SOURCE APPORTIONMENT OF VOLATILE ORGANIC COMPOUNDS IN 3 FRENCH SITES BY DESCRIPTIVE ANALYSES AND RECEPTOR MODELLING

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ABSTRACT

Large quantities of volatile organic compounds (VOC) are emitted into the atmosphere by different sources such as the automobile traffic, residential and biogenic sources or industrial emissions. Consequently, it is interesting to evaluate the temporal and spatial contribution of the different sources to the ambient concentrations. In France, VOC measurements are carried out by air quality monitoring networks. Continuous hourly measurements of 31 VOC from C_2 to C_9 were performed since 2001 in 3 regional networks (Marseille, Strasbourg and Grenoble). Preliminary results show that Marseille site present an average VOC concentration two to three times higher than the other sites and Grenoble site seems to be the most sensitive to seasonal variation. Simple mathematical and descriptive analyses (daily variation and wind roses) have been made and, so, a great majority of the compounds seems to result from the sources related to the urban traffic. Some compounds have singular behaviour: notably, for Marseille site, benzene and cyclohexane concentrations are very influenced by a far chemical factory emission. Lastly, receptor modelling results confirm the substantial prevalence of the urban traffic sources among the involved sources whatever the site (between 35 and 60% of total emissions) and some sources such as automobile exhaust source have a clear daily variation.

Key Words: volatile organic compound, source attribution, data analysis, receptor models

1. INTRODUCTION

Appendix VI of the European directive on ozone 2002/3/EC specifies that the measurement of the ozone precursors has to relate to a "suitable" list of Volatile Organic Compounds (a list of 31 VOC is recommended). VOC coupled with NO_x are the most important precursors of tropospheric ozone formation and VOC are especially important in urban areas because their reaction with the hydroxyl radical (OH) plays a critical role in atmospheric photochemical reactions. Many studies present several sites (Colòn and al., 2001; Tanaka and Samukawa, 1996) or long measuring campaigns (Hakola and al., 2003) but few have three different sites at three different latitudes with hourly measurements since many years as describing below. Since 2001, the hourly measurement of the NMHC has been started in several

French air quality monitoring networks and consequently a large VOC concentration databases is now available. Each site presents a specific typology: urban, periurban and rural site under industrial influence for Marseille, Strasbourg and Grenoble networks respectively. Three databases were made up both with VOC data concentrations and weather data collected on the three sites. The mains sources influencing the ambient VOC concentrations at each site of measurement were systematically indexed. To date, the three databases join more than 1.200.000 data of VOC concentration. For this study, we have done in first time descriptive analyses and in second time receptor modelling analysis.

2. SAMPLING AND CHEMICAL ANALYSIS METHODS

The analytical method used for VOC measurements was developed in the Chemistry and Environment department of the Ecole des Mines de Douai (EMD) in the framework of Central Laboratory of Air Quality Survey (LCSQA). It is based on:

1-preconcentration of volatile organic compounds of ambient air sample on a trap filled with a mixture of adsorbents maintained at - 30°C thanks to a system of Peltier cooling, followed by a thermal desorption until a temperature of 300°C (Turbo Matrix Auto System provided by Perkin Elmer)
2-analysis by gas chromatography (GC Perkin Elmer) using a dual capillary columns system (CP Sil 5CB, 50 m x 0,25 mm, and Plot Al_2O_3/Na_2SO_4, 50 m x 0,32 mm)
3-detection by FID (flame ionisation detector) whose answer is proportional to the effective carbons number of the detected molecule (Tranchant et al., 1995).

For more explanation, the analytical procedure was described in details in a previous paper (Badol et al., 2004).

The measuring device produces large numbers data each day (744 per 31 measured VOC). It is essential to apply check procedures quality in order to validate these data:
1-Checking of the identification of the peaks
Measurements on the long term often involve a drift of the retention time, which can imply misidentifying. Thus peaks assignment is checked for any chromatogram while representing the evolution of the peaks retention time according to time. A rupture in the curve of retention times is due to a misidentifying (Veillerot et al., 1998).
2-Reproducibility
The study of reproducibility is done by the follow-up of the evolution of the peaks surfaces of the target compounds during the checking of the calibration (analyses of a standard mixture every two weeks). It is generally not tolerated a difference higher than 10% between the unit of the values of the surfaces of each injection compared to a reference value. Beyond the tolerance of 10%, the analytical device is examined in order to locate the dysfunctions (Badol et al., 2004).
3-Intercomparison
Each year, canisters containing a gas mixture of VOC are analysed and circulate between the networks and the "Ecole des Mines de Douai" whose values are taken as reference. Any important difference between measurement and the actual value in

the canisters can be proposed. Thus the networks can validate their results and locate possible dysfunctions of their analytical device (Borbon et al., 2003).

3. FIELD STUDIES AND SAMPLING SITES

For this work, we systematically listed the whole of the sources of VOC likely to influence the three receptor sites located near 3 large French cities: Marseille, Strasbourg and Grenoble.

For Marseille, VOC monitoring is led on the station of Prado (urban station, 43°27'N, 5°13'E) located in the Southern half of the city near a busiest artery of Marseille (27000 vehicles per day). Near the site a lot of trade such as laundries or petrol stations can influence ambient VOC concentrations. In addition, two far important factories sites in terms of VOC emissions will be likely to have a sufficient influence to be detected on the sampling site:
  - a chemical factory specialized in the manufacture of an amino acid (approximately 10 km in the East of the site)
  - the port of Marseille which extends between 3 and 11 km in the North-West from the receptor site and which has an varied activity like naval repair or freight transport

For the zone covered by Strasbourg network, the monitoring of the VOC is led in Schiltigheim (48°21'N, 7°25'E), town of approximately 31000 inhabitants being next to Strasbourg (North-West). It is a periurbain station located in office and school zone. Near the site, few specific local sources seem likely to influence VOC measurements. However, the presence in the vicinity (approximately 50 meters) of the monitoring site of a small gasoline depot is likely to influence VOC concentrations. Strong sources of VOC (such as oil or chemical industries, printing works, etc) but relatively far away from the site of measurement (up to 10 kilometers) are likely to be able to influence the measured concentrations. Thus, some industrial emissions seem likely to have a sufficient contribution to be measured when the dominant winds blows in direction of the sampling site.

For the zone covered by Grenoble network, the 31 VOC monitoring is led on a rural station under industrial influence: the station of Champagnier (45°06'N, 5°43'E). The monitoring site can be described as slightly influenced. Indeed, it does not have activities recognized like strongly transmitting of VOC (laundry, garage, petrol station…) except the relatively limited automobile traffic (proximity of a little attended road). Consequently, of share its geographical situation, the station could be subjected mainly to the action of a near factory site which produces mainly polychloroprene rubber. According to the direction of wind, the site could be also influenced by the emissions of a chemical pole (South-eastern) or the emissions of far important industries (North-western, about 5 kilometers).

4. CHEMICAL MASS BALANCE RECEPTOR MODEL

For this study, we have used the Chemical Mass Balance receptor (CMB, Watson et al., 1994, 1998, 2001). It consists of a least-squares solution to a set of mass-balances equations that express each receptor chemical concentration as a linear sum of products of source profile abundances and source contribution. Mathematically the system is written:

$$C_i = \sum_{j=1}^{J} F_{ij} \cdot S_j, \quad i = 1,...,I \tag{1}$$

where C_i is the concentration of compound i, F_{ij} is mass fraction of compound i from source j (weighting percentage), S_j is the mass concentration from source j ($\mu g/m^3$), J is the number of sources and I is the number of compounds.

In contrast to other receptor models (PMF and UNMIX for example), which extract source compositions from the data, CMB requires the user supply source profiles. Also in contrast to the other models, CMB is applied separately to each observation, rather than operating on the data set as a whole. CMB is largely used for environmental data and produce generally good results for VOC data (Vega et al, 2000; Miller et al., 2002). Consequently, according to our good knowledge of field studies (see section 3), we have chosen to use this receptor model.

5. RESULTS

5.1. Preliminary results

First, for each site, the sum of the medians and means of the 31 VOC were calculated (see table 1). Thus the exposure of sites to the VOC can be quantified. The site of Marseille presents an average VOC concentration two to three times higher than the sites of Grenoble and Strasbourg in agreement with its urban localisation. Strasbourg and Grenoble show similar lowest concentrations. For the first quoted, the explanation lies in the fact that it is located in a little village subjected to few VOC emissions sources. For Strasbourg, the site area corresponds in a fairly inhabited zone, made up of offices, small companies and school establishments. The site of measurement is thus far away from the principal sources of VOC and will be subjected punctually to the emissions of distant industries.

Table 1: Sums of medians and means ($\mu g/m^3$) of the 31 targets VOC

Marseille		Strasbourg		Grenoble	
median	mean	median	mean	median	mean
66.22	94.76	26.05	39.67	22.71	36.00

Secondly, a substantial difference in the distribution of the involvement of the measured total concentrations of each VOC family is noticed from the winter months to the summer ones (see table 2). For the site of Grenoble, an increasing of 11% for aromatics family and a decreasing of 9% for alkenes family is observed during the

passage of the winter to the summer months and, so, it is possible to affirm that this site is the most sensitive to seasonal variation. Its rural aspect and the proximity of mountainous massif responsible for very cold winter temperatures (about 1°C on average for a winter day) require higher winter heating. The reduction of olefinic hydrocarbons percentage (25% in winter and 16% in summer) would be directly related to the residential heating whose emissions profiles show a prevalence of the alkenes family (GENEMIS profile available on www.ier.uni-stuttgart.de). Likewise the increase of aromatics compounds percentage can be see as the increase of solvent evaporation source which profile is made up almost exclusively by aromatics compounds (Passant, 2002). For Strasbourg site, we have almost the same phenomenon: decrease of alkenes percentage and increase of aromatics compounds percentage during the passage of the winter months to the summer ones. The same argument as Grenoble can be developed but we can also think that important variation of wind direction with season is also an important factor. In fact, if winter and summer wind roses of Grenoble are almost similar, Strasbourg ones are very different.

Table 2: Seasonal variation of medians sums ($\mu g/m^3$) of each family compound

Family compound	Marseille		Strasbourg		Grenoble	
	Winter	Summer	Winter	Summer	Winter	Summer
Alkenes + acetylene	13%	11%	23%	17%	25%	16%
Alkans	39%	43%	51%	50%	43%	41%
Aromatics	48%	46%	26%	33%	32%	43%

5.2. Spatial and temporal analysis

The analyses of the daily and seasonal variations and concentration roses were then carried out for the whole of the compounds. Generally, a great majority of compounds exhibit a shape with a "double wave": first sharp maximum in the morning and a second one in the afternoon both corresponding to traffic rush hours (see figure 1, ethylbenzene measured on Strasbourg site). Thus, the urban traffic seems to be the principal source of the majority of compounds.
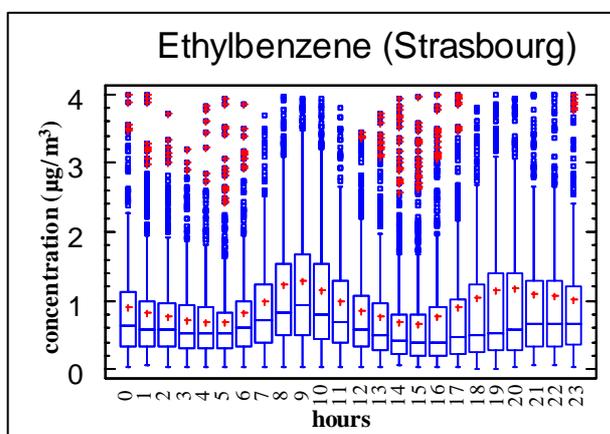

Figure 1: "Double wave" profile of majority of compounds

However, on each site, some compounds showed a singular behaviour (in this study only one singular behaviour were developed). For example, daily variation analyses show high night values for benzene and cyclohexane measured on the site of Marseille (see figure 2, benzene profile). According to this very singular profile (see majority of compounds profile), winds roses were looked with much meticulousness. These ones exhibit high concentrations for a wind direction between 50° and 80°. To explain these observations, it is necessary to know the localisation of Marseille: in the South of France and near the Mediterranean Sea. During the night, the ground cools quickly while the sea keeps approximately the same temperature. It results a land breeze, which blows from East to West on Marseille. Consequently, in the light of these information, the high night values of benzene and cyclohexane can be allotted to emissions related to a factory specialized in the chemistry located in the East of the city (see field studies and sampling sites section).
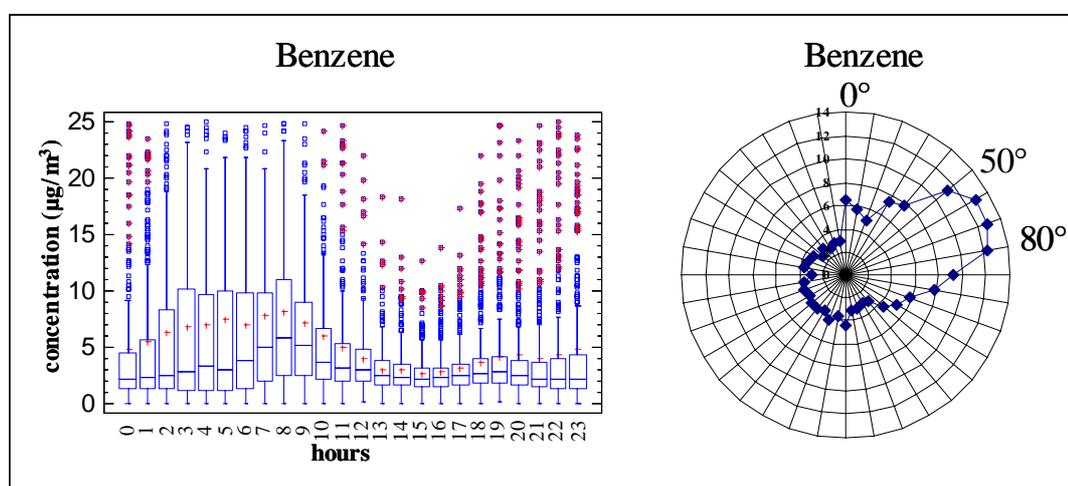

Figure 2: Daily and concentration roses analysis of benzene measured on Marseille site

5.3. Receptor modelling analysis

These basic descriptive analyses seen above have been only the first stages necessary to the attribution of the emissions sources for the measured concentrations. Thus CMB and PMF models were applied on the three databases. In this study, only CMB results are shown. Discriminations between summer and winter data have been done previously. Thus monthly, summer and winter runs are carried out for the three sites. For CMB modelling, the whole of sources profiles likely to influence concentrations measured on the three sites (see section 3) were tried. Whatever the season and the site, very few sources seem able to influence ambient concentrations. There are 5 common sources (vehicle exhaust, gasoline evaporation, leaks of natural gas and GPL, biogenic and domestic heating) to which we must add:
- rubber factory source for Grenoble
- printing works and solvent sources for Strasbourg
- printing works/ink, solvent and amino-acid factory sources for Marseille

For the three sites, during the passage of the summer to the winter months, we can observe a variation in the percentage explained by each emission source to the total concentration. Whatever the site, vehicle exhaust is the most important source (35 to 61% of the total concentration depending of the season and the site, see table 3). Despite Marseille site is the most submit to urban traffic (27000 vehicles per day), surprisingly, relative percentage of vehicle exhaust source of Marseille is the lowest of the three sites. Relative percentage of vehicle exhaust source depend not only of urban traffic intensity but also of the number and the intensity of the others sources on which the receptor site is submitted. Thus, the urban situation of the Marseille site, with much of small punctual sources, makes that this one presents the lowest relative percentage for vehicle exhaust source.

Table 3: Seasonal relative percentage of vehicle exhaust source on the three sites

Marseille		Strasbourg		Grenoble	
summer	winter	summer	winter	summer	winter
35.4%	41.1%	46.0%	53.8%	58.9%	61.4%

Concerning the daily evolution of the vehicle exhaust source, CMB modelling exhibit a shape with a "double wave" with first sharp maximum in the morning and a second one in the afternoon for each site, whatever the season (see figure 3).
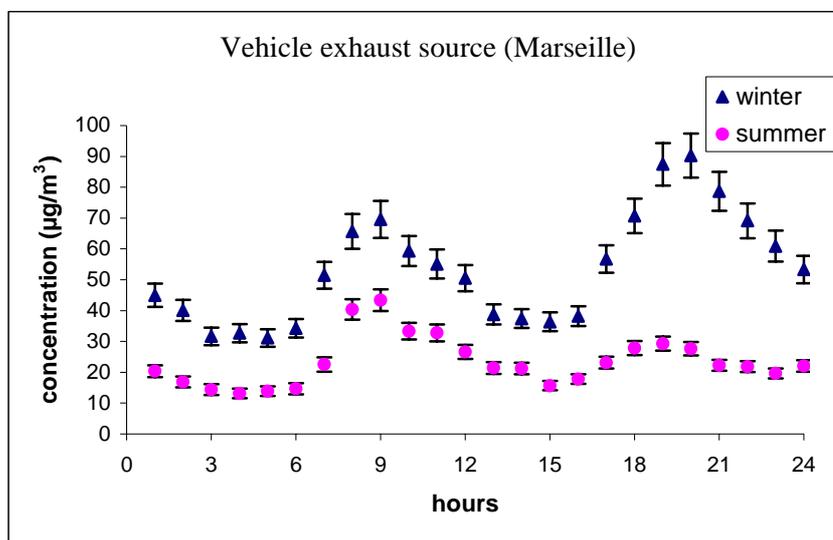

Figure 3: Summer and winter daily concentration variation of vehicle exhaust source of Marseille site

Only this source presents this behaviour. The same daily variation could be characterised for the daily variation of the majority of compounds concentrations. This result confirms the assumptions of section 5.2: majority of compounds stems from urban traffic and particularly from the vehicle exhaust (notably for Grenoble and Strasbourg site). For Marseille site, this assertion seems more debatable because

the part of the vehicle exhaust source decreases until 35.4% in summer. Consequently, the importance of this source remains sufficiently large to influence daily profile of the majority of compounds. But, we can see from this result that the only one examination of the daily profile is not sufficient to affirm that the majority of compounds comes principally from urban traffic and particularly from the vehicle exhaust. Winter modelled concentrations of vehicle exhaust source are stronger than the summer ones and the summer and winter profiles show a sensible difference for the second wave (see figure 3). Besides, the hourly source variation, scattering dispersion can have also an important role for the scale of measuring concentrations. Thus, the seasonal difference observed can be explained by a night boundary layer for winter decreasing mixing layer and increasing the concentrations and a diurnal boundary layer for summer increasing mixing layer and, so, decreasing the concentrations (Seinfeld and Pandis, 1997).

Daily evolution of the whole of source can be represented according to CMB modelling. Each of them has a singular evolution. For example, the source representing the amino-acid factory of Marseille has a singular profile with high night and weak constant diurnal concentrations (see figure 4). A very similar profile has been shown in section 5.2. for two compounds (benzene and cyclohexane). Consequently, according to their lifetime (4.7 days and 20 hours for benzene and cyclohexane respectively) and their transport time (about one hour for land breeze of 2m/s) these compounds are principally allotted to emissions related to the factory specialized in the chemistry located in the East of Marseille.
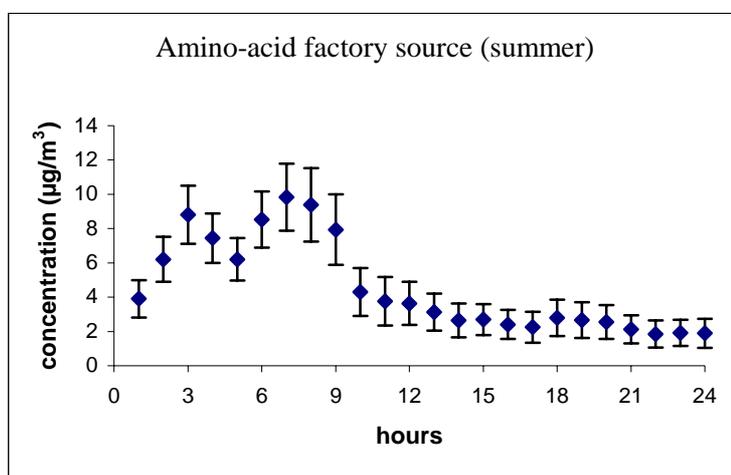

Figure 4: Daily concentration variation of amino-acid factories source on Marseille site

Lastly, for Grenoble site, we can see the increase of evaporative source (EVAP + RUBBER) during the passage of the winter to the summer months and the lost of heating source (see figure 5). The disappearance of this source characterised by a strong prevalence of olefinic family confirms the assumption given to explain "preliminary results" (section 5.1)
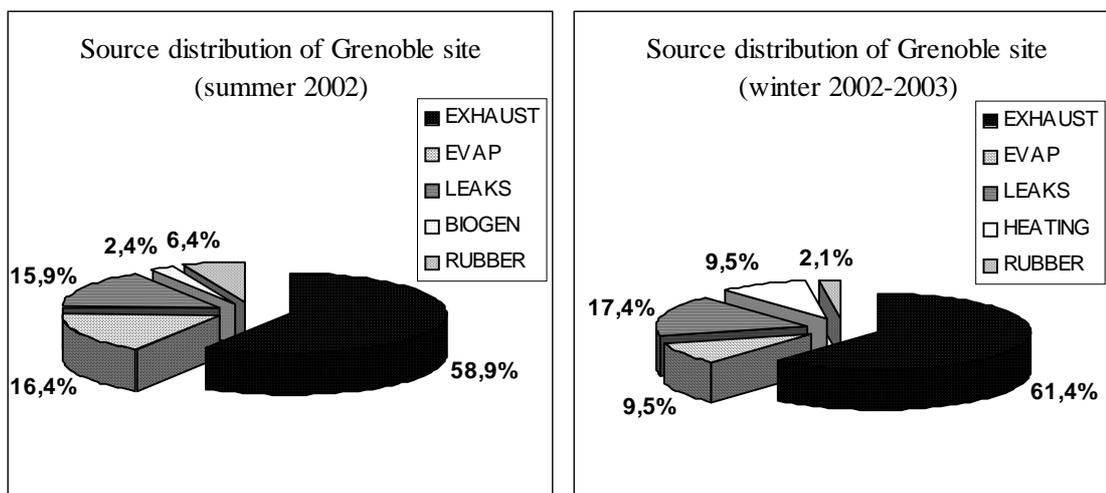
Figure 5: Seasonal variation of source distribution of Grenoble Site. Sources: EXHAUST = vehicle exhaust, EVAP = gasoline evaporation, LEAK = leak of natural gas + liquefied petroleum gas vapour, HEATING = domestic heating, BIOGEN = isoprene emission from biogenic sources, RUBBER = rubber factory

6. CONCLUSION

Many analyses have been made on three VOC databases coming from three French regional networks. Preliminary, spatial and temporal analyses have been made. Seasonal study of relative percentage variation of each family compound allows affirming that the site of Grenoble is the most sensitive to seasonal variation. Most of compounds seem to come, for the most part, from vehicle exhaust source. In addition, we see that the simple descriptive mathematical and statistical methods allow a partial attribution of the VOC sources in particular for the compounds resulting mainly from the industrial sources. VOC daily and seasonal distributions are controlled by a combination of emission factors, dispersion conditions and respective lifetime of the compounds. Thus, meteorological conditions can have an important effect and singular or exceptional wind direction can bring back far factories emissions. Receptor model have also been used. The results confirm the substantial prevalence of the urban traffic source (especially for Grenoble site) among the involved sources. In addition, in the summer months, evaporation sources can have a great importance (up to 50% of total VOC emission according to the receptor site). Lastly, some sources have a clear daily and/or seasonal variation. Thus, some assumptions formulated with preliminary, temporal and spatial analysis could be checked.

7. ACKNOWLEDGEMENTS

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