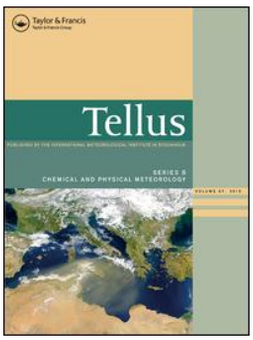

Tellus B: Chemical and Physical Meteorology

ISSN: (Print) 1600-0889 (Online) Journal homepage: http://www.tandfonline.com/loi/zelb20

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To cite this article: Ulrike Dusek, David S. Covert, Alfred Wiedensohler, Christian Neusúss & Diana Weise (2004) Aerosol number to volume ratios in Southwest Portugal during ACE-2, Tellus B: Chemical and Physical Meteorology, 56:5, 477-491, DOI: 10.3402/tellusb.v56i5.16461

To link to this article: https://doi.org/10.3402/tellusb.v56i5.16461

Published online: 18 Jan 2017.

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TELLUS

Aerosol number to volume ratios in Southwest Portugal during ACE-2

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(Manuscript received 30 July 2003; in final form 17 February 2004)

ABSTRACT

Past studies have indicated that long-term averages of the aerosol number to volume ratios (defined as the number of particles larger than a certain diameter divided by the particle volume over some range less than 1 μm) show little variability over the Atlantic. This work presents number to volume ratios (R) measured during the ACE-2 experiment on the land-based Sagres field site located in Southwest Portugal. The values of R measured in Sagres compare reasonably well with previous measurements over the Atlantic. The main emphasis of this work is therefore to investigate more closely possible reasons for the observed stability of the number to volume ratio. Aerosol number size distributions measured in Sagres are parametrized by the sum of two log-normal distributions fitted to the accumulation and to the Aitken mode. The main factor that limits the variability of R is that the parameters of these log-normal distributions are not always independent but show some covariance. In polluted air mass types correlations between parameters of the Aitken and accumulation mode are mostly responsible for stabilizing R. In marine air mass types the variability of R is reduced by an inverse relationship between the accumulation-mode mean diameter and standard deviation, consistent with condensational processes and cloud processing working on the aerosol. However, despite this reduction, the variability of R in marine air mass types is still considerable and R is linearly dependent on the number concentration of particles larger than 90 nm. This partly due to a tail of Aitken-mode particles extending to sizes larger than 90 nm.

1. Introduction

The modification of cloud albedo and lifetime by an increase in anthropogenic aerosol particles in the atmosphere is generally called the indirect effect of aerosols on climate. Marine stratus clouds are considered to be of special importance to the effect of aerosols on cloud albedo. They cover large fractions of the world's oceans, where the aerosol concentrations are low, which makes the cloud albedo especially sensitive to an increase in particle number concentration. Droplets usually nucleate on aerosol particles larger than 70–120 nm at supersaturations typical for marine stratus cloud systems (e.g. Hoppel et al., 1994). It is thus important to have a good estimate of the number concentration of particles in that size range to model the indirect effect of aerosols on climate.

Most of the chemical transport models used to estimate the global distribution of aerosols are only able to predict aerosol mass concentration. The particle number is diagnosed by prescribing or parametrizing a size distribution (e.g. Chuang and Penner, 1995), or the increase in cloud droplets due to anthropogenic aerosol is parametrized directly using empirical relationships (e.g. Boucher and Lohmann, 1995). Only recently have models become available that predict the aerosol size distribution (e.g. Ghan et al., 2001a,b; Adams and Seinfeld, 2002).

Empirical studies of the aerosol number to volume ratio (R, defined as the number of particles larger than a specified, critical diameter, d_c, divided by the submicrometre aerosol volume) are useful for both kinds of models. For models that predict only aerosol mass, typical values of R could provide an empirical link between aerosol mass and the number of particles large enough to nucleate cloud droplets. For models that predict the size distribution, a comparison of modelled and empirical number to volume ratios can serve as an important verification of the predicted size distributions.

Number to volume ratios of the aerosol over the Atlantic Ocean have been studied in the past (e.g. Hegg and Kaufman, 1998; Hegg and Jonsson, 2000; Hegg and Russell, 2000; VanDingenen et al., 2000, and references therein). Depending on the lower and upper cut-off diameters of the instruments used for the size distribution measurements, the definition of R in those

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past studies has not always been the same, but some general conclusions can be summarized. Long-term averages of R have been found to be surprisingly constant (e.g. Hegg and Jonsson, 2000; Hegg and Russell, 2000, and references therein) and are comparable between several studies. Some studies indicate that the relationship between submicrometre aerosol number and volume is approximately linear (Hegg and Kaufman, 1998).These findings support the use of a constant number to volume ratio to derive particle concentrations in large-scale models, even though they are strictly applicable only for the region in which they were acquired.

However, previous results also indicate that there are more fundamental reasons why R is relatively confined in regions far from local pollution sources. VanDingenen et al. (1999) find that dilution by entrainment is the main process that explains a linear relationship between aerosol number and volume and thus constant R. Assuming that the size distribution of the aerosol is log-normal, Hegg and Russell (2000) inferred that a constant R of approximately 200 μm^{-3} implies an inverse relationship between mean diameter and standard deviation. This inverse relationship is shown to be consistent with condensational growth as the main process acting on the size distribution. VanDingenen et al. (2000) found that a simple analytical model for the relationship between submicrometre aerosol number and volume can explain observed number to volume ratios and especially the dependence of R on aerosol volume. The modelled number to volume ratios are mostly governed by entrainment and coagulation, which suggests, in contrast to the results of Hegg and Russell (2000), that these two processes mostly determine the aerosol size distribution over the Atlantic.

In the light of such different conclusions it is useful to investigate more closely why the number to volume ratio of aerosols is relatively confined. The conclusions of the above studies are mainly drawn from comparing model results or theoretical, monomodal size distributions with the observed number to volume ratios. This work builds on the theoretical considerations of Hegg and Russell (2000), but takes a more empirical approach in comparing these theoretical considerations with actually measured size distributions. Bimodal size distributions are considered to provide a more realistic link between aerosol processes and the number to volume ratio. Additionally, the data are analysed separately for different air mass histories to disentangle the effect of aerosol processes on the size distribution from the effects of different aerosol origins.

The aerosol measurements used in this paper were made as a part of the second Aerosol Characterization Experiment (ACE-2) (Raes et al., 2000; Verver et al., 2000). ACE-2 was one of several large-scale aerosol characterization experiments designed to understand aerosol radiative forcing in key areas of the globe and was held in the subtropical North Atlantic region during June and July 1997. The data set used in this study was measured in Sagres, in the southwest of Portugal. It is presented in an overview figure in VanDingenen et al. (2000), but not further analysed in that work.

In previous studies R has been defined in various ways, often limited by the size range of the instrument used to measure the size distribution. For example, in Hegg and Jonsson (2000) and Hegg and Russell (2000) R is defined as the number of particles between 120 nm and 3000 nm divided by the volume in the same size range. VanDingenen et al. (2000) define R as the number of particles between 80 nm and 500 nm divided by the volume from 0 to 500 nm. Since the size distributions in Sagres were measured from 3 to 5000 nm, the definition of R was not subject to instrumental constraints. Thus, we defined R as the number of particles between 90 and 1000 nm divided by the total submicrometre volume (between 3 and 1000 nm). The upper cut-off was chosen because 1000 nm roughly separates the fine and coarse fractions of the aerosol that have different generation mechanisms and are often modelled separately. The lower cut-off diameter of 90 nm is consistent with the location of the minimum in the number size distribution between Aitken and accumulation modes in marine air mass conditions in Sagres during ACE-2. This minimum is usually attributed to cloud processing of aerosol and is a measure of the minimum size of the particles that are activated to cloud droplets (e.g. Hoppel et al., 1994; Cantrell et al., 1999). The lower volume integration limit of 3 nm was used to be consistent with models that usually calculate the whole submicrometre volume concentration.

The definition of cut-off diameters has strong implications for the numerical values of R. The number to volume ratios reported in Hegg and Jonsson (2000) and Hegg and Russell (2000) will be lower than in this study because they include larger particles that contribute mostly to the aerosol volume. The number to volume ratios reported by VanDingenen et al. (2000) will be higher than in this study because of inclusion of smaller particles and the omission of particles larger than 500 nm that can contribute significantly to the submicrometre volume. However, the different cut-offs also have consequences for how different processes affect the number to volume ratio. In the case of Hegg and Jonsson (2000) and Hegg and Russell (2000) initially small particles that grow larger than the 120 nm lower cut-off size (either by coagulation, condensation or cloud processing), more evenly increase both the number and the volume concentration used to calculate R. In this work and in the work of VanDingenen et al. (2000) particles that grow larger than the cut-off size will increase the number concentration at the same rate as in Hegg and Jonsson (2000) and Hegg and Russell (2000). However, the volume concentration used to calculate R will increase less (or not at all, if the particles are growing by coagulation). Additionally, in the case of VanDingenen et al. (2000) particles growing larger than the upper cut-off of 500 nm could potentially move the volume out of the size range and thus increase R. These differences should be kept in mind for comparisons between the results of those studies.

2. Number to volume ratios of log-normal size distributions

The size distribution of the atmospheric aerosol can usually be approximated with good accuracy by log-normal distributions. This is also true for aerosol size distributions measured during the ACE-2 experiment in Sagres. Therefore, the log-normal size distribution is chosen as a model distribution in the following theoretical considerations. However, any distribution that approximates the aerosol size distributions similarly well and has a measure of the maximum and width of the distribution should give qualitatively similar results.

The formulation of R in terms of a log-normal size distribution follows the same principle as Hegg and Russell (2000), but with one important difference: while Hegg and Russell (2000) investigated the relationship of the total number and volume of a log-normal distribution, the discussion here explicitly takes into account the cut-off diameter. This is necessary for a quantitative comparison with experimental data. Considering the total number instead of $N > 90$ would lead to differences in modelled versus measured values of R greater than 100% for size distributions with a mean diameter less than 90 nm.

For a log-normal distribution the number of particles larger than a cut-off diameter d_c, can be calculated by integrating the number distribution from d_c to infinity. This results in:

$$N(d > d_c) = N_0 \left[\frac{1}{2} - \frac{1}{2} \mathrm{erf} \left(\frac{\ln (d_c/d_g)}{\sqrt{2} \ln \sigma_g} \right) \right], \quad (1)$$

where N_0 is the total number concentration, d_g is the number mean diameter and σ_g is the geometric standard deviation of the distribution. erf is the so-called error function, the cumulative normal distribution. If $d_c = 0$, then erf(− inf) = − 1 and $N(d > 0) = N_0$.

To obtain the number to volume ratio, we divide $N(d > d_c)$ by the total volume concentration V_0. V_0 can be expressed in terms of the diameter of average volume (d_v), which is in turn related to d_g by the second Hatch–Choate equation (see Hinds, 1999, p. 99):

$$V_0 = N_0 \frac{\pi}{6} d_v^3 = N_0 \frac{\pi}{6} \left[d_g \exp \left(\frac{3}{2} \ln(\sigma_g)^2 \right) \right]^3 = N_0 \frac{\pi}{6} d_g^3 \exp \left(\frac{9}{2} \ln(\sigma_g)^2 \right). \quad (2)$$

Thus, R is given as:

$$R = \frac{N(d > d_c)}{V_{tot}} = \frac{6}{\pi d_g^3 \exp \left[(9/2) \ln {\sigma_g}^2 \right]} \times \left[\frac{1}{2} - \frac{1}{2} \mathrm{erf} \left(\frac{\ln (d_c/d_g)}{\sqrt{2} \ln \sigma_g} \right) \right]. \quad (3)$$

The dependence of R on the parameters of a single-mode, log-normal size distribution is shown in Fig. 1. It is notable that if a lower cut-off diameter for number is included, R cannot become arbitrarily large but has an upper limit (Fig. 1a). Thus, just the assumption that the aerosol is log-normally distributed, results in an upper limit for R. The reason for this is as follows: if the mean diameter of the log-normal size distribution is much smaller than d_c, only the large size tail of the log-normal distribution lies in the size range greater than d_c. R initially increases

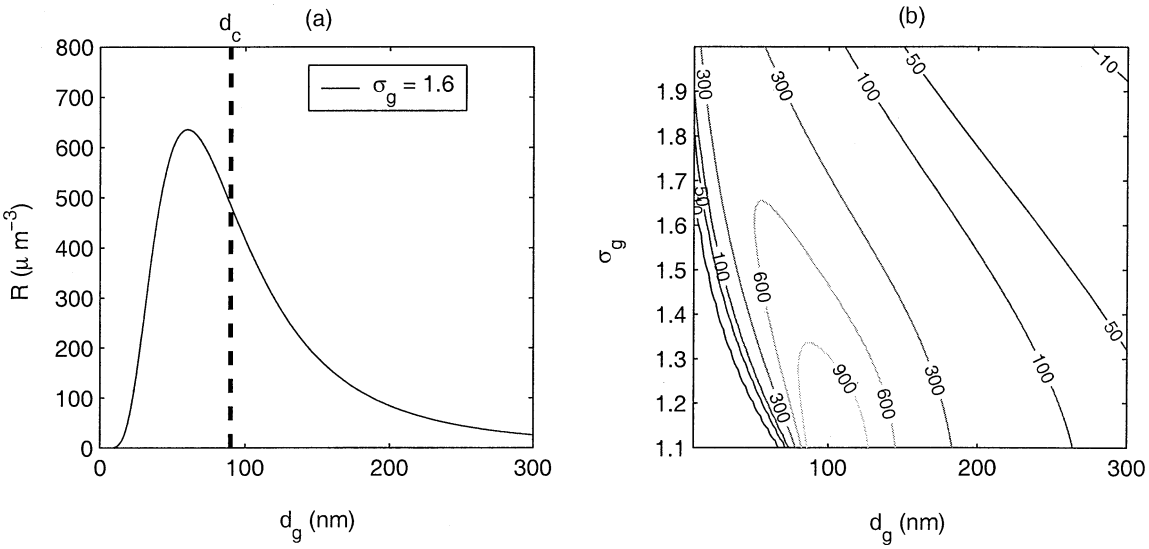

Fig 1. Number to volume ratio (R) of a log-normal distribution. (a) Dependence of R on the geometric number mean diameter d_g. The cut-off diameter, $d_c = 90$ nm, is shown as a dotted line. (b) Contour plot showing the range of R for log-normal size distributions with mean diameters d_g between 10 and 300 nm and geometric standard deviations σ between 1.2 and 2.5. Again the cut-off diameter d_c is 90 nm.

with increasing mean diameter, d_g, because the number concentration of particles exceeding 90 nm increases more rapidly than the total volume concentration. R reaches a maximum at a diameter smaller than d_c and then starts to decrease. In this regime the increase in d_g increases the total volume concentration more strongly than the number of particles whose diameters exceed 90 nm.

In Fig. 1b this one-dimensional analysis is generalized as a contour plot of R for wide ranges of both d_g and of σ_g comparable to atmospheric observations. The number to volume ratio of log-normal size distributions with d_g between 10 and 300 nm and σ_g ranging from 1.2 to 2.5 can be seen to vary between 10 and 1000 μm^{-3}. The increase in R with increasing d_g for small particle sizes and the decrease at larger particles sizes is evident regardless of the standard deviation of the size distribution. However, the location of the maximum shifts to smaller particle diameters with increasing standard deviation. For d_g larger than d_c, R decreases with increasing standard deviation since an increase in σ_g shifts more particles to larger sizes where they contribute more strongly to the volume concentration. For d_g smaller than d_c the dependence of R on σ is more complex.

The assumption that the particle size distribution has log-normal shape implies the existence of an upper limit to possible values of R. This maximum (R_{max}) is shown in Fig. 2 as a function of σ_g for several possible cut-off diameters d_c. The maximum possible R decreases with increasing standard deviation as well as with increasing cut-off diameter. The dependence of the maximum value of R on d_c is quite pronounced. A cut-off diameter of 120 nm limits R to values less than 500 μm^{-3} and to less than 200 to 250 μm^{-3} for a σ_g between 1.6 and 1.8. Similarly for a d_c of 90 nm the R values become 1200 and 550 to 650, respectively.

The next sections compares measured number to volume ratios with these theoretical considerations. If R from measurements is found to be more confined than the upper limit of roughly 600–1000 μm^{-3}, suggested by Fig. 2 for reasonable size distributions, some additional factors must be taken into account that could be responsible for the stability of R. For example the size distribution could be relatively invariant and mostly be governed by dilution processes as suggested by VanDingenen et al. (1999). Another possibility is an inverse dependence of σ on d_g as suggested by Hegg and Russell (2000) and illustrated in Fig. 1b. If the standard deviation of the size distribution decreases as the mean diameter increases R can be confined or even held constant over large ranges of mean diameter; or the size distribution could be bimodal and processes not considered in this simple theoretical example could be responsible for the stability of R.

3. Observed number to volume ratios in Sagres during ACE-2

The number to volume ratios of the aerosol are analysed separately for the four main air mass conditions encountered during the ACE-2 experiment. Thus, the influence of pollution on the number to volume ratio can be analysed. Moreover, relationships between parameters of the aerosol size distribution can be more easily observed within a particular air mass type, since different air masses are often associated with different mean states of the aerosol or different processes that act on the aerosol. This section presents actual observations of R in Sagres during the ACE-2 measurement period. During the ACE-2 field experiment the measurement site at Sagres was influenced by several different air mass types. For the first half of the experiment relatively clean air coming from the North Atlantic Ocean prevailed. During the second half of the experiment polluted air masses originating over the European continent reached Sagres more frequently.

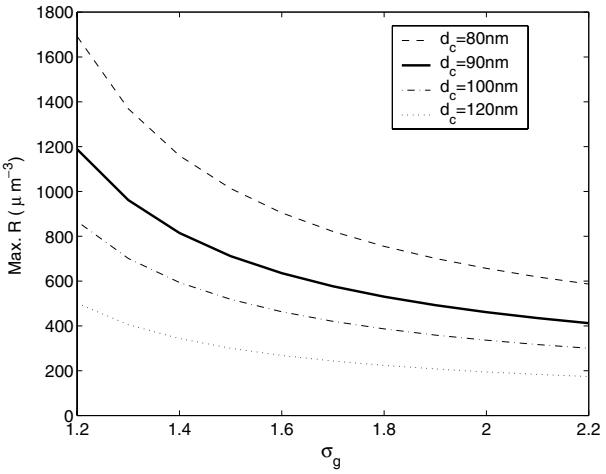

Fig 2. Upper limit of R for a log-normal size distribution as a function of geometric standard deviation σ_g.

3.1. Experimental

Aerosol number-size distributions in Sagres during ACE-2 were measured using a twin differential mobility particle sizer (TDMPS) (Birmili et al., 1999). Two Vienna-type differential mobility analysers (DMAs) (Winklmayr et al., 1991) of different lengths, a DMA and an ultrafine DMA (UDMA), were used to measure aerosol particles from 20–800 nm and from 3–20 nm respectively. Both DMAs select the common particle size of 20 nm at the beginning of each size distribution measurement. Subsequently, the voltage is decreased stepwise in the UDMA to reduce the size of particles in the sample stream and increased in the DMA to increase the particle size. The particles are counted using a condensation particle counter (CPC) and an ultrafine CPC respectively at each voltage. The final number-size distributions are derived by the inversion routine of Stratmann and Wiedensohler (1996). The particle size distribution above 800 nm is measured using an aerodynamic particle sizer. The size distribution measurements are described in more detail in Neusüss et al. (2000).

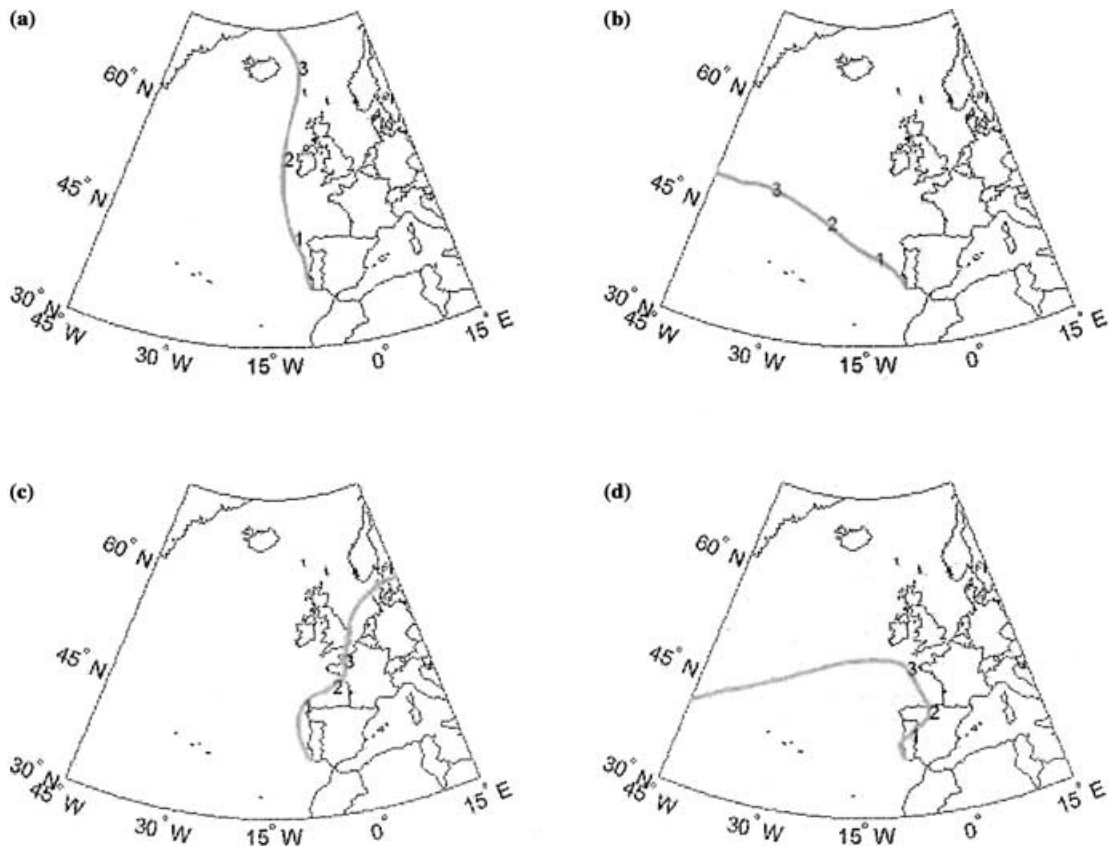

Fig 3. Typical air mass back trajectories associated with the 4 main air mass types during ACE-2: (a) marine Arctic conditions, (b) marine Atlantic conditions, (c) aged pollution and (d) recent pollution.

Aerosol volume-size distributions are derived from the number-size distributions assuming a spherical particle shape. The number to volume ratios are calculated by dividing the number concentration of particles with a diameter between 90 and 1000 nm ($N > 90$) through the corresponding submicrometre volume concentration. Submicrometre mass concentrations derived from DMPS measurements were previously compared with gravimetrically determined mass concentrations (Neusüss et al., 2000). The agreement was satisfactory despite uncertainties in the particle densities, which suggests that the DMPS measurements are suitable for deriving the particle volume.

3.2. Main air mass conditions

Trajectories for the relatively clean time periods originated over the North Atlantic or the Arctic Ocean. In many cases, air masses approached the Iberian Peninsula to the north of Sagres and the boundary layer flowed south along the coast to the Sagres measurement site. These cases are not included in the marine data set to avoid the influence of contamination from local sources along the coast. Trajectories for the polluted time periods are subdivided into two categories according to the distance, time and pathway from the source region. Air masses containing aged pollution originated over France or Great Britain and flowed out over the Atlantic, where they spent several days before reaching Sagres. Air masses containing more recent pollution crossed the Iberian Peninsula immediately before arriving at Sagres from inland.

Figure 3 shows typical 6-day air mass back trajectories associated with the four main air mass types encountered in Sagres: marine Arctic, marine Atlantic, aged pollution and recent pollution. The location of the air mass 1, 2 and 3 d before reaching Sagres are indicated along the trajectory. Arctic air mass trajectories (Fig. 3a) originated above the Arctic Circle and the air mass moved rapidly southward to the measurement site at Sagres. The air mass travelled from latitudes of above 65°N to Sagres in only 3 d. Subsidence was evident during that transport towards Sagres from roughly 1000 m at 3 d from Sagres. Atlantic air mass trajectories (Fig. 3b) originated over the Atlantic and usually spent more time in the marine boundary layer, before reaching Sagres. On some occasions the air travelled for some distance close to the coast, where it might have been influenced by pollution from regional sources or ships. Air mass back trajectories typical for aged pollution are shown in Fig. 3c. The air mass moved from the continent to the eastern Atlantic approximately 2 d before arriving at Sagres. The typical aging time of the aerosol in

European outflow conditions was thus approximately 2 d. Figure 3d shows typical air mass back trajectories for recent pollution. The trajectory originated over the ocean, but spent approximately 2 d over land before reaching Sagres.

3.3. Number to volume ratios in different air mass types

The average number to volume ratio over all air mass types during the ACE-2 field experiment in Sagres was 220 ± 80 μm^{-3}. This is somewhat higher than the number to volume ratios of 168 to 206 μm^{-3} found by Hegg and Jonsson (2000), Hegg and Russell (2000) and Hegg and Kaufman (1998). However, due to different methods for calculating R the numerical values of R are not strictly comparable. The larger cut-off diameters for N and V used in those studies (120 nm lower and 3 μm upper cut-off diameter) lowers the particle number concentration and at the same time increases the particle volume concentration, thereby reducing R.

One reason for the relatively high average number to volume ratio measured in Sagres is the proximity of pollution sources. For several days during the ACE-2 experiment the air flow crossed the Iberian Peninsula before reaching Sagres from inland. These air masses brought relatively recent pollution from inland to the measurement site. During these time periods R is significantly higher ($\bar{R} = 340 \pm 50$ μm^{-3}) than during time periods not influenced by recent pollution ($\bar{R} = 190 \pm 70$ μm^{-3}). R is particularly low in air masses containing aged pollution ($\bar{R} = 170 \pm 30$ μm^{-3}). This dependence of R on the air mass history suggests that generally number to volume ratios are quite high (around 350 μm^{-3}) near pollution sources. After the aerosol ages for a few days over the Atlantic, R decreases quickly to a lower (background) value while both the total number and the total volume are still significantly higher than in background conditions. R seems to relax much more quickly to background conditions than either number or volume concentration of the aerosol. VanDingenen et al. (2000) modelled a decrease of R to background values with a similar timescale of a few days for the ACE-2 experiment.

The frequency distributions of R are illustrated in Fig. 4. The distributions are similar in Arctic and Atlantic air mass conditions. The mean value of R is about 180 μm^{-3} and 90% of the values fall between 100 and 250 μm^{-3}. In aged pollution R has approximately the same mean value, but is significantly less variable with approximately 90% of the values lying between 110 and 200 μm^{-3}. In recent pollution R is higher than in the other air mass conditions with a mean of 340 μm^{-3} and a [5, 95] percentile range of 250 to 425 μm^{-3}. Although VanDingenen et al. (2000) do not give mean values of R in their paper, the range of R can be estimated from an overview figure that includes all air mass types in Sagres. Their R varies between 150 and 600 μm^{-3} and is thus skewed to higher values, which may reflect to their definition of cut-off diameters.

The range of R is in all cases relatively constrained compared with the range theoretically possible for a log-normal size distribution (see Fig. 1). Except for cases of recent pollution observed R is confined between 100 and 300 μm^{-3}, a much narrower range than suggested by Fig. 1b. This suggests that either the aerosol size distribution is almost invariant throughout the ACE-2 experiment or that there is a compensating relationship between mean diameter and standard deviation of the size distribution, as suggested by Hegg and Russell (2000). The first option can be excluded, since the size distribution has been shown to vary considerably during the ACE-2 experiment. The second option will be investigated in the following sections.

4. Variability and stabilization of number to volume ratios in marine air mass types

4.1. Observed variability of R

The marine air masses are characterized by air mass back trajectories from the Arctic or Atlantic Ocean. In those conditions the number to volume ratios average around 200 μm^{-3} which is comparable to the overall average number to volume ratio that we observed in Sagres. However, as can be seen in Figs 4a and 4b R is more variable than in polluted conditions. The reasons for this higher variability are investigated in this section.

The submicrometre particle number size distributions in marine air mass types are bimodal, consisting of an Aitken and an Accumulation mode, separated by a minimum around 80–100 nm (see Fig. 5). In Arctic air mass types the Aitken-mode particles do not contribute very much to the number of particles larger than 90 nm. In Atlantic air mass conditions the Aitken mode has larger mean diameters and a tail of Aitken-mode particles sometimes extends to particle sizes larger than 90 nm. In both cases the Aitken-mode particles do not account for a significant fraction of the total aerosol volume. It can thus be expected that R is mostly determined by the number to volume ratio of accumulation-mode particles, with occasional increases in the number concentration of particles larger than 90 nm ($N > 90$) due to an increase in the diameter or the number concentration of the Aitken mode.

In marine air masses the variability in R is mainly due to the fact that $N > 90$ varies much more strongly than V. Therefore R itself is to a first order linearly dependent on $N > 90$ (Figs 6a and b). Approximately 70% of the variance in R can be explained by a linear dependence of R on $N > 90$ in Arctic air mass types and approximately 50% of the variance in Atlantic air mass types. The regression equations are given in Fig. 6. They are only valid for this temporally and regionally limited data set. There are no statistically significant relationships between R and the total volume concentration. A possible interpretation of the slope and offset can be explained by the example of a single-mode log-normal size distribution: If such a size distribution were invariant, then

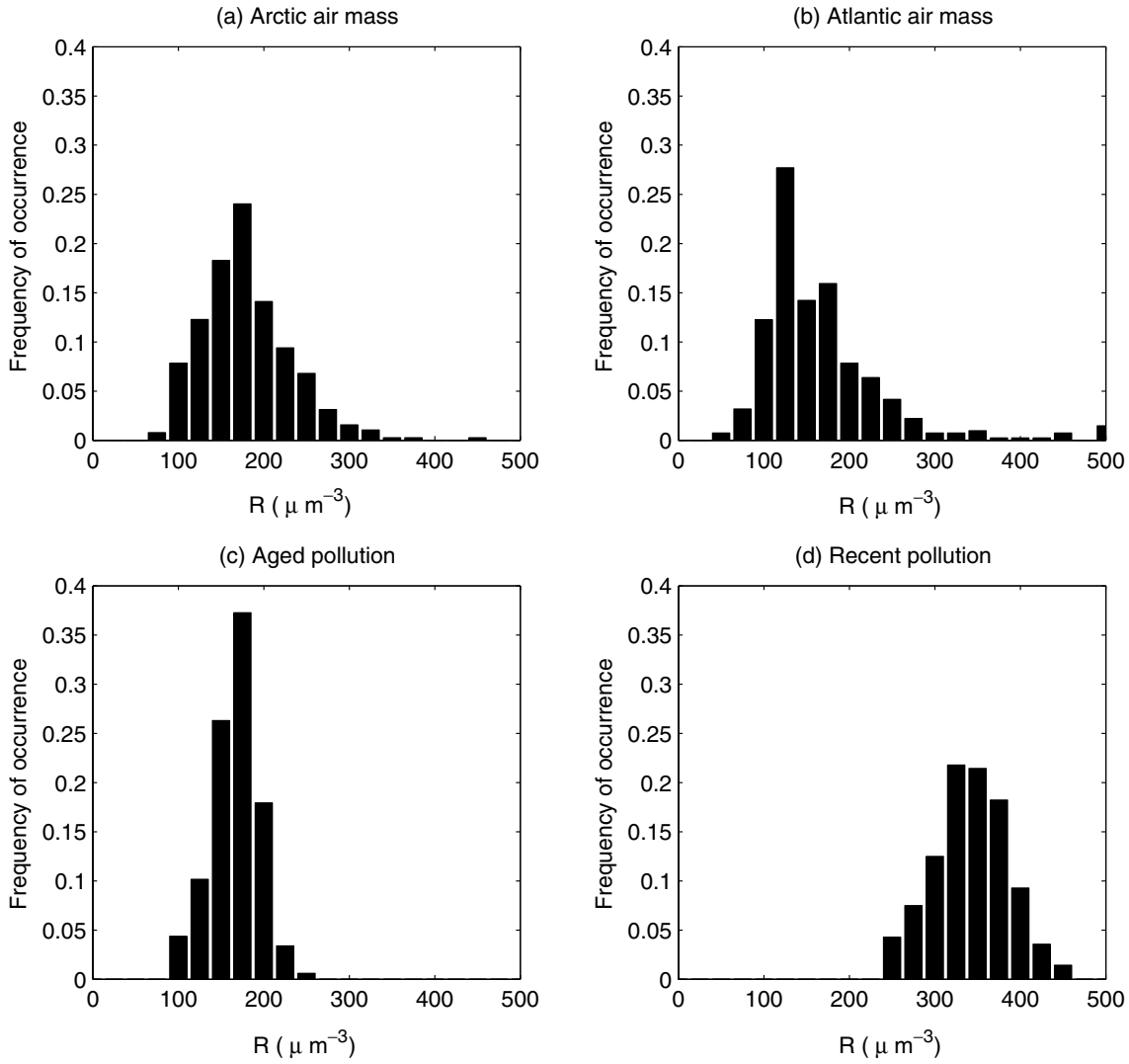

Fig 4. Frequency distribution of R in different air mass conditions.

as the aerosol was further and further diluted the relationship between R and $N > 90$ would be represented by a horizontal line in Figs 6a and b. A slope different from 0 means that a change in $N > 90$ also implies a change in the aerosol size distribution. In marine air masses R decreases with decreasing number concentration. A comparison with Fig. 1b shows that, considering one variable at a time, this could either mean an increase in the mean diameter or standard deviation of the distribution, unless the mean accumulation-mode diameter is unrealistically small, $<$100 nm. Note that according to Fig. 1b an offset very close to 0 would imply either unrealistically large or small mean diameters and standard deviations of the size distribution at infinite dilution, i.e. for practical considerations $R_{\min}$ is approximately 50 μm^{-3}.

The number concentration $N > 90$ consists both of accumulation-mode particles ($N > 90_{\text{acc}}$) and a tail of Aitken-mode particles extending to sizes larger than 90 nm ($N > 90_{\text{ait}}$) (see Fig. 7). This addition of small particles can increase $N > 90$ without changing the volume significantly, which acts to increase the variability of R. In Atlantic air mass types a linear dependence of R on $N > 90_{\text{ait}}$ explains more than 40% of the variance of R, which is almost as high as the 50% explained by dependence of R on all $N > 90$ (see Fig. 6). This highlights the role of Aitken-mode particles in making R more variable. In Arctic air mass types, however, where the Aitken-mode particles do not contribute much to $N > 90$, the accumulation-mode particles themselves cause much of the variability in R.

Figure 7 shows that in these Arctic air mass types the volume concentration of accumulation-mode particles is rather constant with respect to d_{acc}, whereas the number concentration decreases with increasing d_{acc}. Several processes could contribute to this in varying degrees. Coagulation is not a likely

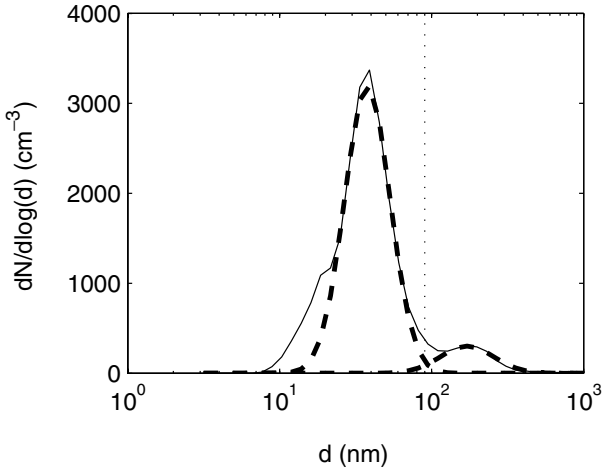

Fig 5. Typical number size distribution for marine air mass types.

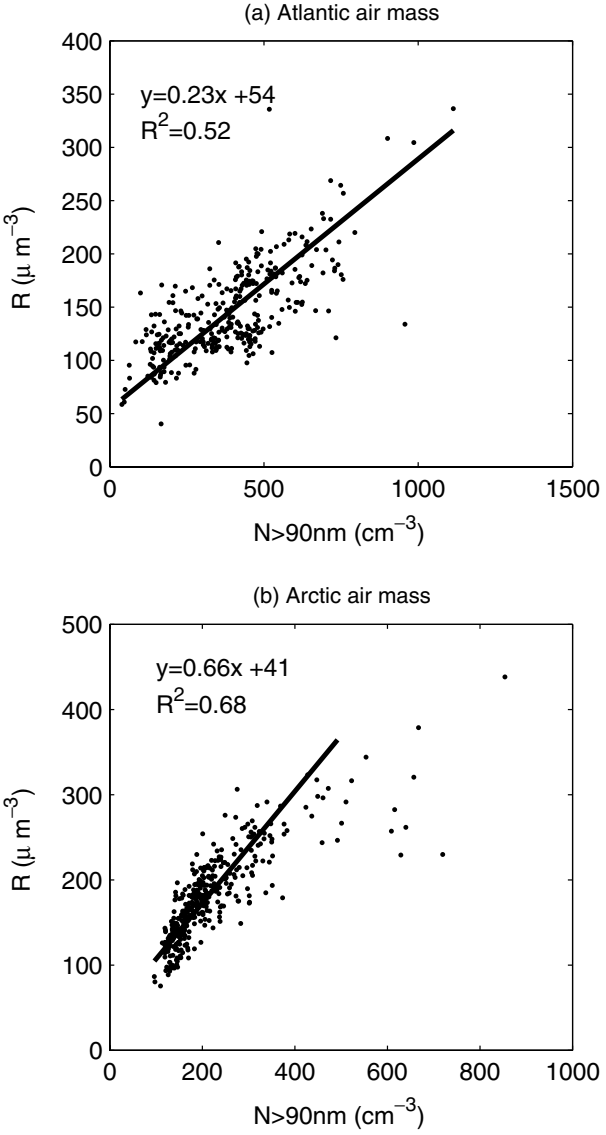

Fig 6. Number to volume ratios in marine air mass types: R as a function of the number concentration of particles larger than 90 nm in air masses originating over (a) the Atlantic and (b) the Arctic.

explanation for this dependence given the number-size distribution that existed in the region. An increase in the mean diameter of the accumulation mode from 100 nm to 200 nm by coagulation would require a timescale of close to 100 d at the observed number concentrations of below 600 cm^{-3}. Moreover, Aitken-mode particles are present at higher concentrations than accumulation-mode particles. Coagulation between Aitken- and accumulation-mode particles would approximately be 80 times faster than the self-coagulation of accumulation-mode particles. The former process, if dominant, would lead to an increase in accumulation-mode volume with increasing mean diameter at constant accumulation-mode particle number, contrary to the observations in Fig. 7.

Other explanations could involve the condensation of mass from the gas phase, or production of accumulation-mode particles by cloud processing in an environment limited in SO_2, or coalescence. Measurements of aerosol size distributions in the Arctic show that the accumulation mode typically has number concentrations around 50 cm^{-3}, corresponding to a volume of roughly 0.4 μm^3 cm^{-3} (Covert et al., 1996) at typical mean diameters, whereas in Sagres typical number and volume concentrations are 100 to 250 cm^{-3} and 0.7 μm^3 cm^{-3} in Arctic air masses. The accumulation mode thus gains in number and volume during the transport from the Arctic. The increase in volume is plausible as the air mass crosses productive ocean surface and shipping channels and is thus enriched in SO_2 and small particles. Condensational growth in fact results in a relation between σ_{acc} and d_{acc} that is very similar to what we observed in the Sagres data in air masses with Arctic and Atlantic trajectories (Hegg and Russell, 2000). For non-precipitating cloud processing, accumulation and the largest Aitken-mode particles nucleate to form cloud droplets in stratus and stratocumulus clouds, SO_2 is converted to sulfate in the droplets (Hoppel et al., 1994) and the resulting residual aerosol distribution upon evaporation becomes larger and narrower. Due to the similarity in air mass back trajectories it is plausible that roughly the same amount of SO_2 is converted. The variation in particle number can be explained by varying cloud supersaturation and the variations in Aitken-mode mean diameter and number concentration. If the same amount of sulfate is distributed among fewer particles (low $N > 90$), each individual particle can accumulate more material and the mean diameter of the accumulation mode increases. If more particles are present (high $N > 90$), each individual particle accumulates less material and the mean diameter of the accumulation mode stays smaller. This leads to an inverse relationship between the mean diameter and number concentration of the accumulation mode and to rather variable R that is evident in the data at

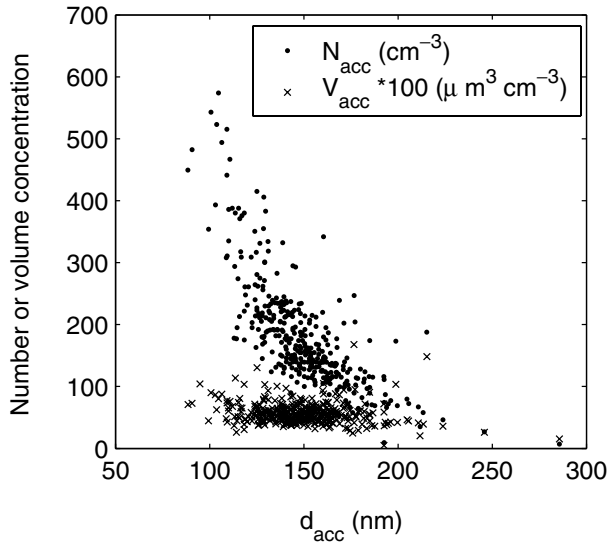

Fig 7. Observed accumulation-mode number and volume concentration as a function of mean diameter in Arctic air mass types.

somewhat less than the expected d_{acc}^{-3} functionality and explains some 50 to 70% of the factor of two variance in R shown by the histograms in Figs 4a and b.

Another process that could reduce accumulation-mode particle numbers with increasing mean diameter is coalescence. It is very likely that some coalescence occurs during the cloud processing of the aerosols; however, it is probably not the main player and the process is more complex with aerosol removal. If the cases with large d_{acc} and low number concentrations were solely due to coalescence then it is likely that in these cases the particle volume would be reduced due to precipitation processes.

Additional variability in R could be caused by sea-salt particles. Due to their relatively large sizes, sea-salt particles contribute significantly to the submicrometre volume concentration but not to the number concentration. Analysis of impactor data shows that in clean conditions NaCl on average accounts for submicrometre mass fractions of between 20 and 30%. However, the concentration of sea-salt particles might fluctuate more strongly on timescales shorter than the impactor sampling time. Thus they have the potential to significantly increase the variability of R in marine air mass types.

4.2. Mechanisms for stabilizing R

As shown in the previous section, the tail of Aitken-mode particles extending to larger diameters acts to increase the variability of R. In fact it explains much of the dependence of R on $N >$ 90. Thus, compensation effects that stabilize the number to volume ratio, will be found primarily in the accumulation mode. The accumulation mode of the aerosol encountered during the ACE-2 experiment was to a good approximation of log-normal shape. In the theoretical section of this paper, it has been shown that for a log-normal size distribution R is only dependent on the geometric mean diameter (d_g) and the standard deviation (σ_g) of the distribution and that R can be stabilized by an inverse dependence of σ_g and d_g.

Figure 8 shows the measured dependence of the accumulation mode standard deviation (σ_{acc}) on the accumulation-mode diameter as black dots overlaid on isolines of R. As postulated by Hegg and Russell (2000), the standard deviation of the accumulation mode decreases with increasing mean diameter. This narrowing of the size distribution as the particles grow stabilizes the number to volume ratio.

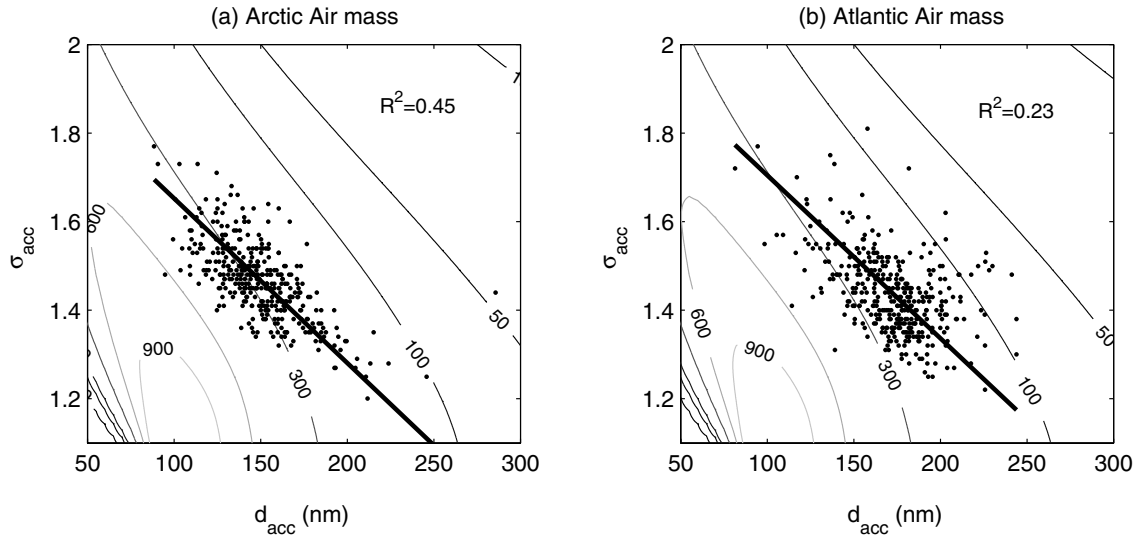

Fig 8. The dependence of the accumulation-mode standard deviation (σ_{acc}) on the accumulation-mode geometric mean diameter (d_g) in (a) Arctic and (b) Atlantic air mass types. Isolines of constant R are shown as shaded lines.

The inverse dependence of σ_{acc} on the accumulation-mode mean diameter d_g can be seen more clearly in the Arctic data set, in which d_g varies over a larger range and the data have a little less scatter than in the Atlantic data set. A linear regression line has been fitted to the data to show the impact of an inverse relationship between mean diameter and standard deviation on R more clearly. The regression line is tilted in the direction of the lower-valued isolines of R. As a result, R is approximately 400 μm^{-3} at a mean diameter of 100 nm and a little more than 100 μm^{-3} at a mean diameter of 250 nm. If σ_{acc} were independent of the mean diameter and held constant at its mean value of 1.45, R would vary from approximately 800 μm^{-3} to below 100 μm^{-3}, for an increase in the mean diameter from 100 to 250 nm. The inverse dependence of σ_{acc} results in a reduction in variation of R by 50%. The decrease of σ_{acc} with mean diameter is not strong enough to achieve constant R, but sufficient to confine R to a narrower range than could be expected, if the mean diameter and the standard deviation of the accumulation mode were not inversely correlated.

In Atlantic air mass conditions most of the data points are confined between mean diameters of 150 and 200 nm. In this size range R is not as strongly dependent on the mean diameter (*cf.* Fig. 8) and thus more stable than in Arctic air mass types. Therefore, the decrease of σ_{acc} with the mean diameter does not play such a big role in stabilizing the number to volume ratio.

5. Stabilization of number to volume ratios in polluted conditions

The number to volume ratios during polluted conditions are also relatively stable, but unlike in marine conditions show no dependence on the number concentration of particles larger than 90 nm ($N > 90$). The size distribution in air mass types associated with either aged or recent pollution is not as clearly bimodal as the size distribution in marine background conditions. The accumulation mode and the Aitken mode overlap to some extent, and in some cases it is necessary to consider both the number and the volume concentration to show that two separate log-normal modes are present. A typical example of the number- and volume-size distribution in recent pollution and aged pollution is shown in Fig. 9. Aitken-mode particles contribute considerably to the number concentration of particles larger than 90 nm and also account for a significant fraction of the of the submicrometre volume concentration.

In recent pollution (Figs 9a and b) Aitken-mode particles account for the majority of $N > 90$. The Aitken-mode particles are so abundant that the particle volume contained in the Aitken mode is comparable to the particle volume of the accumulation mode. Since most of the $N > 90$ are smaller than 120 nm the aerosol number to volume ratios in recent pollution are significantly higher than in the other air mass types. The volume provided by the few particles in the accumulation mode is not large enough to lower R to marine conditions.

In aged pollution (Figs 9c and d) the accumulation mode often appears only as a shoulder on the Aitken mode in the number size distribution. From the number size distribution alone it is not completely clear if it is justified to fit this shoulder as a separate mode. But in the volume size distribution it is obvious that the accumulation mode has log-normal shape and is distinguished from the Aitken mode. Both modes contribute to the total number as well as to the total volume concentration.

In polluted air mass conditions both Aitken- and accumulation-mode particles have an important influence on the number to volume ratio. The total number to volume ratio can be written as:

$$R = \frac{N > 90_{acc} + N > 90_{ait}}{V_{acc} + V_{ait}} = \left(\frac{N > 90_{acc}}{N > 90_{ait}} + 1\right)\left[\frac{N > 90_{acc}}{N > 90_{ait}}\left(\frac{1}{R_{acc}} + \frac{1}{R_{ait}}\right)\right]^{-1}, \quad (4)$$

where $N > 90_{acc}$ is the number concentration of accumulation-mode particles larger than 90 nm, $N > 90_{ait}$ is the number concentration of Aitken-mode particle larger than 90 nm, R_{ait} the number to volume ratio of the Aitken mode and R_{acc} the number to volume ratio of the accumulation mode. From this equation we can draw two conclusions. First, the total number to volume ratio R lies between the number to volume ratio of the Aitken mode and the number to volume ratio of the accumulation mode:

$$\min(R_{acc}, R_{ait}) < R < \max(R_{acc}, R_{ait}). \quad (5)$$

Second, if $N > 90_{acc}$ and $N > 90_{ait}$ are of the same order of magnitude, the total number to volume ratio cannot increase very strongly even if R_{ait} gets arbitrarily large. These conclusions are independent of the actual shape of the size distribution as long as it is bimodal.

Figure 10 illustrates the range of R_{acc} and R_{ait} measured during polluted conditions. The relationship between the standard deviation and the mean diameter of both the Aitken and accumulation mode are overlaid on lines of constant R as in Fig. 8. In most cases R_{ait} is larger than R_{acc}; the only exception is when the Aitken-mode mean diameter is unusually small, below 30–40 nm.

There are important differences in conditions of aged pollution and recent pollution. In air mass conditions influenced by aged pollution (Fig. 10a), the number to volume ratio of the Aitken mode is highly variable (90% of the values between 100 and 600 μm^{-3}. However, since in those conditions $N > 90_{acc}$ is comparable to $N > 90_{ait}$ even a strong increase in the number to volume ratio of the Aitken mode increases the overall R only moderately. The number to volume ratio of the accumulation mode itself is relatively stable (75 to 200 μm^{-3}) for accumulation-mode mean diameters between 100 and 250 nm. For this range of diameters, σ_{acc} decreases with increasing accumulation-mode diameter at a ratio that stabilizes R_{acc}, as in marine conditions. Once the mean diameter is larger than 200 nm the standard deviation levels off and does not fall below 1.2. This results in low

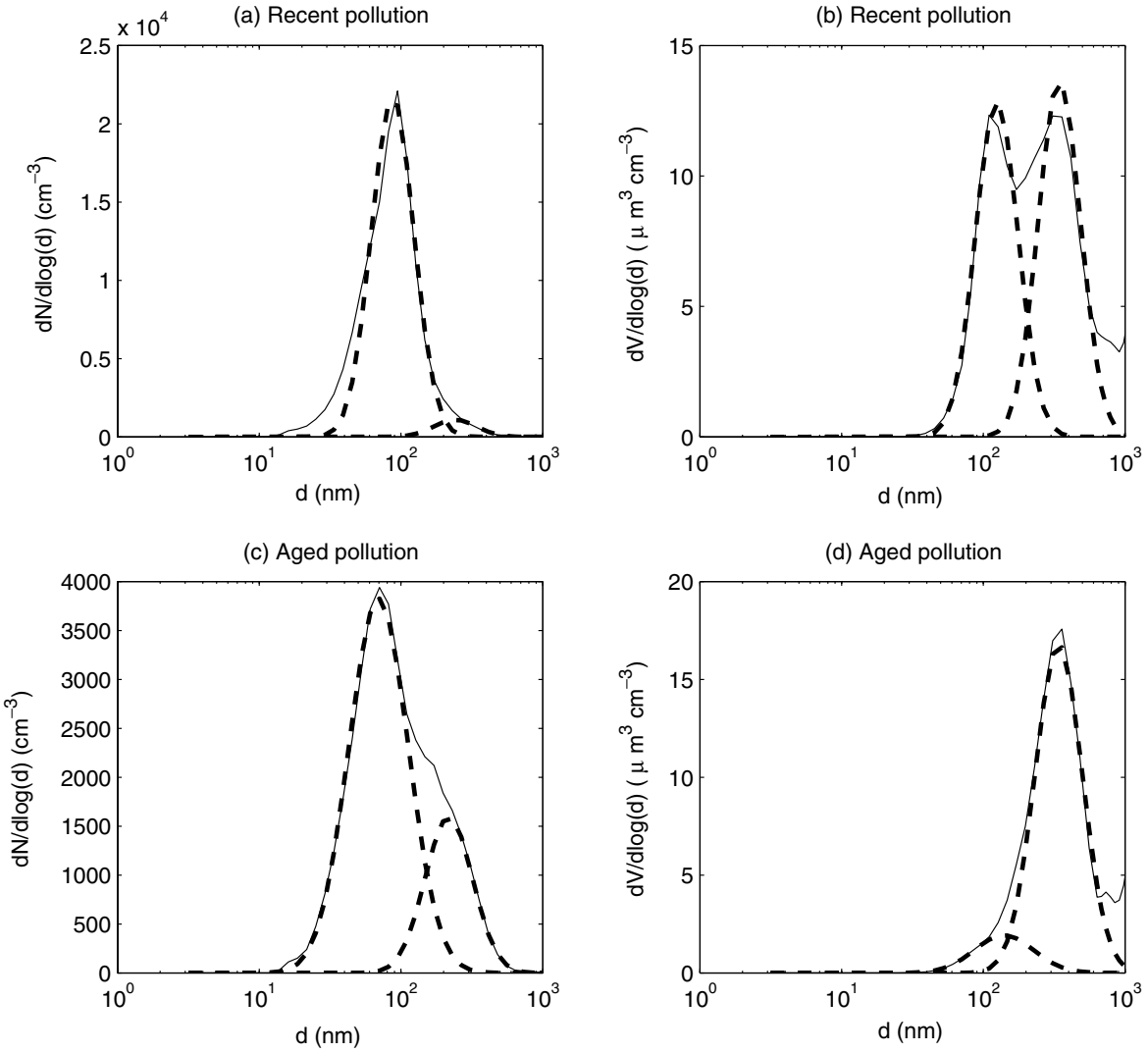

Fig 9. Typical size distribution in polluted conditions: (a) number size distribution in air masses influenced by recent pollution, (b) corresponding volume size distribution, (c) number size distribution in air masses influenced by aged pollution, (d) corresponding volume size distribution.

values of R_{acc} for very large mean diameters of the accumulation mode.

In recent pollution, Fig. 10b, the number to volume ratios of the Aitken mode are large and relatively stable between 600 and 900 μm^{-3}. The mean diameters of the Aitken mode are in the size range where the number to volume ratio of a log-normal distribution reaches its maximum. R_{acc} is more variable than in aged pollution, because there is a less strong inverse relationship between accumulation-mode diameter and standard deviation. Despite the fact that R_{acc} is generally low, the high number concentration of Aitken-mode particles larger than 90 nm combined with a high R_{ait} makes the overall R larger than in other air mass types.

The stability of R in air mass types influenced by aged pollution is quite remarkable and the general principles contained in eq. (4) are not sufficient to explain why R is so confined. The reason for the constancy of R seems to be that in aged pollution the parameters of Aitken and accumulation modes are not completely independent. This is demonstrated in Figs11a–c. The data presented in Fig. 11 are taken from a selected time period during one of the aged pollution episodes that spans a little over 2 d. Including longer time periods and other episodes tends to obscure correlations between aerosol parameters due to synoptic variations and possible changes in the aerosol origin.

In Fig. 11a it can be seen that during the time period of interest the standard deviation of the accumulation mode is strongly inversely dependent on its mean diameter. A second-order polynomial was fitted to the data yielding an R^2 of 0.86. Fig. 11b shows that the accumulation-mode mean diameter (d_{acc}) and the Aitken-mode mean diameter (d_{ait}) are somewhat correlated. Of special importance is that the ratio of $N > 90_{ait}$ to $N > 90_{acc}$

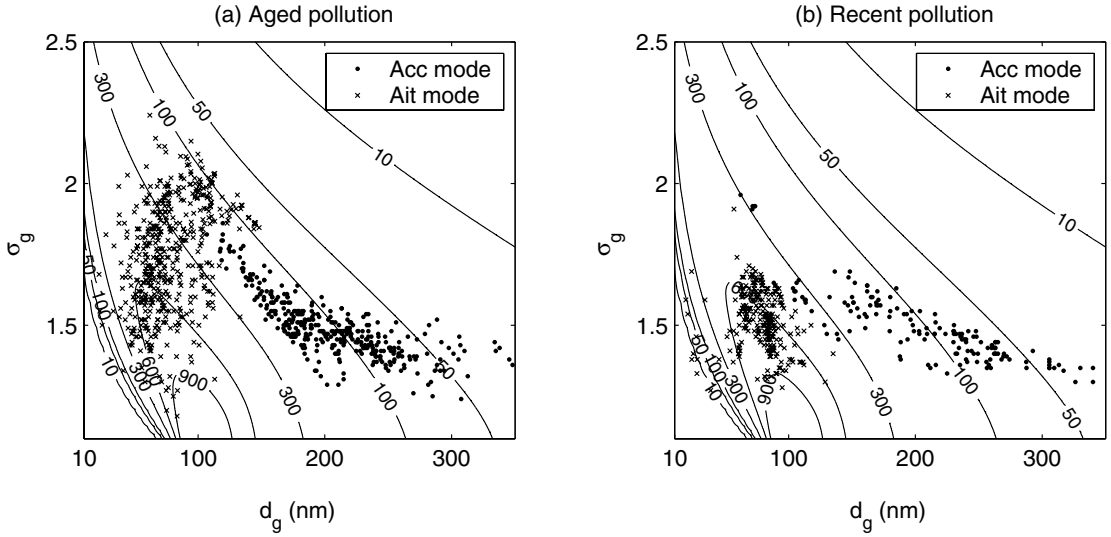

Fig 10. Dependence of the standard deviation on the mean diameter of the Aitken mode (crosses) and the accumulation mode (dots): (a) aged pollution, (b) recent pollution. Isolines of R are shown.

depends on the mean diameter of the accumulation mode as shown in Fig. 11c. Both axes are logarithmic, so the dependence is exponential. This increase of $N > 90_{\mathrm{ait}}/N > 90_{\mathrm{acc}}$ with increasing d_{acc} is not limited to the time period shown here, but typical for the whole ACE-2 data set with a slightly lower R^2 of 0.65. The ratio of $N > 90_{\mathrm{ait}}$ to $N > 90_{\mathrm{acc}}$ determines how sensitive the total number to volume ratio R is to an increase in the number to volume ratio of the Aitken mode. If $N > 90_{\mathrm{ait}}/N > 90_{\mathrm{acc}}$ is close to 1, R can at most achieve a maximum of $R = 2\ R_{\mathrm{acc}}$ as the number to volume ratio of the Aitken mode goes to infinity. However, if $N > 90_{\mathrm{ait}}/N > 90_{\mathrm{acc}} = 10$, R can be up to 10 times larger than R_{acc}. Figure 11c offers a simple explanation for why R of ambient aerosol usually does not get arbitrarily small. As the d_{acc} increases, $N > 90_{\mathrm{ait}}$ increases relative to $N > 90_{\mathrm{acc}}$. The decrease in R_{acc} (as shown in Fig. 10a) is balanced by an increase in Aitken-mode particles that grow larger than the 90 nm cut-off diameter.

To demonstrate that the number to volume ratio of the ambient aerosol is actually limited by these correlations, R was simulated in the following manner. Two sets of 1000 bimodal number size distributions were generated. One set does not allow for covariation in the size distribution parameters, whereas the second set includes the observed correlations. The bimodal distributions are described by the sum of two log-normal distributions each parametrized by a mean diameter, standard deviation and number concentration.

In the first set of simulations the mean diameter, the standard deviation and the number concentration of both the Aitken and of the accumulation mode are each chosen randomly from a normal distribution. The parameters of this normal distribution are derived from the measurements during the time period considered in Fig. 11. For example, the mean and standard deviation of the normal distribution from which random values for d_{ait} are selected are equal to the mean and standard deviation of measured values for the Aitken-mode mean diameter.

In the second set of simulations, only the mean diameter and the number concentration of the accumulation mode are randomly chosen as described above. The standard deviation is calculated for each mean diameter according to the fitted relationship shown in Fig. 11a. Then the Aitken-mode standard deviation is randomly chosen, but the Aitken-mode mean diameter and number concentration are calculated using the relationships shown in Figs 11b and c. Finally R is calculated for each set of 1000 distributions.

The results of the two sets of simulations simulations are compared in Figs 11d and e, which show the frequency distribution of the resulting number to volume ratios. If there is no covariance between the six size distribution parameters (Fig. 11d), the frequency distribution of R is relatively broad and high values of R (up to 800 $\mu\mathrm{m}^{-3}$) are occasionally found. The frequency distribution of R calculated in the second set of simulations is much narrower. Taking into account the observed relationships between size distribution parameters constrains R closely to values around 200 $\mu\mathrm{m}^{-3}$. The frequency distribution of R resulting from the second set of simulations is very close to the frequency distribution of R derived from the actual measurements of the size distributions (Fig. 11f). Additional simulations (not shown here) demonstrate that the relationship in Fig. 11c is mainly responsible for confining R, whereas the effect of relationships 11a and 11b on R is relatively small.

The increase of $N > 90_{\mathrm{ait}}/N > 90_{\mathrm{acc}}$ with increasing d_{acc} could have the following simple physical explanation. The mean diameter of the accumulation mode can only increase above 200 nm if a large amount of precursor gas is converted to aerosol (in or out of cloud). But if the size of the accumulation-mode particles is increased, the Aitken-mode particles are likely to

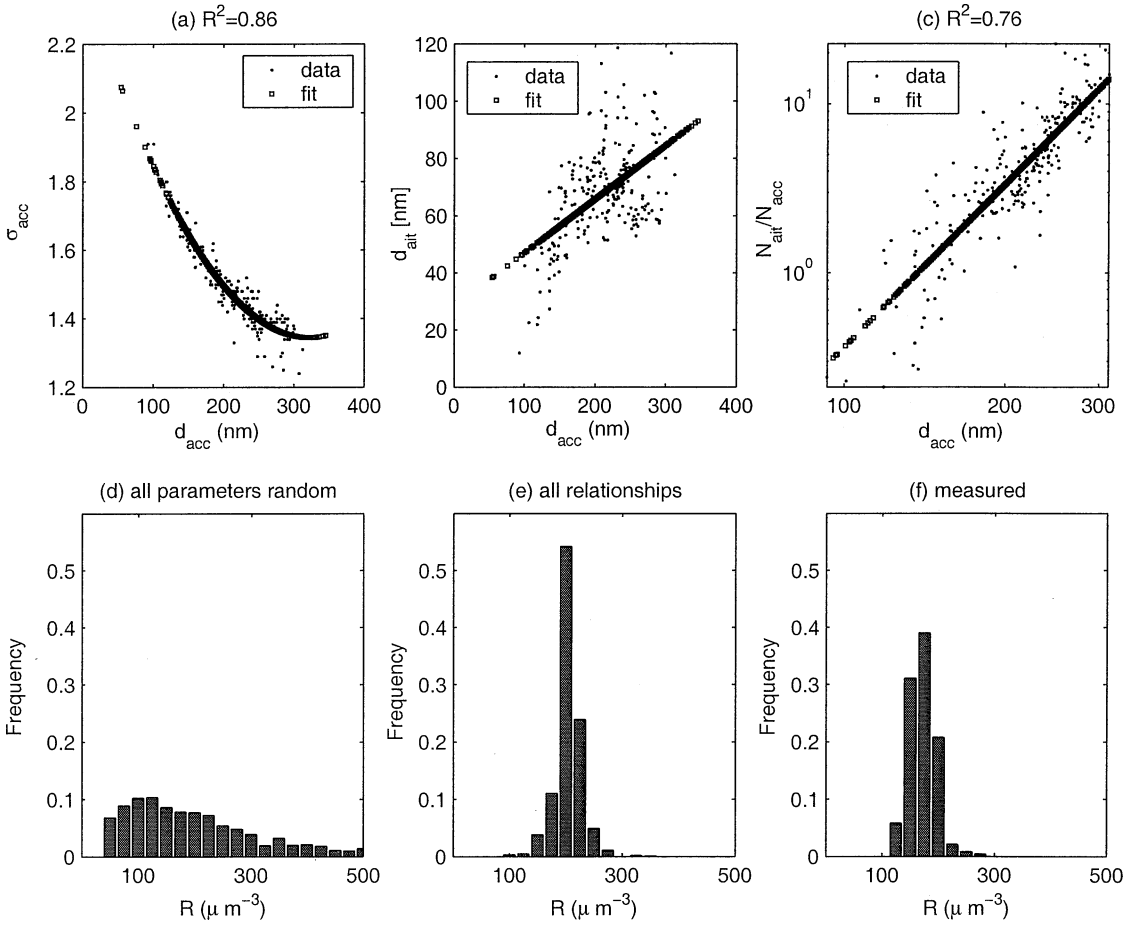

Fig 11. Correlations between parameters of the size distribution in aged pollution and their influence on the number to volume ratio. (a) Dependence of the accumulation-mode standard deviation on the mean diameter. (b) Relationship between accumulation-mode mean diameter and Aitken-mode mean diameter. (c) Dependence of $N > 90_{ait}/N > 90_{acc}$ on the mean accumulation-mode diameter. (d) Simulated frequency distribution of R using uncorrelated size distribution parameters. (e) Simulated frequency distribution of R using the measured relationships shown in (a)–(c). (f) Measured frequency distribution of R.

grow by condensation as well and thus increase $N > 90$. This is further supported by a moderate correlation between the mean diameters of the Aitken and accumulation modes. Coagulation could theoretically lead to a similar behaviour if the accumulation-mode particles grow mainly from coagulation with Aitken-mode particles. However, then relationship in Fig. 11c should involve the total number of Aitken-mode particles instead of only the fraction of Aitken-mode particles larger than 90 nm. Not nearly as good a correlation between the total number of Aitken-mode particles and accumulation-mode particles can be found.

Similar to marine conditions, self-coagulation of accumulation-mode particles cannot be responsible for the inverse dependence of σ_{acc} and d_{acc} because the timescales involved would be larger than 50 d. This inverse dependence could either be explained by condensation of precursor gases on the cloud-processed mode or cloud processing itself might lead to an inverse dependence of σ_{acc} and d_{acc}.

6. Conclusions

The number to volume ratios (R) of the aerosol measured in coastal Southwest Portugal during ACE-2 are comparable to previously and concurrently measured number to volume ratios over the Atlantic and are similarly narrowly constrained. Classification of R by air mass types according to 6-day back trajectories allows us to compare R in marine and polluted air masses. Only in air masses that were recently in contact with continental pollution sources is R significantly higher than average. The number to volume ratios in air mass types containing aged European pollution were even slightly lower than in marine air mass types.

In Atlantic and Arctic air masses R shows relatively greater variability and increases with increasing number concentration of particles larger than 90 nm. A linear dependence of R on Aitken-mode particles larger than 90 nm can explain much of the variance of R in these air mass types. Despite the fact that R

is variable, the observed range of R is smaller than predicted by a random set of bimodal size distributions with log-normal parameters within the observed range, but not undergoing correlated atmospheric processes affecting N and V.

In the Arctic and Atlantic marine air masses the limited range of R is due to the fact that the number to volume ratio is dominated by accumulation-mode aerosol, whose geometric standard deviation depends inversely on the mean diameter of the mode. This inverse dependence has been suggested by Hegg and Russell (2000) and has now been shown to exist in the ambient aerosol. It indicates that condensational processes determine the size distribution of the accumulation-mode aerosol or that cloud processing of the aerosol results in an inverse dependence of the standard deviation of the processed aerosol on the mean diameter.

In aged pollution the variability of R is further reduced due to correlations between the mean size and standard deviation of the Aitken and accumulation modes. These correlations reduce the variability of the number to volume ratio when it is determined by a bimodal number size distribution. The main factor in stabilizing R is the increase of Aitken-mode particles larger than 90 nm relative to accumulation-mode particles as the mean diameter of the accumulation mode increases. This behaviour can be expected if a large number of gaseous aerosol precursors are converted to aerosol, increasing the mean size of the accumulation mode and letting a significant number of Aitken-mode particles grow to diameters larger than 90 nm.

These findings support the hypothesis that R is actively constrained by processes that shape the aerosol size distribution. If there are fundamental reasons why R should be commonly quite confined, the use of empirical number to volume ratios as parametrizations in climate models could be more easily justified. However, more data from different areas of the globe might be needed to justify that hypothesis more generally.

7. Acknowledgments

This research is a contribution to the International Global Atmospheric Chemistry (IGAC) Core Project of the International Geosphere–Biosphere Programme (IGBP) and is part of the IGAC Aerosol Characterization Experiments (ACE). Financial support for the measurements and analyses by the University of Washington was provided by the US National Science Foundation ATM 9619984. Financial support for the size distribution measurements was provided by the DGXII of the European Commission (contracts nos ENV4-CZ95-0032 and ENV4-CT95-0108) and by the Institute for Tropospheric Research, Leipzig. This publication was supported by the Joint Institute for the Study of the Atmosphere and Ocean (JISAO) under NOAA Cooperative Agreement #NA67RJ0155, contribution #994.

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