

Continental pollution in the Western Mediterranean basin: large variability of the aerosol single scattering albedo and influence on the direct shortwave radiative effect

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1	Continental pollution in the Western Mediterranean basin: large variability of
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3	radiative effect
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34 Abstract

35 Pollution aerosols strongly influence the composition of the Western Mediterranean basin, 36 but at present little is known on their optical properties. We report in this study in situ 37 observations of the single scattering albedo (ω) of pollution aerosol plumes measured over 38 the Western Mediterranean basin during the TRAQA (TRansport and Air QuAlity) airborne 39 campaign in summer 2012. Cases of pollution export from different source regions around 40 the basin and at different altitudes between ~160 and 3500 m above sea level have been 41 sampled during the flights. Data from this study show a large variability of ω , with values 42 between 0.84-0.98 at 370 nm and 0.70-0.99 at 950 nm. The single scattering albedo generally 43 decreases with the wavelength, with some exception associated to the mixing of pollution 44 with sea spray over the sea surface. Lowest values of ω (0.84-0.70 between 370 and 950 nm) 45 are measured in correspondence of a fresh plume possibly linked to ship emissions over the 46 basin. The range of variability of ω observed in this study seems to be independent of the 47 source region around the basin, as well as of the altitude and ageing time of the plumes. The 48 observed variability of ω reflects in a large variability for the complex refractive index of 49 pollution aerosols, which is estimated to span in the large range 1.41-1.75 and 0.002-0.068 for the real and the imaginary parts, respectively, between 370 and 950 nm. 50

51 Radiative calculations in clear-sky conditions have been performed with the GAME radiative 52 transfer model to test the sensitivity of the aerosol shortwave Direct Radiative Effect (DRE) 53 to the variability of ω as observed in this study. Results from the calculations suggest up to a 50% and 30% change of the forcing efficiency (FE), i.e. the DRE per unit of optical depth, at 54 the surface (-160÷-235 Wm⁻² τ^{-1} at 60° solar zenith angle) and at the Top-Of-Atmosphere (-55 $137 \div -92 \text{ Wm}^{-2} \tau^{-1}$) for ω varying between its maximum and minimum value. This induces a 56 change of up to an order of magnitude (+23÷+143 Wm⁻² τ^{-1}) for the radiative effect within the 57 58 atmosphere.

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Keywords: pollution aerosols, single scattering albedo, direct radiative effect, WesternMediterranean

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66 1. Introduction

67 Atmospheric aerosols play a crucial role on climate by affecting the radiative transfer of atmospheric radiation and by modifying cloud properties and lifetime (Boucher et al., 2013). 68 The capability of atmospheric aerosols to interact through processes of scattering and 69 70 absorption with the atmospheric radiation, so to exert a direct radiative effect (DRE), depends 71 on their spectral optical properties (extinction efficiency, k_{ext} , single scattering albedo, ω , and 72 asymmetry factor, g). In particular the single scattering albedo has been demonstrated to be a 73 key parameter in modulating the surface, Top-of-Atmosphere (TOA), and atmospheric 74 aerosol DRE (e.g., Ramana and Ramanathan, 2006; Di Biagio et al., 2010; Loeb and Su, 75 2010). Aerosol optical properties can largely vary depending on the particles composition, 76 size distribution, and shape, which are function of the aerosol source, type, and processing 77 occurring during atmospheric lifetime. At present, the capability of climate models in 78 reproducing all the possible heterogeneity in aerosol optical properties represents one the 79 main source of uncertainty in evaluating their DRE on climate (McComiskey et al., 2008; 80 Stier et al., 2013). In this sense, intensive studies providing with the characterization of the 81 aerosol optical properties and their local and regional variability are of great importance in 82 order to reduce these uncertainties.

83 This is particularly the case of the Western Mediterranean basin. Indeed, the Mediterranean is 84 a very complex region, characterized by the presence of air masses carrying aerosols of different origins and types (Gkikas et al., 2012). On its northern bound, it is limited by 85 Europe, which makes that anthropogenic pollution is usually exported from the continent 86 87 towards the basin (Lelieveld et al., 2002; Pace et al., 2006). In particular, the Western part of 88 the Mediterranean basin, surrounded by large coastal megacities, commercial harbours, and 89 under the direct influence of some of the most industrialized areas of the continent (such as 90 the Po Valley in Northern Italy or the Fos/Berre area in Southern France), is strongly affected 91 by continental pollution outflows (Pérez et al., 2008; Pey et al., 2010; Di Biagio et al., 2015). 92 The build-up of high pollution levels over the Western basin is particularly favoured during 93 summer when the strong insolation enhances photochemical reactions and the stable 94 meteorological conditions promote the stagnation of pollutants (Millan et al., 2000; Mallet et 95 al., 2005).

In spite of this, the characterization of the optical properties of anthropogenic aerosols in this
part of the basin remains only limited to coastal and inland regions (Mallet et al., 2003, 2011,
2013; Lyamani et al., 2006; Estelles et al., 2007; Saha et al., 2008; Esteve et al., 2012;





99 Piazzola et al., 2012; Pandolfi et al., 2011 and 2014), or remote islands actually far from the strong influence of continental outflows (Lyamani et al., 2015). Moreover, the majority of 101 these studies uses remote sensing measurements and analyse aerosol properties integrated 102 over the entire atmospheric column, without information on their vertical variability. Thus, at 103 present, we miss a detailed characterization of the optical properties of the pollution aerosol 104 over the entire region, in particular over the remote sea, and its vertical distribution.
105 To fill this gap, the international ChArMEx (Chemistry-Aerosol Mediterranean Experiment;

105 To fill this gap, the international ChArMEX (Chemistry-Aerosof Mediterranean Experiment;
 106 http://charmex.lsce.ipsl.fr) research program has supported in recent years two airborne
 107 campaigns over the Western Mediterranean basin: TRAQA (Transport and Air QuAlity) in
 2012 and SAFMED (Secondary Aerosol Formation in the MEDiterranean) in 2013.

In a recent paper, Di Biagio et al. (2015) have presented in situ measurements of the aerosol vertical profiles acquired over the remote sea during these campaigns. Observations from TRAQA and SAFMED have shown that in the Western basin pollution plumes extend as far as hundreds of km from the coastline and reach up to ~4000 m, presenting a complex stratified structure, and pollution plumes show a large heterogeneity in terms of composition, origin, and lifetime.

Following these observations, we may ask: does the heterogeneity in pollution plume composition, origin, and lifetime as observed in Di Biagio et al. (2015) induce heterogeneity on the optical properties (in particular the single scattering albedo) of pollution aerosols in this part of the basin? And, if observed, does this heterogeneity on the optical properties influence the aerosol DRE? Is it necessary to take it into account to better evaluate the aerosol radiative impact in the Western Mediterranean?

121 With the aim of answering these questions, in this paper we analyse data of the optical 122 properties (spectral scattering and absorption coefficients, and single scattering albedo) and 123 size distributions of pollution aerosols measured over the Western Mediterranean basin 124 during TRAOA. SAFMED observations have been excluded here given that only limited data 125 on the aerosol optical properties are available from this campaign. The objective of the paper is twofold: to provide a new dataset of aerosol single scattering albedo values which can be 126 127 representative of the polluted aerosols over the Western basin, and investigate the sensitivity 128 of the aerosol direct DRE to the variability of this parameter.

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132 2. Overview of flights during the TRAQA campaign

133 The TRAQA campaign took place in the period 20 June -13 July 2012. Instruments were 134 installed on board the SAFIRE (Service des Avions Français Instruments pour la Recherche 135 en Environnement, http://www.safire.fr/) tropospheric aircraft ATR-42, based in Toulouse (43° 36' N, 1° 26' E, France). A total of seventeen flights, most often two flights per day, 136 137 with intermediate stops in different airports in southern France and Corsica, were performed 138 (flight numbers V16 to V32). The majority of flights were over the sea, with some exceptions 139 investigating inland areas in southern France. The flight altitude for the ATR-42 ranged 140 between a minimum of ~ 60 m to a maximum of ~ 5000 m above sea level (a.s.l.), and the 141 maximum flight time was 4 h. The general flight strategy consisted of legs at constant altitude 142 to sound the vertical structure by lidar observations, vertical ascents/descents to describe the 143 vertical atmospheric column and identify the main aerosol plumes, followed by straight 144 levelled runs (SLRs) within the detected aerosol layers. In the present study we will 145 exclusively consider measurements acquired during SLRs, since only during these phases the 146 whole set of aerosol optical properties (scattering and absorption coefficients) were 147 measured. A total of 21 SLRs were performed over the sea surface or inland close to the coastline and will be considered in this study. Figure 1 and Table 1 summarise the 148 geographical location, time, and altitude of these 21 SLRs. As indicated in Table 1 each SLR 149 was about 15-20 min long. At the cruise speed of the ATR (93 ms⁻¹), this integration time 150 151 corresponds to about 100 km.

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153 **3. Measurements and methods**

154 **3.1 Aircraft observations**

155 Aerosol sampling on the ATR-42 was performed using the AVIRAD system. AVIRAD is an iso-axial and iso-kinetic inlet which samples air at a volumetric flow of ~350 L min⁻¹. The 156 50% passing efficiency of the inlet is 12 µm diameter. Various lines depart from AVIRAD to 157 158 connect to different instruments for the measurement of the aerosol physico-chemical and 159 optical properties. Additionally, several sensors for the measurements of the atmospheric 160 composition were installed on the ATR-42 aircraft as basic equipment. A brief description of 161 the different in situ measurements considered in this study from the AVIRAD system and the 162 ATR-42 equipment and their data analysis is reported in the following.





165 nephelometer was calibrated prior the campaign by using air and CO₂ as reference gases. 166 Nephelometer measurements have been corrected for angular truncation and Lambertian 167 non-idealities by applying the formula by Anderson and Ogren (1998), appropriated to 168 submicron aerosols which we expected in the pollution plumes sampled during the 169 campaign. The measurement uncertainty on σ_s , calculated taking into account for the 170 photon counting, gas calibration, and angular corrections uncertainties, is estimated to be 171 lower than 10% at the three wavelengths. Averages of the scattering coefficient are calculated over the different SLRs. The uncertainty on the SLR average values is 172 173 estimated as the combination of the measurement uncertainty and the standard deviation 174 along each individual run. For each SLR, the particle scattering Ångström exponent (SAE) has been calculated as the power law fit of the measured scattering coefficients versus 175 176 wavelength to extrapolate the scattering coefficient at other wavelengths than those of 177 operation.

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 increase in the sensing volume of the instrument due to illumination. The relative humidity measured during the flights inside the nephelometer cavity was <25% in more than 90% of cases, with values up to ~40% occasionally observed <200 m over the sea surface.

183 The aerosol absorption coefficient (σ_{abs}) at 370, 470, 520, 590, 660, 880, and 950 nm has 184 been measured by a 7-wavelengths aethalometer (Magee Sci., model AE31, 2min 185 resolution). The principle of operation of the aethalometer consists in measuring the 186 attenuation of light through an aerosol-laden filter compared to that of another portion of 187 the filter which is unexposed to the air flow and is used as a reference (Weingartner et al., 188 2003). To yield the aerosol absorption coefficient, the spectral attenuation $\sigma_{ATT}(\lambda)$ 189 measured by the aethalometer has been corrected following the procedure described by 190 Collaud Coen et al. (2010):

191
$$\sigma_{abs}(\lambda) = \frac{\sigma_{ATT}(\lambda) - \alpha(\lambda)\sigma_{s}(\lambda)}{C_{ref}R(\lambda)}$$
(1)

192 The different terms in equation 1 are: (i) $\alpha(\lambda)\overline{\sigma_s(\lambda)}$ or "scattering correction". In this work 193 $\alpha(\lambda)$ has been calculated with the formula by Arnott et al. (2005) and varies between 0.02 194 and 0.07, while $\overline{\sigma_s(\lambda)}$ is the average of the scattering coefficient along the considered SLR 195 extrapolated at the aethalometer wavelengths; (ii) C_{ref} or "multiple scattering correction".





196 C_{ref} is set to 2.14 ± 0.21 (wavelength-independent) following Weingartner et al. (2003); 197 (iii) $R(\lambda)$ or "shadowing effect correction". $R(\lambda)$ depends on the charge and 198 absorptivity properties of the sampled aerosol and can be calculated as a function of the 199 particle single scattering albedo (ω). In this study, because of the absence of an 200 independent determination of ω , we used an estimated "first-guess" single scattering 201 albedo (ω^*) to calculate R. This has been determined as the ratio of the measured scattering (σ_s) to extinction ($\sigma_s + \sigma_{abs}^*$) coefficients, with σ_{abs}^* corrected for the scattering 202 203 and the multiple scattering corrections, but not for the shadowing effect. The obtained $R(\lambda)$ varies between 0.75 and 1 for ω^* between 0.75-0.99 at 370 nm and 0.70-0.99 at 950 204 205 nm. The whole uncertainty on the absorption coefficient has been estimated with the 206 propagation error formula taking into account for the different factors in Eq. (1) and varies 207 between 11-36% at 370 nm and 12-70% at 950 nm.

It has to be noticed that an enhanced absorption at single wavelengths has been observed in several cases for the aethalometer. This is possibly due to the absorption on the exposed filter of gases or volatile compounds absorbing at some of the instrument operating wavelengths (Weingartner et al., 2003). These anomalous points have been accurately selected and screened from the dataset. As a result of this screening, data in correspondence of only 60% of the considered SLRs are available for aerosols analyses.

The measured aerosol scattering and absorption coefficients have been used to calculate
 the particle spectral single scattering albedo (ω) between 370 and 950 nm as:

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$$\omega(\lambda) = \frac{\sigma_s(\lambda)}{\sigma_s(\lambda) + \sigma_{abs}(\lambda)}$$
(2)



Additionally, for each SLR for which aethalometer data are available, the particle
 absorption Ångström exponent (AAE) has been calculated as the power law fit of the
 measured absorption coefficients versus wavelength.

The aerosol number size distribution (dN/dlogDg) has been measured by two different optical particle spectrometers: the passive cavity aerosol spectrometer probe (PCASP, model 100-X, 1-s resolution, 31 size classes between 0.1 and 3.0 μm diameter, operating wavelength 632.8 nm), and the optical particle spectrometer SkyGRIMM (GRIMM Inc., model 1.129, 6-s resolution, 32 size classes between 0.3 and 32 μm diameter, operating





227 wavelength 655 nm). For both the PCASP and the SkyGRIMM, the measured sphere-228 equivalent optical diameter has been converted in a sphere-equivalent geometrical 229 diameter (D_g) by taking into account the complex refractive index of the sampled aerosol 230 (Liu and Daum, 2000). Calculation are performed by fixing the imaginary part of the 231 refractive index at 0.01, thus representing a medium absorbing aerosol, while varying the 232 real part between 1.50 and 1.72, following the range of variability found in the literature 233 for pollution aerosols in the Mediterranean (see Di Biagio et al., 2015 for further details). 234 D_g is then set at the mean \pm one standard deviation of the values obtained for the different 235 n. After refractive index correction the Dg ranges for the PCASP and the SkyGRIMM 236 become 0.10-4.47 and 0.28-65.80 µm, with an uncertainty between 1 and 25%. The 237 smallest and the largest size bins of both instruments, for which the minimum and 238 maximum edges respectively are not defined, have been excluded from the datasets, thus 239 reducing the PCASP and SkyGRIMM Dg ranges to 0.11-4.17 µm and 0.31-56.21 µm, 240 respectively.

241 Corrected data from the PCASP and the SkyGRIMM are then merged to obtain the aerosol 242 size distribution over a larger size range. The two instruments superimpose in a large 243 interval covering the diameter range $\sim 0.31-4.17$ µm. In this interval the PCASP and the GRIMM show a good agreement below 0.4 μ m and above 1.0 μ m (less than ~10% 244 245 difference), while significant differences are observed in the 0.4-1.0 µm range where the 246 PCASP underestimates the SkyGRIMM measurements by more than ~50%. This 247 difference is of great relevance in terms of optical properties because particles in the 0.4-248 1.0 µm size interval are very efficient for interaction with shortwave radiation. With the 249 aim of understanding which of the two instruments measures correctly in the 0.4-1.0 μ m 250 range we have performed an optical test, which consisted in calculating with Mie theory 251 the scattering coefficient at 450, 550, and 700 nm based on the PCASP and SkyGRIMM 252 size data, and then in comparing it with simultaneous nephelometer measurements. Optical 253 calculations have been performed by fixing the complex refractive index at 1.6-0.01i, so at 254 the mean of the range of values reported in the literature for pollution aerosols (Ebert et 255 al., 2002 and 2004; Mallet et al., 2003 and 2011; Müller et al., 2002; Raut and Chazette, 256 2008). SLRs characterized by a low variability in terms of scattering coefficient and 257 particle concentration have been selected. The results of the optical test indicate that in the 258 0.4-1.0 µm range the size distribution of the SkyGRIMM is more accurate since it permits 259 to most closely reproduce nephelometer observations (<5% mean difference between





260	calculations and observations at the three wavelengths, compared to differences up to 15-
261	21% if PCASP data are used in the 0.4-1.0 μm size range). Thus, a combined PCASP-
262	SkyGRIMM number size distribution $dN/dlogD_g$ in the 0.11 to 56.21 μm diameter range
263	has been calculated by considering PCASP data up to 0.31 μm and SkyGRIMM data
264	above. Together with the number size distribution, for each SLR also the volume size
265	distribution dV/dlogD _g = $\pi/6 D_g^3 dN/dlogD_g$ has been calculated.

266 Nonetheless, due to a technical problem, SkyGRIMM data were only available below
267 ~350 m (~970 hPa).

The total particle number concentrations in the Aitken (4 nm-0.1 μ m; dN_{Aitken}) and 268 accumulation (0.1-1.0 μ m; dN_{Acc}) modes have been calculated by combining condensation 269 particle counter measurements of particle concentration in the $0.004 - 3 \mu m$ range (CPC, 270 271 TSI Inc., model 3775, 5-s resolution) and size distribution data. Due to the fact that above 272 350 m the SkyGRIMM is not available, only PCASP data are used in the calculations of 273 dNAitken and dNAcc over the whole altitude range. dNAitken is estimated as the difference 274 between CPC concentration and the integral of PCASP data between 0.1 and 3.0 µm, 275 while dN_{Acc} is obtained by integrating the PCASP number concentrations in the 0.1-1.0 276 µm interval. The underestimation of the PCASP number concentration between 0.4 and 1.0 μ m, as discussed above, is estimated to induce a ~20% underestimation of the dN_{Acc} 277 278 calculated here, whilst it has almost a negligible impact on dNAitken. The dNAcc and dNAitken 279 obtained in correspondence of each SLR have been used to calculate the Aitken-toaccumulation ratio dNAitken/dNAcc. 280

281 The carbon monoxide (CO) and ozone (O_3) mixing ratios have been measured by the MOZART instrument (CO, 30-s resolution and ±5% nominal uncertainty, O₃, 4-s 282 283 resolution and $\pm 2\%$ nominal uncertainty) (Nedelec et al., 2003). Starting from the 284 measured O₃ and CO, the ozone enhancement ratio ($\Delta O_3/\Delta CO$) has been calculated, i.e. 285 the ratio of the ozone to carbon monoxide variations compared to their baseline values. A 286 background value of ~70 ppbv in the boundary layer and ~60 ppbv in the free troposphere 287 has been used for CO, while the background has been set at \sim 30 ppbv for O₃ at all levels 288 (Di Biagio et al., 2015). $\Delta O_3/\Delta CO$ data have been used together with dN_{Aitken}/dN_{Acc} to 289 retrieve information on the age of the sampled air masses, as discussed in Di Biagio et al. (290 2015).

In order to compare SLRs measurements obtained at different altitudes, the data analysed here are reported to standard temperature and pressure (STP) using T=293.15 K and





- P=1013.25 hPa. In this case, the scattering and absorption coefficients are scaled to STP
 conditions and the particle concentrations (in number or volume) are given as particles per
- 295 standard cm⁻³ (scm⁻³). Where not explicitly indicated, data refer to STP conditions.
- In Table 2 we summarize main information and uncertainties for the different aerosolinstruments considered in this study.
- 298

299 3.2 Boundary layer height estimation

The planetary boundary layer (BL) top height has been estimated from meteorological observations (temperature, T, potential temperature, θ , and relative humidity, RH) for each vertical sounding performed during TRAQA flights (see Di Biagio et al., 2015). The boundary layer top height is between 730 and 1500 m, with an average of ~1000 m. The location of each SLR, so if it is within the boundary layer or in the free troposphere, has been determined based on the planetary boundary layer top height estimated from the closest vertical sounding performed during each flight.

307

308 **3.3 Tracking the origin of the sampled air masses**

309 As discussed in Di Biagio et al. (2015), aerosol observations during TRAQA were mostly 310 influenced by pollution/anthropogenic particles exported from different sources around the 311 basin (Northern Italy/Po Valley, Southern France, Barcelona area). The Lagrangian trajectory 312 model FLEXPART (FLEXible PARTicle dispersion model, Stohl et al., 1998), adapted for 313 the WRF (Weather Research and Forecasting) meteorological input (Brioude et al., 2013) 314 has been used here to track the origin of air masses sampled during SLRs. Five-day three-315 dimensional back-trajectories have been calculated using the WRF meteorological output at a 316 30 km horizontal resolution and 28 vertical model levels up to 50 hPa. The model specific 317 humidity and potential vorticity is also interpolated along the trajectory path. Based on 318 FLEXPART simulations, data for the different SLRs have been separated as a function of the 319 origin of the sampled air masses. Three different sectors have been defined: the Western 320 sector, which includes trajectories coming from the Atlantic Ocean and travelling over France 321 or northern Spain before reaching the Western basin; the Eastern sector, including air mass 322 trajectories from continental Europe that have travelled over northern Italy-Po Valley before 323 entering the basin; and the Open Sea sector, which consists of trajectories coming from the 324 Western or Eastern sectors which have experienced at least 2 days of subsidence over the sea 325 in the Western basin and thus can be taken as representative of the regional background





326 aerosol or local pollution sources, i.e. ship emissions. The three different selected Sectors are 327 shown in Fig. 1, while Table 1 also reports the identified Sector of origin for the air masses 328 sampled during the different SLRs. As discussed in Di Biagio et al. (2015), several flights 329 were affected by dust particles exported over the basin from Northern Africa. SLRs data 330 dominated by dust have been identified based on the combined analysis of back-trajectories, 331 lidar profiles and optical data, and have been excluded from the dataset. However, for some 332 SLRs, the possible mixing of dust aerosols with pollution particles cannot be a priori 333 excluded.

334

335 3.4 Radiative model calculations

336 Radiative transfer calculations have been performed to estimate the instantaneous aerosol 337 direct radiative effect in the shortwave spectral range for different cases and in clear-sky 338 conditions. The objective of the calculations is to test the sensitivity of the DRE to the 339 variability of the aerosol optical properties, in particular the single scattering albedo, as 340 observed in this study. The GAME radiative transfer model (Dubuisson et al., 1996 and 341 2006) has been used in this study to compute the vertical profiles of downward and upward shortwave irradiances over the 0.28-3.0 µm spectral range. The model calculates radiances 342 and irradiances at various atmospheric levels at 400 cm⁻¹ spectral resolution between 0.28 and 343 344 0.5 µm and 100 cm⁻¹ resolution between 0.5 and 3 µm. Spectral absorption by principal 345 atmospheric gases (H₂O, CO₂, O₃, CH₄, N₂O, O₂) is taken into account in the model. The 346 discrete ordinate method (Stamnes et al., 1988) with twelve streams is used in the simulations 347 to describe multiple scattering. Simulations have been performed with and without aerosols by fixing the solar zenith angle (θ) at 60°, i.e. at about the mean of the diurnal value at the 348 349 latitudes of north-Western Mediterranean, and for a mid-latitude climatological summer 350 meteorological profile. The aerosol optical properties that are used as input in the GAME 351 radiative code are the spectral variation of the optical depth (τ), the asymmetry parameter (g) 352 and the single scattering albedo (ω). The difference of the net shortwave fluxes (downward 353 minus upward irradiances) with and without aerosols at the surface and at TOA is used to 354 estimate the aerosol DRE at these two levels. The atmospheric DRE is then calculated as the 355 difference between the TOA and the surface values. Finally, the ratio of the DRE to the 356 aerosol optical depth at 500 nm, i.e. the aerosol forcing efficiency (FE), is obtained. The shortwave heating rate at the altitude z is also calculated as: 357





358

$$\frac{\partial T}{\partial t} = -\frac{1}{\rho C_{p}} \frac{\partial F(z)}{\partial z} \qquad (3)$$

359 where T is the air temperature, ρ is the air density, C_p is the specific heat of the air, and F(z) 360 is the net flux at the altitude z.

361

362 **4. Results**

363 4.1 Overview over the different SLRs

Figure 2 shows the averages altitude, spectral scattering (σ_s) and absorption (σ_{abs}) coefficients, scattering and absorption Ångström exponent (SAE and AAE, respectively), ozone enhancement factor ($\Delta O_3/\Delta CO$), and Aitken-to-accumulation ratio (dN_{Aitken}/dN_{Acc}) measured for the different SLRs during TRAQA.

As shown in Fig. 2 and Table 1, the large majority of the SLRs were performed within the boundary layer at an altitude <1000 m. Only four SLRs (V25_R2, V25_R3, V26_R1, and V30_R1) measured aerosols in the free troposphere between 1800 and 3500 m. The sampled aerosols originated in each of the three different source sectors identified based on FLEXPART back-trajectories (Western, Easter, and Open Sea), with a larger number of cases from the Western sector compared to the Eastern and the Open Sea areas.

For all the different cases, the measured scattering coefficient is in the range 16-73 Mm⁻¹ at 374 375 450 nm and 8-30 Mm⁻¹ at 700 nm. The absorption coefficient is generally below 10 Mm⁻¹ at 376 all wavelengths, with the exception of V27 R1 and V32 R1 for which values up to ~20 Mm⁻ ¹ at 370 nm have been measured. For these two cases also the highest values of the particle 377 concentration in the accumulation mode (~1700-2200 # cm⁻³, not shown) and among the 378 379 highest values of the scattering coefficient are measured. For all cases, both σ_s and σ_{abs} 380 decrease with the wavelength. The pronounced spectral variability of σ_s , in particular, 381 indicates the dominance of pollution/anthropogenic fine particles in the sampled plumes.

The SAE varies between 0.96 and 1.94, while the AAE varies between 0.92 and 1.65, with an average of ~1.20. The AAE has been not calculated for few cases with very low values of the absorption coefficient (σ_{abs} at 370 nm < 1.5 Mm⁻¹). Both the SAE and the AAE obtained in this study fall in the range of variability indicated by several authors to identify pollution/anthropogenic aerosols or pollution mixed with other aerosol types in the Mediterranean basin (SAE>1-1.5, and AAE~1-1.5; Pace et al., 2006; Toledano et al., 2007; Mallet et al., 2013). Values of AAE larger than unity, in particular, might suggest the possible





389 mixing of pollution with brown carbon or dust particles over the basin (Russell et al., 2010;

- 390 Mallet et al., 2013).
- 391 For all the measured SLRs the $\Delta O_3/\Delta CO$ and the dN_{Aitken}/dN_{Acc} ratios vary in the range 0.37-392 1.02 and 1-50, respectively, for O₃ and CO varying between 24-78 and 69-136 ppbv and dN_{Aitken} and dN_{Acc} between 320-22500 and 100-2170 # cm⁻³. $\Delta O_3/\Delta CO$ and the dN_{Aitken}/dN_{Acc} 393 394 are linked to the photochemical (rate of ozone formation) and physical (rate of Aitken to 395 accumulation particle conversion) processes responsible for the ageing of the aerosol plumes. 396 The range of measured values here includes both cases with high dN_{Aitken}/dN_{Acc} and low 397 $\Delta O_3/\Delta CO$, typical of fresh plumes, and cases with low dN_{Aitken}/dN_{Acc} and high $\Delta O_3/\Delta CO$, 398 indicative of more aged air masses (Di Biagio et al., 2015).
- The summary of these observations suggests that the set of SLRs measurements considered in this study can be considered representative of a wide range of different atmospheric conditions occurring over the basin both in terms of sources, loadings, and lifetime for pollution aerosols.
- 403

404 4.2 Particle size distributions

405 Figure 3 shows the mean and the range of variability of the number and volume size 406 distributions measured during horizontal SLRs within pollution layers during TRAQA. Data 407 refers only to cases at <350 m altitude within the boundary layer. The absolute uncertainty on 408 the measured concentration, as also reported in Table 2, is ~15% for particle diameters below 409 $0.31 \,\mu\text{m}$ and $\sim 10\%$ at larger sizes. The grey shading indicates considerable variability in the 410 number concentration of the size distributions, of approximately one order of magnitude for 411 much of the size range measured. This reflects the relative wide range of aerosol loadings 412 encountered during the campaign.

The measured number size distribution from each SLR has been fitted with multi-modelognormal functions:

415
$$\frac{\mathrm{dN}}{\mathrm{d}\log \mathrm{D}_{\mathrm{g}}} = \sum_{\mathrm{i}} \frac{\mathrm{N}_{\mathrm{tot,i}}}{\sqrt{2\pi} \log \sigma_{\mathrm{g,i}}} \left(-\frac{\left(\log \mathrm{D}_{\mathrm{p}} - \log \mathrm{D}_{\mathrm{g,i}}\right)^{2}}{2 \log^{2} \sigma_{\mathrm{g,i}}} \right) \qquad (4).$$

416 For each mode I, N_{tot} represents the total aerosol number concentration, D_g the median 417 diameter, and σ_g the geometric standard deviation. The logarithm refers to base 10. Size data 418 were fitted automatically using the MPCURVEFIT IDL routine available at 419 http://www.physics.wisc.edu/~craigm/idl/fitting.html. Since the aim of the fitting is to





420 describe as closely as possible the measured number size distributions for subsequent optical 421 calculations (Sect. 4.4), up to seven modes were used to fit the data. The parameters of the 422 lognormal fits are reported in Table 3. The first mode of the size distribution is generally at 423 $0.13-0.14 \mu m$, whilst the largest mode is between ~5 and 8 μm for the different cases.

424

425 4.3 Spectral single scattering albedo: variability as a function of air mass origin and426 height

427 Figure 4 shows the spectral ω for the different SLRs considered in this study. Data have been 428 separated based on the origin of the sampled air masses. The single scattering albedo varies in 429 the range 0.84-0.98 at 370 nm and 0.70-0.99 at 950 nm and generally decreases with the 430 wavelength, as it is typical for pollution particles (Dubovik et al., 2002). Only in two cases (V19 R1 and V30 R2) the single scattering albedo increases with wavelength. For these 431 432 cases also very high values of ω are observed (0.92-0.97 for V19 R1 and 0.98-1.0 for 433 V32 R2), which may suggest the possible mixing of pollution with sea spray. The lowest 434 values of the single scattering albedo are measured for V27 R1 (0.84-0.70 between 370 and 435 950 nm) sampled at ~160 m and originated in the Open Sea sector. Data in Fig. 2 also 436 indicate for V27_R1 very low values of $\Delta O_3/\Delta CO$ (~0.37) and a relatively high 437 dN_{Aitken}/dN_{Acc} (~7), which suggests that V27 R1 is a fresh plume possibly associated to local 438 emissions, i.e. ship plumes, over the basin. If we exclude V27 R1, the range of measured 439 values appears comparable (within error bars) for the three considered sectors (Western, Eastern, and Open sea; ω between 0.88 and 0.98 at 370 nm and 0.83 and 0.99 at 950 nm. 440

441 The vertical variability of ω , together with dN_{Attken}/dN_{Acc} , $\Delta O_3/\Delta CO$, SAE, and AAE, is 442 shown in Fig. 5 for the different considered cases. With the only exception of V27_R1, for 443 which the lowest values are observed below 200 m, the single scattering albedo does not 444 show a clear trend with height, with a similar range of values measured in the boundary layer, 445 below ~1000 m, and in the free troposphere up to ~3500 m. As for ω , the AAE does not 446 significantly vary with height. At the same time, dNAitken/dNAcc and SAE decrease with 447 height, with a concurrent slight $\Delta O_3/\Delta CO$ increase, which may suggest an increase of plume 448 age with height. The ensemble of these observations seems to indicate that, for our observed 449 cases, the absorptivity properties of the sampled plumes do not depend on altitude and 450 associated air mass age of the plume. It should be pointed out, however, that the majority of 451 cases considered here have been sampled below 1000 m, so in the boundary layer, and the 452 statistics in the free troposphere is only limited to a few events.





Values of the single scattering albedo measured in this study are comparable with values reported at several other sites in the Central and Western Mediterranean region for pollution aerosols (Mallet et al., 2003 and 2013; Meloni et al., 2006; Saha et al., 2008; Di Biagio et al., 2009; Pandolfi et al., 2011). The single scattering albedo from these studies is observed to vary in the range 0.84-0.95 at 440 nm, 0.76-0.98 at 500-550 nm, and 0.80-0.87 at 870 nm. Compared with the literature, larger and lower values are obtained in the present study for few cases mostly influenced by sea spray and local fresh emissions, respectively.

461 **4.4 Optical closure and estimation of the aerosol complex refractive index**

As discussed in the previous section, the single scattering albedo of pollution aerosols shows
a relatively large variability. Here we investigate the impact of this variability on the complex
refractive index (m=n-ik) of the particles.

465 For eight selected SLRs for which both complete optical (scattering and absorption 466 coefficients, and single scattering albedo) and size distribution measurements were available, 467 the aerosol spectral complex refractive index has been estimated by optical closure study. 468 These cases correspond to V19 R1, V21 R1, V21 R3, V23 R2, V27 R1, V31 R1, 469 V32 R1, V32 R3 sampled within the boundary layer at <350 m altitude. The optical closure 470 consisted in recalculating the spectral scattering σ_s and absorption σ_{abs} coefficients measured 471 for each SLR by using the measured size distribution as input and by varying the real (n) and 472 imaginary (k) parts of the complex refractive index in the calculations. Then, n and k are 473 fixed when the best agreement between measurements and calculations is found. Optical 474 calculations have been performed using Mie theory for spherical particles. The Mie single.pro IDL routine available at http://www.atm.ox.ac.uk/code/mie/mie single.html 475 has been used. In the calculations the real part of the refractive index is varied in the range 476 477 1.30-1.80 at steps of 0.01, while the imaginary part in the range 0.001-0.1 at steps of 0.001, 478 for a total of 5100 inversions for each SLR dataset. The uncertainty on the real and imaginary 479 parts of the refractive index has been estimated with a sensitivity study. To this purpose, the values of n and k are also obtained by using as input the observed σ_s , σ_{abs} , and $\frac{dN}{d\log D_a}$ plus 480 or minus one standard deviation on their measurement. The deviations of the values of n and 481

 of minus one standard deviation on their measurement. The deviations of the values of n and k retrieved in the sensitivity study with respect to those obtained in the first inversions are assumed to correspond to the one standard deviation uncertainty. The estimated uncertainty is <5% for n and ~25-30% for k.





The comparison of the measured and calculated σ_s and σ_{abs} are shown in Fig. 6, while the retrieved real and imaginary parts of the refractive index for the different SLRs are reported in Fig. 7. Data in Fig. 7 are also compared to the real and imaginary parts of the refractive index for the single components (insoluble, water soluble, soot, and sea salt) considered in the OPAC model (Optical Properties of Aerosols and Clouds, Hess et al., 1998) to represent continental, urban and maritime polluted aerosols.

491 As shown in Fig. 6, a very good agreement is found between the calculated and the measured 492 scattering and absorption coefficients, with an average difference of less than 5% for both σ_s and σ_{abs} . For our analysed cases n and k vary in the range 1.67-1.75 and 0.003-0.038 at 370 493 494 nm and 1.41-1.75 and 0.002-0.068 at 950 nm, respectively. The imaginary part of the 495 refractive index slightly increases with wavelength, while a decrease is observed for the real 496 part in most cases. Highest values of k are obtained for V27 R1, which also shows the 497 absolute lowest values of ω in our dataset (0.84-0.70), followed by V32 R1 and V32 R2, which also present relatively low values of ω (0.95-0.83). The lowest k, as well as among the 498 499 lowest n, is instead obtained for V19 R1 (ω =0.92-0.96). The comparison of our data with 500 OPAC values for single components suggests that in most cases particles are composed of a mixing of insoluble and water soluble components, with possible contributions of soot 501 502 (V27 R1) ad sea salt (V19 R1). The results of the complex refractive index obtained in this 503 study are in agreement with previous estimates obtained for pollution aerosols in continental 504 Europe ($n \sim 1.50 - 1.72$ and $k \sim 0.001 - 0.1$ for UV-visible wavelengths e.g. Ebert et al., 2002, 505 2004; Müller et al., 2002; Mallet et al., 2003, 2011; Raut and Chazette, 2008). Larger values 506 of both n and k are instead obtained here compared to AERONET retrievals at different sites 507 in the Western Mediterranean (1.38-1.46 for n and 0.003-0.01 for k at 440 and 670 nm; 508 Mallet et al., 2013).

509 Figure 8 shows the results of the correlation analysis between the single scattering albedo and 510 the complex refractive index obtained for the analysed cases. For the real part, the range of retrieved n values is larger (1.41-1.70) for ω greater than ~0.95, while as the single scattering 511 512 albedo decreases the real part converges to ~1.70-1.75 at all wavelengths. A strong 513 correlation is observed between ω and k at all wavelengths, that is the lower the single 514 scattering albedo, the higher the imaginary part. A linear regression fit was applied to the ω -k datasets at the seven wavelengths ($R^2=0.83-0.95$ at all wavelengths for the different fits). The 515 516 intercept for all cases is lower than 1 (0.94-0.97), with lowest values (0.94) obtained at 880 517 and 950 nm. This is possibly associated to a slight underestimation of ω which, especially at





- 518 these wavelengths, is difficult to determine given the high uncertainty on the particle 519 absorption coefficient. Another source of uncertainty is the size distribution, which influences
- 520 the results of Mie calculations, and thus has a direct impact on the refractive index retrieval.
- 521

4.5 Influence of the single scattering albedo variability on the aerosol direct shortwaveradiative effect (DRE)

524 Radiative transfer model calculations with the GAME model have been performed with the 525 aim of investigating the impact of the variable optical properties, and in particular the single 526 scattering albedo, on the shortwave direct radiative effect of pollution particles in the Western 527 Mediterranean basin.

528 Simulations have been performed by considering three different vertical aerosol profiles, 529 based on observations reported by Di Biagio et al. (2015): i. aerosols only confined in the BL 530 (whose altitude is fixed at 1000 m, in the mean of observations during TRAQA); ii. 50% of 531 the aerosol optical depth in the BL and 50% in the FT (which is considered to extend between 532 1000 and 4000 m); iii. 20% of the aerosol optical depth in the BL and 80% in the FT. For the 533 different cases we fixed the total aerosol optical depth at 0.2 at 550 nm, which corresponds to 534 the mean of observations obtained over the Western basin during TRAQA (Di Biagio et al., 2015). However, results will be given as FE so they are independent on the chosen optical 535 536 depth. We assume a uniform aerosol distribution and constant optical properties within the 537 BL and the FT for the three different considered profiles. This assumption comes from the 538 observations of the present study, which do not evidence any significant change of the 539 aerosol properties with height. Aerosol spectral optical properties, both in the BL and in the 540 FT up to 4000 m, are assumed from observations, as explained in the following.

541 The GAME model requires as input the aerosol optical depth, single scattering albedo, and 542 asymmetry factor at 7 wavelengths between 330 and 1500 nm. The spectral optical depth 543 between 330 and 1500 nm is extrapolated from the fixed value of 0.2 at 550 nm by assuming 544 a Ångström exponent of 1.5, in the mean of our observations for pollution aerosols (see Fig. 545 2). For the single scattering albedo, we considered 3 different sets of values which correspond 546 to the minimum, maximum, and mean of the values observed in this study (the absolute 547 minimum for V27 R1 has been excluded for calculations since it represents an outlier in our data). The ω values at 370-950 nm as obtained from experimental data are then extrapolated 548 549 at the 7 GAME wavelengths (Table 4). The asymmetry factor is calculated from Mie theory 550 based on the refractive index values and size distribution data for the eight cases considered





551 in the previous Section. The spectral variation of g used in the radiative transfer calculations

552 is estimated as the mean of the values obtained for these eight cases extrapolated at the 7

553 GAME wavelengths. The obtained g varies between 0.60 at 330 nm and 0.51 at 1500 nm.

554 These values are consistent with previous estimates of g obtained for pollution aerosols over

the Mediterranean basin (Meloni et al., 2006; Saha et al., 2008; Mallet et al., 2011).

Background stratospheric aerosols (above 12 km) are also taken into account for radiative
calculations; optical properties from the OPAC stratospheric aerosol model (Hess et al.,
1998) are assumed.

559 Finally, in addition to aerosol optical properties, the GAME model requires as input the albedo of the surface (A_s) at 5 wavelengths between 448 nm and 2130 nm. In this study, 560 561 simulations are performed over the sea surface. The albedo of the sea surface is obtained from Jin et al. (2004), which provide a parameterisation of As as a function of chlorophyll 562 concentration (Chl), wind speed (w), aerosol optical depth at 500 nm (τ), and the solar zenith 563 angle (θ). For this study A_s is estimated for Chl=0, w=6-9 m s⁻¹, τ =0.24 (extrapolated from 564 the value of 0.2 at 550 nm), and θ =60°, and it varies between 0.009 and 0.005 in the 565 566 considered 448-2130 nm spectral range.

Results of the radiative transfer simulations are shown in Fig. 9, which reports the FE at the 567 568 surface, TOA, and atmosphere (FE_S, FE_{TOA} and FE_{ATM}) for the maximum, mean, and 569 minimum of the single scattering albedo observed in this study. Results of the simulations are 570 mostly independent on the vertical distribution of the aerosols (less than $\sim 5\%$ changes for 571 FE_S, FE_{ATM}, and FE_{TOA} for the three different profiles used in the simulations), so the mean 572 of the results obtained for the three cases is reported in Fig. 9. The forcing efficiency varies between -160 and -235 (FE_s), -137 and -92 (FE_{TOA}), and +23 and +143 (FE_{ATM}) W m⁻² τ^{-1} for 573 ω varying between its maximum and minimum values. Estimates of the forcing efficiencies 574 in correspondence of the mean of ω are -198, -113, and +85 W m⁻² τ^{-1} at the surface, TOA, 575 576 and atmosphere, respectively. The corresponding instantaneous shortwave heating rate at the surface varies between 0.2 and 2.0 K day⁻¹ for ω between its maximum and minimum. 577

As expected, the lower the single scattering albedo, the larger in absolute value the FE_s and FE_{ATM} and the lower the FE_{TOA}. This is due to the impact of absorption on the amount of radiation trapped in the atmosphere and transmitted towards the surface, which thus enhance the radiative effect in the atmosphere and at the surface for decreasing ω . Conversely, the larger the particle absorption, the lower the effect on the radiation reflected back to space, and thus the decrease of the intensity of the cooling effect at the TOA. Changes in the single





scattering albedo of the particles between its maximum and minimum ($\Delta \omega$ =0.1-0.2 at the different wavelengths) determine about a 50% strengthening of the direct shortwave radiative effect at the surface, and a reduction of ~30% the effect at the TOA. Consequently, the atmospheric FE may vary up to an order of magnitude. These results thus highlight the sensitivity of the DRE on the absorptivity properties of the particles, as well as the importance of accurately reproducing the single scattering albedo of aerosols to correctly evaluate their direct radiative effect.

591 The results of the present study are in quite good agreement with previous estimates of the 592 aerosol forcing efficiency for pollution aerosols in the Mediterranean area. FE_S, FE_{ATM}, and 593 FE_{TOA} obtained here compare well with data obtained in the Central Mediterranean by Di 594 Biagio et al. (2009, 2010), who provide estimates based only on observational data, i.e. 595 without any assumption on the aerosol optical properties. In these studies they report a forcing efficiency of ~-200 and -164 W m⁻² τ^{-1} at the surface and TOA at solar zenith angles 596 597 of 50°-60° for mixed aerosols (pollution plus sea salt particles). They estimate an increase in 598 absolute value of FEs of about 20-40% due to a decrease of 0.1-0.2 of the single scattering 599 albedo (at 415 and 868 nm) of the aerosols, as well as a concurrent increase of FE_{TOA} of about 10-40%. The observations obtained in this study fall in the range of variability reported 600 601 by Di Biagio et al. (2009, 2010). Our data also agree with estimates of Saha et al. (2008), 602 reporting for pollution aerosols measured in the French Mediterranean coast up to 40% 603 variability in the FEs and FE_{TOA}, concurrently with 70% increase of FE_{ATM}, due to a ω 604 change of 0.15 at 525 nm. Conversely, our estimates at the surface and TOA are larger in absolute value compared to data reported for continental Europe by Horvath et al. (2002), 605 who estimated a FEs of ~-164 W m⁻² τ^{-1} and a FE_{TOA} of -50 W m⁻² τ^{-1} for polluted aerosols 606 with ω =0.90 at 520 nm, thus comparable with our mean values of single scattering albedo for 607 608 pollution aerosols.

609

610 **5.** Conclusions

In this study we have presented measurements of the spectral optical properties (scattering and absorption coefficients and single scattering albedo) and particle size distributions for pollution aerosols obtained over the remote sea in the Western Mediterranean basin during the TRAQA campaign in summer 2012. The set of observations analysed in this study can be assumed to be representatives of a wide range of different conditions that can be observed over the basin, both in terms of pollution sources, aerosol loadings, and lifetimes of the





617 plumes. The detailed characterization of the spectral optical properties of pollution aerosols

618 in the Western basin was missing to date.

619 Observations from the present study show a large variability of the optical properties of 620 pollution aerosols over the basin, in particular of the spectral single scattering albedo. Values of ω in the range 0.84-0.98 at 370 nm and 0.70-0.99 at 950 nm are observed in this study. 621 622 This variability of ω does not seem to be clearly linked neither to the particle origin, nor to 623 the altitude and associated ageing of the sampled plumes. The variability of ω reflects in a 624 large variability for the complex refractive index of pollution aerosols, which is estimated to 625 span in the range 1.41-1.75 for the real part and 0.002-0.068 for the imaginary part between 626 370 and 950 nm. The analysis of the complex refractive index suggests that possible 627 differences in terms of particle compositions can explain in part the observed variability of ω . 628 A large range of compositions has been however reported for pollution aerosols in Europe 629 and the Mediterranean basin (Mallet et al., 2003; Ebert et al., 2004; Pey et al., 2010; Piazzola 630 et al., 2012) and a more detailed analysis of the composition for the cases obtained in this 631 study should be addressed.

Based on the observations of the present study, the variability of optical properties for pollution aerosols can arise from the combination of different factors, linked to the origin, production mechanism, and ageing of the plumes along their lifetime, as well as the possible mixing of different plumes with different characteristics. So, the inherent heterogeneity of sources, coexistence of different air masses, and multiple physical and chemical processes occurring in a complex environment such as the Western Mediterranean may give rise to this inherent variability of the particle single scattering albedo.

639 This observed variability on ω has a large influence on the direct shortwave radiative effect of pollution aerosols at the surface, TOA, and within the atmosphere. For instance, a change 640 of up to an order of magnitude (from +23 to +143 W m⁻² τ^{-1} at 60° solar zenith angle) in the 641 642 atmospheric radiative effect is estimated due to the variability of the single scattering albedo 643 within the range of values observed in this study. The change in the amount of atmospheric 644 absorbed solar radiation may have a strong impact on the temperature profile and the 645 atmospheric thermal structure, with important consequences on several processes, such as 646 cloud formation and precipitations. The strong sensitivity of the DRE also at the surface, up 647 to 50% for varying ω , on its turn, may largely impact the rate of evaporation over the basin, 648 which is also a crucial component of the hydrological cycle (Nabat et al., 2015). Given the 649 large sensitivity of the Mediterranean area and the high risk of desertification for this region





(Giorgi and Lionello, 2008; IPCC, 2013) any factor possibly impacting the hydrological cycle should be taken carefully into account by regional climate models. In this view, results from the present study can be used to provide a constraint of the absorption properties of pollution particles in the Western Mediterranean basin to use in regional modelling studies. Constraining these properties constitutes a crucial step in order to better assess the role of aerosols on the radiative balance of this region and to ameliorate the capability of making projection on future climate changes.

657

658 Author contributions

J.-L. Attié, F. Ravetta, G. Ancellet, and P. Formenti designed the TRAQA experiment and coordinated the campaign. C. Gaimoz, N. Grand, and C. Di Biagio operated the instruments on board the ATR-42 during the flights. C. Di Biagio performed the data analysis with contributions from L. Doppler and P. Formenti. S. Bucci and F. Fierli performed the FLEXPART simulations. M. Mallet and P. Dubuisson provided the GAME code for radiative calculations. C. Di Biagio wrote the manuscript with contributions from the co-authors.

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863 Tables

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Table 1. Summary of information on the SLRs analysed in this study. The SLR location (within the boundary layer or in the free troposphere) has been determined based on the boundary layer top height estimated for the closest vertical sounding performed during each flight (see Di Biagio et al., 2015). The Sector of origin for sampled air masses has been determined based on FLEXPART back-trajectories.

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Flight				Altitude		
number	SLR_ID	Date	Time start-stop	(m)	Location	Sector of origin
V19	V19_R1	26/06/2012	11:23-11:38	322	Within the boundary layer	Eastern
V19	V19_R2	26/06/2012	11:44-11:59	897	Within the boundary layer	Eastern
V21	V21_R1	27/06/2012	10:54-11:12	312	Within the boundary layer	Eastern
V21	V21_R2	27/06/2012	11:48-12:04	629	Within the boundary layer	Eastern
V21	V21_R3	27/06/2012	12:05-12:19	311	Within the boundary layer	Western
V22	V22_R1	29/06/2012	7:42-8:01	478	Within the boundary layer	Eastern
V23	V23_R2	29/06/2012	12:05-12:20	319	Within the boundary layer	Open Sea
V25	V25_R1	04/07/2012	9:08-9:24	639	Within the boundary layer	Western
V25	V25_R2	04/07/2012	9:32-9:48	2015	Free troposphere	Western
V25	V25_R3	04/07/2012	9:50-10:08	2538	Free troposphere	Western
V26	V26_R2	04/07/2012	17:08-17:25	1877	Free troposphere	Western
V27	V27_R1	06/07/2012	9:28-9:47	164	Within the boundary layer	Open Sea
V28	V28_R2	06/07/2012	15:58-16:13	927	Within the boundary layer	Open Sea
V30	V30_R1	07/07/2012	14:09-14:28	3498	Free troposphere	Western
V30	V30_R2	07/07/2012	14:51-15:07	549	Within the boundary layer	Open Sea
V31	V31_R1	10/07/2012	15:44-16:20	322	Within the boundary layer	Western
V31	V31_R2	10/07/2012	16:31-16:59	954	Within the boundary layer	Western
V32	V32_R1	11/07/2012	12:52-13:13	250	Within the boundary layer	Western
V32	V32_R2	11/07/2012	13:22-13:48	788	Within the boundary layer	Western
V32	V32_R3	11/07/2012	14:02-14:12	336	Within the boundary layer	Western
V32	V32_R4	11/07/2012	14:18-14:35	802	Within the boundary layer	Western

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Table 2. Summary of the aerosol in situ measurements on the ATR-42 during the TRAQA campaign. Details on the data treatment and uncertainty estimation for the different instruments are provided in Sect. 2.

Property measured	Instrument	Location on aircraft	Flow rate (l min ⁻¹)	Time resolution	Size range	Sensitivity or uncertainty	Comments
Aerosol number concentration	Condensation Particle Counter (CPC 3775)	in the cabin behind AVIRAD inlet	1.5	5 sec	0.004 – 3 μm	±10% (concentration)	
	Passive cavity aerosol spectrometer probe (PCASP 100x)	aircraft fuselage, left side before the wing	0.06	1 sec	Nominally 0.1 – 3.0 µm Corrected for refractive index 0.10 – 4.47 µm	<±25% (diameter optical to geometric conversion) ±15% (concentration) (e.g., Highwood et al., 2012)	Aerosol concentration underestimated by 50% between 0.4 and 1.0 μm
Aerosol size distribution	SkyGRIMM 1.129	in the cabin behind AVIRAD inlet	1.3	6 sec	Nominally 0.3 – 32 μm Corrected for refractive index 0.28 – 65.80 μm (AVIRAD 50% cut-off efficiency at ~12 μm diameter)	<±25% (diameter optical to geometric conversion) ±10% (concentration)	Data not available >350 m
Dry aerosol scattering coefficient σ _s (450, 550, 700 nm)	TSI 3563 integrating nephelometer	in the cabin behind AVIRAD inlet	30	6 sec	50% cut-off efficiency at ~ 12 μm diameter	<±10% for σ _s at 450, 550, and 700 nm	
Aerosol absorption coefficient (σ_a) (370, 470, 520, 590, 660, 880, 950 nm)	Magee AE31 aethalometer	in the cabin behind AVIRAD inlet	13	2 min	50% cut-off efficiency at ~12 μm diameter	11-70% variable at the different wavelengths	Data available only for 60% of SLRs





Table 3. Lognormal mode parameters of the measured aerosol size distribution (total aerosol number concentration, N_{tot}, median diameter, D_g, and geometric standard deviation, σ_g). Data corresponds to SLRs below ~350 m altitude. Diameters are given in microns and number concentrations refer to ambient conditions.

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		Mode 1	Mode 2	Mode 3	Mode 4	Mode 5	Mode 6	Mode 7
V19_R1	N _{tot}	498.00	160.00	20.00	4.50	1.95	0.10	
	D_{g}	0.13	0.24	0.38	0.66	1.55	4.85	
	$\sigma_{\rm g}$	1.19	1.16	1.17	1.29	1.60	1.38	
V21_R1	N _{tot}	600.00	210.00	29.00	5.50	0.55		
	D_{g}	0.13	0.24	0.37	0.52	1.56		
	$\sigma_{\rm g}$	1.20	1.17	1.15	1.40	1.62		
V21_R3	N _{tot}	600.00	195.00	30.00	2.80	0.48	0.02	
	D_{g}	0.13	0.23	0.37	0.57	1.55	4.95	
	$\sigma_{\rm g}$	1.19	1.16	1.18	1.33	1.66	1.41	
V23_R2	N _{tot}	660.00	195.00	25.00	3.20	0.75	0.03	
	D_{g}	0.13	0.23	0.37	0.57	1.59	5.69	
	$\sigma_{\rm g}$	1.19	1.16	1.16	1.37	1.69	1.33	
V27_R1	N _{tot}	930.00	264.00	40.00	4.60	0.52	0.04	0.004
	D_{g}	0.13	0.23	0.37	0.55	1.57	3.85	8.20
	$\sigma_{\rm g}$	1.19	1.17	1.18	1.38	1.68	1.12	1.26
V31_R1	N _{tot}	482.00	278.00	48.00	2.70	0.55	0.01	
	D_{g}	0.14	0.24	0.35	0.54	1.82	7.14	
	$\sigma_{\rm g}$	1.20	1.16	1.17	1.39	1.65	1.17	
V32_R1	N _{tot}	1135.00	413.00	55.00	5.00	0.65	0.01	
	D_{g}	0.13	0.23	0.37	0.50	1.65	7.30	
	$\sigma_{\rm g}$	1.19	1.18	1.16	1.37	1.66	1.11	
V32_R3	N _{tot}	235.00	84.00	12.00	1.80	0.12	0.02	0.004
	$\overline{\mathrm{D}_{\mathrm{g}}}$	0.14	0.23	0.38	0.50	1.57	3.75	7.99
	$\sigma_{\rm g}$	1.19	1.16	1.16	1.32	1.68	1.12	1.31

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889	Table 4. Maximum,	mean, and	minimum	of the	single	scattering	albedo	considered	for	radiative
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890	transfer calculations.	Values are reported at the	7 wavelengths used	as inputs in the GAME model.

	330 nm	400 nm	550 nm	670 nm	870 nm	1020 nm	1500 nm
SSA max	0.98	0.98	0.99	0.99	1.00	0.99	0.99
SSA mean	0.93	0.93	0.92	0.91	0.90	0.90	0.89
SSA min	0.88	0.87	0.85	0.85	0.83	0.82	0.80

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895 Figures

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897 Figure 1. Upper panel: geographical position of the different straight levelled runs (SLRs) 898 performed during the TRAQA campaign and analysed in this paper. The label for each point in the 899 figure identifies the flight number and the corresponding SLR: for example V22 R1 indicates the 900 coordinates of the first SLR of flight V22. Lower panel: definition of three different source areas for 901 the various SLRs (see Sect. 3.1 for more details). The Western sector includes trajectories coming 902 from the Atlantic Ocean and travelling over France or northern Spain before reaching the Western 903 basin; the Eastern sector includes air mass trajectories from continental Europe that have travelled 904 over northern Italy-Po Valley before entering the basin; and the Open Sea sector consists of 905 trajectories which have experienced at least 2 days of subsidence over the sea in the Western basin. 906









Figure 2. Averages over the different TRAQA straight levelled runs (SLRs) of the measured: altitude, spectral scattering coefficient (σ_s ; 450, 550, and 700 nm), scattering Ångström exponent (SAE), spectral absorption coefficient (σ_{abs} ; 370, 470, 520, 590, 660, 880, and 950 nm), absorption Ångström exponent (AAE), ozone enhancement factor ($\Delta O_3/\Delta CO$) and Aitken-to-accumulation ratio (dN_{Aitken}/dN_{Acc}). Uncertainties indicate the 1- σ standard deviation. The x-axis indicates the flight number (19 to 32 for flights V019 to V032); each point for the same flight number represents a different SLR.

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Figure 3. Number size distributions (left panel) and volume size distributions (right panel) measured over the different SLRs for the TRAQA flights. Data corresponds to measurements performed within the boundary layer at altitudes <350 m (V19_R1, V21_R1, V21_R3, V23_R2, V27_R1, V31_R1, V32_R1, V32_R3). Concentrations are given at ambient conditions. Grey shading represents minimum and maximum measured values, while the black curve is the average size. Measurement uncertainties are also reported for the average curve.

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Figure 4. Spectral single scattering albedo at seven wavelengths between 370 and 950 nm
calculated from nephelometer and aethalometer measurements for the different SLRs within
pollution layers. Data are separated based on the different air mass origin (Western Sector, Eastern
Sector, and Open Sea).

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- 942 Figure 5. Single scattering albedo (370, 660, and 950 nm), ozone enhancement factor ($\Delta O_3/\Delta CO$),
- 943 Aitken-to-accumulation ratio (dNAitken/dNAcc), and scattering (SAE) and absorption Ångström
- 944 exponent (AAE) versus height for all analysed SLRs cases.
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Figure 6. Comparison of the aerosol scattering (σ_s , left panel) and absorption (σ_{abs} , right panel) coefficients measured by the nephelometer and the aethalometer and calculated from measured size distribution data with Mie theory. Data are given at ambient conditions.

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955 Figure 7. Spectral real (n, left panel) and imaginary (k, right panel) parts of the complex refractive 956 index obtained by optical closure for the 8 selected case studies. For sake of clarity, uncertainties on 957 n and k are not reported in the plot. The values of the single scattering albedo measured at 370 and 958 950 nm for the different cases are reported in the legend. The spectral real and imaginary parts of 959 the complex refractive index as obtained from the Optical Properties of Aerosols and Clouds 960 (OPAC, Hess et al., 1998) database for insoluble, water soluble, soot and sea salt components are 961 also reported in the plot. These components are used in OPAC to model continental polluted, 962 continental rural, urban, and maritime polluted aerosols.

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966 Figure 8. Spectral single scattering albedo plotted against the real (left panel) and the imaginary 967 (right panel) parts of the complex refractive index.

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- 970 Figure 9. Aerosol shortwave forcing efficiency at 60° solar zenith angle calculated at the surface,
- 971 TOA, and within the atmosphere for the maximum, mean, and minimum of the single scattering
- 972 albedo (ω) observed in this study (Table 4).

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