc} (>0.3 µm)

[d] Junkermann (2009), Po Valley, July-August 2002 and Septmember-October 2003; ; size range dN_{Aitken} (>0.01 µm)

[e] Hamburger et al. (2012), central Europe, May 2008; size range dN_{Aitken} (0.004-0.15 µm), dN_{Acc} (>0.15 µm)

[f] Highwood et al. (2012), central Europe, May 2008; size range dN_{Aitken} (0.004-0.15 µm), dN_{Acc} (>0.15 µm)

Figures

Figure 1. (Upper panel) Flight trajectories of the TRAQA (20 June - 13 July 2012) and the SAFMED (24 July - 1 August 2013) campaigns. The aircraft was based in Toulouse (43°36'N, 1°26'E, France) during TRAQA and in Genoa (44°24'N, 8°55'E, Italy) during SAFMED. (Lower panel) Zoom on the investigated area and geographical position of the different vertical soundings analysed in this paper. The position of the three AERONET stations of Barcelona, Frioul, and Ersa considered in this study is also shown.

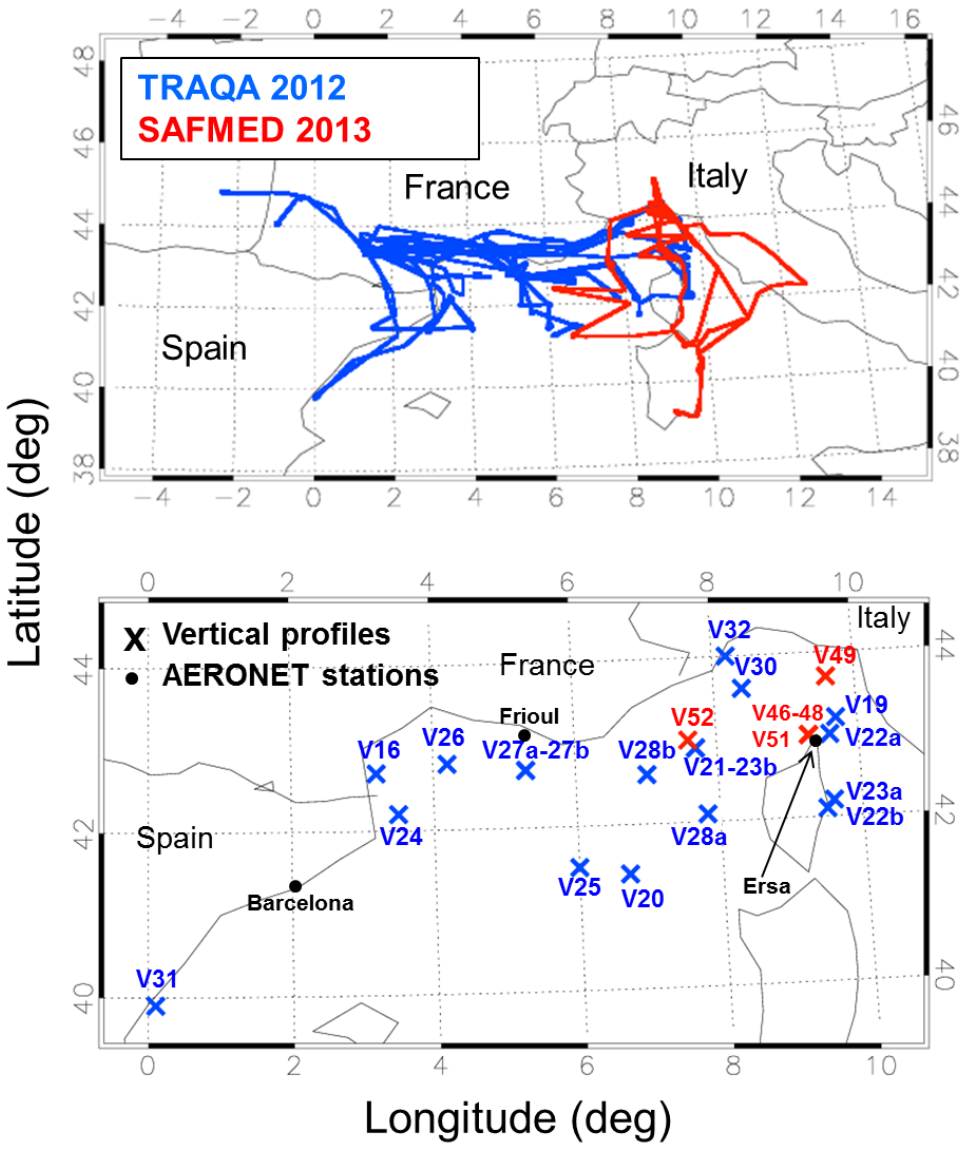

Figure 2. Aerosol optical depth at 440 nm (τ) and Ángström exponent (α) measured at the Barcelona, Frioul, and Ersa AERONET stations during the TRAQA 2012 (left panels) and the SAFMED 2013 (right panels) campaigns. The time period for the different plots is ±10 days around the beginning/end of the two campaigns (data for the Barcelona station are not available over the entire period for 2012). The label D indicates the days affected by Saharan dust.

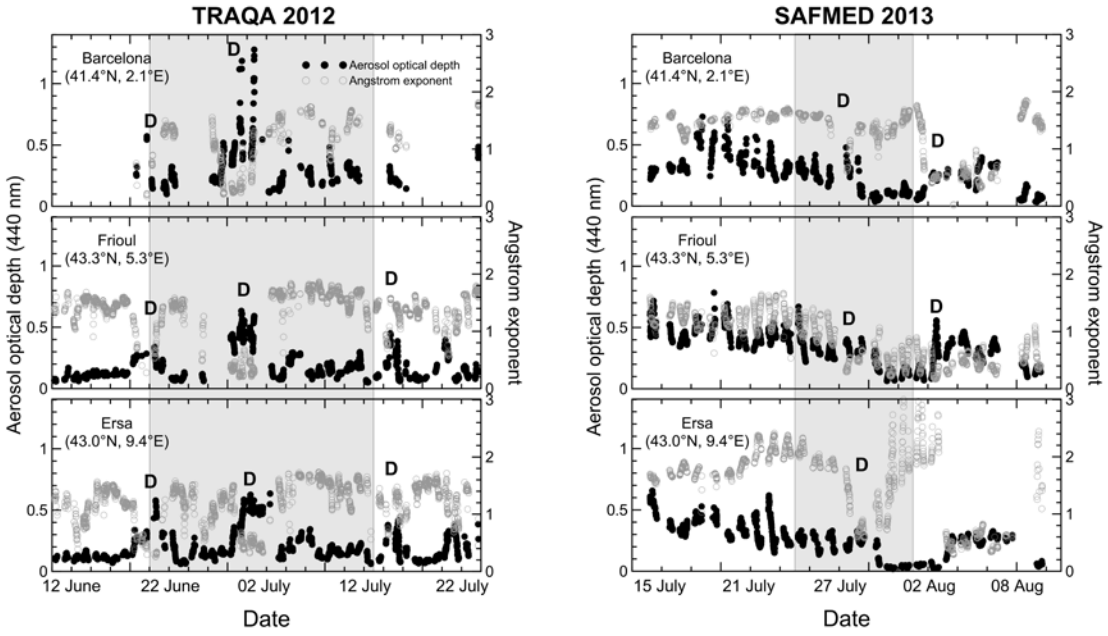

Figure 3. Example of wind maps at 925 mbar for 26 June and 3 July 2012. The maps are obtained from the WRF-Chem model (Weather Research and Forecasting – Chemistry) at 10-km horizontal resolution.

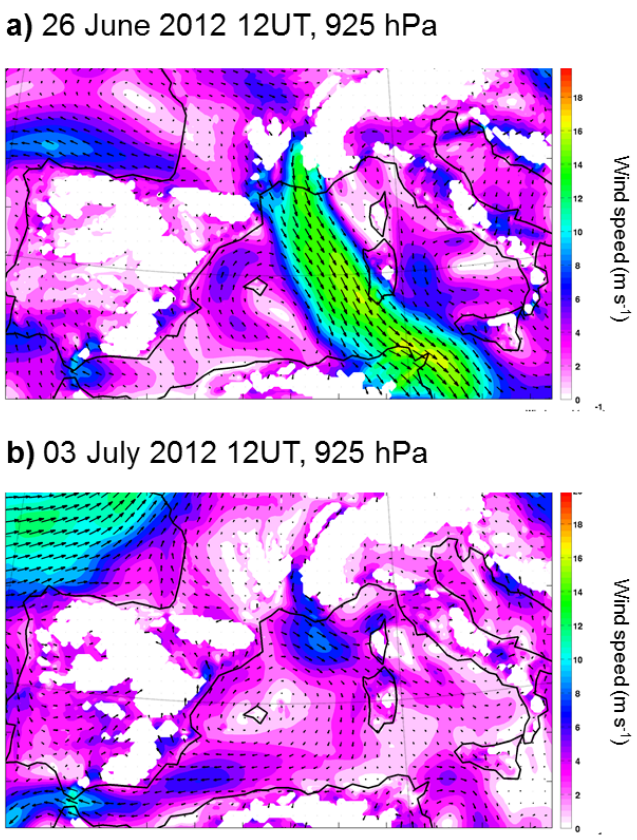

Figure 4. (Left) Scattering coefficient σ_s at 450, 550, and 700 nm versus the scattering Ångstrom exponent α_s. Cases with extremely negative (<−2) and positive (>4) values of α_s are always related with very low scattering coefficients, and are likely due to instrumental noise under low scattering conditions. (Right) Frequency of occurrence of α_s obtained considering vertical profiles data from all TRAQA and SAFMED flights.

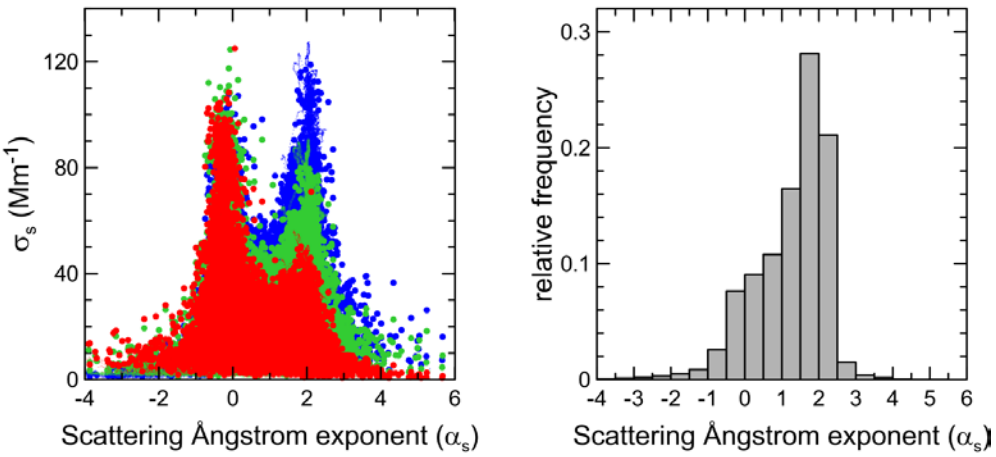

Figure 5. Box and whisker plot of the aerosol scattering coefficient (σ_s) at 450, 550, and 700 nm, particle concentration in the Aitken (dN_{Aitken}) and accumulation (dN_{Acc}) modes, and CO and O_3 measured within pollution plumes in the boundary layer (BL) and in the free troposphere (FT).

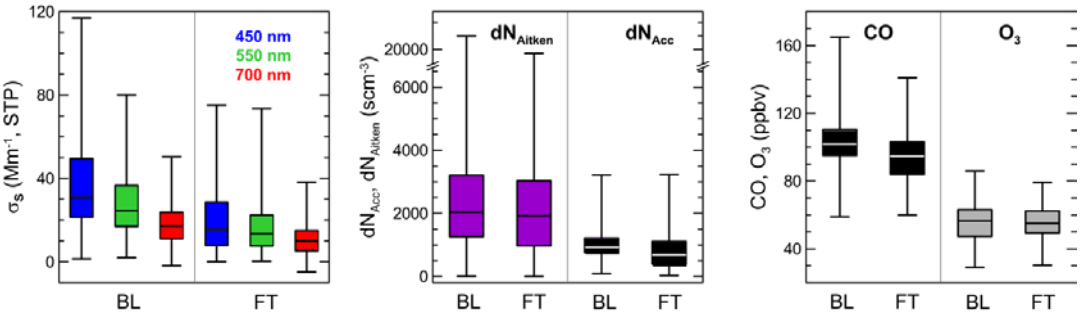

Figure 6. Vertical profiles of the spectral scattering coefficient σ_s at 450, 550, and 700 nm and particle number concentration in the 0.1-1.0 µm (dN_{Acc}) and 1.0-4.0 µm (dN_{Coarse}*) diameter ranges observed during TRAQA and SAFMED. Data are reported at STP (standard temperature and pressure, T =293.15 K and P=1013.25 hPa). The heights of the top of the marine aerosol boundary layer (MABL) and planetary boundary layer (BL) estimated from the meteorological profiles are also indicated in the plots. The label D is used to identify the aerosol layers affected by Saharan dust. For certain flights (V22, V23, V27, and V28) two vertical soundings were performed; the letters "a" and "b" after the flight number in this plot specify if the considered data are taken from the first or the second sounding, respectively.

(* data for dN_{Coarse} are multiplied by 100 in the plot).

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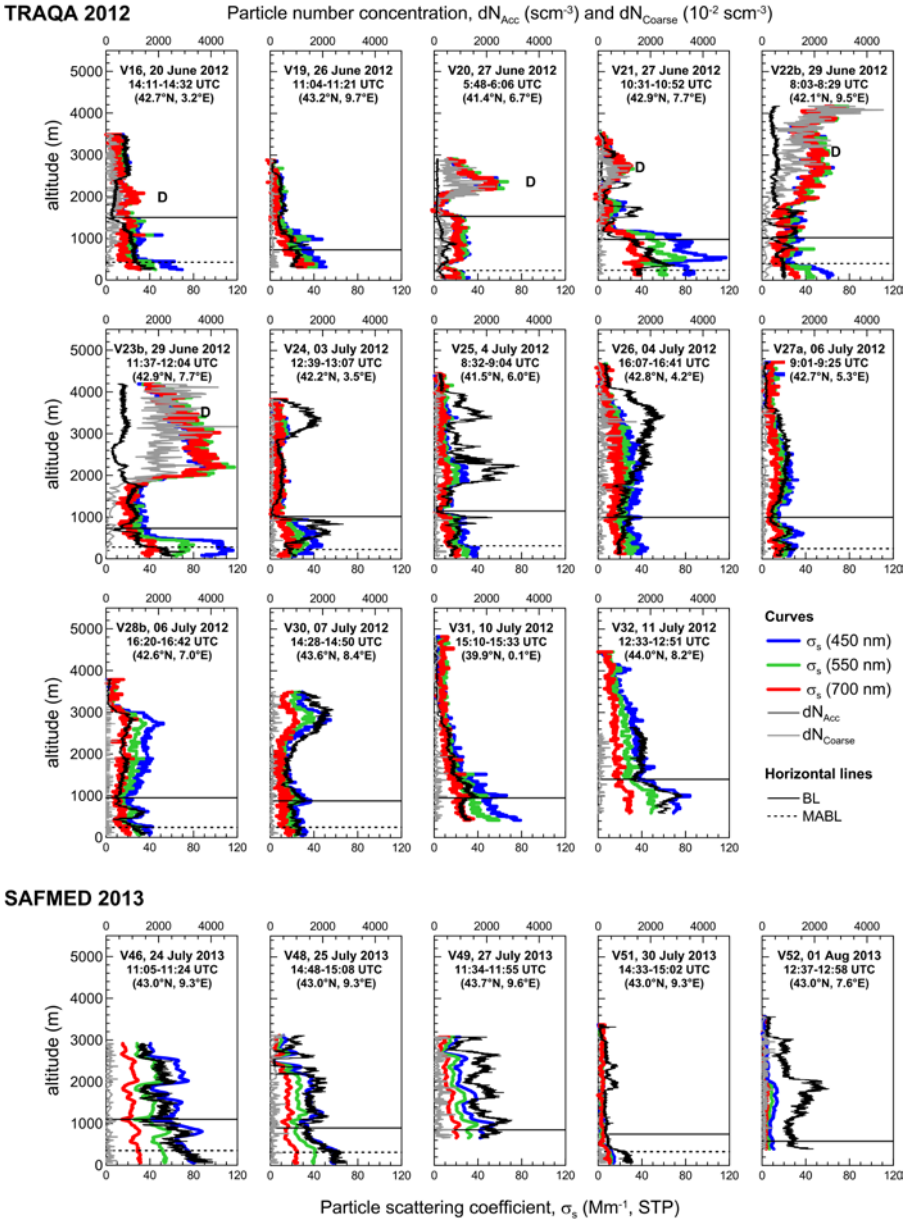


Figure 7. O_3 versus CO in the boundary layer (BL) and the free troposphere (FT) for all TRAQA and SAFMED vertical profiles (dust observations excluded).

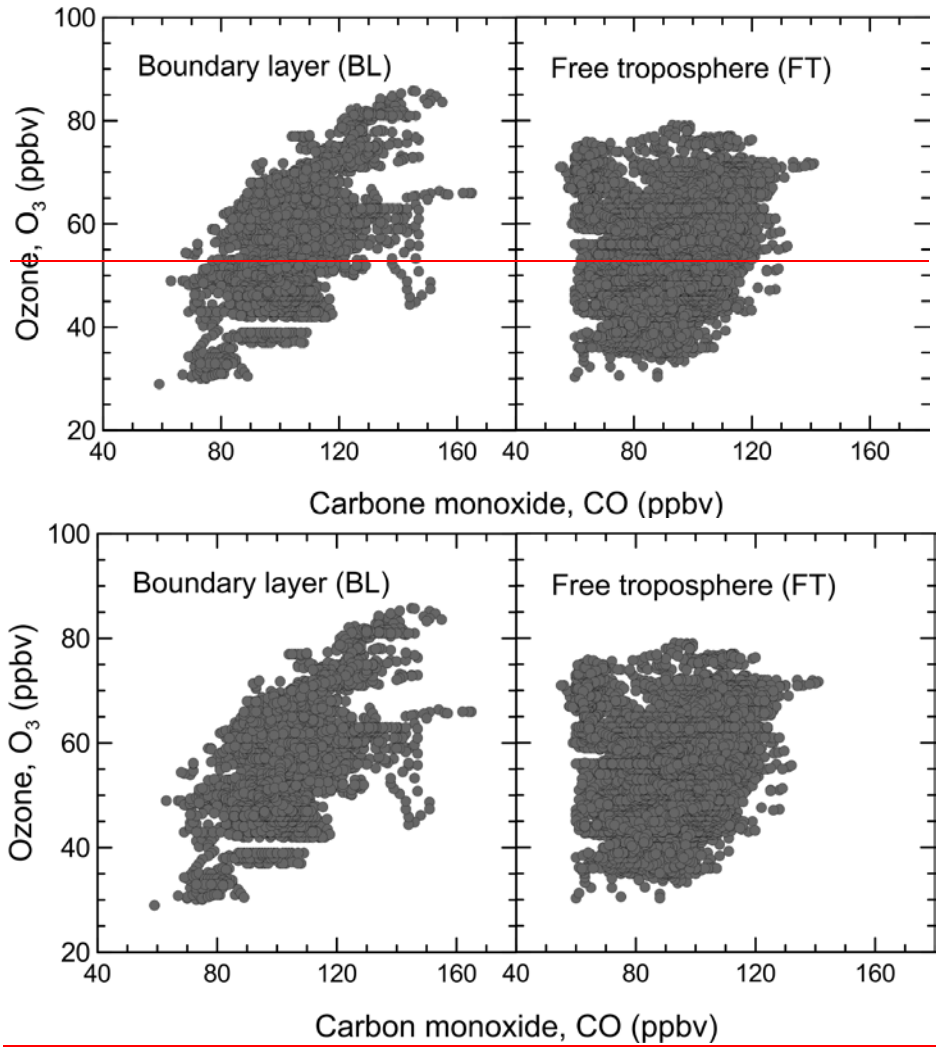


Figure 8. Aerosol and trace gases vertical profiles for flights V19 (export from northern Italy/Po Valley), V20 (Mistral event), and V24 (export from the Barcelona area). The plots show the: (a) spectral scattering coefficient σ_s at 450, 550, and 700 nm (blue, green, and red lines, respectively), temperature (T, black line), and relative humidity (RH, light blue line); (b) particle number concentration in the 0.004-0.1 μm (dN_{Aitken}, purple line) and 0.1-1.0 μm (dN_{Acc}, black line) diameter ranges, (c) CO (black dots) and O_3 (grey dots) mixing ratios, (d) ozone enhancement factor $\Delta O_3/\Delta CO$ (grey dots) and Aitken to accumulation ratio dN_{Aitken}/dN_{Acc} (pink dots) and (e) horizontal wind vector. The heights of the top of the MABL (dotted line) and BL (solid line) are also indicated.

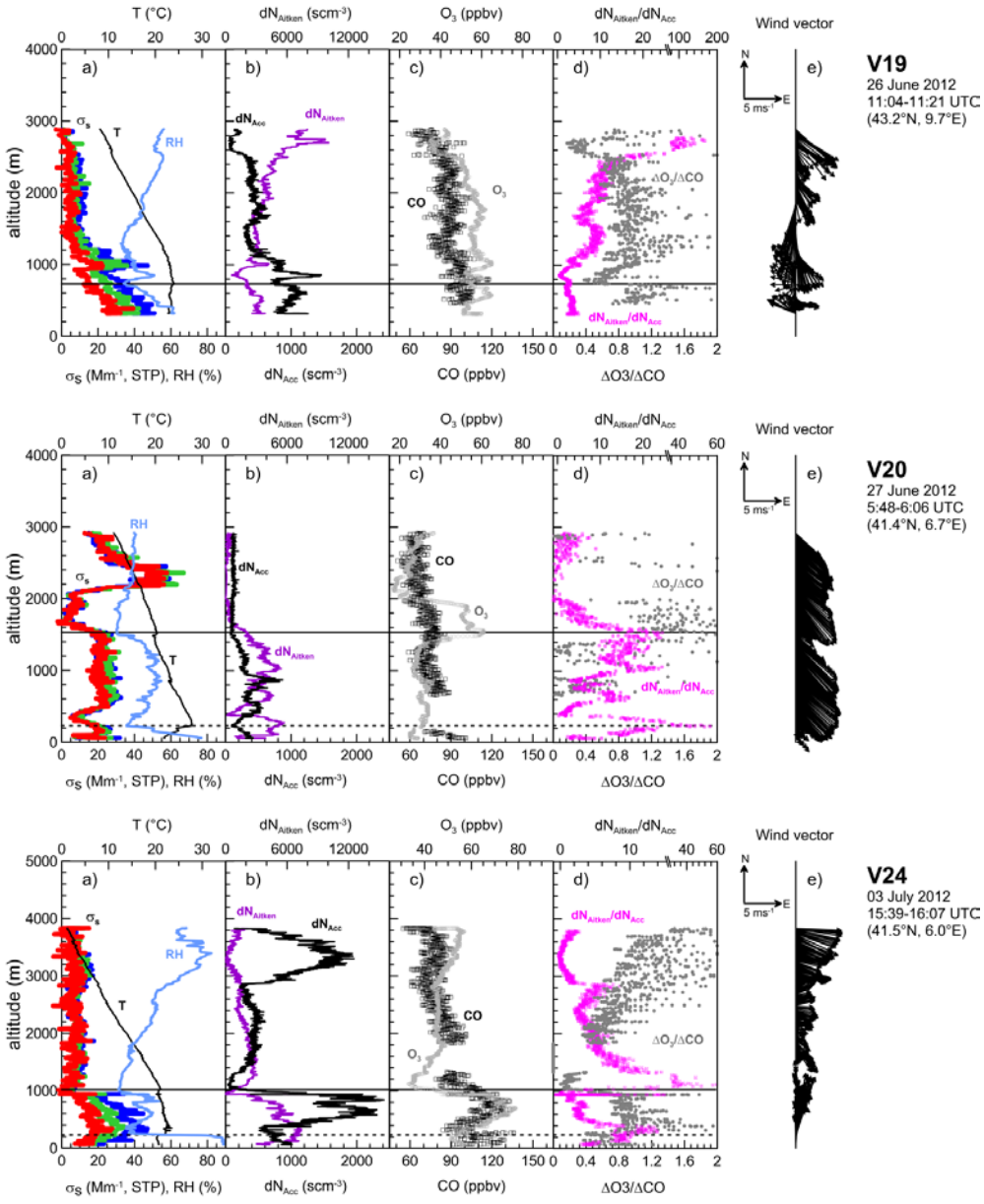


Figure 9. Five-days backward air mass trajectories for the V19, V20, and V24 flights calculated with the FLEXTRA model. The upper panel shows the trajectories over an extended latitude-longitude region, while the central panel zooms on the Western Mediterranean area. The altitude of the air masses and its temporal evolution along the five days trajectories is reported in the lower panel of each plot.

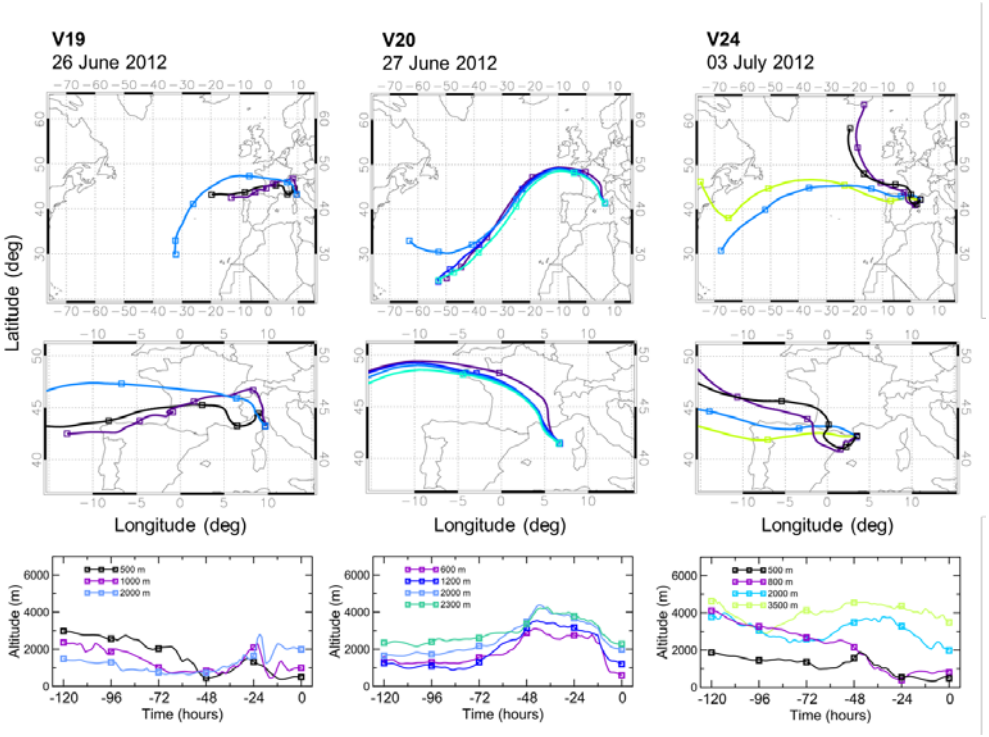
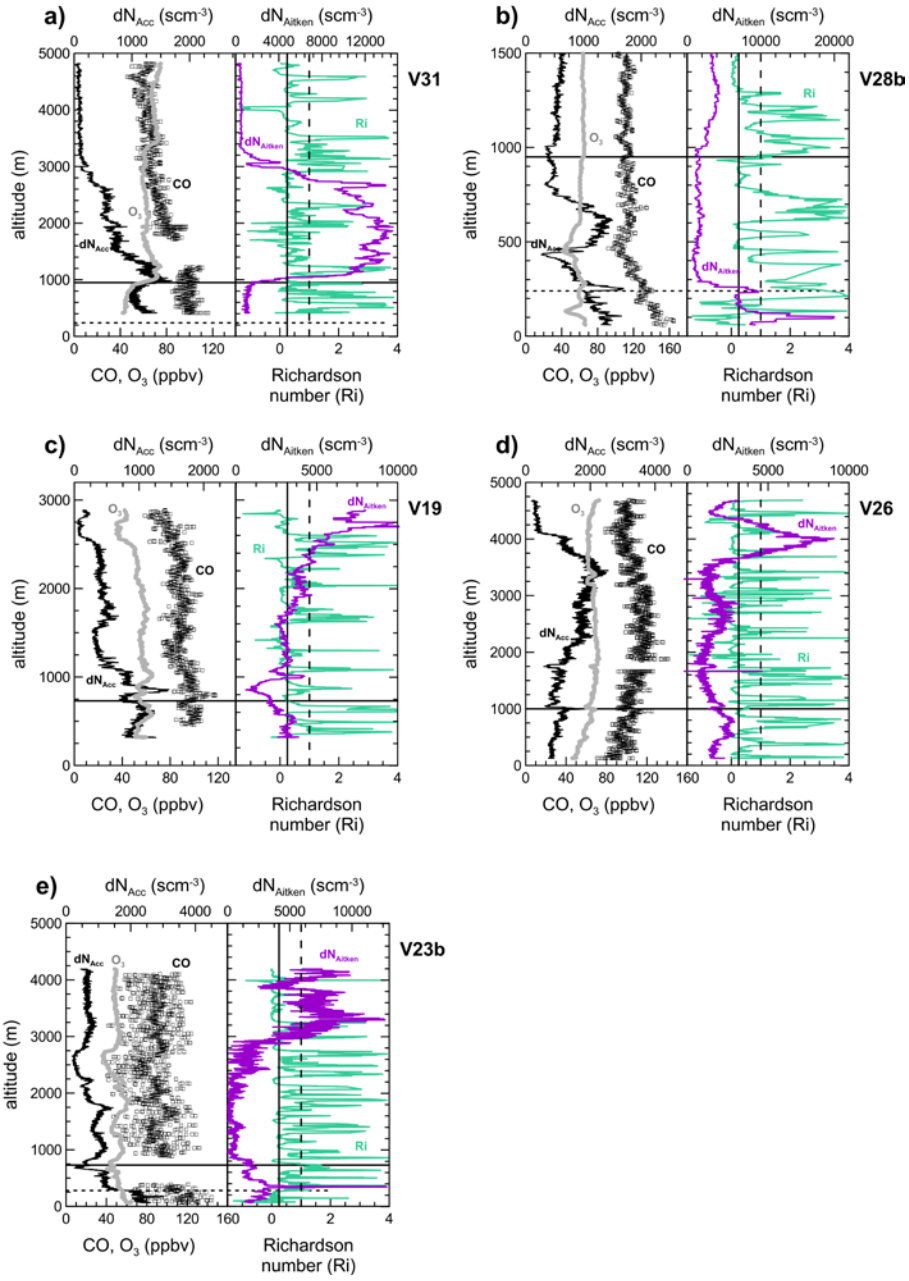


Figure 10. Vertical profiles of the accumulation and Aitken particle concentrations (dN_{Acc}, black line, and dN_{Aitken}, purple line), CO (black dots), O_3 (grey dots), and gradient Richardson number (Ri, green line) for flights a) V31, b) V28, c) V19, d) V26 and e) V23b. The horizontal lines indicate the height of the marine boundary layer MABL (dotted line) and the planetary boundary layer BL (continuous line), while the vertical lines indicate Ri_{crit}=0.25 and Ri=1 (continuous and dashed lines, respectively).


a)
b)
c)
d)
e)
V31
V28b
V19
V26
V23b
altitude (m)
CO, O3 (ppbv)
Richardson number (Ri)
CO
O3
Ri

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