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SUMMARY

As part of a regional project of the study of pollution in two alpine valleys (POVA), an intensive campaign of measurements for **VOCs, carbonyl compounds, PM₁₀, particles and major ionic species** was performed in Maurienne Valley (French Alps) during one week in August 2000. In summer, under anticyclonic conditions, the dispersion of air pollutants in deep valleys is mainly dependent on an usual characteristic cycle: up-valley wind for the day, down-valley wind for the night. During the sampling campaign, the diurnal variation west-east wind was changed by a South wind for two days. A **saharan dust episode** occurred, characterized by large increases of **PM₁₀, large particles, and Ca²⁺**. This dust episode was followed by an increase of **fine particles** (0.3 μm) and of **SO₄²⁻**, indicating the intrusion of an anthropogenic air mass. The evolution of VOCs have been influenced by these events and the concentration levels were higher during this period. The ratio **benzene/ toluene** was low (**0.7**) during the episode, which indicates an **urban pollution**.

KEYWORDS : VOCs, Saharan episode, particles concentration, transport of air pollutants, alpine valley pollution.

INTRODUCTION

Volatile organic compounds (VOCs) are important precursors for the formation of ozone and photooxidant in the atmosphere [1, 2]. In the mid latitudes of the Northern Hemisphere, their main sources are either biogenic [3] or anthropogenic, primarily with combustion of fossil fuel in industrial processes, domestic heating and road traffic. In the mountainous areas, the anthropogenic sources are concentrated in the valleys where most residences, industries and traffic are located [4]. Specifically, in the alpine

valleys supporting international traffic, the concentration of VOCs is generally largely influenced by vehicles' emissions and this source is becoming more and more important because of the increased traffic over the last decades.

When anticyclonic conditions prevail in summer, the dispersion of the atmospheric concentrations in deep valleys is mainly dependent upon the atmospheric mixing according to an usual characteristic cycle. On days with enhanced radiation, up-valley winds are formed during the day, transporting air from the foreland into the mountains. During the night, down-valley winds yield a reversal of the daytime flow system [5]. The study of such meteorological processes within valleys has a long tradition and has led to a good understanding of valley winds, slope winds and the vertical thermal mixing [6 – 9]. Some recent work also focused on the implication of ozone concentrations in alpine regions [10, 11]. However, only a few studies have been published about ozone precursors in the Alps [4, 12 - 14]. Most of them (POLLUMET: air pollution and meteorology [15] or TRACT: transport of air pollutions over complex terrain [16] focused on ozone formation during summer conditions with weak winds, while the program VOTALP focused on the vertical ozone transport over the Alps [17, 18].

The present paper describes some measurements of VOCs, especially BTEX (benzene, toluene, ethylbenzene, (m+p)-xylene) and carbonyl compounds, obtained in the Maurienne valley of the French Alps during August 2000, when a large episode of dust of Saharan origin took place. These data were collected during an intensive field campaign from the POVA (**P**ollution des **V**allées **A**lpines) program, that was initiated after the closing of the Mont-Blanc tunnel in march 1999. The goals of POVA are to evaluate (before and after the reopening of the Mont-Blanc tunnel) the respective influence of anthropogenic and biogenic sources of emission in the Chamonix and Maurienne valleys, and to develop a model of atmospheric pollution dispersion in these complex alpine terrains to perform studies of different scenarios of devel-

opment. In the present paper, the interpretation of the VOC data is focused on the differences observed in the concentrations during a regular period of up-slope/ down-slope system, and the specific period with Saharan dust intrusion.

MATERIALS AND METHODS

Field campaign and measurements: The field campaign took place from August 22nd to August 30th 2000 in the Maurienne Valley (French Alps) (Figure 1) within the frame of the POVA (Pollution des Vallées Alpines) program. The upper part of the Maurienne valley where the sampling sites are located (from Saint Michel de Maurienne and Lanslevillard), is about 40 km long and is roughly oriented SW-NE. The valley is about 6 km wide on average in this part (crest to crest), the valley floor being surrounded by mountains reaching more than 3000 m above sea level on average. While the lower part of the valley (before Saint Jean) comprises several industries (in-

cluding some large aluminum making factories), the upper part (after Modane) is more agricultural and less densely populated. The highway leading to the tunnel du Fréjus at Modane (supporting most of the transalpine traffic between France and Italy since the closing of the Mont Blanc tunnel) is a major source of emission from vehicles, including heavy duty traffic. Several sites were instrumented for the measurement of different parameters, including Orelle (altitude 950m above sea level), Modane (1050m above sea level) and Sollières (1340m above sea level). Modane is a small town with a population of 5200 inhabitants, while Orelle and Sollières are little villages (populations of 360 and 170 inhabitants, respectively). Sollières is located near the end of the valley, 17 km below the Col du Mont Cenis pass going to Italy (with the large city of Torino 95 km away). The sampling site at Orelle is on a flat area about 100 m above the valley floor, that in Modane is about 800 m out of the city center (on the opposite side of the Frejus Tunnel), while that in Sollières is on a grassy flat and wide open area used occasionally as an airfield.

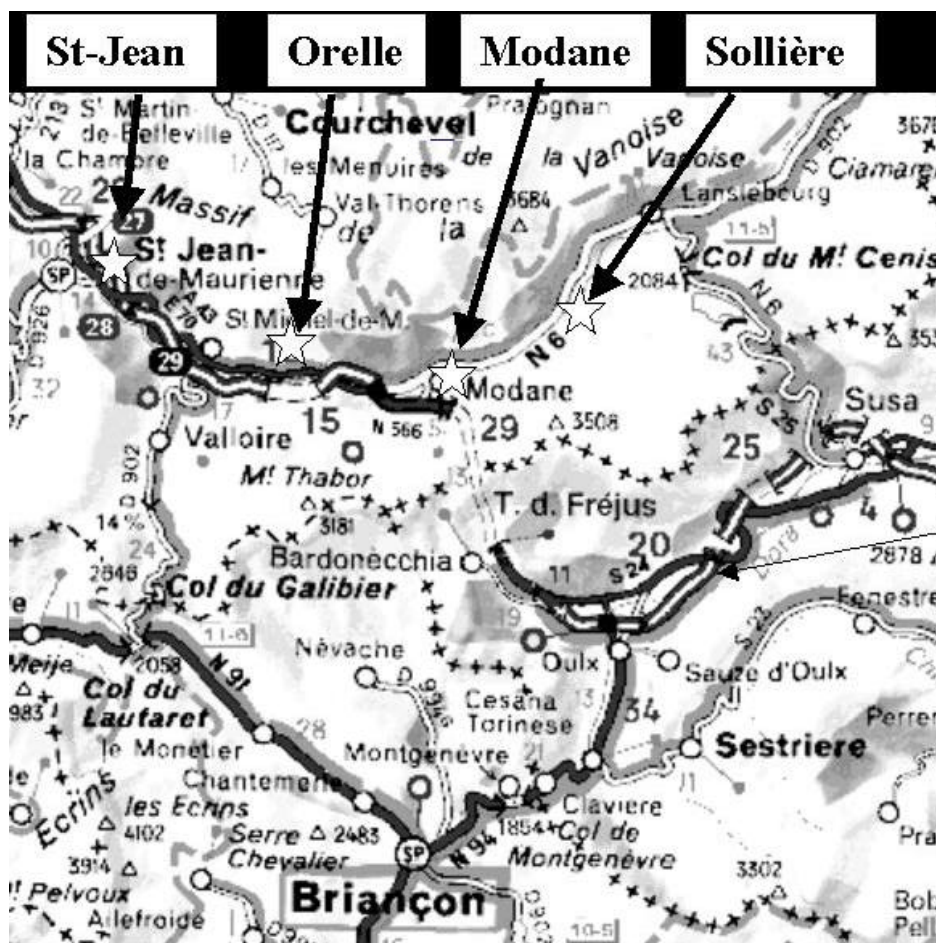


FIGURE 1 - Situation of the different sampling sites in Maurienne valley during POVA.

A wind profiler (Degreane SA, Toulon, France) was installed in Modane. This device measured the vertical profiles above the site for the wind direction and horizontal speed up to an altitude of 2000 m above the valley floor with 25 m resolution. Data were gathered during the whole week with a 15 min time resolution. Meteorological data (temperature, wind direction and wind speed as 1h averages) are also available from several stations from the national network of Météo France, in Lanslevillard (8 km further inside the valley compared to Sollières) and Modane. PM 10 measurements performed with Tapered Element Oscillating Microscale (TEOM) were maintained for the all week at the three sites (Orelle, Modane, Sollières) with a 15 min time resolution. We are presenting 1h averages of these data. The air inlets of the TEOM were heated up to temperature of 50 °C. Particles number concentrations were measured in Sollières during the whole period with a laser particle counter (Malvern MPC 301X/501X), with a resolution time of 15 min. Aerosols were classified in 4 size ranges (diameter of 0.3 /0.5; 0.5/1; 1/5, > 5 µm). The air intake was 90 cm long, with a flow rate of 2.83 lmin⁻¹.

Aerosol sampling for the determination of ionic species was maintained at Orelle and Sollières during the whole period with a resolution time of 3 h. The sampling was performed on Teflon Zefluor filters (0,5 µm pore size) with an open face filter holder at a flow rate of 1 m³hr⁻¹. Filters were changed manually and stored individually in air tight glass bottles in a cold place until their analysis at LGGE. Filter blanks were collected systematically every day and processed as actual samples. Both actual filters and blanks were cleaned in methanol baths before the campaign in order to reduce their background content for the chemical species analyzed [19].

VOCs sampling was maintained at Sollières and Orelle during the whole period. The sampling for carbonyl compounds (especially aldehydes) was performed on 2,4-DNPH coated silica cartridges (Waters) with a flow rate of 1l.min⁻¹, controlled by mass flow controllers. The sampling time was 2 h. Sampling for other VOCs (especially aromatic compounds) was performed on an absorbent, 200 mg of Tenax TA (60-80 mesh), in stainless steel tube (Perkin Elmer) previously conditioned 4 h at 300 °C. The sampling flow was set at 100 ml.min⁻¹ and controlled by a massflow controller. The sampling duration was set to 30 min. to avoid breakthrough. The series in Sollières suffered from several interruptions due to logistical constraints. Cartridges were changed manually and stored individually in a cold place until their analysis at GRECA. Cartridges blanks were collected systematically every day and processed as actual samples.

Analytical methods: Teflon filters were analyzed for soluble ionic components with ionic chromatography in a class 10000 clean room at LGGE. All handling procedures took place under a class 100 laminar flow hood. Filters were extracted for 10 min in their storage bottle

using 0.8 ml of methanol (Baker CMOS grade) in order to first wet the Teflon filters, followed by 9.2 ml of Milli-Q water (resistivity 18 M.Ω.m⁻¹). Cations (Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺) were analyzed with a DIONEX 100 chromatograph, using a CS12 column, following the conditions prescribed by the DIONEX company. Anions (Cl⁻, NO₃⁻, SO₄²⁻ and a suite of organic acids) were analyzed with a DIONEX 500, using an AS11 column, as described elsewhere [19, 20]. Only data from a selection of these ionic species are presented here to substantiate the general aerosol chemistry during the Saharan dust episode. The overall series will be discussed in another publication.

All tubes containing 200 mg Tenax were analyzed by an automatic thermodesorption device (Perkin Elmer ATD 400) connected to a gas chromatograph (Perkin Elmer Autosystem XL) coupled with a mass spectrometer (GC/MS) (Perkin Elmer Turbomass). Desorption conditions were set as follows : desorption temperature of 300 °C, cryofocussing on 20 mg Tenax TA at -20 °C and flash injection at 300 °C for 90 s. The temperature of the transfer line was 225°C and it was directly connected to a capillary column PM-5MS Perkin Elmer (50 m x 0.25 mm, 0.5 µm film thickness) flushed with 1 ml.min⁻¹ helium carrier gas. The analysis started at 50°C for 5 min and temperature was increased by 5 °C.min⁻¹ up to 300 °C, maintained for 5 min.

Identification of the compounds with the mass spectrometer was accomplished by the retention times, standards compounds, and GC/MS library. Full scan mode was used with a mass range from 35 to 350 and a scan speed of 1 scan. s⁻¹. The compounds measured were: aromatic compounds (benzene, toluene, ethylbenzene, m+p-xylene, o-xylene, o,m+p-ethyltoluene, 1,2,4-trimethylbenzene), isoprene and terpenes (α-pinene, β-pinene, myrcene, limonene). Calibration curves were obtained for all compounds using standards prepared in an atmospheric simulation chamber in the laboratory. The uncertainty obtained with this method is lower than 10 %.

The DNPH-coated cartridges were eluted with 3 ml of acetonitrile (HPLC grade). Chromatographic analysis was performed on an HPLC system wequipped with a Jasco PU-980 intelligent HPLC pump, with an AS-950 intelligent sampler and a variable wavelength 875 UV-detector adjusted to 365 nm. The compounds measured were formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, valeraldehyde, hexaldehyde, benzaldehyde, and tolualdehyde. Calibration curves were obtained using standards prepared by hydrazones synthesis in the laboratory. The uncertainty obtained with this method is lower than 10%.

RESULTS AND DISCUSSION

Dust episode

The general meteorological situation during the early part of the week long experiment in the Maurienne valley was classical for the summer season in the area, with marked diurnal cycles of the temperature between 5 °C at

night and up to 30 °C at day (Figure 2a). The temperature at Sollières showed larger diurnal variation than in Orelle, partly due to the higher elevation of the former site. Very few clouds were seen during the whole period, and no precipitation was recorded between August 22nd – 29th. As indicated by the record of the wind profiler in Modane, the wind direction pattern inside the valley up to 2000 m is clearly dominated by diurnal changes between up slope (ie from the west) (during the day) and down slope (at night) directions, driven by thermal heating. The wind speed is higher during the day than at night, but generally stays below 4 m s⁻¹. This diurnal pattern is also clearly seen in the wind records at the surface at Modane and Lanslevillard. This situation changed on August 26th and 27th, with a

strong input of south wind reaching the valley floor in the morning of the 26th. The wind record in Lanslevillard clearly indicates sustained wind speeds of 10-12 ms⁻¹ coming from south during the whole period, while the wind speed is lower in Modane. Visual observation at ground indicates a highly turbid atmosphere at that time, persisting till the end of 27th August. A SeaWiFS satellite picture of the Mediterranean area taken on August 25th indicates the occurrence of Saharan dust plumes over the Mediterranean Sea, together with plumes from biomass burning out of the African coast. The situation returned to normal during the 27th August, with much cooler temperatures than in the early part of the week and reinstallation of the up-slope/ down-slope system.

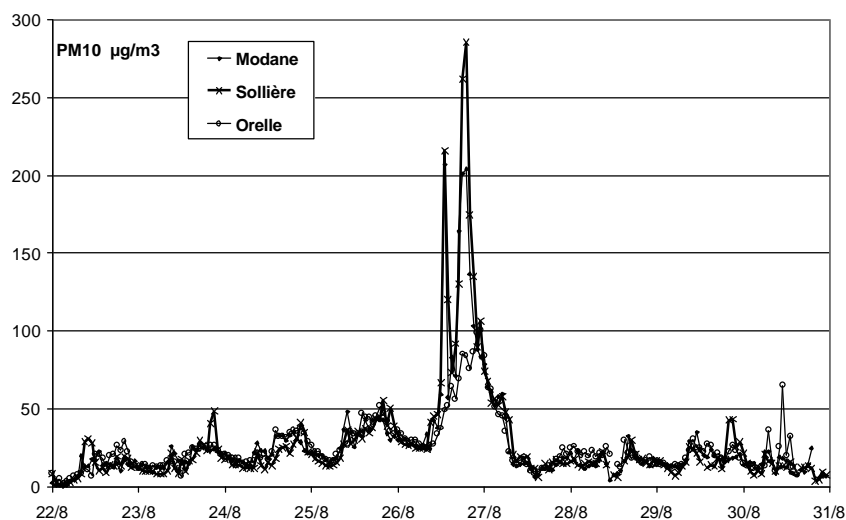
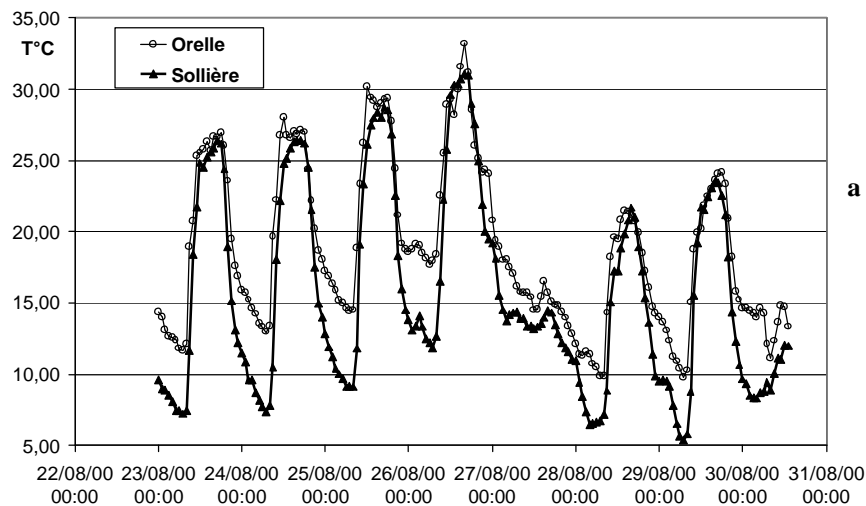


FIGURE 2a - Hourly average temperatures(°C)

b - Hourly average of PM10 (µg.m⁻³) at Sollières, Modane and Orelle during the weeklong campaign.

The occurrence of dust with a northern African origin is a well-known phenomenon over southern Europe [21, 22], which is well recorded in Alpine ice cores [23]. It is often associated with south winds that can create foehn conditions. During the Mesoscale Alpine Program (MAP) special observation period (SOP) between 7 September and 15 November 1999, ground-based and airborne measurements have been conducted in Rhine valley south of the Lake of Constance to investigate the non-stationary aspects of foehn. Ozone concentrations in the valley tend to increase at the onset of foehn. This results in higher ozone concentrations in the valley at night and in the morning hours. These ozone concentrations are usually not as high as the highest ozone concentrations reached during photochemical smog episodes. Foehn events do not necessarily cause ozone peaks but prolong the duration of ozone stress in Foehn areas [24]. In our case, we will investigate the influence of such a south wind episode on some VOCs concentrations

PM10, size distributions, and ionic chemistry of the aerosol

Figure 2b presents the hourly average of PM10 measurements during the whole campaign at the 3 sites. Concentrations are slowly increasing during the first part of the experiment (August 22nd – 26th) with daily averages in the 20 - 30 $\mu\text{g} \cdot \text{m}^{-3}$ range, marked diurnal variations, and

maxima during late afternoon / early evening. All 3 sites are behaving in much the same way despite being separated by about 22 km. A very large increase in the concentrations is seen in the late morning of the 26th for the sites of Modane and Sollière, coincident with the turn to south winds observed with the wind profiler. Hourly averages are reaching 285 $\mu\text{g} \cdot \text{m}^{-3}$ for the latter site at 19:00h while, in the mean time, the concentrations at Orelle are increasing only moderately, with maximal concentration of 100 $\mu\text{g} \cdot \text{m}^{-3}$. The situation is back to low concentrations for all three sites at noon on the 27th August.

The record provided by the particle counter set in Sollières allows to characterize more precisely the aerosol during this period. Figure 3 presents the record for the 4 channels together with the record of the PM10 measurement at Sollières between August 25th – 27th.

The PM10 increase takes place in two distinct periods on the 26th, the first one from 11:30h to 14:00h, and the second one from 15:00h to midnight. During both periods the mass increase is very well correlated with the change in the concentrations of the particles in the supermicron channels ($d > 5 \mu\text{m}$ and $1 \mu\text{m} > d > 0.5 \mu\text{m}$). The increase is also substantial in the lower channel ($0.5 \mu\text{m} > d > 0.3 \mu\text{m}$), while the smaller particles ($0.3 \mu\text{m} > d > 0.1 \mu\text{m}$) do not experience much changes.

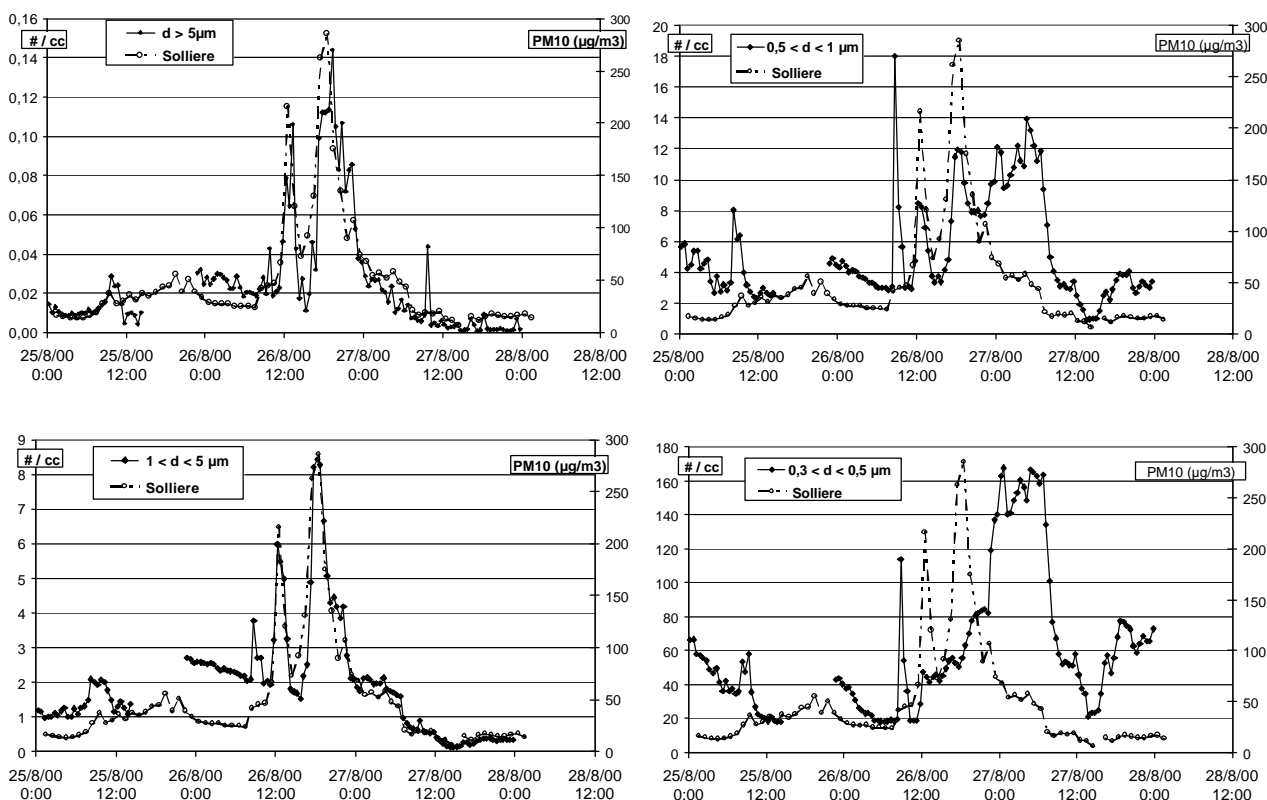


FIGURE 3 - Hourly average concentration of PM10 ($\mu\text{g} \cdot \text{m}^{-3}$) and of particles number concentrations (in particles number (#)/ cubic centimeter (cc) in 4 size ranges.

Indeed, Figure 3 indicates a very different behavior of the particle number in this last size range. There is a first short term episode of high concentrations in the early morning of the 26th (before the large particle increase), but the most striking feature is an episode of very high concentrations (also seen for the particles in the $0.5 \mu\text{m} > d > 1\mu\text{m}$ channel) starting during the dust episode and lasting till noon on the 27th of August. Despite its large increase compared to the background level, it is not influencing the particle mass much, as seen with the PM10 series. All of these observations are consistent with an episode of Saharan dust input (split in two parts), fol-

lowed by the intrusion of an air mass contaminated by anthropogenic emissions. The PM10 results show that the largest part of the dust plume did not influence all the sites in the valley in the same way, but was more important at the higher altitude sites. However, the maximum hourly value ($69.8 \mu\text{g} \cdot \text{m}^{-3}$) reached in the town of Saint Jean de Maurienne (30 km further down the valley compared to Modane, 550 m above sea level) during this episode is in the upper 1.5 % of the range of hourly measurements maintained between March 1st, 1998 and December 1st, 2001, indicating that the dust plume was still present in the whole area.

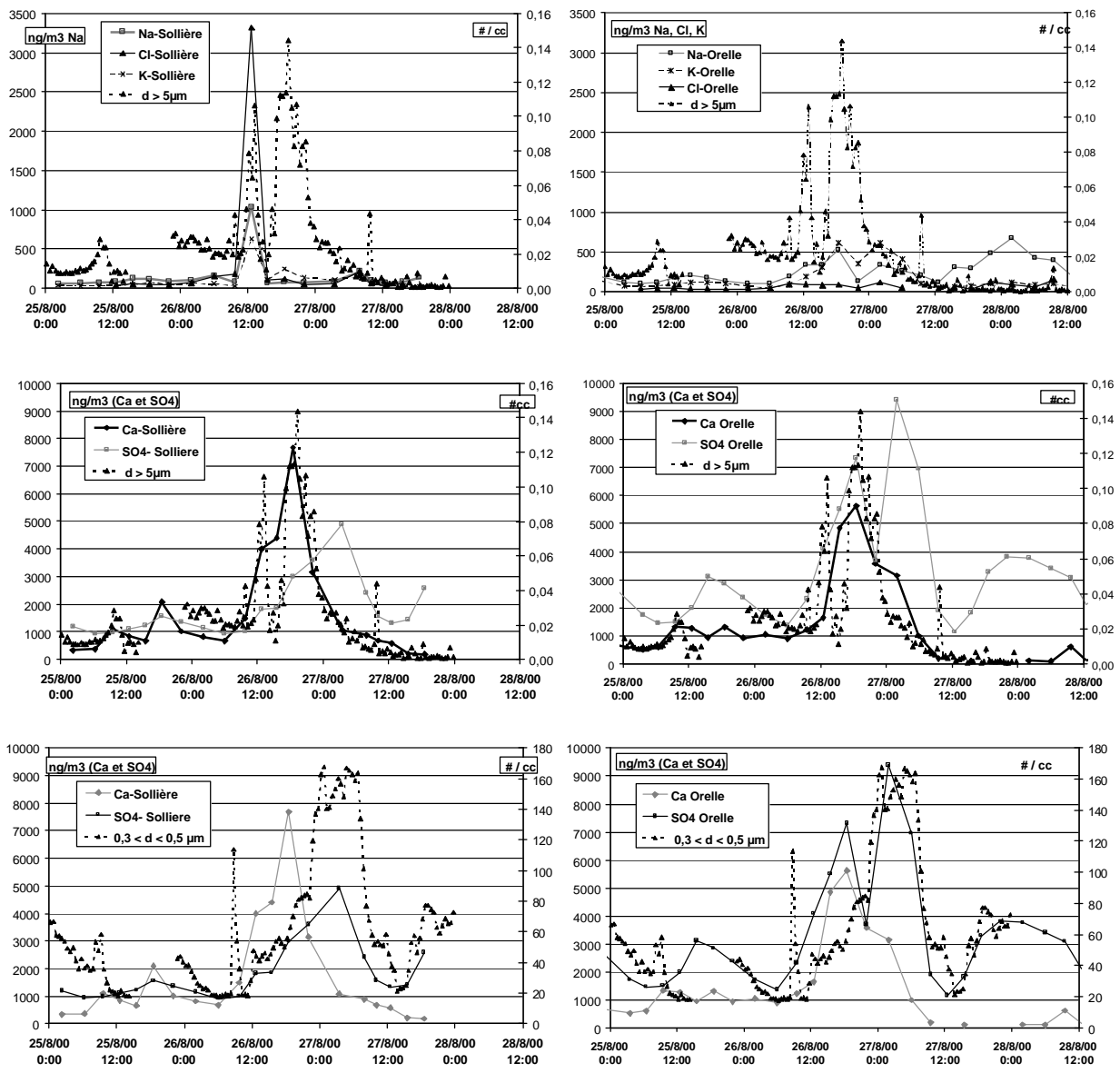


FIGURE 4a - Evolution of Na^+ , Cl^- and K^+ ($\text{ng} \cdot \text{m}^{-3}$) and particles number concentration ($d > 5 \mu\text{m}$).
b - Evolution of Ca^{2+} , SO_4^{2-} ($\text{ng} \cdot \text{m}^{-3}$) and particles number concentration ($d > 5 \mu\text{m}$).
c - Evolution of Ca^{2+} , SO_4^{2-} ($\text{ng} \cdot \text{m}^{-3}$) and particles number concentration ($0.3 > d > 0.5 \mu\text{m}$).
 Left side : Sollières, right part Orelle.

This scenario can be corroborated with the chemistry of the aerosol as measured with ion chromatography. In Sollières, the first episode recorded for the large particles and for PM10 (from 11.30h to 14:00h on the 26th) corresponds to the beginning of the increase in calcium concentration (Figure 4b), but the most striking features are the very large increases of concentrations for Na⁺, Cl⁻, and K⁺ (Figure 4a), with an enrichment of Cl⁻ by more than a factor of 55 over the background level of the previous days. The large enrichment in Na⁺ may be an indication of marine influences during this first part of the episode. However, the mass ratios Cl⁻/Na⁺ and K⁺/Na⁺ (at 3.20 and 0.61, respectively) are much larger than the sea water ratios (1.75 and 0.035, respectively) suggesting the strong influence of other types of sources for these species. The enrichment in Cl⁻ and K⁺ could be due to a mixing of large particles with biomass burning emissions [25], an hypothesis not substantiated by the lack of large increase of the fine particles concentrations and of that of organic acids (including oxalate) generally associated with this type of emissions [26]. Finally, there is a possibility that the enrichment in Na⁺, Cl⁻, and K⁺ is linked with a dust source containing halite as a sediment, as seen in a previous dust episode over the Alps [21]. Figure 4a also shows that this first episode is not seen at Orelle, in agreement with the change in the PM10 concentrations at both sites (Figure 2b).

The second part episode (from 15:30h to midnight on the 26th) recorded for the large particles and for PM10 is characterized by the large increase of the concentrations of Ca²⁺ both at Orelle and Sollières (Figure 4b), that already started during the first part of the episode in Sollières. Soluble calcium can be considered as a good surrogate for the occurrence of crustal species in the aerosol, and the very large concentrations reached in this case, are in agreement with a desert dust plume reaching the site. There is an excellent correlation between the concentrations of calcium, large particles, and PM10, despite the fact that soluble calcium represents only 3.5 % on average of the PM10 mass during the entire period in Sollières. We have at present no explanation for the gap between the first and the second part of the episode in Sollières, that is well-marked in the PM10 and particle records, while it is not seen in the calcium concentrations. A detailed chemical balance (including insoluble species) would have been needed in order to propose a comprehensive scenario.

As shown in figure 4c, the concentrations of sulfate are also increasing during both periods. This increase is much higher in Orelle than in Sollières for the first part, when the dust is at its maximum. It is possible that this large increase at Orelle is produced by interaction of SO₂ from sources in the valley with the alkaline dust. However, in both places, the maximum concentrations are reached only well after the dusty period, in the early hours of the 27th. Figure 4c indicates that in Sollières this gradual increase is strictly parallel to a change in concentra-

tions of the small particles in the 0.3 μm to 0.5 μm size range, that starts slowly during the entire dust episode, but reaches its maximum during the first part of the 27th. As these particles containing sulfate are the (direct or indirect) products of combustion, this third episode is most probably related to an anthropogenic plume. In Sollières, the very high concentrations reached at that time compared to the background of the early week are in favor of an origin from outside of the valley, a hypothesis also substantiated by the wind direction still coming from the south at that time.

Overall, these measurements are in agreement with the parallel intrusion of a dust episode at the two sites, with some differences in their characteristics. The input of dust seems more limited in Orelle (as indicated by the lower PM10 and calcium concentrations), but the timing is similar. At both sites, this dust event is followed by an anthropogenic episode with an origin from the outside of the Maurienne valley.

Evolution of VOC concentrations:

Only the most important and characteristic anthropogenic compounds are discussed in this paper, including the aromatic compounds (BTEX: benzene, toluene, ethylbenzene and xylene), as well as formaldehyde and acetaldehyde. The concentration of other carbonyl compounds are very low, near their detection limits. The arithmetic mean concentrations obtained at the two sites (Orelle and Sollières) are presented in Table 1 (for BTEX) and Table 2 (for aldehydes). Separate averages are proposed for the periods before and during the “dust episode” with the “dust episode” including the 3 periods described above. The calculation takes into account 43 samples in Orelle and 31 samples in Sollières before the episode, and 12 samples at both sites during the dust event. These tables also report previous results from the literature.

Taking the variability into account, the mean concentrations of BTEX before the dust episode are rather equivalent at the two Maurienne sites. Toluene is generally the most abundant aromatic compound in urban atmospheres. Its mean concentration in the Maurienne valley, about 0.34 ppbv, is comparable to that in a rural atmosphere, as can be observed in a pine forest site in Germany (Table 1). It is about 10 times lower than that in the down town area of Grenoble. Benzene mean concentrations in the Maurienne valley, about 0.5 ppbv, characterize a moderately polluted atmosphere, as can be observed in the Grono Valley, as opposed to an urban one (like Grenoble) (Table 1). The concentrations of the other compounds (ethylbenzene and m&p-xylene) are low, and similar to the concentration in a rural atmosphere in a forest in Germany. The average concentration is larger for benzene than for toluene at our two sites, which is also rather typical for an atmosphere away from direct exposition to sources, and is related to the larger reactivity of toluene, particularly with the hydroxyl radical, OH [32]. The mean concentrations for carbonyls (formaldehyde

TABLE 1 - VOCs concentrations in ppbv.

ppbv		Benzene	Toluene	Ethylbenzene	(m+p)-Xylene
Before dust episode	Orelle	0.52 ± 0.05	0.35 ± 0.03	0.04 ± 0.01	0.10 ± 0.01
	Sollières	0.46 ± 0.04	0.33 ± 0.03	0.06 ± 0.01	0.14 ± 0.01
During dust episode	Orelle	0.65 ± 0.06	0.90 ± 0.09	0.09 ± 0.01	0.22 ± 0.02
	Sollières	0.57 ± 0.05	1.16 ± 0.11	0.09 ± 0.01	0.10 ± 0.01
Pine forest (Germany). July, 1991	[27]	0.17	0.49	0.11	0.17
Everest . Sept., 1991-South wind	[27]	0.61	8.19	0.47	0.79
Everest . Oct., 1993-North wind	[27]	0.15	0.04	-	-
Grono (Italy). August 1996	[4]	0.40	0.80	-	0.30
Grenoble, downtown. Mai 2000	*	0.85	3.03	0.51	1.42

* : GRECA, unpublished data

TABLE 2 - Carbonyl concentrations in ppbv.

ppbv		Formaldehyde	Acetaldehyde
Before dust episode	Orelle	1.90 ± 0.19	0.55 ± 0.05
	Sollières	1.46 ± 0.14	0.53 ± 0.05
During dust episode	Orelle	2.27 ± 0.22	0.59 ± 0.06
	Sollières	0.87 ± 0.08	0.38 ± 0.03
Rural Schauinsland. Sept. 1992	[28], [31]	1.0	0.7
Ontario. July, 1988	[29]	1.7	0.5
Wank. October, 1991	[30]	1.3	0.6
Grenoble, down town. Apr. 2001	*	6.1	2.5

* GRECA, unpublished data

and acetaldehyde) at Orelle and Sollières before the dust episode are also rather similar. Again, they are typical for rural atmospheres, as in Ontario or Wank (Table 2). These average concentrations are lower than the measurements at urban sites like Grenoble.

Table 1 and 2 indicate large increases of the average concentrations during the dust period, with an increase of 25 % for benzene at the two sites, and a much larger change (+250 % at Orelle and +350 % at Sollières) for toluene. In the same way, concentrations of ethylbenzene and xylene are nearly doubling at the two sites from one period to the other. The changes in aldehyde concentrations are less clear, with the concentrations at Orelle increasing and the concentrations at Sollières slightly decreasing compared to the previous period.

The time series of concentrations for these species before the dust episode show parallel evolution for some of the compounds, as indicated by the correlation coefficients presented in Table 3. The concentrations of toluene, ethylbenzene, and (m+p)-xylene are highly significantly correlated at the two sites, allowing the hypothesis of a common dominant source and/or influence of the same atmospheric processes (dispersion, reactivity) for these species. The correlations are larger in Orelle than in Sollières, in agreement with a lower influence of the reactivity and dispersion processes at the former site, closer to the sources related to traffic. Conversely, the lack of correlation between benzene and the other species on both sites results most probably from the very large difference in their respective reactivity (Table 4) leading to a larger life time of benzene than toluene.

TABLE 3 - Correlation coefficient (R^2) and slope of the linear regression between BTEX and carbonyl compounds before the dust episode, for 43 samples in Orelle and 31 samples in Sollières.

	Orelle		Sollières	
	slope	R^2	slope	R^2
Benzene / Toluene	0.61	0.060	0.71	0.202
Toluene / Ethylbenzene	0.10	0.873	0.16	0.743
Toluene / (m+p)-Xylene	0.27	0.871	0.44	0.748
Ethylbenzene / (m+p)-Xylene	2.67	0.991	2.65	0.954
Formaldehyde / Acetaldehyde	0.26	0.508	0.33	0.09

TABLE 4 - Rate constant for reaction with the hydroxyl radical OH.

	Rate constants (from ref 32) ($k \times 10^{12} = \text{molecules.cm}^3.\text{s}^{-1}$)
Benzene	1.23
Toluene	5.96
Ethylbenzene	7.1
(m+p)-Xylene	14.3
Formaldehyde	9.37
Acetaldehyde	15.8

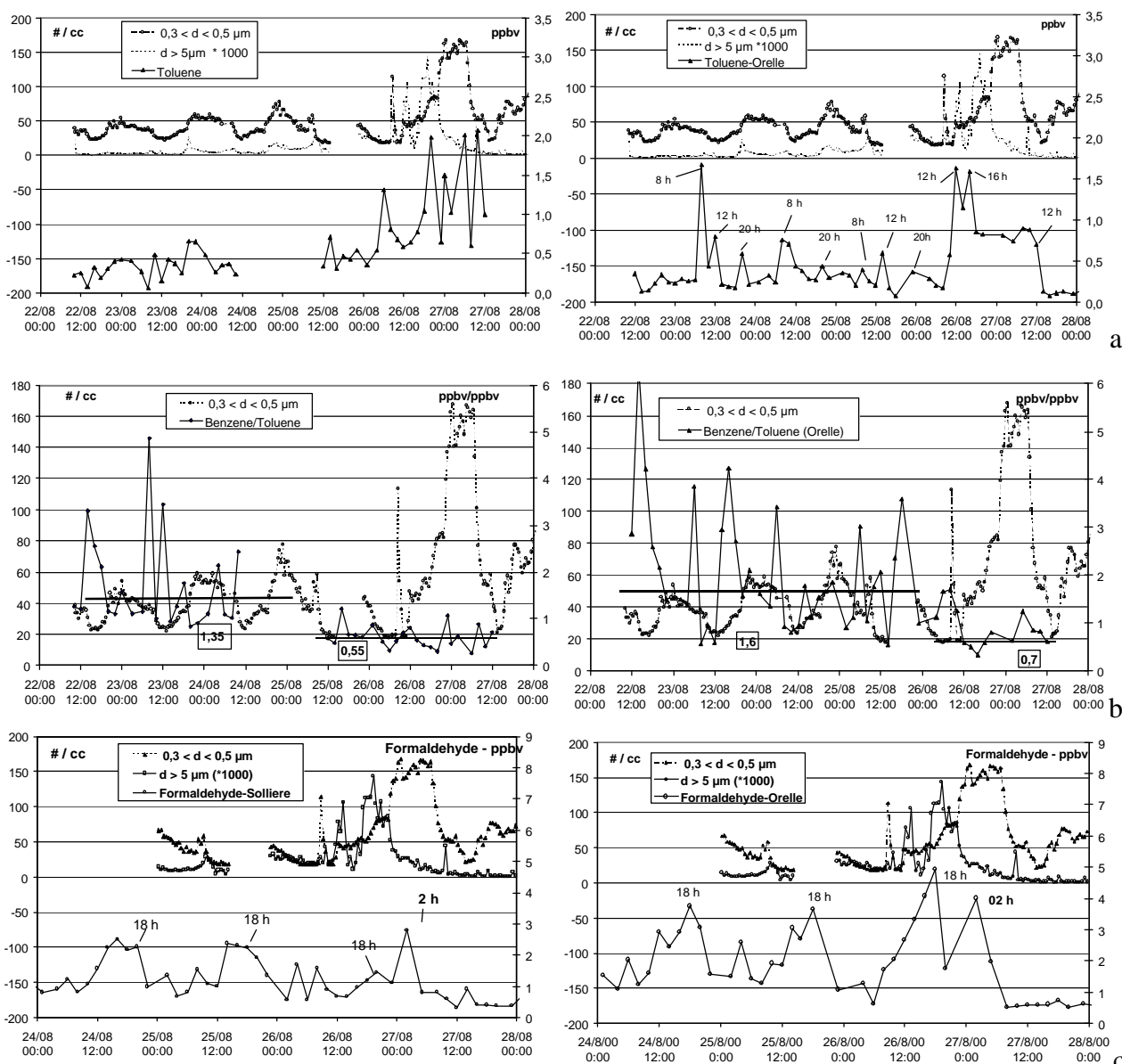


FIGURE 5a - time series of toluene concentrations (ppbv) in Sollières (left) and Orelle (right)
 b - time series of the ratio benzene/toluene (ppbv/ppbv) in Sollières (left) and Orelle (right)
 c - Evolution of formaldehyde (ppbv) in Sollières (left) and Orelle (right)
 The number concentration of particles in 2 size ranges in Sollières is shown for comparison.

The evolution of the toluene concentrations between August 22nd - 28th at the two sites are presented in Figure 5a, with Figure 5b showing the evolution of the benzene/toluene ratio. The time series of concentrations of formaldehyde are presented in Figure 5c. In both figures, the evolution of the particle concentrations are also given for two size ranges of interest.

The time series in both Sollières and Orelle do not show well-marked diurnal variations before the dust episode, like the one demonstrated during the VOTALP program (4). The low concentrations, the distance from the sources, and the local geomorphology around the site (with several converging secondary valleys in the area) most probably explain this lack of diurnal pattern for Sollières. More structures can be observed in the time series at Orelle, with systematic peaks of toluene concentrations at 8 h, 12 h and 20 h on the first days of the campaign. The geometry of the valley is simpler at that site, and the variations of the concentrations result from a complex interplay between the emissions (larger during day time), the variation in the height of the inversion layer (smaller during the first part of the night, as indicated by the clear cycle of PM10 concentrations), the dispersion with the up-wind/ down-wind system (the former bringing higher concentrations from the lower portion of the valley) and the increased reactivity linked with photochemistry during day time.

At both sites, carbonyl concentrations show clearer diurnal variations before the dust period, with a daily broad maximum during the afternoon. As these carbonyl compounds are essentially formed from the degradation of primary pollutants following photochemical reactions, this cycle underlines the importance of the formation process compared to the change in concentrations linked to the dynamics (by changes of the height of the inversion layer or by dispersion with increasing wind speed).

Perturbation during the dust event

As mentioned earlier, the average concentrations of BTEX and carbonyls are clearly perturbed by the intrusion of south winds linked to the dust episode (Tables 1 and 2). In Sollières, the toluene concentrations increase in parallel with the submicron aerosol number concentration and reach a maximum at the same time (Figure 5a). In Orelle, the increase is concurrent with that of sulfate (Figures 5a and 4c), with a couple of peaks during the crustal event and a sustained level during the anthropogenic part of the episode. At both sites, the average concentrations for all BTEX compounds are much higher than that of the previous days. Particularly, the high levels reached at night are unusual considering the evolutions observed in Orelle the previous days.

The carbonyl concentrations also present the same kind of perturbations (Figure 5c). The daily maximum during the afternoon (concurrent with the dust maximum) is followed by an unusual maximum at night, in parallel with the anthropogenic inputs linked with south winds. This southern air mass brings into the Maurienne valley chemical species from a polluted area, that have already been degraded photochemically the previous afternoon and leading to high concentrations of formaldehyde at night. The impact of the high wind speed during this episode on the structure of the inversion layer close to ground remains to be evaluated, but most probably allows more mixing than during the previous period.

It is possible to evaluate the origin of this air mass by a rough calculation of its age. The air mass photochemical age can be characterized by the benzene/toluene ratio. Benzene and toluene are emitted by automobiles in a ratio around 0.5 (benzene (ppbv) / toluene (ppbv)). During the dust episode, the average ratio benzene/toluene is about 0.7 (0.55) in Orelle (Sollières), compared to mean values of 1.4 (1.3) for the previous days (Table 5 and Figure 5b). It should be emphasized that the ratio in the days before the dust episode are rather variable, with large changes in the course of the day.

TABLE 5 - Ratio Benzene/Toluene (ppbv/ppbv).

	benzene/toluene	
	Before dust episode (Orelle / Sollières)	1.5 ± 0.3
During dust episode (Orelle / Sollières)	0.7 ± 0.15	0.55 ± 0.1
Pine forest (Germany), July, 1991 [27]		0.34
Foot of Everest , Sept, 1991-South wind [27]		0.07
Foot of Everest , Oct., 1993 – north wind [27]		4.21
Grono (Italy), August1996 [4]		0.50
Grenoble, down town , Mai 2000		0.28

If we consider that the reaction with OH is the main pathway leading to the destruction of benzene and toluene, (1) and (2) lead to (3) :

- (1) Benzene + [OH] → Products (k_B) and $-d[\text{Benzene}]/dt = k_B[\text{OH}][\text{Benzene}]$
- (2) Toluene + [OH] → Products (k_T) and $-d[\text{Toluene}]/dt = k_T[\text{OH}][\text{Toluene}]$
- (3) $T = (\text{Ln}[(\text{Benzene})_0/(\text{Toluene})_0] * (\text{Toluene})/(\text{Benzene})) / [(k_B - k_T) * [\text{OH}]]$

With :

$[\text{OH}] = 1.5 \times 10^{-6}$ molecules.cm⁻³ in a moderate polluted valley.
 $k_B = 1.23 \times 10^{-12}$ molecules.cm⁻³.s⁻¹,
 $k_T = 5.96 \times 10^{-12}$ molecules.cm⁻³.s⁻¹
 $(\text{Benzene})_0/(\text{Toluene})_0 = 0.5$ (Concentrations at emission)
 $(\text{Benzene})/(\text{Toluene}) =$ results in Table 3

TABLE 6 - Age of the air mass in Orelle and Sollières before and during the dust episode.

	T = Air mass age (hours)	
Before dust episode (Orelle / Sollières)	42 ± 9	13 ± 6
During dust episode (Orelle / Sollières)	13 ± 7	4 ± 4

The results of this estimation are presented in Table 6. Among the many very restrictive hypotheses made for this calculation, these results do not take into account the emissions between the sources and the sampling site, nor the change in OH concentrations during night time. However, it shows that during the dust episode, the air mass age is younger than before the episode. In Sollières, the estimated air mass age (4 hours) and the southern average wind speed of 10 m. s⁻¹ recorded in Lanslevillard means that the air mass could have been transported from Italy to France across the border in a distance of about 140 km. This is roughly the distance from the industrialized areas of the upper Po valley with the large city of Torino, which is connected to the Maurienne valley via the Mont-Cenis Pass and the Susa valley in Italy. The older estimated age before the dust episode may be an indication of the stagnation of the air masses within the valley during the regular up-slope/down-slope cycle, and the large variations observed for the ratio benzene/toluene during this period could be an indication of the complex dynamic processes involved.

Finally, it should be noted that the impact of interactions between VOCs and the dust particles remains to be investigated. Several previous studies indicate that the heterogeneous reactions can take place between organics and crustal particles (33, 34, 35), including reversible or irreversible adsorption and chemical reactions. A rough calculation based on particle number concentrations indi-

cates that the surface area of the aerosol increases from about 5-8 μm² cc⁻¹ on average before the dust episode up to 40-50 μm² cc⁻¹ on average during the dust period, largely changing the surface available for potential heterogeneous reactions to take place. An evaluation of the impact of such heterogeneous reactions would require investigations on the chemistry of the particulate phase, including a specification of the organic matter.

CONCLUSION

Investigations on atmospheric chemistry were conducted at several sites in the Maurienne valley (France) during August 2000 in the course of the POVA program, including measurements for PM10, particle number concentrations, aerosol chemistry and VOCs with short sampling time. The week long sampling includes a 2 day period perturbed by a large dust input that largely changed the characteristics of the aerosol chemical and physical profiles compared to the previous period. Chemical and meteorological evidences indicate that it is associated with the intrusion of an anthropogenic air mass with an origin from the south of the Maurienne valley, most probably from the northern part of Italy in the Torino area. The VOCs and aldehyde concentrations during this period of south winds are much larger than during the previous days, including unusual sustained high concentrations at night and changes in the ratios of some BTEX compounds. The impact of the changes in the atmospheric dynamic (particularly the height of the inversion layer and the perturbation of up-slope/ down-slope wind system), as well as the impact of potential heterogeneous reactions between gas and crustal particles remain to be evaluated.

Finally, these observations indicate that the emission sources inside the Maurienne valley (including emissions from the heavy duty traffic linked with intense international exchanges through the Frejus Tunnel) are not always dominant, but that large changes of the concentrations can also be linked with larger scale transport from regional source areas.

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