Applying Receptor Models To Analyze Urban/Suburban VOCs Air Quality in Martorell (Spain)

3 AUTHORS, INCLUDING:

José M Baldasano
Polytechnic University of Catalonia

299 PUBLICATIONS **3,539** CITATIONS

Josep Calbo
Universitat de Girona

111 PUBLICATIONS **1,030** CITATIONS

Applying Receptor Models To Analyze Urban/Suburban VOCs Air Quality in Martorell (Spain)

JOSÉ M. BALDASANO,*
ROSA DELGADO, AND JOSEP CALBÓ[†]

Institut de Tecnologia i Modelització Ambiental (ITEMA), Universitat Politècnica de Catalunya (UPC), Apartat de Correus 508, 08220 Terrassa, Barcelona, Spain

Airborne concentrations of several VOCs were measured in the city of Martorell (Spain) and analyzed by using a receptor modeling approach in order to assess the contribution of several potential sources of VOCs. In addition, VOC concentrations in Martorell are compared to VOC levels in 16 other cities of the world. Special attention throughout the paper is focused on the comparison between results obtained with data from an urban environment and data from a suburban area. Compared to the other cities, VOCs air quality in Martorell do not stand out for being neither among the worst nor among the best. The goal of setting relationships between airborne concentrations and pollutant sources is approached by a principal component analysis coupled to multiple linear regression. These procedures allow one to identify sources of VOCs pollution. A subsequent multiple linear regression allows us to estimate emission profiles for significant sources. The main source of VOCs pollution in Martorell is road traffic, contributing 62% of total pollution. Other identified sources of VOCs are the manufacture of aromas and essences (17%), a chemical industry of chlorinated compounds, and a wastewater facility (together, 6%). These latter three point sources are located by establishing relationships between wind directions and peak concentrations.

Introduction

Volatile organic compounds (VOCs) are important contributors to the formation of ozone and other photochemical oxidants (*i.e.*, urban smog). Some VOCs have been identified as toxic or mutagenic at concentration levels sometimes found in urban environments (*1*). Because of increasingly more sensitive sampling and analytical techniques, some species can be detected and reported at parts per billion or even parts per trillion levels (*1−3*). In order to devise efective VOC control strategies, it is necessary to know the sources of VOCs in a given region, but the traditional approach of dispersion modeling is not always effective. Emission factors of VOCs from some sources and some speciation profiles, that is, the relative amount of each species that is released from a source, can be found in the literature (*4, 5*). Emission inventories, however, may be uncertain due to changes in fuel characteristics, operating conditions, equipment failures, etc. (*6*). These limitations make the use of alternative methods such as receptor models necessary.

* Corresponding author e-mail: baldasano@pe.upc.es.
† Present address: Dept. d'Enginyeria Industrial, Universitat de Girona, Avda. Lluís Santaló, s/n, 17071 Girona, Spain.

Receptor models assess contributions from various sources based on observations at sampling sites (receptors) (*7*). Several kinds of exploratory or confirmatory receptor models (*8*) have been used in the past; most of them were applied on the basis of chemical composition of particulate matter. For example, a principal component analysis (PCA) of particulate elemental data recorded in Boston allowed Thurston and Spengler (*9*) the estimation of mass contribution for five fine particles sources (soil, motor vehicles, coal, oil, and marine salt). Pirrone at al. (*10*) applied a hybrid-receptor deposition model to estimate the dry deposition flux to Lake Michigan of trace elements associated with particles in the fine and the coarse size range using ambient air concentrations measured during the Lake Michigan Urban Air Toxic Study (LMUATS).

Receptor models have also been applied to interpret VOC data. Sweet and Vermette (*11*) applied chemical mass balance (CMB) and wind trajectory analysis to 13 toxic VOCs in Illinois. Scheff and Wadden (*12*) used CMB to analyze 23 non-methane organic compound (NMOC) concentration patterns for each of 55 samples obtained in Chicago. They considered eight source categories (vehicles, gasoline vapor, refineries, degreasing, coatings, graphic arts, dry cleaning, and wastewater treatment plant). In a more recent work, Wadden et al. (*13*) combined CMB along with the carbon bond reaction kinetics model (CBM-IV) to develop an exploratory method to investigate the potential effect of VOCs reduction from several sources on maximum ozone concentration. Kupiszewska and Pilling (*14*) applied CMB and factor analysis (FA) to concentrations of 20 VOCs sampled at three sites in Leeds, U.K., in order to identify major sources. Fujita et al. (*15*) used data for several NMOC obtained during the South California Air Quality Study (SCAQS) to assess the CMB performance. They considered several potential sources, including biogenic emissions. Pirrone et al. (*16*) modified the hybrid-receptor deposition model used in ref 10 to estimate both gas exchange across the air−water interface and particle dry deposition of a number of semi-volatile organic compounds (SOCs).

In this paper, measurements of airborne concentrations of several VOCs in the city of Martorell (Spain) are presented. These data were obtained and interpreted in order to assess air quality due to VOCs in this city. In particular, pollutant concentrations in Martorell were compared to VOCs air quality elsewhere. In order to set relationships between airborne concentrations and pollutant sources, an exploratory modeling approach (principal component analysis coupled to multiple linear regression) was used. This allowed the verification of the main sources of VOCs pollution in Martorell. Furthermore, a simple wind directional analysis allowed location of some of these sources. Special attention throughout this paper is focused on the comparison between results obtained with the data collected in an urban environment and the data collected in a suburban area.

Study Area

The area of interest for this study is the city of Martorell, Spain. This city is located in the northeast of the Iberian Peninsula, some 20 km NW of Barcelona and 24 km from the Mediterranean coast. It covers an area of 12.9 km² and has a population of approximately 16 000 inhabitants. The city is placed at the confluence of two rivers: the Llobregat River, which runs from NNW to SSE, and the Anoia River, which runs from SW to NE (Figure 1).

Despite its relatively small population, Martorell is an important transportation hub. Most traffic between Bar-
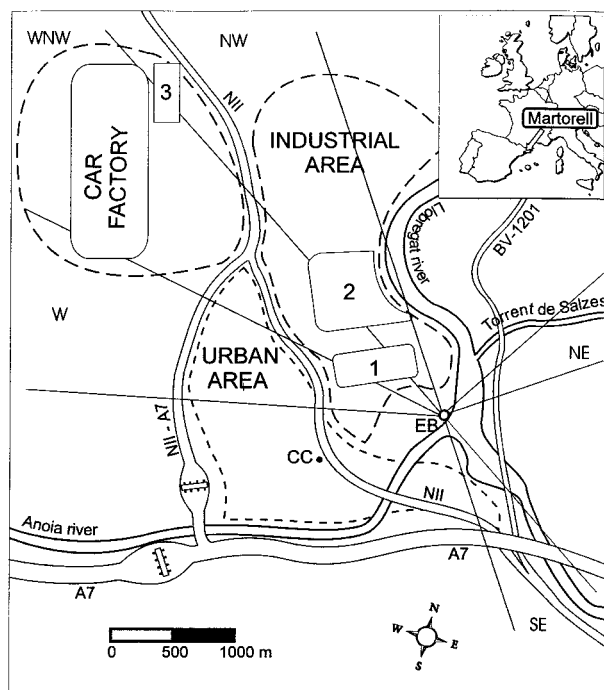
FIGURE 1. Study area (city of Martorell), with the two receptor sites (CC and EB). Main highways and industries (1, food manufacture; 2, chemical industry; 3, wastewater treatment facility) are shown as well as wind directions as seen from the suburban (EB) receptor point.

TABLE 1. Mean Concentrations (μg/m^3 $\pm$ SD) of Analyzed VOC at CC and EB

code	compound	CC (urban) ($n = 34$)	EB (suburban) ($n = 44$)
	Alkanes		
C6	hexane	4.0 ± 5.9	2.0 ± 3.6
C7	heptane	1.0 ± 0.9	0.43 ± 0.44
C8	octane	0.65 ± 0.65	0.65 ± 0.84
C9	nonane	0.78 ± 0.76	1.2 ± 1.7
C10	decane	4.1 ± 5.7	2.1 ± 1.6
C11	undecane	1.0 ± 2.6	0.48 ± 0.39
C12	dodecane	2.6 ± 4.2	2.1 ± 2.3
C13	tridecane	0.8 ± 1.6	0.86 ± 0.77
C14	tetradecane	3.1 ± 4.3	3.3 ± 4.0
	Alkylbenzenes		
BENZ	benzene	3.8 ± 3.5	1.3 ± 1.3
TOLU	toluene	14 ± 11	9.0 ± 11
ETBZ	ethylbenzene	3.8 ± 3.1	1.8 ± 1.8
MPXY	$m+p$-xylene[a]	11 ± 8	5.2 ± 4.3
OXYL	o-xylene[b]	3.6 ± 2.0	1.4 ± 1.0
3MBE	trimethylbenzene[c]	18 ± 14	6.7 ± 5.5
	Chlorinated Hydrocarbons		
12CE	1,2-dichloroethane	0.9 ± 2.6	1.6 ± 2.1
111C	1,1,1-trichloroethane	3.1 ± 5.2	2.4 ± 6.1
PERC	perchloroethylene	1.5 ± 2.9	1.3 ± 1.73
3CET	trichloroethene	1.6 ± 2.3	1.5 ± 2.54
CMT	tetrachloromethane	0.25 ± 0.59	0.18 ± 0.40
112C	1,1,2-trichloroethane	0.09 ± 0.25	0.08 ± 0.13
	Terpenes		
APIN	α-pinene	1.2 ± 1.4	1.2 ± 1.5
BPIN	β-pinene	0.11 ± 0.25	0.10 ± 0.18
CARE	carene	ND[d]	0.19 ± 0.35
LIMO	limonene	0.21 ± 0.39	0.38 ± 0.51
	Miscellaneous		
EACE	ethyl acetate	1.3 ± 2.1	0.47 ± 0.86
BACE	butyl acetate	0.70 ± 0.73	0.37 ± 0.51
ACPH	acetophenone	1.9 ± 6.3	5.2 ± 6.6
AAOL	α,α-dimethylbenzylalcohol	1.4 ± 5.2	2.2 ± 2.5

[a] Sum of the meta and para isomers of xylene. [b] Ortho isomer of xylene. [c] Several isomers of this compound are given as a single species. [d] This species always showed concentration below detection limit (0.1 μg/m^3) at this station.

celona and the southern and central areas of Catalonia and Spain must go through Martorell. Highway NII from Barcelona to Madrid, Highway A7 from Barcelona to Madrid and Valencia, and several regional highways cross each other in this city. Large traffic flows are found: in 1990, the annual average daily traffic (AADT) was 38 957 vehicles through NII (that crosses the urban area of the city); 48 754 vehicles through the connection between NII and A7; and 78 539 vehicles through A7.

The most important economic activity in Martorell is industry. Large industries are located close to the Llobregat river: a petrochemical industry that produces chlorine, caustic soda, and polyvinyl chloride; a food processing industry that produces glucose; and a car factory. In addition, a large number of less important industrial companies are located in and around Martorell. Almost one-fourth of the city area is dedicated to industrial uses. There is a small fraction of agricultural land (orchards) within the city boundaries, but most of the area not used as industrial, residential, or commercial is unimproved terrain covered by shrubs.

Sampling Sites and Methods

Air samples were collected at two different receptor sites between October 1992 and July 1993. The first site, called Cabina de Control (CC), was located within downtown Martorell; the second point, called Estació de Bombeig (EB), was placed away from the city center in a suburban area (Figure 1). The distance between the two sites is 1.2 km. The urban station (CC) was surrounded by a number of large buildings. These buildings block and modify wind direction, especially when the wind blows from N, NE, or W. The suburban station (EB) was free of obstacles around it. At this latter station, records of wind direction show that the wind is driven mainly by the topography of the area: the valleys of Llobregat River, the Anoia River, and a third, smaller water stream, called Torrent de Salzes, which runs from NE to SW.

At both sites, measurement equipment that recorded meteorological variables and a device to collect air samples were installed. Meteorological data (wind speed and direction, temperature, humidity, solar radiation) were continuously recorded every half hour, while air samples were collected approximately once per week. Samples of different time length duration (between 5 and 24 h) were collected at a flow rate of 30 mL/min with a filter containing three kinds of molecular carbon (Carbotrap B, Carbotrap C, and Carbosieve III). Air samples were analyzed using gas chromatography (GC) coupled to mass spectrometry (MS) and based on protocols TO-01 and TO-02 provided by the U.S. EPA (17). We used a Hewlett-Packard 5890 gas chromatograph coupled to a MSD 5970 mass spectrometer. The GC column was a 25 m $\times$ 0.25 mm Rescom OV-1 column (0.3 μm film thickness), and helium was used as the carrier gas. The column temperature was increased from 35 to 200 °C at a rate of 4 °C/min and then from 200 to 240 °C at a rate of 6 °C/min. Ambient concentrations of 29 VOC species were determined (Table 1). Several audit samples were analyzed for quality assurance purposes. The mean percent recovery for the analyzed species was 75%. The relative standard deviation (RSD) obtained after an analysis of duplicate samples was typically less than 20%. In general, blank concentrations were less than 1%.
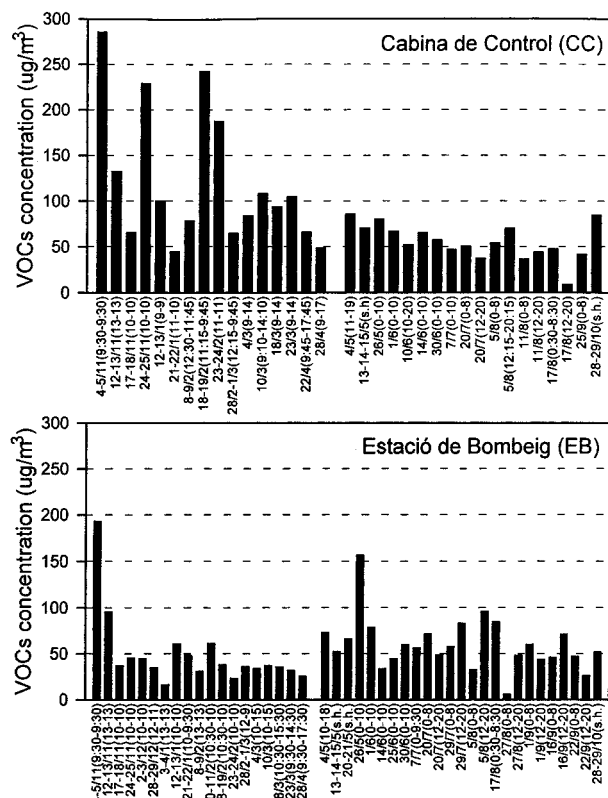
FIGURE 2. Seasonal variation of VOCs concentration at the two stations: top, urban site (CC); bottom, suburban site (EB). In each graph, winter samples are on the left and summer samples are on the right.

Data Analysis: Air Quality

Thirty-four samples at CC and forty-four samples at EB were analyzed. A summary of the data collected is shown in Table 1. For most VOCs considered in this study, mean concentrations at CC are higher than those at EB. This is particularly true as far as the n-alkanes and alkylbenzenes are concerned. Since alkanes and alkylbenzenes are mainly released by road traffic (4), it seems that the impact of traffic is larger at CC, in the urban area, than at EB (suburban). For heavy alkanes ($C_{12}-C_{14}$), however, concentrations at both stations are equivalent. This fact reflects that the ratio of diesel vehicles to total traffic is higher in the suburban area. On the other hand, we can see that acetophenone, a typical product of manufacturing artificial aromas and essences (18), reaches a much higher mean concentration at EB. This probably corresponds to a short distance between the source of this species and that station. Concentrations of terpenes, VOCs of biogenic origin, are almost equivalent at both stations. This reflects that terpenes recorded at both sites are well mixed in the air when they reach the area under study, since they are released by widely spread sources around the city. In general, concentrations recorded at CC show larger standard deviation than those measured at EB, which indicates that the CC site is more influenced by local sources.

Total concentrations of VOCs against time are plotted in Figure 2 to allow an analysis of seasonal evolution of air quality. Samples are split in two groups: one for summer samples (from May to October) and the other for winter samples (from November to April). We can see that the duration of the sampling period does not have a relevant influence. At the urban site, the mean summer concentration is lower, by a factor of 2, than the winter average. Several factors can explain this behavior. First, the radiative warming of the surface in the summer is stronger than in the winter.

This warming induces higher atmospheric turbulence and deeper mixing layers. There are several air soundings and acoustic soundings in Barcelona (unpublished) that reflect this phenomenon. Since air pollutants are uniformly distributed in the mixing layer, the deeper the layer, the lower the concentrations. The second factor is related to emissions. Summertime is when many people take vacations. That means a decrease of local traffic and emissions inside the city downtown. Besides, domestic heating is also turned off during summer. Finally, the photochemical activity of VOCs is the third factor that may explain differences between summer and winter concentrations. In summer, the increase of incoming solar radiation makes the photochemical reaction rates increase, and consequently concentrations of primary VOCs decrease. For the suburban site, we can see that the mean concentration of VOCs in winter is equivalent to the summer average. Since the above meteorological effects should result in lowering concentrations in the summer, an increase of emissions affecting this site relative to winter emissions is the only factor that can explain such equivalence. Indeed, traffic emissions in highway A7 increase because this route is an intensively used way to many vacation destinations.

Data Analysis: Receptor Modeling

Sources of the Analyzed VOCs. Several documents were examined in order to obtain approximate emission profiles (*i.e.*, including speciation) of the most important potential sources for the species considered. The VOCs analyzed in the present study are described, and their main sources are listed in refs 4, 18, and 19. In particular, Hampton (4) distinguishes 22 species released by vehicles, differencing between emissions from diesel and gasoline engines. In 1989, Scheff et al. (5) published emission factors and complete profiles of a large number of sources, including those of vehicle traffic, gasoline vapor, refineries, architectural coatings, wastewater treatment, graphic arts industries, and others. Subsequent studies made use of these data (11−13, 20, 21). Almost the same information can be found from other reports; for example, in the United Kingdom emission inventory (22). Müller and Buser (23) show very detailed profiles for vehicle emissions, but they include some VOCs that we did not measure in Martorell. Contrarily, Obermeier et al. (24) describe the emissions for families of VOC, not for species. As far as biogenic emissions are concerned, emission profiles of deciduous and evergreen trees according to families of VOCs are given in Pierce et al. (25). More detailed profiles of VOC emissions for a number of Mediterranean trees are shown in ref 26. Fehsenfeld et al. (27) summarized information on biogenic emissions, distinguishing several classes of forests and a large number of chemical species.

This bibliographic information is summarized according to our interests in Table 2. So, the 29 VOCs analyzed at the receptor points and the sources that are a priori present in the area are included in the table. When numbers (*i.e.*, speciation profiles) are given, the values must be used carefully when applying them to Martorell or any other particular site. Since actual emission profiles were not measured in the study area, Table 2 was used in identifying sources from the air quality measurements.

Database. A total of 78 samples taken at the two points, with 29 analyzed VOCs in each sample, formed our initial database. Since we were interested in studying typical VOCs pollution in Martorell, samples that presented total airborne concentrations of VOCs much higher or lower than usual were removed from this data set. Five samples were discarded that did not meet the criterion of the annual mean plus or minus twice the standard deviation. In addition, VOC species that were not detected in more than 80% of the samples were also removed from the VOCs profile. Tetra-

TABLE 2. Source Profiles Normalized to the Analyzed Compounds (wt %)

species	vehicles[a,b]	gasoline vapor[c]	architec. coatings[a,c]	wastewater treatments[c,d]	graphic arts[a]	vapor degreasing[a,c]	dry cleaning[a,c]	automotive painting[a,e]	chlorinated products[f]	use of solvents[g−i]	aromas essences	wood combustion[j]	biogenic emissions[k]
hexane	3.0	56.8						1.8		*		*	
heptane	*									*		*	
octane	*									*		*	
nonane	*									*		*	
decane	*									*		*	
undecane	*									*		*	
dodecane	*									*		*	
tridecane	*											*	
tetradecane	*											*	
benzene	14.6	14.2	0.3	4.5				*				54.9	
toluene	31.0	25.7	81.1	11.7	76.9			68.8		43.0		29.7	
ethylbenzene	4.4	1.1	1.4	1.4				6.4		*			
m+p-xylene	14.3	1.1	8.3	*	5.7			17.4		38.0		10.9	
o-xylene	8.6	1.1	8.9	*				5.6		19.0		4.5	
trimethylbenzene	24.1												
1,2-dichloroethane				*					75.0				
1,1,1-trichloroethane				44.1		82.6	*		25.0[l]	*			
perchloroethylene				38.3		17.4	100		l				
trichloroethene									l				
tetrachloromethane									l				
1,1,2-trichloroethane										*			
α-pinene													*
β-pinene													*
carene													*
limonene													*
ethyl acetate					17.4			*		*	*		
butyl acetate										*	*		
acetophenone											*		
α,α-dimethylbenzyl alcohol										*			

[a] Scheff et al. (5). [b] Numbers correspond to gasoline vehicles. Diesel vehicles are responsible for emissions of heavy alkanes (C7 and up). [c] Scheff and Wadden (12). [d] Bell et al. (28). [e] Kelly and Callahan (29). [f] Personal communication from the industry located in the city of Martorell. [g] Heyes and Williams (22). [h] Kupiszewska et al. (14). [i] Sweet and Vermette (11). [j] Zwedinger et al. (30). [k] After several references cited in the text (24−26). [l] The 25% corresponds to the emission of this four species together. *These species are released by the corresponding source, but at unknown rates. So, they have not been included when normalizing.

chloromethane, 1,1,2-trichloroethane, α-pinene, carene, and limonene were affected by this criterion. Finally, trimethylbenzene was also removed from the database since its values actually included the sum of its different isomers. This could have led us to incorrect results when applying receptor models since different isomers of trimethylbenzene can come from different sources. Thus, after the filtering process, the database contained a total of 23 VOCs in 73 samples.

Principal Component Analysis/Multiple Linear Regression (PCA/MLR). The basic hypothesis of receptor modeling is mass conservation, *i.e.*, assuming that the levels of pollution observed somewhere can be explained as the summation of the emissions from different sources in the area under study, each one of them multiplied by a coefficient concerning its contribution to total concentration (*8*). Principal Component Analysis (PCA) followed by a Multiple Linear Regression (MLR) is an exploratory receptor modeling approach. The only data required for its application are measurements of airborne concentration of several chemical species. First, a large number of interrelated variables (concentrations of each species) is reduced to a lower number of independent variables (components) by means of the PCA statistical procedure. The components can often be identified as the main sources of pollution in the studied area. Second, the mass contribution of these sources in the total level of each VOC in the air is found by doing a MLR. A subsequent MLR allows one to estimate the emission profiles of each source. This methodology is equivalent to that used by Thurston and Spengler (*9*) in their study of the contribution of fine particles sources. The main difference from chemical mass balance as applied by other authors (*11–13*) is that our methodology does not require emission profiles of potential sources. Emission profiles, however, are used to identify the principal components as sources of VOCs.

PCA starts by building the correlation matrix for the data (previously normalized by mean concentrations). Diagonalization of this matrix provides its eigenvalues and eigenvectors. Since the variance explained by each eigenvector is proportional to its eigenvalue, only those eigenvectors with eigenvalues greater than 1 are selected as significant independent variables (components). The eigenvectors or components are typically more easily interpretable if a VARIMAX rotation, which transforms the eigenvectors to make each of them representative of individual sources of variation, is applied (*8, 9*). Then, each component may be identified as a source of VOCs by determining its most interrelated VOCs. Figure 3 is a graphic representation of the six rotated components that we found to have significance after applying the PCA. Component 1 is mainly related to light alkanes and alkylbenzenes, *i.e.*, VOCs emitted by gasoline vehicles and gas stations. Component 2 appears to be related to acetophenone (orange essence) and α,α-dimethylbenzyl alcohol (mint essence). Therefore, it corresponds to emissions from manufacturing artificial aromas and essences. Several emission sources seem to be mixed in component 3. High correlation with 1,2-dichloroethane shows emissions from manufacturing chlorinated chemicals; the presence of 1,1,1-trichloroethane indicates an emission from a wastewater treatment facility; α-pinene is related to biogenic emissions. The proximity among the three sources involved (at least when they are seen from one of the stations) may explain the correlation among the three species. Component 4 is related to undecane, ethyl acetate, and butyl acetate, compounds that are released by the production and use of solvents and lacquers (*18*). Component 5 shows a strong correlation with heavy alkanes. Thus, it corresponds to the emissions from diesel vehicles. Finally, perchloroethylene and trichloroethene are the most correlated VOCs in component 6. These species do not seem to be related to a single source, and
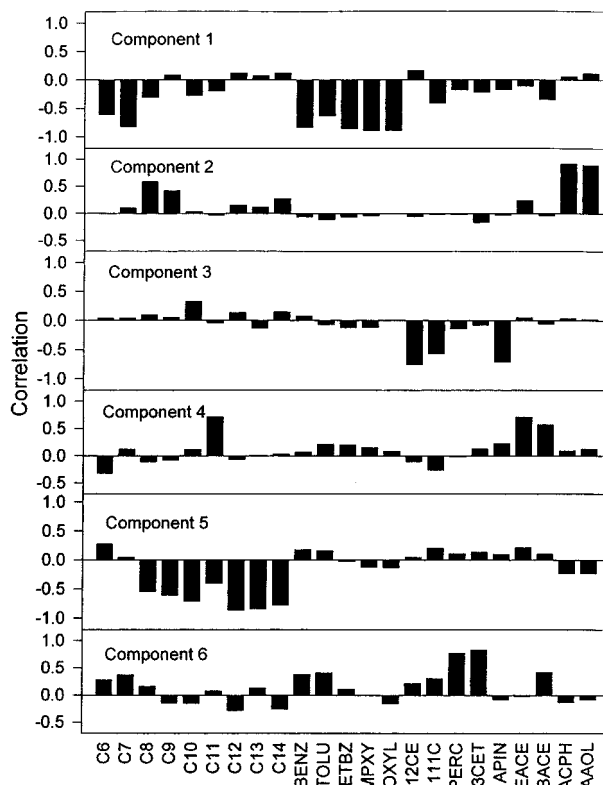

FIGURE 3. Six principal components obtained after applying a PCA (with a VARIMAX rotation) to the VOCs data collected in Martorell. The codes for the species correspond to those of Table 1.

therefore we called this latter component "noise". In Table 3, a summary of the components, their corresponding sources, and the variance explained by each one is shown. Concerning the variance, we can see that the six identified components together explain 76% of the variance of the original data. The components related to road traffic emissions, *i.e.*, components 1 and 5, explain 36% of the variance.

After identifying the six most significant components with the main sources of VOCs in the area, the impact of each component on the samples was calculated. Since the components form a new coordinate system, the impacts are the coordinates of the samples referred to this new system. Then, we carried out a MLR of total concentration of VOCs in each sample against the impacts. The product of the regression coefficients by the impacts is the mean mass contribution of each principal component (*i.e.*, each source) to the total concentration of VOCs (*9*). Mass contributions are shown in Figure 4. We can clearly see that the largest mass contribution to the VOCs air pollution in Martorell is related to gasoline, that is emissions from gasoline vehicles and from gas stations. The second most important source in the area is the manufacturing of artificial aromas and essences, that is industries of food processing placed inside the city boundaries. Other sources (manufacture of chlorinated chemical products, wastewater facilities, biogenic emissions, diesel vehicles, etc.) contribute about 30% to total mass of pollutants. The contribution of the component identified as production and use of solvents and lacquers is insignificant, so this source does not appear separately in the figure.

A second multiple linear regression allows us to estimate source profiles. Airborne concentrations of each VOC in each sample are regressed against each source mass contribution. The regression coefficients multiplied by the mean mass contribution of each source is the mean contribution of each

TABLE 3. Variance of the Data Explained by the Components Identified after Applying PCA

component	source	% variance	cumulative variance
1	gasoline traffic and gas stations	29.4	29.4
2	manufacture of aromas and essences wastewater facility	20.6	50.0
3	manufacture of chlorinated chemicals biogenic emissions	7.6	57.6
4	use and production of solvents and lacquers	6.9	64.5
5	diesel traffic	6.2	70.7
6	noise	5.3	76.0
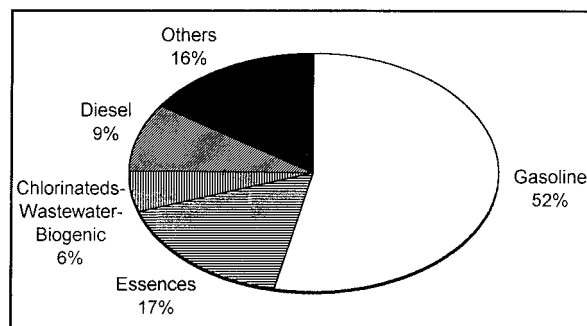
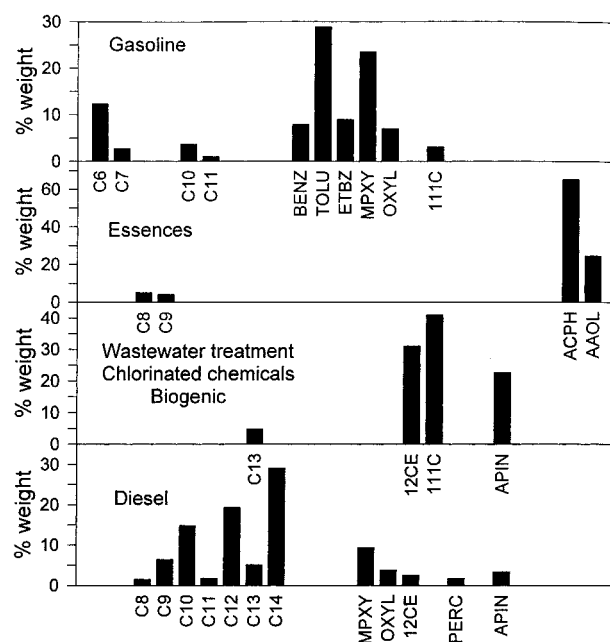FIGURE 4. Mean mass contribution from the main sources of VOCs pollution in Martorell (after a PCA/MLR).

FIGURE 5. Emission profiles for the significant sources of VOCs pollution in Martorell identified after applying a PCA/MLR.

species to the total emission from the source. These contributions, normalized and expressed in percentage, are source profiles, which are shown in Figure 5. As expected, the profile for gasoline emissions shows high values of alkylbenzenes (especially toluene and $m+p$-xylene) and hexane. The calculated profile agrees quite well with the emission profile given in Table 2. The source called production of aromas and essences shows a high percentage of acetophenone and the α,α-dimethylbenzyl alcohol, which is also in agreement with the literature. The third principal component corresponds to three different sources, and accordingly, its profile shows peaks of 1,2-dichloroethane (from production of chlorinated chemicals), 1,1,1-trichloroethane (from a wastewater facility), and α-pinene (from biogenic emissions). Finally, emissions of diesel vehicles

TABLE 4. Wind Direction, Most Influenced VOCs, and Corresponding Sources

wind direction	VOCs	source
NE	tridecane ethylbenzene	traffic
	perchloroethylene	dry cleaning
	limonene	biogenic
SE	undecane butyl acetate	solvents and lacquers
	α-pinene limonene	biogenic
W	heptane octane nonane decane dodecane tetradecane benzene $m+p$-xylene o-xylene	traffic
	carene	biogenic
	ethyl acetate acetophenone α,α-dimethylbenzyl alcohol	essences
WNW	hexane toluene ethylbenzene	traffic
	1,2-dichloroethane 1,1,1-trichloroethene tetrachloromethane	chlorinated chemicals
	α-pinene carene	biogenic
NW	hexane benzene	traffic
	1,1,1-trichloroethane perchloroethylene	wastewater treatment

are responsible for higher alkanes, especially decane, dodecane, and tetradecane.

Wind Direction Relationships. In Table 4, we show a summary of this analysis, which was applied to the database formed by VOC concentrations and winds recorded at the suburban station (EB). Species that reach a concentration peak (defined as concentrations greater that the mean plus 1.5 times the standard deviation for that species) are grouped according to the representative wind direction of the sample in which the peak is reached. In the same table, possible sources of those species are also shown. Then, by locating wind directions on a map of the area, we can locate the particular sources responsible for those maximum concentrations (Figure 1). Compounds related to biogenic emissions appear from several directions. This is logical, since orchards and other vegetation surround the receptor point. Similarly, high values of road traffic-related pollutants are found from

TABLE 5. Mean Airborne Concentrations (μg/m^3) of Five Alkylbenzenes in Several Cities

city	benzene	toluene	ethylbenzene	m+p-xylene	o-xylene
Sydney (Australia)[a]	9.1	37	6.2	8.6	7.1
Hamburg (Germany)[b]	13	38	8.8	22.	9.5
Chicago (USA)[c]	11	10	2.4	4.7	1.6
Leeds (United Kingdom)[d]	9.0	22	4.3	22	8.1
Los Angeles (USA)[e]	21	48	11	22	9.0
Oakland (USA)[e]	5.6	13	2.8	7.1	3.8
Phoenix (USA)[f]	21	68	11	41	15
Denver (USA)[f]	9.4	28	5.7	16	7.6
Houston (USA)[f]	9.4	20	3.3	12	5.2
Philadelphia (USA)[f]	5.2	14	2.8	9.5	7.1
Pittsburgh (USA)[f]	9.1	8.6	1.4	3.3	1.4
San Jose (USA)[f]	8.4	18	7.1	15	7.6
Boston (USA)[f]	3.5	9.5	1.4	5.7	2.4
St. Louis (USA)[g]	11	8.5	6.9	16	3.3
London (United Kingdom)[h]	31	56	4.2	13	5.9
Johannesburg (South Africa)[h]	12	42	8.9	21	7.7
Martorell (Spain)[i]	3.8	14	3.8	11	3.6

[a] Nelson et al. (2). [b] Bruckmann and Kersten (31). [c] Scheff and Wadden (12). [d] Kupizewska and Pilling (14). [e] Harkov et al. (3). [f] Edgerton et al. (1). [g] Sweet and Vermette (11). [h] Finlayson-Pitts and Pitts (32). [i] Present study.

all wind directions. Traffic through road BV-1201 may explain traffic emissions coming from sector NE; traffic through highways NII and NII-A7 and through the urban area may explain high values of traffic related VOCs coming from the W, WNW, and NW. More interesting are the results regarding point sources. In sector NE, a peak concentration of perchloroethylene should come from a dry cleaning activity. Coming from sector SE, we found high concentrations of undecane and butyl acetate that are emitted by the use of solvents and lacquers. No particular source, however, was identified as being responsible for these emissions. From sector W, we found peaks of ethyl acetate, acetophenone, and α,α-dimethylbenzyl alcohol, which are characteristic of the manufacture of aromas and essences. Indeed, a big food processing industry is located in that sector, just a few hundred meters away from the receptor site. In sector WNW, we found high concentrations of 1,2-dichloroethane, trichloroethene, and tetrachloromethane, which must have been released by a factory of chlorinated compounds. Such an industry is placed precisely in that sector, 1 km away from the receptor. In sector NW, high values of 1,1,1-trichloroethane and perchloroethylene indicate emissions from the wastewater treatment facility placed in that sector some 3 km away from the receptor.

Discussion

VOC concentration levels measured at the urban station show some differences with respect to measurements at the suburban site. In agreement with some previously reported results (31), concentrations in the city center were clearly higher than those at the suburban area, which reflects a greater impact of the local sources on the urban site. The seasonal behavior at the urban site is different than the behavior at the suburban site. Since meteorological factors should induce the same variation at both sites, this different behavior is explained by variations of emissions from sources that affect the urban site.

For most of the considered VOCs, a comparison among data from different cities is a useful tool to assess the concentrations measured in the area under study. Concentrations of the five main VOCs released by road traffic (benzene, toluene, ethyl benzene, m+p-xylene, and o-xylene) are available in urban areas only for the following cities: London (England) and Johannesburg (South Africa) (32); Los Angeles and Oakland (USA) (3); Phoenix, Denver, Houston, Philadelphia, Pittsburgh, San Jose, and Boston (USA) (1); and St. Louis (USA) (11). A larger number of VOCs was measured
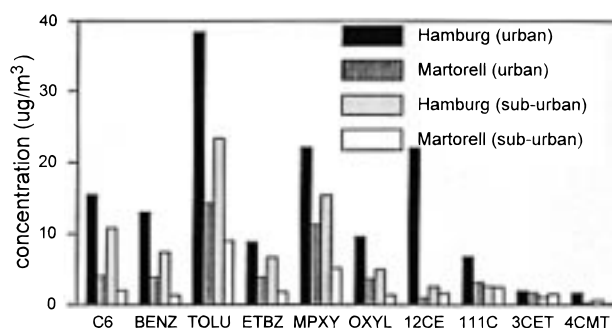

FIGURE 6. Comparison between mean concentrations in Hamburg and Martorell for some selected species and for urban and suburban sites.

in urban and suburban areas of other cities: Hamburg (Germany) (31), Chicago (USA) (12), and Leeds (England) (14). Finally, the concentrations of an even larger number of VOCs measured at one site in an urban area of Sydney (Australia) are given in ref 2. Martorell is smaller than any of these other cities, but we can compare values of airborne concentrations. Mean concentrations in the urban areas of the 17 cities of the five VOCs species related to traffic are shown in Table 5. All the cities show approximately the same pattern: the highest concentration is for toluene, and the lowest is for the ortho isomer of xylene. Nevertheless, differences in relative importance of the five VOCs can be found among the cities; these diverse behaviors may be explained by different fuel formulations or by different composition of the road traffic (2). Phoenix had the highest mean airborne concentrations for all five species. A larger density of gasoline vehicles in Phoenix than in the other cities may explain this fact; unfavorable meteorological conditions may also play a role in explaining such high concentrations (1). Pittsburgh and Boston, on the other hand, are the cities that show the lowest mean concentration of these five alkylbenzenes. Concentrations in Martorell lie within the range of values measured in the other cities.

A more detailed comparison is done with data from Hamburg, by taking into account a larger number of VOCs and comparing urban and suburban sampling sites in both cities (Figure 6). The trend followed by 10 VOCs is practically identical in the two cities: concentrations in Hamburg are higher (by a factor of 2 or 3) than in Martorell, and concentrations in urban areas are higher (by a factor of 1.5) than values in the suburban zone in both cities. Some

chlorinated compounds break this pattern: for example, for urban data a big difference in the concentrations of 1,2-dichloroethane is found. This is due to the presence of several industries that manufacture chlorinated products surrounding the urban sampling points in Hamburg (31), while in Martorell the main source of chlorinated compounds is located closer to the suburban station. In summary, after these comparisons of concentrations measured in Martorell with air quality in other cities of the world, we see that VOCs air quality in Martorell is neither among the worst nor among the best.

The result of applying a PCA and a subsequent MLR is that the main source of VOCs pollution in Martorell is road traffic (as result of traffic through the city and highways NII, A7, and BV-1201). Road traffic contribution is approximately 62% of total pollution, at least as far as the analyzed VOCs are concerned. A food industry that manufactures aromas and essences is responsible for the 17% of VOCs pollution, while an industry of chlorinated compounds together with a wastewater treatment facility and the biogenic emissions account for an extra 6%. Other sources that have not been located concern the use and production of solvents and drycleaning activities. Our results are difficult to compare to other studies because of different analyzed species, different sizes and characteristics of domains, etc. However, the emissions sources that we have identified and located are the typical sources of VOCs found in other studies (5, 11, 12). The impact of vehicles is higher in the present work than in others. This fact can be explained by two reasons: first, one half of the 29 species in the VOCs profile are related to gasoline or diesel vehicles; and second, the very high concentration of important highways in the small area of the city of Martorell.

Acknowledgments

Literature Cited

(1) Edgerton, S. A.; Holdren, M. W.; Smith, D. L. *JAPCA* **1989**, *39*, 729−732.

(2) Nelson, P. F.; Quigley, S. M. *Environ. Sci. Technol.* **1982**, *16*, 650−655.

(3) Harkov, R.; Kebbekus, B.; Bozzelli, J. W. In *Toxic Air Pollution*; Lioy, P., Daisey, J., Eds.; Lewis Publishers Inc.: Chelsea, MI, 1987; pp 69−90.

(4) Hampton, C. V. *Environ. Sci. Technol.* **1982**, *16*, 287−298.

(5) Scheff, P. A.; Wadden, R. A.; Bates, B. A.; Aronian, P. F. *JAPCA* **1989**, *39*, 469−478.

(6) Commitee on Tropospheric Ozone Formation and Measurement, National Research Council. *Rethinking the ozone problem in urban and regional air pollution*; National Academy Press: Washigton, DC, 1991.

(7) Gordon, G. E. *Environ. Sci. Technol.* **1988**, *22*, 1132−1140.

(8) Hopke, P. K. *Receptor Modeling in Enviromental Chemistry*; Wiley-Interscience: New York, 1985.

(9) Thurston, G. D.; Spengler, J. D. *Environ. Sci. Technol.* **1985**, *19*, 9−25.

(10) Pirrone, N.: Keeler; G. J.; Holsen, T. M. *Environ. Sci. Technol.* **1995**, *29*, 2112−2122.

(11) Sweet, C. W.; Vermette, S. J. *Environ. Sci. Technol.* **1992**, *26*, 165−173.

(12) Scheff, P. A.; Wadden, R. A. *Environ. Sci. Technol.* **1993**, *27*, 617−625.

(13) Wadden, R. A.; Scheff, P. A.; Uno, I. *Atmos. Environ.* **1994**, *28*, 2507−2521.

(14) Kupiszewska, D.; Pilling, M. J. In *Air Pollution II, Vol. 2*; Baldasano, J. M., Brebbia, C. A., Power, H., Zannetti, P., Eds.; Computational Mechanics Publications: Southampton, UK, 1994; pp 169−176.

(15) Fujita, E. M.; Watson, J. G.; Chow, J. C; Lu, Z. *Environ. Sci. Technol.* **1994**, *28*, 1633−1649.

(16) Pirrone, N.: Keeler; G. J.; Holsen, T. M. *Environ. Sci. Technol.* **1995**, *29*, 2123−2132.

(17) Winbery, W. T.; Murphy, N. T.; Riggan, R. M. *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*; Report EPA 600/4-89-017 (NTIS/PB90-116989); U.S. EPA: Research Triangle Park, NC, 1988.

(18) Sittig, M. *Handbook of Toxic and Hazardous Chemicals and Carcinogens*; Noyes Publications: Park Ridge, NJ, 1991.

(19) Budavari, S. *The Merck Index*; Merck & Co. Inc.: Rahway, NJ, 1989.

(20) Carmichael, G. R.; Chang, Y. S.; Satsumabayashi, H.; Kurita, H.; Ueda, H. In *Urban Air Pollution, Vol. I*; Power, H., Moussiopoulos, N., Brebbia, C. A., Eds.; Computational Mechanics Publications: Southampton, UK, 1994; pp 185−219.

(21) Scheff, P. A.; Wadden, R. A.; Kenski, D. M.; Chung, J.; Wolff, G. *J. Air Waste Manage. Assoc.* **1996**, *46*, 1048−1057.

(22) Heyes, C. J.; Williams, M. L. In *Proceedings of the TNO/EURASAP workshop on the reliability of VOC emission databases*; Baars, H. P., Builtjes, P. J. H., Pulles, M. P. J., Veldt, Chr., Eds.; TNO Institute of Environmental Sciencies: Delft, The Netherlands, 1993; p 5−18.

(23) Müller, M. D.; Buser, H.-R. *Environ. Sci. Technol.* **1986**, *20*, 1151−1156.

(24) Obermeier, A.; Freidrich, R.; John, C; VoB, A. *Zeitlicher Verlauf und räumliche Verleilung der Emissionen von flüchtigen organischen Verdindungen und Kohlenmonoxid in Baden-Württemberg. Projekt Europäisches Forschwgszentrum für MaBnahnien zur Luftreinhaltung (PEF)*; Institüt für Energiewirtschaft und Rationelle Energieanwendurg (IER), Universität Karlsruhe: Karlsruhe, Germany, 1991.

(25) Pierce, T. E.; Lamb, B. K; Van Meter, A. R. Presented at the 83rd Annual Meeting and Exhibition of the Air & Waste Management Association, Pittsburgh, PA, June 1990.

(26) Street, R. A.; Duckham, S. C.; Brissard, C.; Hewitt, C. N. *Biogenic terpenoid emission from vegetation in Europe. A contribution to subproject BIATEX*; Institute of Environmental & Biological Sciences, Lancaster University: Lancaster, USA, 1993.

(27) Fehsenfeld, F.; Calvert, J.; Fall, R.; Goldan, P.; Guenther, A. B.; Hewitt, C. N.; Lamb, B.; Liu, S.; Trainer, M.; Westberg, H.; Zimmerman, P. *Global Biogeochem. Cycles* **1992**, *6*, 389−430.

(28) Bell, J.; Melcer, H.; Monteith, H.; Osinga, I; Steel, P. *Water Environ. Res.* **1993**, *65*, 708−716.

(29) Kelly, T. J.; Callahan, P. J. *Environ. Sci. Technol.* **1993**, *27*, 1146−1153.

(30) Zweidinger, R. B.; Stevens, R. K.; Lewis, C. W. *Environ. Sci. Technol.* **1990**, *24*, 538−542.

(31) Bruckmann, P.; Kersten, W. *Chemosphere* **1988**, *17*, 2363−2380.

(32) Finlayson-Pitts, B. J.; Pitts J. N. *Atmospheric Chemistry: Fundamentals and Experimental Techniques*; John Wiley & Sons: New York, 1986.