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1 **Continental pollution in the Western Mediterranean basin: large variability of**
2 **the aerosol single scattering albedo and influence on the direct shortwave**
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
50 for the real and the imaginary parts, respectively, between 370 and 950 nm.

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
54 50% and 30% change of the forcing efficiency (FE), i.e. the DRE per unit of optical depth, at
55 the surface ($-160 \div -235 \text{ Wm}^{-2}\tau^{-1}$ at 60° solar zenith angle) and at the Top-Of-Atmosphere ($-$
56 $137 \div -92 \text{ Wm}^{-2}\tau^{-1}$) for ω varying between its maximum and minimum value. This induces a
57 change of up to an order of magnitude ($+23 \div +143 \text{ Wm}^{-2}\tau^{-1}$) for the radiative effect within the
58 atmosphere.

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61 **Keywords:** pollution aerosols, single scattering albedo, direct radiative effect, Western
62 Mediterranean

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66 1. Introduction

67 Atmospheric aerosols play a crucial role on climate by affecting the radiative transfer of
68 atmospheric radiation and by modifying cloud properties and lifetime (Boucher et al., 2013).
69 The capability of atmospheric aerosols to interact through processes of scattering and
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
85 different origins and types (Gkikas et al., 2012). On its northern bound, it is limited by
86 Europe, which makes that anthropogenic pollution is usually exported from the continent
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).

96 In spite of this, the characterization of the optical properties of anthropogenic aerosols in this
97 part of the basin remains only limited to coastal and inland regions (Mallet et al., 2003, 2011,
98 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
100 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 ChArME_x (Chemistry-Aerosol 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
108 2012 and SAFMED (Secondary Aerosol Formation in the MEDiterranean) in 2013.

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

115 Following these observations, we may ask: does the heterogeneity in pollution plume
116 composition, origin, and lifetime as observed in Di Biagio et al. (2015) induce heterogeneity
117 on the optical properties (in particular the single scattering albedo) of pollution aerosols in
118 this part of the basin? And, if observed, does this heterogeneity on the optical properties
119 influence the aerosol DRE? Is it necessary to take it into account to better evaluate the aerosol
120 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 TRAQA. 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
126 is twofold: to provide a new dataset of aerosol single scattering albedo values which can be
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
136 (43° 36' N, 1° 26' E, France). A total of seventeen flights, most often two flights per day,
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
148 coastline and will be considered in this study. Figure 1 and Table 1 summarise the
149 geographical location, time, and altitude of these 21 SLRs. As indicated in Table 1 each SLR
150 was about 15-20 min long. At the cruise speed of the ATR (93 ms⁻¹), this integration time
151 corresponds to about 100 km.

152

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
156 iso-axial and iso-kinetic inlet which samples air at a volumetric flow of ~350 L min⁻¹. The
157 50% passing efficiency of the inlet is 12 µm diameter. Various lines depart from AVIRAD to
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.

163 - The aerosol scattering coefficient (σ_s) at 450, 550, and 700 nm has been measured by a 3-
164 wavelengths integrating nephelometer (TSI Inc., model 3563, 6s resolution). The



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
 172 calculated over the different SLRs. The uncertainty on the SLR average values is
 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)
 175 has been calculated as the power law fit of the measured scattering coefficients versus
 176 wavelength to extrapolate the scattering coefficient at other wavelengths than those of
 177 operation.

178 The nephelometer measured the scattering coefficient in dry air conditions. This is due to
 179 the heating of the airflow while entering the aircraft cabin and the temperature increase in
 180 the sensing volume of the instrument due to illumination. The relative humidity measured
 181 during the flights inside the nephelometer cavity was <25% in more than 90% of cases,
 182 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 $\sigma_{\text{ATT}}(\lambda)$
 189 measured by the aethalometer has been corrected following the procedure described by
 190 Collaud Coen et al. (2010):

$$191 \quad \sigma_{\text{abs}}(\lambda) = \frac{\sigma_{\text{ATT}}(\lambda) - \alpha(\lambda)\overline{\sigma_s(\lambda)}}{C_{\text{ref}}R(\lambda)} \quad (1).$$

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
202 scattering (σ_s) to extinction ($\sigma_s + \sigma_{\text{abs}}^*$) coefficients, with σ_{abs}^* corrected for the scattering
203 and the multiple scattering corrections, but not for the shadowing effect. The obtained
204 $R(\lambda)$ varies between 0.75 and 1 for ω^* between 0.75-0.99 at 370 nm and 0.70-0.99 at 950
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.

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

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

$$216 \quad \omega(\lambda) = \frac{\sigma_s(\lambda)}{\sigma_s(\lambda) + \sigma_{\text{abs}}(\lambda)} \quad (2).$$

217 The uncertainty on ω has been calculated with the propagation error formula and varies
218 between 0.02 and 0.04 at all wavelengths.

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

222 - The aerosol number size distribution ($dN/d\log D_g$) has been measured by two different
223 optical particle spectrometers: the passive cavity aerosol spectrometer probe (PCASP,
224 model 100-X, 1-s resolution, 31 size classes between 0.1 and 3.0 μm diameter, operating
225 wavelength 632.8 nm), and the optical particle spectrometer SkyGRIMM (GRIMM Inc.,
226 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 D_g 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 D_g 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
244 GRIMM show a good agreement below 0.4 μm and above 1.0 μm (less than \sim 10%
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 \sim 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 μm
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 $dN/d\log D_g$ 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 $dV/d\log D_g = \pi/6 D_g^3 dN/d\log D_g$ has been calculated.

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

268 - The total particle number concentrations in the Aitken (4 nm-0.1 μm ; dN_{Aitken}) and
269 accumulation (0.1-1.0 μm ; dN_{Acc}) modes have been calculated by combining condensation
270 particle counter measurements of particle concentration in the 0.004 – 3 μm range (CPC,
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 dN_{Aitken} and dN_{Acc} over the whole altitude range. dN_{Aitken} 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
277 1.0 μm , as discussed above, is estimated to induce a $\sim 20\%$ underestimation of the dN_{Acc}
278 calculated here, whilst it has almost a negligible impact on dN_{Aitken} . The dN_{Acc} and dN_{Aitken}
279 obtained in correspondence of each SLR have been used to calculate the Aitken-to-
280 accumulation ratio $dN_{\text{Aitken}}/dN_{\text{Acc}}$.

281 - The carbon monoxide (CO) and ozone (O_3) mixing ratios have been measured by the
282 MOZART instrument (CO, 30-s resolution and $\pm 5\%$ nominal uncertainty, O_3 , 4-s
283 resolution and $\pm 2\%$ nominal uncertainty) (Nedelec et al., 2003). Starting from the
284 measured O_3 and CO, the ozone enhancement ratio ($\Delta\text{O}_3/\Delta\text{CO}$) 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 ~ 30 ppbv for O_3 at all levels
288 (Di Biagio et al., 2015). $\Delta\text{O}_3/\Delta\text{CO}$ data have been used together with $dN_{\text{Aitken}}/dN_{\text{Acc}}$ to
289 retrieve information on the age of the sampled air masses, as discussed in Di Biagio et al. (
290 2015).

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



293 P=1013.25 hPa. In this case, the scattering and absorption coefficients are scaled to STP
294 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.

296 In Table 2 we summarize main information and uncertainties for the different aerosol
297 instruments considered in this study.

298

299 3.2 Boundary layer height estimation

300 The planetary boundary layer (BL) top height has been estimated from meteorological
301 observations (temperature, T, potential temperature, θ , and relative humidity, RH) for each
302 vertical sounding performed during TRAQA flights (see Di Biagio et al., 2015). The
303 boundary layer top height is between 730 and 1500 m, with an average of ~ 1000 m. The
304 location of each SLR, so if it is within the boundary layer or in the free troposphere, has been
305 determined based on the planetary boundary layer top height estimated from the closest
306 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
342 shortwave irradiances over the 0.28-3.0 μm spectral range. The model calculates radiances
343 and irradiances at various atmospheric levels at 400 cm^{-1} spectral resolution between 0.28 and
344 0.5 μm and 100 cm^{-1} resolution between 0.5 and 3 μm . Spectral absorption by principal
345 atmospheric gases (H_2O , CO_2 , O_3 , CH_4 , N_2O , O_2) 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
348 by fixing the solar zenith angle (θ) at 60° , i.e. at about the mean of the diurnal value at the
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
357 shortwave heating rate at the altitude z is also calculated as:



$$358 \quad \frac{\partial T}{\partial t} = -\frac{1}{\rho C_p} \frac{\partial F(z)}{\partial z} \quad (3)$$

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

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

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

374 For all the different cases, the measured scattering coefficient is in the range $16\text{--}73 \text{ Mm}^{-1}$ at
375 450 nm and $8\text{--}30 \text{ Mm}^{-1}$ 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 $\sim 20 \text{ Mm}^{-1}$
377 at 370 nm have been measured. For these two cases also the highest values of the particle
378 concentration in the accumulation mode ($\sim 1700\text{--}2200 \text{ # cm}^{-3}$, not shown) and among the
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.

382 The SAE varies between 0.96 and 1.94, while the AAE varies between 0.92 and 1.65, with an
383 average of ~ 1.20 . The AAE has been not calculated for few cases with very low values of the
384 absorption coefficient (σ_{abs} at $370 \text{ nm} < 1.5 \text{ Mm}^{-1}$). Both the SAE and the AAE obtained in
385 this study fall in the range of variability indicated by several authors to identify
386 pollution/anthropogenic aerosols or pollution mixed with other aerosol types in the
387 Mediterranean basin (SAE $> 1\text{--}1.5$, and AAE $\sim 1\text{--}1.5$; Pace et al., 2006; Toledano et al., 2007;
388 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 $dN_{\text{Aitken}}/dN_{\text{Acc}}$ ratios vary in the range 0.37-
 392 1.02 and 1-50, respectively, for O_3 and CO varying between 24-78 and 69-136 ppbv and
 393 dN_{Aitken} and dN_{Acc} between 320-22500 and 100-2170 # cm^{-3} . $\Delta O_3/\Delta CO$ and the $dN_{\text{Aitken}}/dN_{\text{Acc}}$
 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 $dN_{\text{Aitken}}/dN_{\text{Acc}}$ and low
 397 $\Delta O_3/\Delta CO$, typical of fresh plumes, and cases with low $dN_{\text{Aitken}}/dN_{\text{Acc}}$ and high $\Delta O_3/\Delta CO$,
 398 indicative of more aged air masses (Di Biagio et al., 2015).

399 The summary of these observations suggests that the set of SLRs measurements considered in
 400 this study can be considered representative of a wide range of different atmospheric
 401 conditions occurring over the basin both in terms of sources, loadings, and lifetime for
 402 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 μm and ~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.

413 The measured number size distribution from each SLR has been fitted with multi-mode
 414 lognormal functions:

$$415 \quad \frac{dN}{d \log D_g} = \sum_i \frac{N_{\text{tot},i}}{\sqrt{2\pi} \log \sigma_{g,i}} \left(-\frac{(\log D_p - \log D_{g,i})^2}{2 \log^2 \sigma_{g,i}} \right) \quad (4).$$

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/~craig/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 μm , 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 and** 426 **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
431 (V19_R1 and V30_R2) the single scattering albedo increases with wavelength. For these
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 $\Delta\text{O}_3/\Delta\text{CO}$ (~ 0.37) and a relatively high
437 $dN_{\text{Aitken}}/dN_{\text{Acc}}$ (~ 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,
440 Eastern, and Open sea; ω between 0.88 and 0.98 at 370 nm and 0.83 and 0.99 at 950 nm.

441 The vertical variability of ω , together with $dN_{\text{Aitken}}/dN_{\text{Acc}}$, $\Delta\text{O}_3/\Delta\text{CO}$, 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, $dN_{\text{Aitken}}/dN_{\text{Acc}}$ and SAE decrease with
447 height, with a concurrent slight $\Delta\text{O}_3/\Delta\text{CO}$ 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.



453 Values of the single scattering albedo measured in this study are comparable with values
454 reported at several other sites in the Central and Western Mediterranean region for pollution
455 aerosols (Mallet et al., 2003 and 2013; Meloni et al., 2006; Saha et al., 2008; Di Biagio et al.,
456 2009; Pandolfi et al., 2011). The single scattering albedo from these studies is observed to
457 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.
458 Compared with the literature, larger and lower values are obtained in the present study for
459 few cases mostly influenced by sea spray and local fresh emissions, respectively.

460

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

462 As discussed in the previous section, the single scattering albedo of pollution aerosols shows
463 a relatively large variability. Here we investigate the impact of this variability on the complex
464 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
475 Mie_single.pro IDL routine available at http://www.atm.ox.ac.uk/code/mie/mie_single.html
476 has been used. In the calculations the real part of the refractive index is varied in the range
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
480 values of n and k are also obtained by using as input the observed σ_s , σ_{abs} , and $\frac{dN}{d \log D_g}$ plus
481 or minus one standard deviation on their measurement. The deviations of the values of n and
482 k retrieved in the sensitivity study with respect to those obtained in the first inversions are
483 assumed to correspond to the one standard deviation uncertainty. The estimated uncertainty is
484 <5% for n and ~25-30% for k .



485 The comparison of the measured and calculated σ_s and σ_{abs} are shown in Fig. 6, while the
486 retrieved real and imaginary parts of the refractive index for the different SLRs are reported
487 in Fig. 7. Data in Fig. 7 are also compared to the real and imaginary parts of the refractive
488 index for the single components (insoluble, water soluble, soot, and sea salt) considered in
489 the OPAC model (Optical Properties of Aerosols and Clouds, Hess et al., 1998) to represent
490 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
493 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
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,
498 which also present relatively low values of ω (0.95-0.83). The lowest k , as well as among the
499 lowest n , is instead obtained for V19_R1 ($\omega=0.92-0.96$). The comparison of our data with
500 OPAC values for single components suggests that in most cases particles are composed of a
501 mixing of insoluble and water soluble components, with possible contributions of soot
502 (V27_R1) and 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
511 retrieved n values is larger (1.41-1.70) for ω greater than ~ 0.95 , while as the single scattering
512 albedo decreases the real part converges to $\sim 1.70-1.75$ 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
515 datasets at the seven wavelengths ($R^2=0.83-0.95$ at all wavelengths for the different fits). The
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

522 **4.5 Influence of the single scattering albedo variability on the aerosol direct shortwave** 523 **radiative 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.,
535 2015). However, results will be given as FE so they are independent on the chosen optical
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
548 data). The ω values at 370-950 nm as obtained from experimental data are then extrapolated
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
555 the Mediterranean basin (Meloni et al., 2006; Saha et al., 2008; Mallet et al., 2011).

556 Background stratospheric aerosols (above 12 km) are also taken into account for radiative
557 calculations; optical properties from the OPAC stratospheric aerosol model (Hess et al.,
558 1998) are assumed.

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

567 Results of the radiative transfer simulations are shown in Fig. 9, which reports the FE at the
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 ~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
573 between -160 and -235 (FE_S), -137 and -92 (FE_{TOA}), and +23 and +143 (FE_{ATM}) W m⁻² τ^{-1} for
574 ω varying between its maximum and minimum values. Estimates of the forcing efficiencies
575 in correspondence of the mean of ω are -198, -113, and +85 W m⁻² τ^{-1} at the surface, TOA,
576 and atmosphere, respectively. The corresponding instantaneous shortwave heating rate at the
577 surface varies between 0.2 and 2.0 K day⁻¹ for ω between its maximum and minimum.

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



584 scattering albedo of the particles between its maximum and minimum ($\Delta\omega=0.1-0.2$ at the
585 different wavelengths) determine about a 50% strengthening of the direct shortwave radiative
586 effect at the surface, and a reduction of $\sim 30\%$ the effect at the TOA. Consequently, the
587 atmospheric FE may vary up to an order of magnitude. These results thus highlight the
588 sensitivity of the DRE on the absorptivity properties of the particles, as well as the
589 importance of accurately reproducing the single scattering albedo of aerosols to correctly
590 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
596 forcing efficiency of ~ -200 and $-164 \text{ W m}^{-2} \tau^{-1}$ at the surface and TOA at solar zenith angles
597 of $50^\circ-60^\circ$ for mixed aerosols (pollution plus sea salt particles). They estimate an increase in
598 absolute value of FE_S 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
600 about 10-40%. The observations obtained in this study fall in the range of variability reported
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 FE_S 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
605 absolute value compared to data reported for continental Europe by Horvath et al. (2002),
606 who estimated a FE_S of $\sim -164 \text{ W m}^{-2} \tau^{-1}$ and a FE_{TOA} of $-50 \text{ W m}^{-2} \tau^{-1}$ for polluted aerosols
607 with $\omega=0.90$ at 520 nm, thus comparable with our mean values of single scattering albedo for
608 pollution aerosols.

609

610 5. Conclusions

611 In this study we have presented measurements of the spectral optical properties (scattering
612 and absorption coefficients and single scattering albedo) and particle size distributions for
613 pollution aerosols obtained over the remote sea in the Western Mediterranean basin during
614 the TRAQA campaign in summer 2012. The set of observations analysed in this study can be
615 assumed to be representatives of a wide range of different conditions that can be observed
616 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
621 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.
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.

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

639 This observed variability on ω has a large influence on the direct shortwave radiative effect
640 of pollution aerosols at the surface, TOA, and within the atmosphere. For instance, a change
641 of up to an order of magnitude (from +23 to +143 W m⁻² τ^{-1} at 60° solar zenith angle) in the
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



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

657

658 **Author contributions**

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

665

666

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681

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863 **Tables**

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

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Flight number	SLR_ID	Date	Time start-stop	Altitude (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	$\pm 10\%$ (concentration)	
Aerosol size distribution	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	$< \pm 25\%$ (diameter optical to geometric conversion) $\pm 15\%$ (concentration) (e.g., Highwood et al., 2012)	Aerosol concentration underestimated by 50% between 0.4 and 1.0 μm
	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 $\sim 12\ \mu m$ diameter)	$< \pm 25\%$ (diameter optical to geometric conversion) $\pm 10\%$ (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 $\sim 12\ \mu m$ diameter	$< \pm 10\%$ 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 $\sim 12\ \mu m$ diameter	11-70% variable at the different wavelengths	Data available only for 60% of SLRs



881 **Table 3.** Lognormal mode parameters of the measured aerosol size distribution (total aerosol
 882 number concentration, N_{tot} , median diameter, D_g , and geometric standard deviation, σ_g). Data
 883 corresponds to SLRs below ~350 m altitude. Diameters are given in microns and number
 884 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	
	σ_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		
	σ_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	
	σ_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	
	σ_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
	σ_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	
	σ_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	
	σ_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
	D_g	0.14	0.23	0.38	0.50	1.57	3.75	7.99
	σ_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
 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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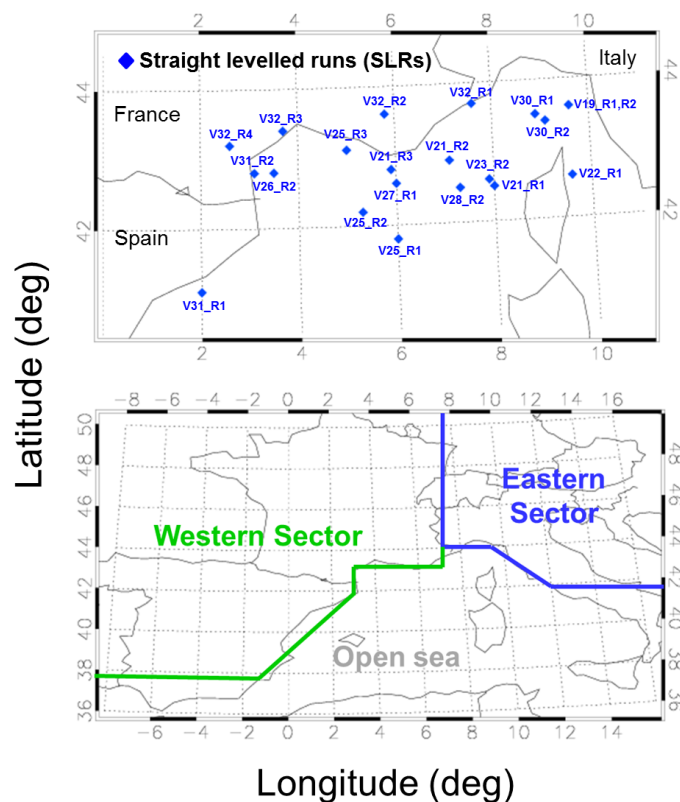
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895 **Figures**

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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.
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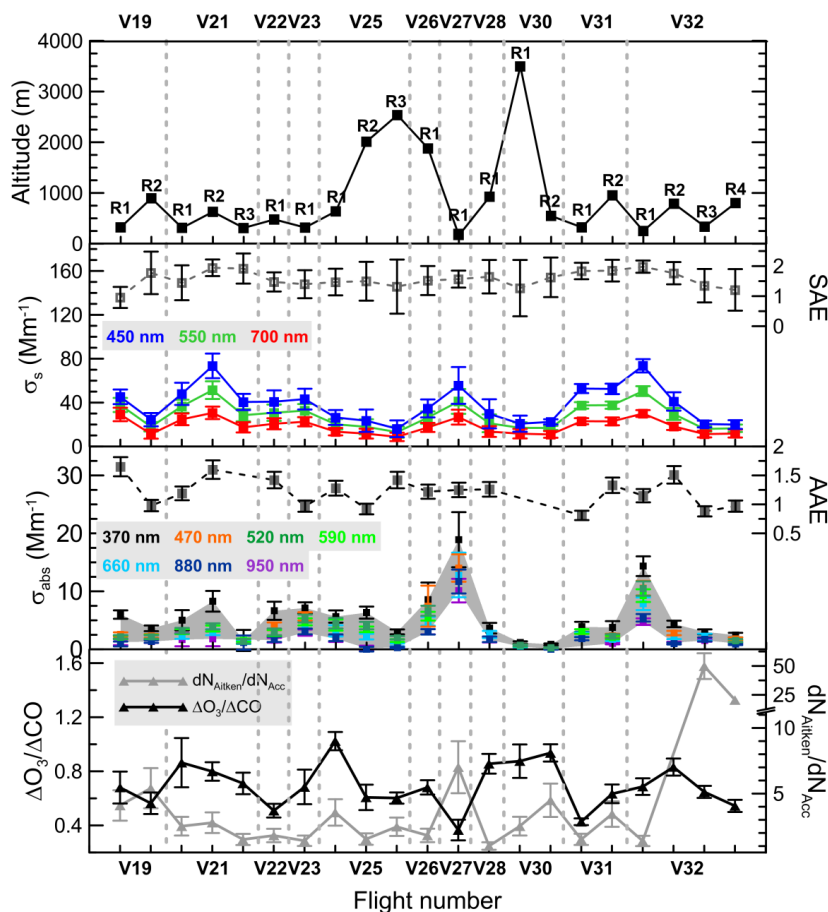


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910 **Figure 2.** Averages over the different TRAQA straight levelled runs (SLRs) of the measured:
 911 altitude, spectral scattering coefficient (σ_s ; 450, 550, and 700 nm), scattering Ångström exponent
 912 (SAE), spectral absorption coefficient (σ_{abs} ; 370, 470, 520, 590, 660, 880, and 950 nm), absorption
 913 Ångström exponent (AAE), ozone enhancement factor ($\Delta\text{O}_3/\Delta\text{CO}$) and Aitken-to-accumulation
 914 ratio ($dN_{\text{Aitken}}/dN_{\text{Acc}}$). Uncertainties indicate the 1- σ standard deviation. The x-axis indicates the
 915 flight number (19 to 32 for flights V019 to V032); each point for the same flight number represents
 916 a different SLR.

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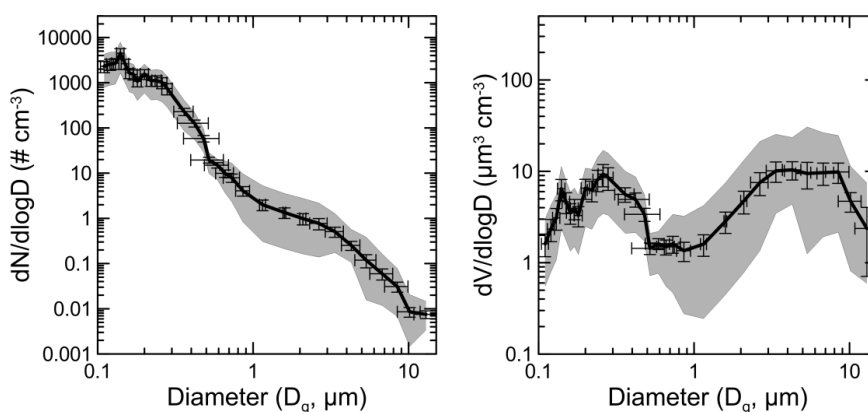


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924 **Figure 3.** Number size distributions (left panel) and volume size distributions (right panel)
925 measured over the different SLRs for the TRAQA flights. Data corresponds to measurements
926 performed within the boundary layer at altitudes 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

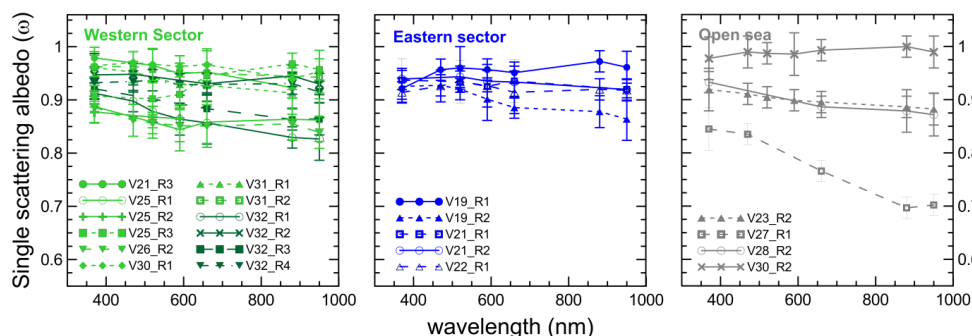
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934 **Figure 4.** Spectral single scattering albedo at seven wavelengths between 370 and 950 nm
935 calculated from nephelometer and aethalometer measurements for the different SLRs within
936 pollution layers. Data are separated based on the different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

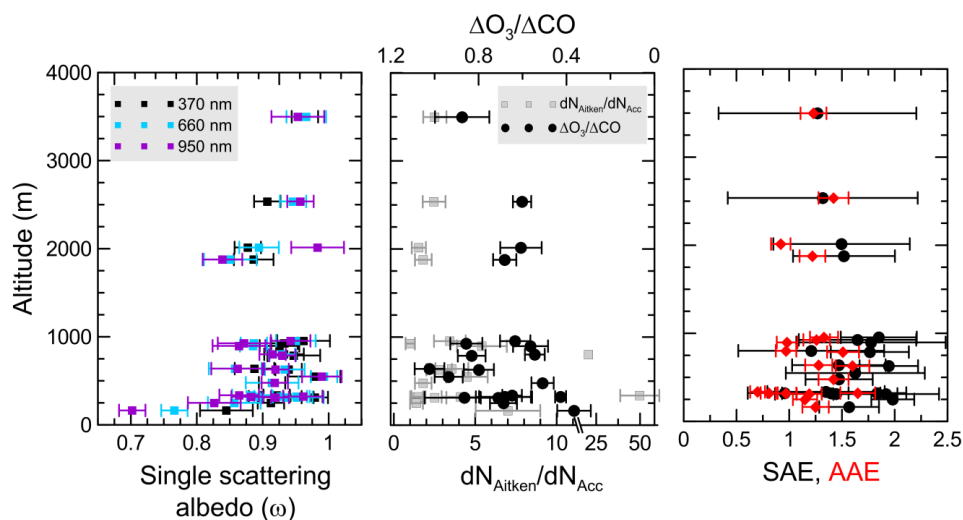
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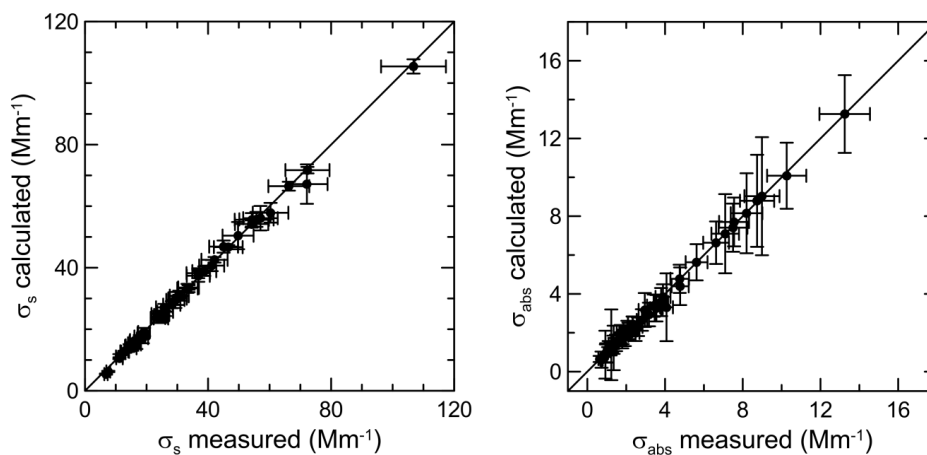


942 **Figure 5.** Single scattering albedo (370, 660, and 950 nm), ozone enhancement factor ($\Delta O_3/\Delta CO$),
 943 Aitken-to-accumulation ratio (dN_{Aitken}/dN_{Acc}), and scattering (SAE) and absorption Ångström
 944 exponent (AAE) versus height for all analysed SLRs cases.
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949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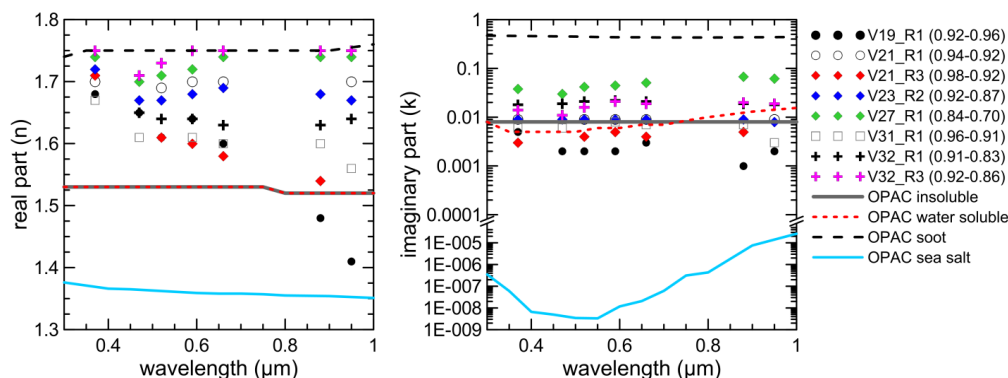


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955 **Figure 7.** Spectral real (n , left panel) and imaginary (k , right panel) parts of the complex refractive
 956 index obtained by optical closure for the 8 selected case studies. For sake of clarity, uncertainties on
 957 n and k are not reported 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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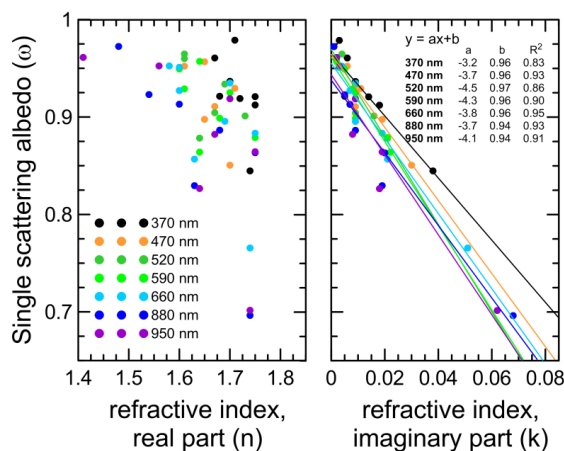


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966 **Figure 8.** Spectral single scattering albedo plotted against the real (left panel) and the imaginary
 967 (right panel) parts of the complex refractive index.

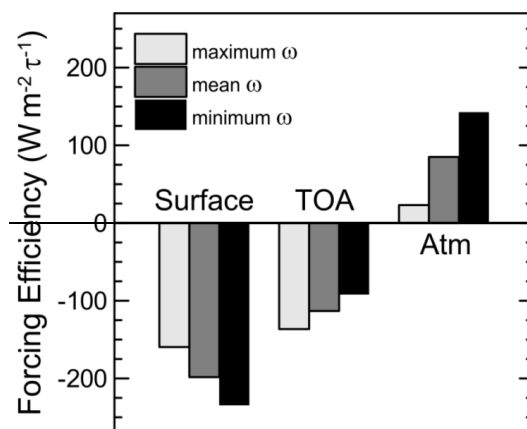
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970 **Figure 9.** Aerosol shortwave forcing efficiency at 60° solar zenith angle calculated at the surface,
971 TOA, and within the atmosphere for the maximum, mean, and minimum of the single scattering
972 albedo (ω) observed in this study (Table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