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### Aerosol modelling and validation during ESCOMPTE 2001

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The ESCOMPTE 2001 programme (Atmospheric Research. 69(3-4) (2004) 241) has resulted in an exhaustive set of dynamical, radiative, gas and aerosol observations (surface and aircraft measurements). A previous paper (Atmospheric Research. (2004) in press) has dealt with dynamics and gas-phase chemistry. The present paper is an extension to aerosol formation, transport and evolution. To account for important loadings of primary and secondary aerosols and their transformation processes in the ESCOMPTE domain, the ORISAM aerosol module (Atmospheric Environment. 35 (2001) 4751) was implemented on-line in the air-quality Meso-NH-C model. Additional developments have been introduced in ORganic and Inorganic Spectral Aerosol M odule (ORISAM ) to improve the comparison between simulations and experimental surface and aircraft field data. This paper discusses this comparison for a simulation performed during one selected day, 24 June 2001, during the Intensive Observation Period IOP2b. Our work relies on BC and OCp emission inventories specifically developed for ESCOM PTE. This study confirms the need for a fine resolution aerosol inventory with spectral chemical speciation. BC levels are satisfactorily reproduced, thus validating our emission inventory and its processing through Meso-NH-C. However, comparisons for reactive species generally denote an underestimation of concentrations. Organic aerosol levels are rather well simulated though with a trend to underestimation in the afternoon. Inorganic aerosol species are underestimated for several reasons, some of them have been identified. For sulphates, primary emissions were introduced. Improvement was obtained too for modelled nitrate and ammonium levels after introducing heterogeneous chemistry. However, no modelling of terrigeneous particles is probably a major cause for nitrates and ammonium underestimations. Particle numbers and size distributions are well reproduced, but only in the submicrometer range. Our work points out to the need of introducing coarse dust particles to further improve the simulation of PM-10 concentrations and more accurate modelling of gas-particle interactions.

Keywords: Aerosol model; Aerosol inventory; Inorganic and organics formation; Size distribution

#### 1. Introduction

\*Corresponding author. Tel.: +33561332759; fax: +33561332790. A previous paper (Cousin et al., 2004) has dealt with dynamics and gas-phase chemistry for 24 June, during the ESCOMPTE 2001 campaign. Here, this work is extended to account for aerosol pollution. Particulate pollution has recently received much interest, due to its

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environmental and health impacts. Up to now, general efforts have been made to model gaseous pollution but there is presently an urgent need for incorporating aerosol processes in air quality simulations in view of forthcoming European legislations on particles. Aerosols have been introduced as air quality indicators through PM-10 (particles of diameters below 10  $\mu$ m) and in the near future, through PM-2.5 (diameters below 2.5  $\mu$ m). Aerosols are known to have an impact on gaseous chemistry (Ravishankara, 1997). They also are essential for the closure of radiative budgets (Charlson et al., 1992; Penner et al., 1996; Adams et al., 2001). Threat to human health is also an important issue (Donaldson et al., 1998).

Aerosol impacts are closely dependent on their chemical composition and size, a very complex issue due to their chemical diversity and evolution in the atmosphere. Carbon is an essential component of the atmospheric particulate matter, mainly issued from combustion emissions (Cachier, 1992). This component comprises of two fractions: the organic carbon (OC), reactive in the atmosphere and the non-reactive black carbon (BC) (Cachier, 1998). Inorganic components such as nitrates, sulphates, ammonium also form a significant part of the aerosols. In most aerosol modelling works, aerosols species are generally assessed as independent passive tracers and any interaction with their gaseous environment is not taken into account. This limiting constraint is overcome with the use of an aerosol module which may simulate in some way gas-particle interactions and the chemical and size evolution ("ageing") of the resulting heterogeneous aerosols. For this purpose, the ORganic and Inorganic Spectral Aerosol Module (ORISAM) has been developed (Bessagnet and Rosset, 2001) and implemented in the 3D mesoscale model Meso-NH-C previously upgraded for dynamics, radiation and gas-phase chemistry (Tulet et al., 2003).

In this work, ORISAM has been tested and improved using an episode of the ESCOMPTE experiment (Cros et al., 2004). Although primarily devoted to gas-phase chemistry and ozone photochemical production, ES-COMPTE has produced an important set of experimental data documenting the aerosol phase and its evolution (Cachier et al., 2004). Indeed, seven representative sites were equipped at ground level (Fig. 1) for the study of particles and some flight tracks devoted to aerosol and gas-phase studies also allowed to gain some information on the particle vertical distribution. As furthermore expected, it has been shown that the domain was subjected to intense primary emissions and secondary anthropogenic and biogenic aerosols formations. All these conditions have resulted in a unique opportunity to test ORISAM. The period of our study, 24 June 2001, during IOP2b, was identified as one characteristic period of sea-breeze regimes and asso44.3N



Fig. 1. Orographic map (height isocontours) of the central ESCOMPTE domain with the main stations and valleys quoted in the text.

ciated high pollution levels (Cousin et al., 2004), probably one of very favourable conditions for gas--particle interactions.

A new BC and OCp emission inventory was specifically designed for ESCOMPTE, and simulations were then performed and compared with aerosol measurements at surface stations and along aircraft flight tracks.

#### 2. Model descriptions

#### 2.1. The organic and inorganic spectral aerosol module

In order to simulate aerosol size distributions, two methods are commonly used: the modal and the sectional ones. In the modal representation, each aerosol subpopulation (mode) is described by an analytical distribution function (e.g. lognormal in Binkowski and Shankar, 1995). This approach has the advantage of limiting the number of prognostic variables but forces the distribution function for each mode. In the sectional approach, the size distribution which is approximated by a set of contiguous, non-overlapping discrete size bins (e.g. Jacobson, 1997; Gong et al., 2003), appears more suitable for a detailed description of the microphysical processes. This has been adopted here for its flexibility in solving aerosol multicomponent systems involving the processes of coagulation, condensation, absorption and chemical reactions.

In the ORISAM module, first developed by Bessagnet and Rosset (2001), there are four bins from 0.03 to  $10 \,\mu$ m. These four sectional bins are chosen as follows:

Table 1 List of aerosol species

Model species	Species	Туре
BC	Anthropogenic black carbon	Primary
OC	Anthropogenic primary organic carbon	Primary
ASOA	Anthropogenic secondary organic aerosol	Secondary
BSOA	Biogenic secondary organic aerosol	Secondary
$H_2SO_4$	Equivalent sulphate <sup>a</sup>	Secondary
HNO <sub>3</sub>	Equivalent nitrate <sup>a</sup>	Secondary
NH <sub>3</sub>	Equivalent ammonium <sup>a</sup>	Primary gas emissions, then secondarily transferred to the aerosol phase
Water	Water	_

<sup>a</sup>Ions, molecules, crystals.

bin 1 between 0.03 and 0.156  $\mu m,$  bin 2 between 0.156 and 0.625  $\mu m,$  bin 3 between 0.625 and 2.5  $\mu m$  and bin 4 between 2.5 and 10  $\mu m.$ 

A detailed aerosol speciation has been adopted (Table 1) to better represent aerosol composition. Initially, this aerosol module comprised six chemical species: anthropogenic carbon, secondary OC, sulphates, nitrates, ammonium and water. Here, carbonaceous anthropogenic primary species have been partitioned into two primary carbon components, BC and primary organic carbon (OCp). We also have partitioned secondary organic aerosols to differenciate between their anthropogenic or biogenic origins. Nitric acid is produced in the gas phase by  $NO_x$  oxidation. Ammonium is considered a primary species converted into the aerosol phase by ammonia neutralization with nitric and sulphuric acids. Secondary Organic Aerosol (SOA) are formed from condensable Volatile Organic Compounds (VOC) using aerosol yields (Moucheron and Milford, 1996) and partition coefficients (Pankow, 1994). Aerosol growth follows condensation/ absorption processes on preexisting particles followed with subsequent coagulation. We also have added the nucleation process for sulphates according to Kulmala et al. (1998). A detailed description can be found in Bessagnet et al. (2004).

## 2.2. The mesoscale non-hydrostatic chemistry model (Meso-NH-C)

The ORISAM module has been implemented on-line within the mesoscale non-hydrostatic Chemistry model (Meso-NH-C), and a full description of that is given in Cousin et al. (2004). The ORISAM module and the gas-phase chemical module ReLACS (Crassier et al., 2000) derived from RACM (Stockwell et al., 1997) are also coupled on-line with Meso-NH.

Particle dry deposition has also been implemented in Meso-NH-C together with chemistry schemes modified for nitrates following Jacob (2000) so as to account for particle impact on gaseous species.

#### 3. Emission inventories

For the gas phase, the GENEMIS anthropogenic emission inventory (Wickert et al., 1999) was first adopted at 9 km horizontal and 1 h time resolutions. For primary aerosols, since no inventory was available at comparable resolutions, two different approaches have been adopted.

In the large domain (Fig. 3a) first, we use global BC and primary OCp inventories at  $1^{\circ} \times 1^{\circ}$  resolutions. These inventories were derived from Cooke et al. (1999) with an updated algorithm for the year 1997. In order to increase the resolution, CO emission inventories developed for mesoscale purposes were used to scale BC and OCp emissions. Since CO emissions are mainly due to combustion sources, they are strongly related to BC and primary OCp. Consequently, inventories were spatialised at 9 km using the GENEMIS inventory for CO. An average CO emission value for each  $1^{\circ} \times 1^{\circ}$  cell in the large domain was computed from this 9 km inventory so as to obtain BC/CO and OC/CO ratios. Then, CO emissions at 9 km resolution were used to scale out primary BC and OCp aerosol emission inventories at this same 9km resolution. With such values at 9km resolution, computing average BC and primary OCp in each  $1^{\circ} \times 1^{\circ}$  cell gave BC and primary OCp values in the updated inventory. Time evolution of BC and OCp emissions were thus assigned to follow CO emissions.

The second approach for the small domain (Fig. 3b) was based on the new fuel consumption data set established on a daily basis for the ESCOMPTE campaign (François et al., 2004). Bottom up primary BC and OCp emission inventories were then determined for the 2001 campaign in the ESCOMPTE domain. These inventories were obtained with a 1 km resolution (Fig. 2a), including combustion of fossil fuels and wood subject to an imposed typical daily evolution. Fig. 2b displays BC emissions scaled with the CO Genemis emissions. When comparing these two figures, it appears in the new inventory that traffic emissions are better

described and primary sources more accurately located. Finally, as previously explained, hourly CO variations (specific to the ESCOMPTE campaign) were used to obtain BC and primary OCp hourly inventories.

Carbonaceous particle emission size distributions were defined using BC and OC measurements obtained with a 13stage impactor (Dekati) at Marseilles on 23 June (Aulagnier, 2003). These distributions display a common mode in the submicrometer size range for BC and OC and an additional coarse mode for OC. These results at Marseilles are in agreement with other measurements performed at Vallon Dol, a station



Fig. 2. BC emission inventory (a) ad hoc ESCOMPTE 2001 inventory and (b) derived from the CO Genemis inventory (scale in  $\mu g m^{-2} s^{-1}$  at the right), for 24 June at 7.00 UTC.

Table 2 Characteristics of the lognormal function for BC and primary OCp emissions (sigma is the dispersion parameter)

	Median diameter (µm)	Sigma	BC (%)	OC (%)
Mode 1	0.197	1.89	100	60
Mode 2	2.905	2.02	0	40

located 10 km north of Marseilles (Mallet et al., 2003). In order to initialise ORISAM, we have used two lognormal functions for the two emission modes, with their characteristics listed in Table 2.

In the ESCOMPTE domain, with strong industrial and urban sources and intense traffic, sulphate formation rapidly occurs very near emission sources, in relation with high water contents within the combustion plumes. Another possibility could be heterogeneous sulphate formation at the particle surfaces in connection with high-aerosol concentrations in these plumes. These processes are not explicitly simulated. Nevertheless, since they can significantly affect initial sulphate concentrations, following Kasibhatla et al. (1997) and Tan et al. (2002), we have considered that a fraction (2% here) of total SO<sub>x</sub> emissions is rapidly transformed into SO<sub>4</sub><sup>2-</sup>.

# 4. Aerosol modelling and comparison with experimental data

## 4.1. Model configuration and meteorological situation on 24 June 2001

Two-way nested grid simulations were performed using the large domain at 9 km resolution (Fig. 3a) and the small domain at 3 km resolution (Fig. 3b) so as to figure out the importance of trans-boundary pollution inputs. It was the same configuration as in Cousin et al. (2004) with dynamic and gas-phase chemistry only, but here it was further supplemented with ORISAM, all models being run in a nested way in the large and small domains.

One crucial problem is chemical initialisation. For gaseous species, initial fields was provided by the global chemistry transport model MOCAGE (Dufour et al., 2003) which also gave the boundary conditions of the large domain every 3 h. The MOCAGE resolution was 0.25°. For carbonaceous aerosols, the MOCAGE CO fields were also used to derive BC and OCp initial fields. For this purpose, using these CO modelled fields and domain averaged measured BC and OC values, uniform surface BC/CO and OC/CO ratios were derived all over the large domain. CO boundary conditions also gave boundary conditions for BC and primary OCp for the



Fig. 3. PM-10 surface concentrations (scales in  $\mu g m^{-3}$  at the right) with superimposed wind fields (vector at bottom left is for  $10 m s^{-1}$ ) on 24 June 2001, at 12.00 UTC in: (a) the large domain (the square delineates the small domain) and (b) the small domain (segments represent ARAT 39 flight trajectory described in section 4.6.2). Isocontour is plot for 15  $\mu g m^{-3}$ 

large domain. Then, BC and primary OCp initial fields for the small domain were deduced through direct nesting in the large domain. Other aerosol species were initialised to zero.

As in Cousin et al. (2004), the dynamical and gasphase chemistry simulations for 24 June began on 21 June 00 UTC. For aerosols run in an on-line mode, spinup began on 23 June, 12.00 UTC, due to much higher computational costs. As shown in Cousin et al. (2004), 24 June is characteristic in the Marseilles region of highpollution episodes following strong northerly mistral winds which have previously cleansed the lower atmosphere. Southerly sea-breeze regimes then appear early in the morning at coastal stations. After progressively penetrating inland, winds turn to the southwest, driving the pollutant plume from the Berre pond within the Durance valley. More generally, high-pollution (gaseous and particulate) levels are reestablished. During 24 June, temperatures were about 15-18 °C in the morning, increasing inland during the day to 28-29 °C, sometimes over 30 °C. Relative humidities were high in the morning and the evening (about 90%). To illustrate this situation, Fig. 3 shows PM-10 fields obtained from the summation of all modelled aerosols species (listed in Table 1), with superimposed winds at 12.00 UTC. The model clearly reproduces chanelling of particle pollution plumes within the Durance valley, as already observed for gases (Cousin et al., 2004).

#### 4.2. BC concentrations

Comparisons between simulated and measured BC concentrations were carried out in order to test the improvements that could be expected with the use of the ad hoc new ESCOMPTE combustion particle emission inventory. Fig. 4 illustrates this comparison for the BC diurnal evolution on 24 June at the stations of Marseilles, Martigues, Dupail, Plan d'Aups and Vallon Dol. For the two sites within the source regions (Marseilles and Martigues), this comparison shows fair agreement both at concentration levels and trends. At Martigues (Fig. 4b), the morning peak is not observed with the correct intensity, perhaps due to close vicinity of intense point sources. However, later this day, BC levels are well simulated. At Marseilles (Fig. 4a), a double peak is observed early in the morning. The second peak is the classical urban traffic peak, whereas the origin of the first peak is not so common. Interestingly, this double peak is reproduced only with the ad hoc ESCOMPTE-derived BC inventory, not in the GENEMIS inventory. In France, the first summer Saturday is the "music day" celebrated by street festivals. The day under study, 24 June, was a Sunday, the day just after this celebration. Thus, the first peak can be attributed to unusually dense traffic at night (2.00-3.00 UTC), between 23 Saturday and 24 Sunday. The model can reproduce this, since ad hoc BC emission evolutions have been specifically designed for the ESCOMPTE campaign, which is not the case for GENEMIS. The comparison between simulated and measured BC concentrations is not so satisfactory at rural sites. For example at Dupail (Fig. 4c), though the mid-day peak is well captured by the model, probably due to sea-breeze transport of the pollutant plumes from Berre and Marseilles, there is a constant significant



Fig. 4. BC time series (scale in  $\mu$ g m<sup>-3</sup> at the left) for 24 June at: (a) Marseilles, (b) Martigues, (c) Dupail, (d) Plan d'Aups and (e) Vallon Dol (grey curve (a) and squares for model, dark curve for measurements)

underestimation of the BC concentrations. This feature points out to the limitations of BC initialization by CO fields. At remote sites such as Dupail, background concentrations issued from the CO-based initialization procedure result in BC underestimation. At Plan d'Aups, a 800 m elevation site (Fig. 4d), the situation is still worse, probably due to steep very local orographic effects non-fully resolved by the model. There, the mid-day peak probably denotes rapid shifting from the free troposphere at night to the boundary layer with pollution from Marseilles and Aix. Eventually, at Vallon Dol, north of Marseilles, the second peak in the morning is well captured by the model. The first peak is measured but not simulated, while in the afternoon, the model overestimates BC levels, perhaps due to very fine orographic effects around Vallon Dol.

#### 4.3. Particulate organic matter concentrations

Due to logistical and technical reasons, measurements at the various sites were made at different time resolutions, the number of samples obtained during 24 June 2001 vary from one to four. Model POM values were obtained by averaging all simulated values over the same time period as the duration of individual measurements. To account for non-carbon atoms in organic matter, primary POM concentrations were deduced from primary OCp concentrations by applying a scaling factor of 1.3 (a minimum value for scaling total primary and secondary OC). Total POM includes both primary POM, anthropogenic ASOA and biogenic BSOA secondary organic aerosols. In sources regions and suburban sites (Marseilles  $(3.42 \,\mu g \, m^{-3} \, measured)$ ,  $6 \mu g m^{-3}$  modelled), Martigues and Realtor (Fig. 5a, b), concentration levels and trends are well reproduced with a tendency for overestimation at night. Conversely, at remote sites (Dupail and Plan d'Aups, Fig. 5c, d), there is a clear trend to underestimate actual concentrations, though analytical artefacts (linked to complex OC analysis) are not excluded, especially for aged aerosols. A reason could be found in the underestimation of primary BC aerosols (as previously seen in Fig. 4c and d), which consequently limits the aerosol surface available for semi-volatile OC condensation. Both BC and OC underestimations are particularly significant at Plan d'Aups. Another cause of discrepancy between experimental and model results could be related to temperature. Organic gas condensation processes onto particle surfaces are known to be limited at high temperatures (Sheehan and Bowman, 2001). This result was discussed by Liousse et al. (2004) who have shown that ORISAM displays a clear temperature dependence in SOA formation. In our case study, temperatures can reach 30-35 °C. It is possible that the temperature condensation threshold above which SOA formation declines, is somewhat too low in the model, thus possibly explaining model underestimation in the afternoon.

#### 4.4. Sulphate concentrations

Comparisons between model results and measurements highlight a general sulphate underestimation, with overestimation only found at Martigues (Fig. 6b), tightly surrounded by strong industrial sulphate sources. At this site, the model overestimates primary sulphate concentrations, particularly in the morning before onset of the dispersing sea-breeze circulations. Several reasons can explain this general underestimation of sulphates. First, even with high SO<sub>2</sub> levels, sulphate formation might be too slow in the model. Homogeneous sulphate production is very slow and less efficient when compared to heterogeneous aqueous production. In our case study, with prevailing dry anticyclonic conditions, no cloud could account for an effective pathway for sulphate production. Moreover, the meteorological analyses forcing the model gave too low relative humidity (RH) at several stations, due to underestimation of the marine boundary layer RH. One consequence would be quite inefficient SO<sub>4</sub> production. To test this modelling artefact, using a 1D version of the Meso-NH-C model, two simulations at Realtor have been made, one using the modelled RH (obtained from 3D simulations) and the other using measured RH during ESCOMPTE. In Fig. 7, it can be observed that sulphate (and other inorganic species) mean concentrations increase with measured RH. Another cause for biases can be found in the ratio value selected for primary sulphate emissions. In the absence of any measurements, a value of 2% has



Fig. 5. Particulate Organic Matter (POM) concentrations (scales in  $\mu g m^{-3}$  at the left) at different time periods (in UTC) on 24 June at: (a) Martigues, (b) Realtor, (c) Dupail and (d) Plan d'Aups (measurements in dark, average model values in grey).



Fig. 6. Sulphate aerosol concentrations (scale in  $\mu g m^{-3}$  at the left) for different time periods on 24 June at: (a) Marseilles, (b) Martigues, (c) Realtor, (d) Dupail (measurements in dark, model in grey)



Fig. 7. Mean inorganic aerosol concentrations at Realtor (scale in  $\mu g m^{-3}$  on the left) on 24 June. 1D comparisons between simulations with measured (in dark) and modelled (in grey) relative humidities.

been applied to  $SO_x$  emission for generating primary sulphates (Kasibhatla et al., 1997; Tan et al., 2002). Other studies refer to different possible values for primary sulphate emissions, ranging from 1.4% (Benkovitz et al., 1994) up to 5% (Eliassen and Saltbones, 1983).

#### 4.5. Nitrates and ammonium

As mentioned in Section 2.2, heterogeneous chemistry of nitrate precursors (NO<sub>2</sub>, NO<sub>3</sub> and  $N_2O_5$  hydrolysis)

has been introduced. The overall effect is an increased  $HNO_3$  production in the gas phase, mainly in the morning and the evening (not presented here). Condensation also results in an increase of particle mass concentrations.

Nevertheless, at all stations, nitrates and ammonium are underestimated in the model. First, this can be explained by modelled low RH on 24 June (Fig. 7), even in the morning and evening when RH are the highest.

In Fig. 8, nitrates and ammonium aerosol concentrations at Realtor are displayed. The model simulates significant nitrate aerosol concentrations only in the morning. During this period, nitrate concentrations are highest in the gas phase, with low temperatures and high humidities favouring the condensation process. However, at other time periods, nitrates are almost zero. Other physical processes could presumably occur, allowing for nitrates to be generated in the aerosol phase. Some studies have hypothesised that terrigeneous mineral aerosols can react with and neutralise  $HNO_3(g)$ (Dentener et al., 1996; Tabazadeh et al., 1998). Furthermore, Cachier et al. (2004) have shown from detailed impactor results that nitrates were mainly in the coarse aerosol fraction, probably attached to dust and sea-salt particles. In our study, measurements show that sea-salt concentrations are very low this day but carbonate concentrations are significant. At present, in ORISAM, ISORROPIA does not account for



Fig. 8. (a) Nitrates and (b) ammonium aerosol concentrations (scales in  $\mu$ gm<sup>-3</sup> at the left) for different time periods on 24 June at Realtor (measurements in dark, model in grey).

carbonates which is probably one major cause of model nitrate underestimation. It was shown also that ammonium could decrease in the accumulation mode, sometimes in the coarse mode too. This artefact has already been noticed by Jacobson (1999).

#### 4.6. Total aerosol investigations

## 4.6.1. PM-10 concentrations and size distributions at the surface

At all stations, simulated PM-10 values (Fig. 9) are too low when compared to measurements. During daytime, a ratio of 2–4 can be found between model and experimental values. This underestimation was to be expected since the model does not consider resuspended particles and dust which may substantially contribute to the total PM loading (Miguel et al., 1999). Lack of prexisting sea-salt particles could also contribute to this discrepancy, though to a lesser extent. It must be underlined that during the day wind speeds were stronger  $(2.25 \text{ m s}^{-1})$  than at nighttime  $(1 \text{ m s}^{-1})$ , which is consistent with this hypothesis.

Focusing on submicrometer aerosols, we have compared particle numbers measured at Marseilles with those in the first and second bins of the model. Experimental data were obtained with a TSI 3010 model CN counter, whereas in the model, the first bin refer to particles with a diameter between 0.03 and 0.156 µm and between 0.156 and 0.625 µm in the second one. This comparison proves to be satisfactory for the first bin (Fig. 10a) though the traffic peaks appear to be somewhat overestimated. The situation is quite different in bin 2, since modelled particle numbers in this bin let appear an important underestimation. This comparison confirms that aerosol underestimation is mainly due to underestimated growth processes (e.g. condensation) and lack of dust resuspension. Furthermore, for all secondary organic and inorganic species, boundary conditions values for the large domain are set to zero. Therefore, there is no transboundary transport of aged aerosols which could generate an important loading by secondary aerosols. This absence could contribute to underestimation of the daytime values.

#### 4.6.2. Aerosol vertical distribution

On 24 June, the morning ARAT aircraft flight (flight 39) was devoted to gas and aerosol measurements. During this flight (Fig. 3b), total particle numbers were measured with a TSI 3022 CN counter. Size distributions (in numbers) were measured in the size range 0.01-3 µm. Fig. 11 displays the comparison between measurements and model results for total particle numbers. Almost all particles are found in model bin 1. This is particularly true when remembering that particles of radii between 0.01 and 0.03 µm are not simulated, which could potentially contribute to underestimation of particle numbers in the submicrometer size range. During the flight, aerosol numbers concentrations are fairly well simulated at all levels in the sampled atmosphere. At 6.45 UTC, the aircraft flew close to the surface, south of Marseilles and the Berre pond. Measurements denote a small increase in particle numbers. At the end of flight 39, the ARAT heading to Avignon airport flew through the Fos-Berre industrial plume. The aircraft then was at 960 hPa (about 400 m) within the boundary layer. The model has well captured the plume which confirms accurate timing of sea-breeze advance at the surface in the simulations. Due to reduced aerosol simulations and our treatment of boundary conditions, the model cannot detect transboundary aerosol transport. Cousin et al. (2004) have shown that regional transport of an ozone layer issued from the Barcelona area has an impact in the ESCOMPTE domain on 24 June. A similar effect could be expected for particles, though if in the ESCOMPTE domain, the particle pollution sources could be more restricted to local emissions. Due to the shorter aerosol spin-up, regional particle layers probably have not enough time to be generated in the model.



Fig. 9. PM-10 time series (scales in  $\mu$ g m<sup>-3</sup> on the left) for 24 June at: (a) Marseilles, (b) Martigues, (c) Dupail, (d) Realtor and (e) Plan d'Aups. (squares for the model, dark curve for measurements)

#### 5. Conclusions

The ORISAM aerosol model initially incorporating coagulation and condensation processes has been improved and coupled on-line with the Meso-NH-C model to better account for interactions between atmospheric dynamics, gaseous chemistry and aerosol processes. Simulations at fine grid resolutions were performed with a new ad hoc emission combustion particle inventory based on the new ESCOMPTE detailed inventory for gases and combustion fuels. One observes overall good agreement between measured and modelled BC concentrations, particularly in urban and industrial source areas. Aerosol modelling fairly reproduces the concentration levels of particulate organic matter, despite underestimation of organics in the afternoon. Ongoing developments aim at to better representing secondary aerosol formation in the model. Aerosol yields can also be replaced by new explicit mechanistic chemical scheme for SOA formation (e.g. Griffin et al., 2002). Inorganic species are underestimated in the model. For sulphates, even with high

sulphur dioxide levels, sulphate oxidation is underestimated. One reason lies in the underestimation of relative humidities affecting the condensation processes. Another important factor requiring further consideration is more precise assessment of primary sulphate emissions especially in areas with many industrial plumes such as the ESCOMPTE domain. Nitrates and ammonium are also affected by RH underestimation. After implementing heterogeneous chemistry for nitrates, aerosol concentrations of nitrates and ammonium increase, particularly in the morning and the evening. Nevertheless, our modelling study underlines the major biaises due to neglecting the terrigeneous species, thus leading to major nitrate and ammonium underestimations. This points out to necessary further developments with incorporation of pre-existing coarse carbonates or dust in order to capture the attachment of acidic gases. Consequently, modelled PM-10 concentrations are underestimated versus measurements. The situation is much more satisfactory for submicron particles. The model could reproduce particle numbers in this submicrometer size range, at the surface and in the



Fig. 10. Particle number time series (scale in part  $cm^{-3}$  on the left) for 24 June at Marseilles in: (a) the first bin and (b) the second bin.



Fig. 11. Time series during the ARAT morning flight 39 for particle numbers (scale in part cm<sup>-3</sup> on the left). Bin 1 particles between 0.03 and 0.156  $\mu$ m, total model particle between 0.03 and 3  $\mu$ m. CNC total particle number between 0.01 and 3  $\mu$ m.

atmospheric column. Future improvements for this sizerange could be identified related to transboundary conditions providing higher background conditions thus enhancing submicron particle concentrations directly or indirectly by offering additional surface areas to further gas-to-particle conversion.

As an extension to a previous paper (Cousin et al., 2004) devoted to dynamics and gas-phase chemistry for 24 June 2001, this study further considers aerosols

coupling in an on-line mode, within Meso-NH-Chemistry using the ORISAM model (Bessagnet and Rosset, 2001). During this exploratory phase of aerosol modelling, some agreement but also limitations have been pointed out, useful for further developments of OR-ISAM, particularly as regards terrigeneous and secondary organic aerosol components.

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