**Atmospheric
Chemistry
and Physics**

Seasonal variation of PM_{10} main constituents in two valleys of the French Alps. I: EC/OC fractions

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Abstract. Daily PM_{10} samples were collected at two urban sites within two valleys in the French Alps (Chamonix and St Jean de Maurienne) during a period of two and a half years. The carbonaceous species EC (elemental carbon) and OC (organic carbon) were analysed to investigate the possible sources of EC and OC, and their seasonal variations. Mean OC concentrations are in the very high range of concentrations measured for other European sites, and represent at least one third of the PM_{10} mass on each site. On the basis of the comparison between EC and OC concentrations with several tracers, we were able to show that their main sources are local primary combustion sources. Biomass burning emissions (residential heating) have a significant impact on OC concentrations while heavy duty traffic emissions have an impact only on EC concentrations. Finally, we estimated the contribution of SOA (secondary organic carbon) to OC, using the EC-to-OC primary ratio method (Castro et al., 1999) and demonstrated that the calculation of SOA mass with this method is highly uncertain, if the hypothesis of a constant primary EC-to-OC ratio is not very closely examined.

1 Introduction

The morphology of deep valleys in mountainous areas, the local meteorology, and high concentration of emission sources create potential conditions for intense pollution episodes in these sensitive areas. Previous programs in European alpine areas include TRANSALP (Ambrosseti et al., 1998), TRACT (Löffler-Mang et al., 1998), POL-LUMET (Lehning et al., 1996), the Bolzano project (Dosio

et al., 2001), VOTALP I (Wotawa and Kromp-Kolb, 2000; Furger et al., 2000) and VOTALP II (http://www.boku.ac.at/imp/votalp/votalpII.pdf), a program over the Grenoble area (France) (Couach et al., 2003), and a study around the "Massif du Mont Blanc" (Espace Mont Blanc, 2003). However, none of these programs really focused on multiphase atmospheric chemistry with emphasis on aerosol, while particle loadings are often one of the most critical aspects of pollution episodes in this kind of environment (Ward et al., 2004). This last point fosters questions on the origin and fate of PM_{10}, as well as on the characteristics of the particles, in order to promote countermeasures for reducing the atmospheric load.

Following the accident in the Mont Blanc Tunnel in the French Alps (cf. Fig. 1) on 24 March, 1999, all international traffic between France and Italy was stopped through the Chamonix valley and mostly transferred to the Maurienne valley. Traffic in this last valley increased from an average of 2150 trucks per day before the accident up to 4250 trucks per day after, on average, under the Frejus Tunnel between France and Italy. In the Chamonix valley, residual traffic after the accident amounted to about 750 trucks per day, mainly local traffic. These very large changes of the traffic patterns created an interesting situation to perform studies for the evaluation of the impact of vehicles emission, particularly those of heavy duty traffic. International transit under the Mont Blanc Tunnel resumed without any restrictions on March 1st, 2003. The program POVA (Pollution des Vallées Alpines) started in May 2000. The objectives were to develop atmospheric modelling at the sub meso scale (Brulfert et al., 2005), in order to perform scenarios studies of the impact on air quality of changes of traffic and of local developments, taking into account gas and particles emissions. One aspect of the program consisted in a longer-term daily sampling at one site in each valley for a set of properties

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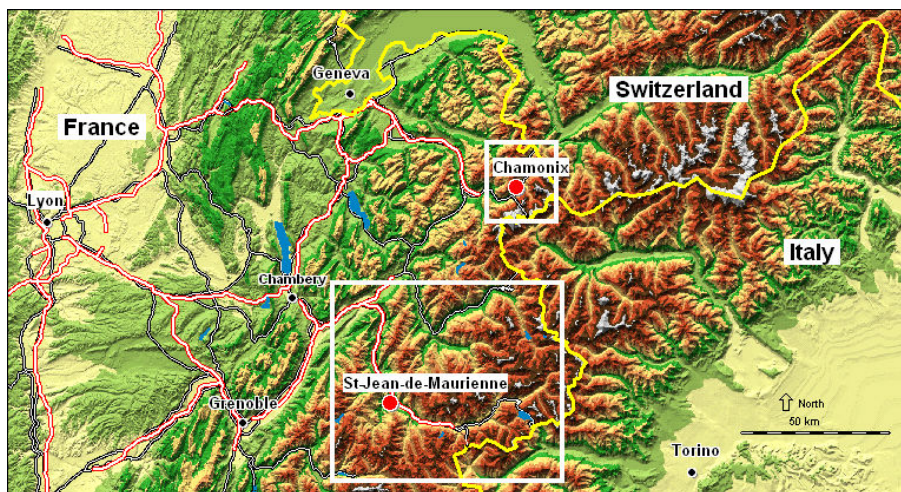
Fig. 1. Sampling areas in the French Alps.

including chemistry of the PM$_{10}$. The goals were to better constrain large-scale processes influencing atmospheric concentrations, including regional transport, meteorological factors, and seasonal variations in the type and strength of the emission sources.

In this paper, we are presenting the results of the PM$_{10}$ speciation for carbonaceous species (elemental carbon (EC) and organic carbon (OC)), conducted during this long-term sampling at the two sites. The general importance of this organic fraction in the particulate phase is well synthesized in Kanakidou et al. (2004) and Putaud et al. (2004). Results are completed with data on regulated atmospheric components (O$_3$, NO, NO$_x$, PM$_{10}$, SO$_2$), and with meteorological and traffic data. Results obtained by ionic chromatography (Jaffrezo et al., 2006a) for concentrations of soluble potassium (K$^+$) in PM$_{10}$ are also presented. K$^+$ is used as a tracer for biomass burning emissions. We are aiming at an evaluation of the variability of the contributions of the carbonaceous components to the PM$_{10}$ mass, with some assessment of the main sources and factors driving the variability of its concentrations in the very specific context of these alpine valleys.

2 Experimental

2.1 Sites and traffic

One sampling site was located in the Chamonix valley. This valley is rather short (23 km long) and narrow (1 to 2 km wide on average on the bottom part), with an average altitude of 1000 m above sea level (masl) at the valley floor. It is surrounded by mountains culminating with the Mont Blanc peak (4807 masl). There are no industries or waste incinerators in the valley, and the main anthropogenic sources of emissions are the traffic, residential heating (mostly with fossil fuel and wood burning), and some agricultural activities. The resident population is about 12,000 but tourism brings in many people (about 10 000 per day on average), mainly for short term visits. There is only one main road supporting all of the traffic in and out of the valley, but many secondary roads spread over all of the valley floor and on the lower slopes. During the closing of the Mont Blanc Tunnel leading to Italy, the traffic at the entrance of the valley was mostly composed of cars (90% of the total, including 50% diesel powered), with a low contribution of local trucks (5%) and of buses for tourism (1%). Natural emission sources are limited to the forested areas. The sampling site was located in the downtown area of the Chamonix town (6°52'16" E; 45°55'26" N; altitude 1038 masl), about 10 meters from a street. It can be considered as a kerbside site.

The second sampling site was located in the Maurienne valley, with Saint Jean de Maurienne being about 80 km from Chamonix, on the SSW (cf Fig. 1). This valley is much longer (about 80 km long) and wider (about 3–5 km wide on average at the valley floor) than the Chamonix one. The surrounding mountains are also lower, peaking at 3852 masl at the Grande Casse. The altitude of the valley mouth is 330 masl, increasing up to 2081 masl at the Col du Mont Cenis, leading to Italy. The lower 30 km of the valley up to the town of Saint Jean de Maurienne support some heavy industries, with among others steel transformation, and aluminium and phosphorus production. Other anthropogenic emissions are linked to the traffic, with a large share of it (95% of the trucks and 55% of the cars) taking place on the 50 km of the highway leading from the valley mouth up to Modane where is located the entrance of the Tunnel du Fréjus leading to Italy. The valley also supports agricultural activities, and some large natural areas. The total population of the valley is about 45 000, with most of it concentrated in the lower 40 km. Tourism is not as important as in Chamonix and brings in people mostly during the winter season and

Table 1. Sampling dates, and statistics on sampling at both sites.

	Chamonix	Saint Jean de Maurienne
Date start	02-21-01	02-10-01
Date stop	07-03-04	06-25-04
Number of days	862	864
Number of valid samples	785	798
% of valid samples	91.1	92.4
Number of EC-OC data	763	788
Number of field blanks	104	113

mostly in the upper part of the valley. The sampling site was located in a residential urban area of Saint Jean de Maurienne (6°21'04" E; 45°16'34" N; altitude 555 masl), about 2 km from the highway and of some large aluminium plants. It can be considered as an urban background site.

2.2 Sampling

Both sites are permanent stations maintained by the local Air Quality Agency, l'Air de L'Ain et des Pays de Savoie (http://www.atmo-rhonealpes.org/). Continuous measurements at the stations were performed on a 15 min basis and included NO_x (Environnement SA, AC31M), O_3 (Environnement SA, O341M), SO_2 (Environnement SA, AS21M), and PM_{10} (TEOM1400, R and P). The TEOMs were heated at 50°C. Air intakes for all these instruments were located about 4 m above ground on the roofs of the shelters.

For this program, we added automatic aerosol sampling with Accu samplers (R and P) on the by-pass flow of the TEOMs. These samplers where kept (together will all of the other instruments) in a non-heated shelter. All the tubing of the Accu systems were replaced with Teflon coated lines. We used stainless steel filter holders with a conical shape to insure homogeneous deposit on the filters. Sampling was conducted on a daily basis, from midnight to midnight (local time), at a flow rate of $0.85 \, m^3.hr^{-1}$. The samplers were serviced once a week, with the collection of 7 samples and one field blank. We used Whatman QM-A quartz fibre filters. These were pre-washed for 3 days in 3 successive bathes of Milli-Q water for lowering blanks for ionic species. Then, after drying at low temperature in an oven, they were fired for 1 h at 800°C to lower the blank levels for EC and OC. Filters were kept and transported to the field by packs of 20 in leak proof glass jars before sampling. After sampling, exposed filters were downloaded directly in the field and stored at –5°C in individual Petri slides wrapped up in aluminium foil in sealed bags, until analysis. All handling procedures were designed to reduce potential contaminations.

Sampling was maintained between 21 February 2001 and 3 July 2003 in Chamonix and between 10 February 2001 and 25 June 2003 in Saint Jean de Maurienne. The number of samples and field blanks are presented in Table 1. More than 760 concentrations for EC and OC were determined for each site. While the data series are not totally continuous, the numbers of samples are high enough to give a very good representation of the variability of the concentrations over the sampling periods.

2.3 Analysis for EC and OC

Samples were analyzed for EC and OC using the Thermo-Optical Transmission (TOT) method on Sunset Lab analyzers (Birch and Cary, 1996). Operating principles of this analyser are now well known. The main difficulty is in the correct separation between EC and OC: several temperature programs and results of intercomparison exercises are described in the literature (Chow et al., 2001; Schmid et al., 2001; Schauer et al., 2003). These studies generally show that the sensitivity of the separation between EC and OC using a TOT analysis method depends mainly on the temperature program and on the type of samples analysed. Our sampling sites are located in urban or sub-urban areas, in mountainous region. Thus, our samples are "urban samples" and are also influenced by wood burning, notably used in these regions for residential heating. TOT methods with temperature program similar to that of the NIOSH or the "base case" ACE Asia methods (see Table 2) are adapted for urban aerosol samples (Schmid et al., 2001; Schauer et al., 2003). It should be noted that methods reaching lower maximum temperature during the OC part of the analysis (i.e., under pure helium) could be used in order to reduce OC charring (see Table 2: method "alternate 3" ACE Asia). However, Schauer et al. (2003) demonstrated that EC measurements on wood smoke samples were significantly biased with this type of temperature program. Finally, we used a temperature program very close to that proposed by NIOSH or that used in the ACE Asia experiment: temperature up to 870°C for the analysis of OC in 100% He, and up to 900°C for the analysis of EC in 98% He + 2% O_2 (cf Table 2).

Automatic split time was always used for the distinction between EC and pyrolysed OC, except for the blank samples, that was manually corrected. We analyzed fractions of

Table 2. Temperature protocols used for the thermal analysis of EC and OC in different studies of carbonaceous aerosol. 1: this study, 2: Chow al., 2001, 3: Schauer et al., 2003.

Method	POVA[1]		NIOSH[2]		ACE Asia[3] (base case)		ACE Asia[2] (alternate 3)	
	T (°C)	Time (s)	T (°C)	Time (s)	T (°C)	Time (s)	T (°C)	Time (s)
100% He	250	60	250	60	340	60	120	60
	500	50	500	60	500	60	250	60
	650	60	650	60	615	60	450	60
	870	50	850	90	870	90	550	90
Mix He / O$_2$	600	30	650	30	575	45	575	45
	700	30	750	30	625	45	625	45
	850	40	850	60	700	45	700	45
	900	75	940	120	775	45	775	45
					850	45	850	45
					900	120	900	120

Table 3. Statistics for daily atmospheric concentrations of PM$_{10}$ mass, OC, and EC over the campaign. All concentrations are in μg m^{-3}. Mean: arithmetic mean. C. O. V.: coefficient of variation (=standard deviation over mean).

	PM10	OC	EC	OC / PM10	EC / PM10
Chamonix					
Mean	26.6	8.97	1.89	38.4	7.72
Standard dev.	14.7	5.22	1.43	17.9	4.46
C.O.V.	55.5	58.2	75.7	48.7	57.8
Median	23.0	7.22	1.34	35.2	6.56
Saint Jean de Maurienne					
Mean	21.4	6.32	0.95	32.8	4.64
Standard dev.	11. 5	3.08	0.66	11.9	2.46
C.O.V.	53.4	48.7	69.5	36.2	53.0
Median	19.0	5.49	0.77	30.7	4.19

1.5 cm^2 of the filters, without any preparation. A subset of samples (approximately 5%) was analyzed 3 times to check for the even repartition of particles on the filters. This test indicated a really good reproducibility of the deposition, with results within 3% of each other.

A first batch of analyses covering the first year of sampling took place in Gent (Belgium), while the remaining series was later analyzed in Grenoble (France) on the same type of instrument. The temperature programs were identical in both cases. We performed duplicate analyses on both instruments for roughly 10% of the samples, to ensure the continuity in the data series. Again, the results of these tests indicated a very good reproducibility between the two series. Arithmetic average of the concentrations of the field blanks were taken into account for the calculation of atmospheric concentrations. Field blank concentrations (equivalent to concentrations of OC=0.45±0.27 μgC/m^3 and EC =

0.05±0.06 μgC/m^3 for a typical sample of 20 m^3 of air) account for 6.6 and 4.4% of average atmospheric summer concentrations for OC and EC, respectively.

Finally, OC concentrations were not corrected to give organic matter (OM) concentrations. This is not useful in our study, as we do not try to reconstruct the mass of PM$_{10}$. Also, we did not attempted any correction for the possible artefacts on OC sampling, for the results presented in this paper. Therefore, one should keep in mind that this can certainly affect our measurements and especially the comparisons with other studies (Huebert and Charlson, 2000). We will return to these points in the following discussions.

2.4 Final data set

The final data set for this long term sampling campaign includes the data for EC and OC concentrations, as well as

Table 4. Measurements of PM$_{10}$ mass, OC, EC and EC/OC covering at least one year. All concentrations are in μg m^{-3}. (1): this study; (2): Putaud et al. (2004).

Location	Type of site	PM$_{10}$	OC	EC	EC/OC
Chamonix[1]	Kerbside	26.5	9.0	1.9	0.20
St Jean de Maurienne[1]	Urban	21.4	6.3	0.9	0.15
Chaumont (CH)[2]	Rural	10.5	1.2	0.6	0.48
Monagrega (E)[2]	Rural	17.3	1.6	0.6	0.40
Illmitz (A)[2]	Rural	23.9	3.9	2.0	0.52
Ispra (I)[2]	Near-ciy	29.5	5.8	1.5	0.26
Zuerich (CH)[2]	Urban	24.5	3.6	2.1	0.58
Basel (CH)[2]	Urban	25.8	3.6	2.0	0.55
Bern (CH)[2]	Kerbside	40.2	6.5	5.7	0.88
Wien (A)[2]	Kerbside	54.6	7.6	10.7	1.41

daily data for ionic species that were obtained from the same filters (Jaffrezo et al., 2006a). Daily data for NO, NO$_x$, O$_3$, SO$_2$, and PM$_{10}$ mass concentrations were also obtained, by averaging the 15-min measurements. The data base also includes meteorological informations obtained from Météo France (temperature, precipitation, wind speed) from the stations in Chamonix and Saint Jean de Maurienne, with hourly measurements averaged to get daily values. We obtained traffic countings from regional administrations and highway companies, for the sites of Tunnel des Chavants (at the lower entrance of the Chamonix valley) and Saint Michel de Maurienne (10 km upward of Saint Jean de Maurienne). These are daily data sets, with separate countings for individual cars and trucks.

3 Results and discussion

3.1 Seasonal variations of the concentrations and mass fractions

Table 3 presents annual statistics for the concentrations of PM$_{10}$ mass and carbonaceous species at both sites. PM$_{10}$ annual average mass concentrations are rather similar at the two sites, and are comparable to annual average concentrations (see Table 4) measured in the background of some much larger urban areas in Europe, like London, Basel, Zurich, or Ispra (Van Dingenen et al., 2004), despite much lower population and activity in the valleys. There are more differences in the concentrations of OC and EC, with a factor of two between the two sites for the latter species.

There are still few studies in the literature presenting EC and OC concentrations series covering at least one full year for European areas, and the majority of those are compiled in Putaud et al. (2004). Comparison of results (presented in Tabl 4) must take into account that measurements of EC and OC are dependant upon the sampling and analytical meth-

ods. Therefore, only results obtained with the same methods or with intercalibrated methods can really be compared. As an example, this is not the case for the results from Bologna, collected with a 6-stage Berner impactor (Putaud et al., 2004). For other urban and sub-urban results, reported in Table 4, the methods used for EC and OC analysis (EGA and coulometry) give results very close to that obtained with the method used in our study for this type of sample (Schmid et al., 2001). Further, sampling was generally performed with high volume samplers in the studies compiled by Putaud et al. (2004). Key parameters to assess the comparability of different total filters sampling are the face velocity (McDow and Huntzicker, 1990; Turpin et al., 1994, 2000) and the duration of the sampling (Turpin et al., 1994). According to these last authors, the differences in the face velocity between most methods used in Putaud et al. (2004) and that of our study (40 cm.s^{-1} and 20 cm.s^{-1}, respectively) should lead to an overestimation of OC in our study that could reach 20%, also in agreement with findings by ten Brink et al. (2004). Conversely, all studies, including ours, used daily sampling and are comparable in this respect. Taking this into account, Table 4 shows that our OC concentrations are in the high range of those measured at urban sites in Europe (Putaud et al., 2004). In Chamonix, they are even close to concentrations measured at kerbside sites in Bern or in Vienna. In turn, EC concentrations at our two sites are closer to those measured in urban background of the large cities mentioned earlier.

Mean values of the EC-to-OC ratios are 0.19$\pm$33% and 0.14$\pm$46% in Chamonix and St Jean de Maurienne, respectively. Comparison of EC-to-OC ratios between different studies is even more difficult than direct comparison of EC and OC concentrations, as this ratio is more sensitive to the separation between EC and OC performed by the analytical method. Table 4 indicates that the mean ratios measured in Chamonix and St Jean de Maurienne are systematically lower than ratios reported for other sites. The differences with respect to urban and kerbside sites respectively are high
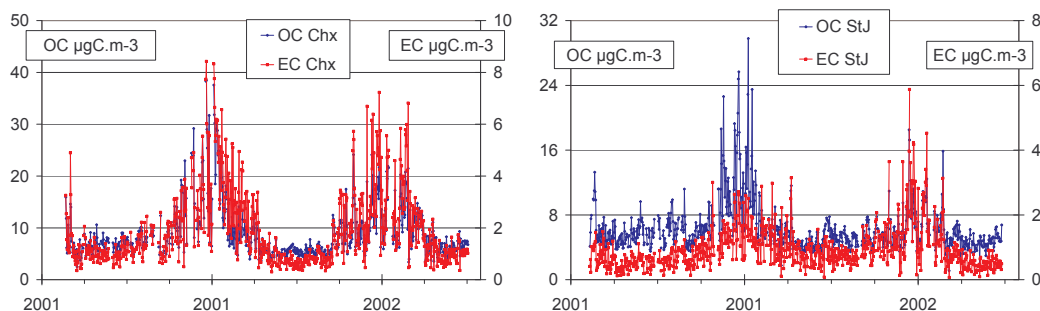
Fig. 2. Daily concentrations of EC and OC at both sites.

enough (a factor higher than 4 for Chamonix compare to kerbside sites, and 3 for St. Jean compare to urban sites) that it cannot be explained only with sampling and analysis uncertainties. This is an indication that it certainly reflects real differences. A more detailed examination of the information brought in by these ratios is proposed in the next section.

For both sites, the variability of OC concentrations (as described by the coefficient of variation) is close to that of PM_{10} mass (cf. Table 3), while that of EC is much higher, underlining much larger day-to-day changes in the concentrations of the primary species EC compared to that of OC or PM_{10}. These variabilities are well described in Fig. 2 that presents the daily concentrations of OC and EC during the whole sampling period for Chamonix and Saint Jean de Maurienne, respectively. This figure also shows that the daily variability is lower, for both species and both sites, than the strong seasonal variations of the concentrations, with large maxima during winter. The amplitudes of these seasonal cycles are larger in Chamonix than in Saint Jean de Maurienne. These cycles are similar, albeit more pronounced, to that of the PM10 concentrations (Aymoz, 2005). Such seasonal cycles with maxima in winter can also be recalculated for many European sites (like for Ispra, Zurich, Barcelona, Bern, or Vienna) from the data provided in Putaud et al. (2004) (Aymoz, 2005). In our case, several hypotheses can be proposed to explain such large seasonal variations, including an impact of the meteorology, a change in the sources between summer and winter, or (for OC) the impact of physicochemical processes. Each of these aspects is discussed in the following sections.

At both sites, OC is by far the larger component of the PM_{10} mass, on average, with annual mean contributions above 30% (cf. Table 3). It dominates the sulphate contribution (Jaffrezo et al., 2006a), even without counting a mass conversion factor between OC and organic matter. OC contribution to PM_{10} is slightly larger in Chamonix than in Saint Jean de Maurienne. These contributions are much larger than those reported in Putaud et al. (2004) for any European city, and in the high range of the values presented by Na et al. (2004) for TC (= EC + OC) in $PM_{2.5}$ for studies worldwide.

However, they can compare with values up to 60% reported by Ruellan and Cachier (2001) for a kerbside site on a busy highway in Paris, or to values between 30 and 40% reported by Ward et al. (2004) for a town in a valley of the Rocky Mountains (USA). The mass fraction of EC to PM_{10} is also larger in Chamonix than in Saint Jean de Maurienne, and the annual mean value, up to 7%, is again in the range of those from urban background of large European cities. A more thorough discussion on these comparisons would require, as mentioned above, a detailed examination of the sampling and analysis techniques used in each study, including those for the PM_{10} measurements.

Figure 3 indicates that the mass fractions of OC and EC to PM_{10} vary seasonally, with maxima during winter time. These seasonal cycles are stronger at the kerbside site (Chamonix) than at the urban background site (Saint Jean de Maurienne). The influence of strong differences in the respective climate of the valleys (induced by a much narrower valley at higher altitude in the case of Chamonix) is not excluded to explain this difference of seasonality, on top of that of the nature of the sampling site. It is particularly striking that during winter the PM_{10} fraction of EC in Chamonix can reach very high values, up to 14% on a monthly average, indicating a much stronger impact of combustion sources on the composition of the aerosol at that time. It is also striking that no large increase of the PM_{10} mass fraction is seen for OC in summer, when the formation of Secondary Organic Aerosol (SOA) is expected to be favoured (Kanakidou et al., 2004).

3.2 Concentrations, mass fractions, and meteorological conditions

The strong seasonal variations depicted in Figs. 2 and 3 call for a close examination of the impact of meteorological conditions on the concentrations. Particularly, the relationship with temperature is interesting, all the more in our context with large amplitudes between summer and winter conditions. Figure 4 shows the evolution of EC and OC concentrations according to the temperature, for Saint Jean and Chamonix. As expected from Fig. 2, the concentrations largely increase for lower temperatures, for both sites and
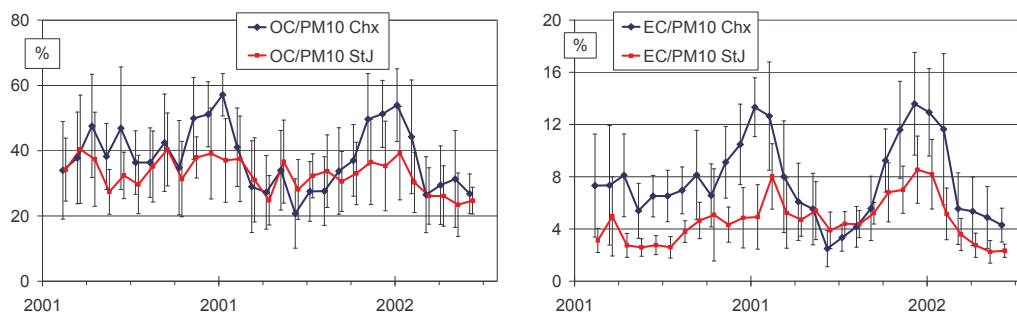
Fig. 3. Monthly arithmetic average mass fraction of EC and OC at both sites and standard deviation.
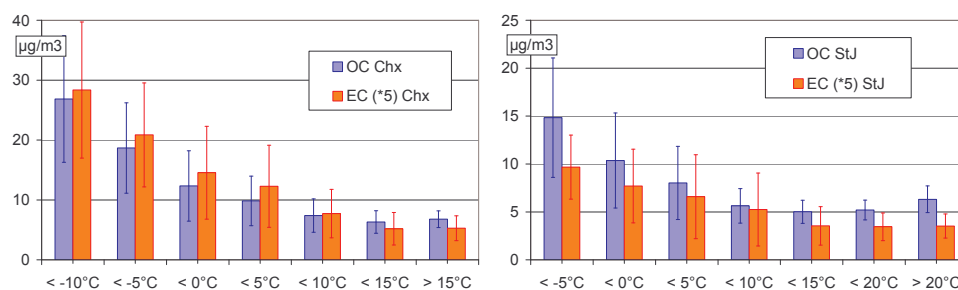
Fig. 4. Average concentrations of EC and OC according to the temperature in Chamonix and St Jean de Maurienne.

both species. The increases in EC concentrations are much larger in Chamonix (a factor of 4.2) than in Saint Jean (a factor of 3.0) for changes in the temperature between T°C < -5°C and 10 < T°C < 15, while those in OC are closer (factors of 3.1 and 2.7 for the two sites, respectively) for the same temperature ranges. One hypothesis to explain this difference between the two sites could be in differences in the sources of particulate matter they experience as the temperature changes. For the warmer temperature ranges, small increases in average OC concentrations are seen at both sites, which are not associated with changes in EC concentrations. They could be linked either with the formation of SOA, in agreement with a smaller increase at the site close to sources (Chamonix) than further away from direct emissions (Saint Jean), or with an increase of the impact of primary sources with low EC to OC ratios.
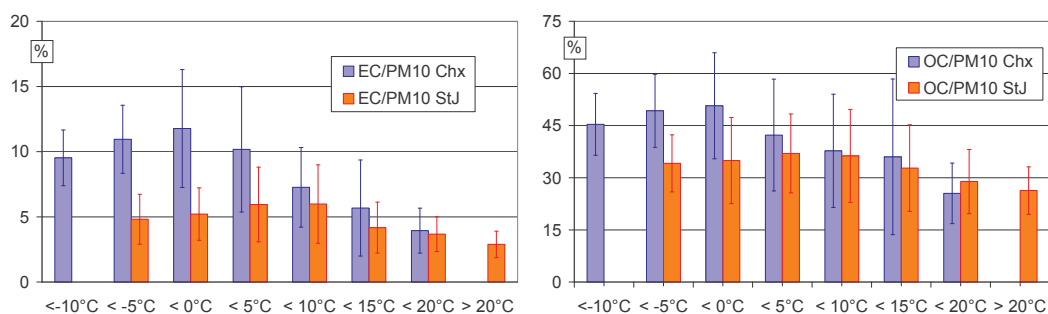
Figure 5 presents the evolution of the mass fraction of EC and OC to the PM$_{10}$ according to the temperature ranges at the two sites. Despite the much larger concentrations for the lower temperatures mentioned above, the maxima in the mass fraction of both EC and OC are not measured for the coldest conditions. Further, these maxima are not found for the same temperature range for the two sites, but between –5°C and 0°C in Chamonix and between 0°C and 5°C in Saint Jean. A first hypothesis to explain these results would be that some chemical species other than EC or OC are making up an increasing fraction of the mass as the temperature

decreases. However, the PM$_{10}$ mass fractions of sulphate and nitrate (the only other major components of the aerosol mass) do not increase at low temperature (Jaffrezo et al., 2006a) and therefore cannot explain the missing mass. Another hypothesis is that the OC-to-OM conversion factor is higher at lower temperatures, with the mass fraction of OM increasing proportionally. Very few data are available in the literature on the evolution of this conversion factor, and a value of 1.4 is generally considered for urban sites (Turpin and Lim, 2001). This assumption is discussed later, in relation with potential changes in the sources of EC and OC in the valleys.

Figure 6 shows the evolution of EC-to-OC ratios according to the temperature. Values reported for St Jean are systematically lower than that for Chamonix for each temperature interval. This could be in agreement with an "older" aerosol at this site (i.e., in agreement with our assumptions on the respective proximity of the sources for the two sites), or more generally with different chemical emission profiles between the two valleys. Also, the evolution of this ratio with respect to the temperature is indicative of changes in the relative influences of different sources of EC and OC to the atmosphere of our sites. This ratio is maximum for intermediate temperatures. It is noted that this maximum does not appear for the same range of temperature at the two sites. This difference seems difficult to explain, even if this temperature difference is of the same order of magnitude as the average deviation of the mean annual temperature between the two

Table 5. Linear correlation parameters between the concentrations of OC, EC and PM_{10} mass, NO, NO_2 and K^+. All concentrations in $\mu g.m^{-3}$.

	Chamonix		St Jean de Maurienne	
	OC	EC	OC	EC
EC	OC = 3.3*EC + 2.7		OC = 3.0*EC + 3.5	
	r^2 = 0.83 N = 763		r^2 = 0.41 N = 788	
PM_{10}	OC = 0.22*PM_{10} + 3.3	EC = 0.053*PM_{10} + 0.49	OC = 0.20*PM_{10} + 2.0	EC = 0.033*PM_{10} + 0.23
	r^2 = 0.36 N = 753	r^2 = 0.29 N = 753	r^2 = 0.60 N = 778	r^2 = 0.32 N = 778
NO	OC = 0.19*NO + 5.4	EC = 0.052*NO + 0.92	OC = 0.15*NO + 4.8	EC = 0.030*NO + 0.64
	r^2 = 0.78 N = 744	r^2 = 0.79 N = 744	r^2 = 0.55 N = 703	r^2 = 0.45 N = 703
NO_2	OC = 0.25*NO_2 + 1.6	EC = 0.075* NO_2 - 0.28	OC = 0.16*NO_2 + 2.4	EC = 0.035*NO_2 + 0.056
	r^2 = 0.60 N = 744	r^2 = 0.69 N = 744	r^2 = 0.44 N = 763	r^2 = 0.45 N = 763
K^+	OC = 62*K^+ + 3.3	EC =15*K^+ + 0.51	OC = 16*K^+ + 3.7	EC =2.9*K^+ + 0.47
	r^2 = 0.83 N = 738	r^2 = 0.65 N = 738	r^2 = 0.62 N = 775	r^2 = 0.44 N = 775

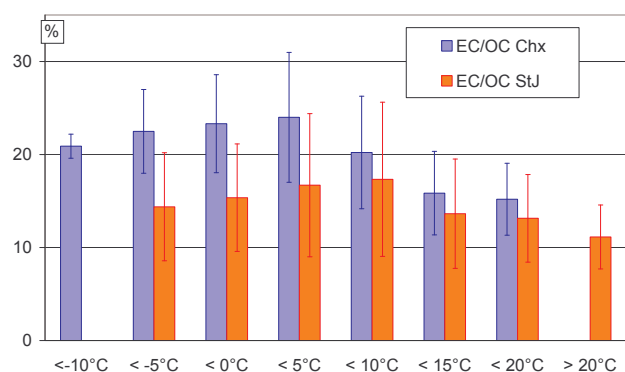**Fig. 5.** Average mass fractions of EC and OC at both sites according to the temperature.

sites (approximately 5°C warmer in St. Jean de Maurienne) (Jaffrezo et al., 2005).

At both sites, the EC-to-OC ratio tends to decrease with higher temperatures. An assumption is that the increase in slope breezes with an increase in the temperatures promotes vertical mixing and increases the influence of more remote sources, bringing less primary aerosols (more typical of rural sites, i.e., lower EC-to-OC ratio). It is also possible that some agricultural practises (burning of meadows) and burning of organic waste by inhabitants (with low EC-to-OC ratios) in summer are at the origin of this evolution. Two assumptions can be proposed to explain the tendency to the decrease of the EC-to-OC ratio with the lowest temperatures. A first assumption is the possible impact of the condensation of semi-volatile organic species, a process favoured at low temperatures. This is well known to be one of the governing processes for the modulation of particulate concentrations of chemical species like PAHs or POPs (Leach et al., 1999) and of SOA (Sheeman and Bowman, 2001). It is however difficult to evaluate with the data we have in hand the impact of such a process on the EC-to-OC ratio in our case. A second hypothesis (non exclusive of the first one) could be a change in the sources of carbonaceous matter between seasons, with an increasing importance of the sources having

a low EC-to-OC ratio at low temperature. This tendency is compatible with a probable increasing influence of emissions from wood combustions, with emissions characterized by a low EC-to-OC ratio, typically between 20 and 40 (Schauer et al., 2001; Oros and Simoneit, 2001a, b). This would also have an impact on the evolution of the OC-to-OM conversion factor (mentioned above), as it is generally believed (Turpin and Lim, 2001) that this ratio is higher for biomass burning emissions. The importance of this source is further discussed below (Sect. 3.5), using soluble potassium as an additional tracer.

The temperature is the most prominent parameter related with the changes in concentrations of EC and OC in the valley. However, evolution of concentrations according to the wind speed measured at each site shows, without too much surprise for sites located close to sources, that concentrations tend to be higher during conditions of low dispersion, that this feature is more pronounced at the kerbside site than at the urban background site and, further, is way more pronounced for EC than for OC (Aymoz, 2005). Again, this is associated with an increase of the mass fractions of both EC and OC to the PM_{10} for low wind speed, well pronounced for EC in Chamonix, indicative of the predominance of the emissions from local combustion sources in the formation of the aerosol

Fig. 6. Average EC-to-OC ratio at both sites according to the temperature.

Fig. 7. Aritmetic mean and standard deviation of the percentage of change between values on Sunday and the weekday of the same week, for HD (number of heavy duty trucks), PV (number of personal vehicles), and concentrations of OC, EC, PM_{10} mass, NO, NO_2, SO_2, K^+, and O_3 for the whole study.
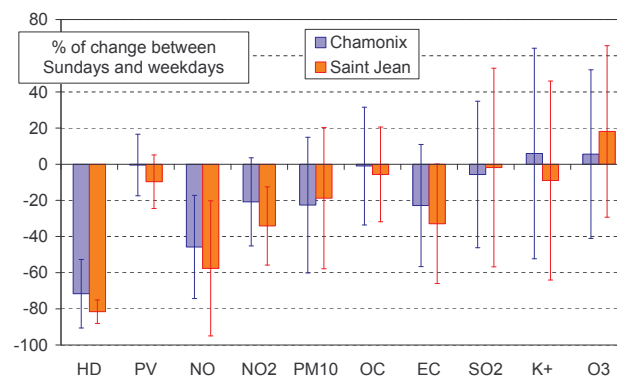
load for these two sites.

Overall, all of these observations do not allow delineating the respective impacts, on the concentrations of EC and OC, of the factors mentioned in the previous section. Particularly, it is challenging to evaluate the respective roles for the seasonal cycles of the concentrations of the changes in emission sources and of the impact of the local meteorology characterized by an increase of the frequency of the inversion layers in winter. Nevertheless, the quantification of the impact of meteorology on the observed concentrations is out of the scope of this paper, and we attempted rather to determine the sources of carbonaceous matter in the aerosol. The goal of the next sections is to examine successively the role of known combustion sources on the concentrations of organics and to test the method of the "primary ratio" (Turpin et al., 1991) to evaluate the SOA formation and contribution to OC.

3.3 The influence of combustion sources

Table 5 presents the correlations between the concentrations of OC, EC, and PM_{10} mass, NO, and NO_2 for the two sites. These tables indicate that both EC and OC are closely correlated with NO and NO_2. To the best of our knowledge, no such data sets are available in the literature, for comparison. These close links between gaseous and particulate concentrations are most probably due in part to a common impact of local meteorological conditions on all atmospheric species, as described above. However, the correlations with NO and NO_2 being much higher for EC and OC than for PM_{10} are a strong indication that local combustion sources represent a main factor in the modulation of EC and OC concentrations. Two of the main combustion sources in the valleys are the traffic and the biomass burning.

3.4 The influence of heavy duty traffic

A direct comparison between any series of concentrations and traffic data do not lead to significant correlations (Aymoz, 2005), despite the favourable conditions of our study

considering the limited systems of the valleys. This results from the large influence of other parameters, as mentioned above. However, we can take advantage of the strong weekly cycle of the heavy duty traffic (that is forbidden on weekends in France) to try to evaluate its impact on atmospheric concentrations. Figure 7 shows the average differences between the averages on Sunday and on workdays of the same week for several parameters during the whole study. In Chamonix and St Jean de Maurienne, the decreases of the number of heavy duty trucks (HD) amount to 72% and 82%, respectively, due to the regulation of traffic for this type of vehicles. This represents a large change in the emissions, either directly from the combustion exhaust, or indirectly with the resuspension of soil dust. Conversely, the traffic of personal cars is the same between the two types of periods. Further, it is very likely that emissions from other main sources are also stable between weekdays and weekends, including that from residential heating with wood burning and that from industries, as indicated by small changes, on average, in K^+ and SO_2 concentrations, respectively (cf. Fig. 7).

Therefore, the important decreases of NO and NO_2 concentrations at both sites (58 and 34% for Saint Jean, respectively) on Sundays shown on Fig. 7 are probably mainly linked with the changes in the HD source. The decreases are larger in Saint Jean (for a site closer to the highway, with a much larger traffic in the valley) than in Chamonix, and larger for NO than NO_2 (again, in agreement with the location of the sites only a couple of km away from the highways supporting this heavy duty traffic). The decreases are lower, but still significant for PM_{10} mass, with values about 20% for both sites, associated with large standard deviation. The changes are also well marked for EC (averages decreases of 23 and 33% for Chamonix and Saint Jean, respectively), but are not significant for OC (changes below 5% for both sites). These results are similar to those presented by Röösli et al.
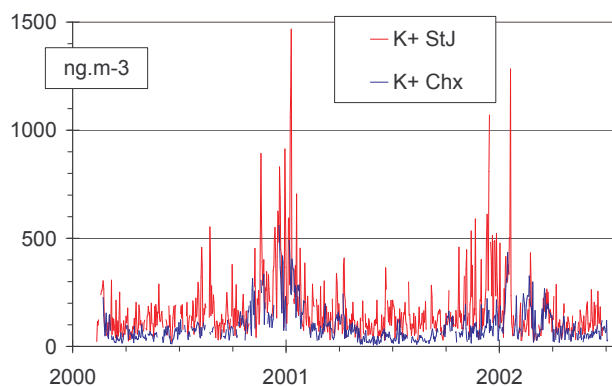
Fig. 8. Daily concentrations of K+ at both sites.

(2001) for a study in Basel (Switzerland), with changes in concentrations between Sundays and weekdays being larger for EC than for PM_{10} mass and OC.

According to the emission rates for EC and OC for heavy duty diesel trucks proposed by Schauer et al. (1999) (these species representing about 31 and 20% of the fine particle mass emitted, respectively), the decreases observed on average for EC on Sundays should lead to a change of about 3% of the average OC mass for both sites, which is compatible with our observations. It shows that Heavy Duty traffic is a major source of EC in the valleys, but is not so important for OC. Finally, it should also be pointed out that the decreases in the PM_{10} mass on Sundays (changes of 6.1 and 4.0 $\mu g/m^3$ on a yearly average for Chamonix and Saint Jean, respectively) are far from being totally explained by the decreases of the two main components (EC and OC). These decreases of the aerosol load on weekends are also not associated to large changes in sulphate or nitrate concentrations (Jaffrezo et al., 2006a). The influence of the resuspension of soil dust should therefore be suspected (Röösli et al., 2001) but elemental compositions were not investigated in our study. This difference between EC and OC weekly cycles, associated with the "primary" character of EC and OC previously observed, and with the weak EC-to-OC ratio confirm that there is not a unique source of carbonaceous matter in the valleys. One important point is that the impact of HD source on OC concentrations is clearly limited. We can investigate the potential impact of another source of OC represented by the biomass burning.

3.5 Influence of wood combustion

Wood combustion is a known source of particles in the valley, as demonstrated with measurements of molecular tracers performed during short term campaigns conducted during the POVA program (Marchand et al., 2004; 2006). We can try to get more information on the influence of this source during all seasons, using soluble potassium as an additional tracer.

Potassium in aerosol samples has several natural sources including the marine and crustal ones. It was also detected in biomass burning plumes (Andreae et al., 1988; Echalar et al., 1995) then used as tracer of this type of source in natural sites (Ruellan et al., 1999; Allen and Miguel, 1995) or in remote ice core records (Savarino et Legrand, 1998). However, in a study of emission profiles from different sources (vehicular, biomass combustions, crustal matter and coal combustion) Watson et al. (2001) showed that soluble potassium (K^+) is also an unambiguous tracer of biomass burning emissions in areas influenced by human activity. K^+ was subsequently used to investigate the role of biomass burning in such areas, like the mega-cities Beijing in China (Duan et al., 2004) or Dhaka in Bangladesh (Salam et al., 2003).

Jaffrezo et al., 2005b investigate the size distribution of K^+ on the sites of our study. Authors show that the size distributions of soluble potassium in winter and summer are monomodal, with mass median diameters centred in the interval 0.40 to 0.65 μm. This sub-micronic mode is a very strong indication that soluble potassium originate from combustion and not from sea-salt, soils or re-suspension of dust.

In our case, soluble potassium was measured with ion chromatography in 738 and 775 of the samples from the Chamonix and St Jean de Maurienne series, respectively (Jaffrezo et al., 2006a). Mean annual concentrations of K^+ amount to 166 and 90 ng/m^3 for Chamonix and St Jean de Maurienne, respectively. However, large seasonal cycles with well defined maxima in winter are experienced at both sites (Fig. 8). These cycles are somewhat weaker than that of EC, but larger than that of OC and PM_{10} mass.

Table 3 presents correlation between K^+, OC and EC. The correlation between OC and K^+ is high and stronger in Chamonix ($r^2 = 0.83$) than in St Jean de Maurienne ($r^2 = 0.62$). It indicates that biomass combustion is a very important source of OC, particularly in Chamonix. Correlation between EC and K^+ is also significant, but weaker at the two sites ($r^2 = 0.65$ and 0.44 for Chamonix and St Jean de Maurienne, respectively). This indicates that EC concentrations are less influenced by biomass burning emission than OC concentrations. Emissions from biomass combustion are generally characterised by low EC-to-OC ratios, compared to those from diesel and gasoline vehicle emissions. Ratios reported for diesel engines (between 1.0 and 1.3 (Schauer et al., 2002)) and recent gasoline engines (between 0.25 and 0.45 (Schauer et al., 1999; Rogge et al., 1993)) are highs compared to those reported for biomass or coal burning emissions (between 0.025 and 0.05 (Schauer et al., 2001; Oros and Simoneit, 2000, 2001a, 2001b)). We can thus conclude that EC concentrations are linked both with HD and biomass burning emissions, while OC concentrations are much more influenced by biomass burning emissions with an impact of HD emission being not obvious.

Mean K^+-to-EC and K^+-to-OC ratios at both sites are respectively 5.2 and 1.0% in Chamonix, and 19.0 and 2.4% in St Jean de Maurienne. The differences observed between
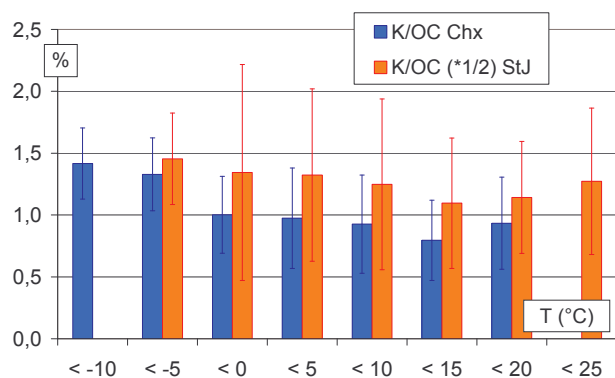
Fig. 9. Average K^+-to-OC ratio at both sites according to the temperature.

Chamonix and St Jean de Maurienne can tentatively be explained by differences in the type of biomass burned. Indeed, there are no specific values of these ratios ascribed to biomass burning emissions, because they vary notably with the type of wood burnt and the amount of branches and foliage (Oros and Simoneit, 2000, 2001a, b). Nevertheless, the ratios we observed in the valleys are close to those reported in Chow et al. (1994) for different urban sites in Los Angeles (CA, USA), with mean K^+-to-EC and K^+-to-OC comprised in the range 4–20% et 1–5%, respectively.

Figure 9 shows the evolution of the K^+-to-OC ratio according to the temperature at both sites. The ratio shows an evolution, relatively similar at both sites, with maximum values for the lowest temperature (rather marked in Chamonix), and for highest temperature (rather marked in St Jean de Maurienne). For the lowest temperature ranges, it confirms that the impact of biomass burning on OC concentrations is maximum because of residential heating in winter. This is in agreement with lower EC-to-OC ratios at this temperature, as seen in the Sect. 3.2 and Fig. 6. It can also explain the evolution of the OC-to-PM_{10} ratio (cf Fig. 5). According to Turpin and Lim (2001), wood burning emissions show OC-to-OM conversion factors that can exceed 2.4. Conversion factors that are considered characteristic of other primary sources are generally lower, with a value of 1.4 or less generally admitted for vehicle emissions, for example. Thus, the decrease of OC-to-PM_{10} ratio observed at low temperature does not necessarily mean a decrease of the actual contribution of OM to PM_{10} mass, and can hide stability, or even an increase of this contribution. For the ranges of the highest temperatures, a hypothesis to explain the weak increase observed for the K^+-to-OC ratio is possibly linked with local agricultural practices and more generally burning of garden waste in summer. As for low temperatures, it could also explain, at least partially, the observed decreases of EC-to-OC and OC-to-PM_{10} ratios (cf. Figs. 5 and 6). However, and compared to the lowest temperature, the increase of K^+-to-OC is weak.

Other processes are possibly implicated in the evolution of these ratios, like the formation of SOA. We examine in the next section the possibility to evaluate this contribution in our study.

3.6 Calculation of SOA formation

Evidence of the influence of SOA transported or formed in the valley in summer conditions are presented in Jaffrezo et al. (2005) on the basis of the evolution of dicarboxylic acids concentrations. However, the total mass of these last species represents only a few percent of OC, even in summer, and it does not allow to fully appreciate the real influence of the secondary source on OC concentrations. Actually, no experimental method exists to measure directly this fraction, but calculation methods of this fraction from data sets of EC and OC are proposed in the literature. The principle of these calculations is that EC, emitted by combustion sources, can be used as a tracer of primary fraction of OC (Turpin et al., 1991). It means that we make the assumption that, for a given site, there is an EC-to-OC ratio, noted (EC/OC)pri, representative of the primary emissions of these two species. Then, many authors, of which Turpin and Huntzicker (1991) use a very simple expression of primary OC, noted OCpri, and of secondary OC, noted OCsec, starting from the concentrations of EC and total OC, noted OCtot:

(OCpri) = (EC) / (EC/OC)pri

(OCsec) = (OC)tot - (OCpri).

Several methods are proposed in the literature to determine (EC/OC)pri. A first one consists in measuring this ratio for each source then, starting from an inventory of the emissions and by taking into account the variations in time of the influence of each source, to calculate the resulting primary ratio for a given receptor site. For example, Gray et al. (1986) calculated a primary ratio of 0.42 in a study concerning the Los Angeles area. However, this approach requires a detailed study of emission sources and a reliable inventory of the emissions of ECpri and OCpri. These conditions are not met in our study. A second method consists in measuring in-situ the primary ratio in the atmosphere for days when the secondary production of OC is expected to be minimal. In a study in the Los Angeles area, Turpin and Huntzicker (1991) estimated this ratio by using only measurements of EC and OC when the weather conditions were unstable (no sun and no drizzle) or with minimal photochemical activity (determined by low ozone levels). Alternatively, a last method used in Castro et al. (1999) consists in determining systematically the minimum ratio for each study and each site (or an average of the minimum ratios) and using it as the primary ratio. For the two last methods, and in agreement with Castro et al. (1999), the result is then subjected to several assumptions:

i) (EC/OC)pri does not evolve significantly over the period of the study,

ii) the effective contribution of SOA is negligible for the samples used in the determination of the primary ratio,
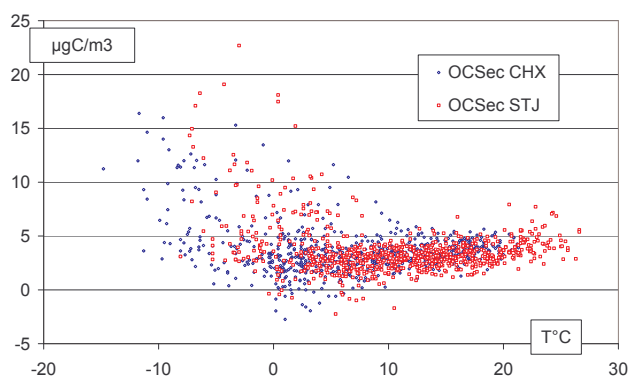
Fig. 10. Concentration of secondary organic carbon calculated at each site according to the temperature. Details of the calculation are given in the text.

iii) the contribution to the primary OC of sources other than combustion sources is low or constant,

iv) the contribution of semi-volatile OC to the primary OC is low compared to the contribution of the non-volatile organic species.

These assumptions are quite constraining and probably not respected in most of the cases. It is obvious in our case that the first assumption is definitely wrong, as we saw in the previous sections that variations of the EC-to-OC ratios are related with changes in the relative influence of different combustion sources to the total amount of OC. However, we performed the calculation of OCsec according to the third method in order to evaluate the level of uncertainties that such a method can bear.

Therefore, OCsec are calculated with a (EC/OC)pri ratio determined for each site for the whole sampling period as the arithmetic mean of the 5% of the highest values of this ratio. This ratio is 0.32 and 0.36 in Chamonix and St. Jean de Maurienne, respectively. This is in the range generally presented in the literature (Na et al., 2004, and references therein). However, it is striking that, if these lower ratios are found essentially in winter, they are not obtained in the conditions that would be seen as the most favourable for the influence of local sources. For example, the average daily values for these episodes are $2.7\pm2.8\,°C$, $35.9\pm21.4\,\mu g.m^{-3}$ and $18.7\pm8.0\,\mu g.m^{-3}$ for temperature, NO, and SO_2 concentrations for Chamonix, as opposed to mean values of $-1.6\pm5.7°C$, $50.5\pm41.1\mu g.m^{-3}$ and $26.6\pm12.0\,\mu g.m^{-3}$ for the same parameters from 1/12/01 to 20/03/02, the winter period concerning most of the episodes with high EC-to-OC ratios. This is a strong indication that the primary ratio of local emissions in winter is indeed higher than the (EC/OC)pri determined by this method, due certainly to the high proportion of biomass burning at that time.

Figure 10 shows the evolution of OCsec according to the temperature, using these primary ratios. At the two sites, OCsec concentrations present a very large maximum for the

colder temperatures, while only a weak increase of the concentrations is observed for the warmer temperatures. The tendency observed for the lowest temperature is clearly influenced, at the two sites, by the increase of the influence of biomass burning emission, and seems totally inconsistent with a real production of secondary organic carbon. It appears clearly that this method is inappropriate in this case. We can then wonder whether the increase we observe for the warmer temperatures, apparently coherent with the formation of SOA, is an acceptable estimation of its concentration. Indeed, the observation of the evolution of K^+-to-OC in the previous section indicated that biomass combustion emission can possibly influence (OC/EC)pri for the range of temperature. Although less drastic than for the lower temperature, it is thus possible that a change of primary sources explains at least a fraction of OCsec calculated for the warmer temperatures.

Because of the large range of conditions encompassed in our study, we can easily show in this case that if the assumption of a constant (EC/OC)pri is not exactly respected, the result for the calculation of SOA formation is not reliable. More generally, if this assumption is not closely examined, the validity of the results given by the calculation of the primary and secondary fractions of OC with this type of method is really questionable. The amplitude of the error induced by the variation of the primary EC-to-OC ratio could, in many studies, lead to OCsec concentrations that would be more or less coherent with an expected result and interpreted as well. Thus, this type of method can only be applied in studies where primary sources of EC and OC are extremely well known, together with their contributions to total EC and OC measured on the receptor site. In all other cases, probably a high majority, this potential error, added to all other uncertainties in the determination of OC concentrations, as described in Huebert and Charlson (2000), makes the result of the calculation of OCsec dubious.

4 Conclusions

Daily PM_{10} samples were collected at two urban sites in valleys of the French Alps (Chamonix and St Jean de Maurienne) during a period of two and a half years. The carbonaceous species EC (elemental carbon) and OC (organic carbon) were analysed to investigate the possible sources of EC and OC, and their seasonal evolutions. Mean EC and OC concentrations were respectively 1.9 and 9.0 $\mu g/m^3$ in Chamonix and 1.0 and 6.4 $\mu g/m^3$ in St Jean de Maurienne. Mean OC concentrations are in the very high range of concentrations measured for other European sites, and represent 33 and 38% of PM_{10} mass for Chamonix and St Jean de Maurienne, respectively, without correction to calculate OM (organic matter) concentrations. Concentrations of EC and OC for both sites show a clear seasonal cycle, with maxima in winter. High correlations with NO and NO_2 show the

importance of local primary combustion sources. The strong increase of EC and OC concentrations as the temperature decreases is probably largely linked with the increase of the frequency and strength of atmospheric inversion layers during winter time in these deep valleys. Nevertheless, the evolution of the EC-to-OC ratio with the temperature demonstrates that the relative contribution of different sources of EC and OC is also changing according to the temperature ranges.

The impacts of heavy duty traffic and residential heating are highlighted by the relations between EC and OC concentrations and the number of heavy duty vehicles (HDV) circulating in the valleys and K^+ concentrations used as a tracer for biomass combustions, respectively. On the one hand, changes in EC concentrations are linked with that of HDV number, which is not the case for OC. On the other hand, the correlation between concentrations of OC and K^+ is very large and stronger than that between concentrations of EC and K^+. Although other potential sources, like primary emissions by cars, or possible impact of semi-volatile organic species condensation with low temperature could not be estimated, it appears clearly that biomass burning emissions have a significant impact on OC concentrations (and consequently on PM_{10} mass concentrations), especially for low temperatures. The impact of this source on PM_{10} mass is probably stronger than that of the HDV source. This can explain both the evolutions of the EC-to-OC ratio and of OC- and EC- to-PM_{10} ratios observed for low temperatures. Further quantification of the contributions of these sources would require measurements of specific tracers (Marchand et al., 2006).

Finally, our data show that the formation of SOA could have an impact on PM_{10} mass during summer time. The EC-to-OC primary ratio method, based on several hypotheses (Castro et al., 1999), was applied to the overall data set to evaluate this SOA fraction. It appears clearly that the SOA mass calculated in our study is largely biased by the variations of the primary EC-to-OC ratio. More generally, it demonstrates that the calculation of SOA mass with this method is highly uncertain, if the hypothesis of a constant primary EC-to-OC ratio is not very closely examined.

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