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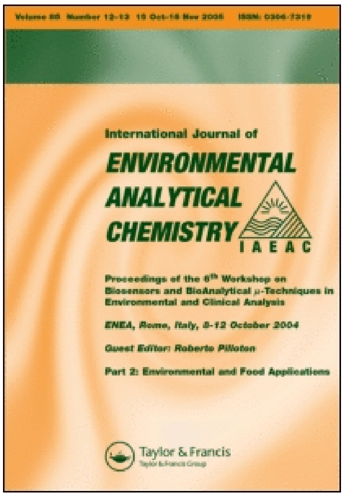

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VOLATILE ORGANIC COMPOUNDS IN URBAN AND INDUSTRIAL ATMOSPHERES: MEASUREMENT TECHNIQUES AND DATA ANALYSIS

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Main results of 62 volatile organic compounds (VOCs) 'continuous' on-line measurement obtained at the Air Quality Monitoring Station sited at the School of Engineering of Bilbao (Northern Spain) are presented. The system has been put into operation between 1997 and 2001 in an area influenced by urban and industrial emissions. Initially, the measurement method and data validation process are described and, then, the application of combined statistical analysis techniques for inferring the mixed organic compound sources impacting the receptor location. The addition of a simple meteorological study for the characterisation of the prevailing winds combined with pollution roses has confirmed this statistical results and allows, for each compound, the discrimination of its urban – mainly traffic – or industrial origin.

Keywords: VOCs; Non-methane hydrocarbons; On-line VOC analysis; Ozone precursors; Air quality

INTRODUCTION

Anthropogenic and natural non-methane hydrocarbons (NMHC) are the fraction of volatile organic compounds (VOCs) that contain only carbon and hydrogen, and constitute the majority of anthropogenic VOC emissions [1]. It is important to monitor these compounds in ambient air due to the following reasons: (a) Their toxicity (as a matter of fact, 97 out of 188 toxic pollutants from 1990 amendments of the US Clean Air Act are VOCs); (b) The key role of the (most) reactive VOCs on photochemical oxidant formation; (c) Their relevance as precursors on fine particulate matter in urban areas [2,3]; (d) The reaction of VOCs with the OH radical, which can lead to enhanced natural CH_4 lifetime by 15% and to increase background O_3 levels by 18% [4] (OH radical is the major atmospheric sink for CH_4); (e) VOCs constitute a source of atmospheric carbon and can thus play a key role in the global carbon budget and

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cycling [5]. Commonly, VOCs and semi-VOCs analysis has been performed using Chromatographic techniques [6], but systematic on-line measurement of speciated VOCs on ambient air is not at all a straightforward task, due to the complexity of the sample, the wide spectrum of compounds to be analyzed, coming from both natural and anthropogenic sources, as well as their atmospheric oxidation products and the low levels of concentration usually found.

Automatic monitoring networks, using flame ionization detector systems, routinely measure the organic matter content in the atmosphere as 'total Non-Methane Hydrocarbons', allowing the assessment of the temporal evolution of such parameter. Total NMHC content, however, does not offer any information regarding chemical reactivity in the atmosphere, ozone formation potential or toxicity. It is, thus, of paramount importance the measurement of individual compounds, especially those identified as toxic or very reactive, for it allows the gathering of important information towards the management and monitoring or air quality in urban and industrial sites, especially nearby some industrial point sources. For that purpose, it is required to cover, with adequate temporal resolution, long periods of automated measurements (when possible, using unattended operation) when the establishment of patterns of behaviour is sought. For each individual VOC, it is possible to assess extreme and average values along the sampling period [7].

In order to study the temporal evolution of VOCs in ambient air, the use of automatic GC systems has grown rapidly in recent years [8–10]. An automatic GC is able to provide frequent analyses (hourly, usually) of VOCs for long periods of time (days to months). The system consists of: (1) sample pre-concentration system; (2) GC with non-specific detectors, such as flame ionization detector (FID), electronic capture detector (ECD), photoionization detector (PID); and (3) data acquisition software and hardware for the automated control of sampling and GC operation.

This paper presents a summary of results obtained at the air quality monitoring station located at the School of Engineering of Bilbao (SEB) in the Basque Country (Northern Spain), where a system has been in operation since 1997. The measuring campaigns between 1997 and 2001 were preceded by many other studies carried out by the Environmental Group of the SEB for the Directorate Of Environmental Quality of the Basque Government [11–13].

ON-LINE MEASUREMENT METHOD

Routinely yet intensively measurements were performed on an hourly basis using an automatic gas chromatograph (VOC Ozone Precursor Analyzer System, from Perkin Elmer). The system (AGC-FID) was optimised for the automatic measurement for a nominal range of C_2–C_{10} hydrocarbons of, initially, 27 non-polar ozone precursors (marked with * in Table I) in urban air (during 1998), and later 62 compounds, achieving sensitivities down to parts per trillion in volume (10^{-6}ppmv). Main elements are as follows: (1) Thermal desorption unit (ATD400) fitted with an air sampler accessory. This system is an adaptation of the standard ATD400 to include a special device for direct introduction of ambient sample air. The de-humidification device used is a semi-permeable membrane (Nafion® by Permapure Inc, Toms Rivers, NJ). Nafion® drying devices are known to cause losses of certain polar VOCs (amines, ketones, alcohols and some ethers), and also rearrangement of several monoterpenes

TABLE I Summary of hydrocarbon concentration at SEB. April–October 2001

No	*Compound*	*Max*	*Min*	*Mean*	*Median*	*S.D.*
1*	Ethane	22.09	0.53	3.09	2.43	2.17
2*	Ethene	42.39	< DL	2.37	1.67	2.43
3*	Propane	12.89	0.15	1.75	1.33	1.41
4*	Propene	14.06	< DL	0.93	0.73	0.75
5*	*i*-butane	26.99	< DL	0.95	0.63	1.17
6*	*n*-butane	30.71	0.10	1.94	1.33	1.82
7*	Acetylene	261.54	< DL	2.69	1.33	6.35
8*	*trans*-2-butene	1.92	< DL	0.13	0.10	0.09
9*	1-butene	1.47	< DL	0.14	0.11	0.12
10	*i*-butene	2.72	0.20	0.62	0.55	0.26
11*	*cis*-2-butene	1.78	< DL	0.11	0.08	0.11
12	Cyclopentane	0.57	< DL	0.04	0.03	0.03
13*	*i*-pentane	27.34	< DL	1.26	0.92	1.14
14*	*n*-pentane	10.22	< DL	0.59	0.44	0.50
15*	1,3-butadiene	2.81	< DL	0.18	0.13	0.17
16	Propyne	3.67	< DL	0.15	0.07	0.26
17	3-methyl, 1-butene	0.70	< DL	0.06	0.05	0.05
19*	*trans*-2-pentene	1.75	< DL	0.13	0.09	0.12
20	2-methyl,2-butene	2.28	< DL	0.18	0.12	0.18
21	1-pentene	0.90	< DL	0.09	0.07	0.07
22*	*cis*-2-pentane	0.95	< DL	0.07	0.05	0.07
23	2,2-dimethylbutane	0.32	< DL	0.03	0.02	0.02
24	2,3-dimethylbutane	0.87	< DL	0.08	0.06	0.07
25*	2-methylpentane	3.28	< DL	0.28	0.20	0.25
26*	3-methylpentane	3.03	< DL	0.20	0.15	0.19
27*	Isoprene	2.34	< DL	0.19	0.15	0.15
28*	*n*-hexane	3.57	< DL	0.21	0.14	0.23
29	Methylcyclopentane	2.51	< DL	0.12	0.10	0.11
30	2,4-dimethylpentane	1.53	< DL	0.05	0.04	0.05
31*	Benzene	15.99	< DL	0.62	0.40	0.78
32	Cyclohexane	17.32	< DL	0.20	0.12	0.48
33	2-methylhexane	2.90	< DL	0.22	0.16	0.19
34	2,3-dimethylpentane	1.21	< DL	0.10	0.07	0.08
35	3-methylpentane	4.03	< DL	0.28	0.19	0.26
36	Trichloroethylene	5.97	< DL	0.20	0.07	0.35
37	1-heptene	1.36	< DL	0.06	0.05	0.07
38	2,2,4-trimethylpentane	2.67	< DL	0.23	0.17	0.22
39*	*n*-heptane	9.49	< DL	0.41	0.30	0.43
40	Methylcyclohexane	5.58	< DL	0.24	0.19	0.27
41	2,3,4-trimethylpentane	1.11	< DL	0.10	0.07	0.09
42*	Toluene	25.54	0.11	2.31	1.71	1.96
43	2-methylheptane	0.87	< DL	0.08	0.06	0.06
44	3-methylheptane	0.79	< DL	0.08	0.06	0.07
45	Octane	1.04	< DL	0.11	0.09	0.07
46	Tetrachloroethylene	4.06	< DL	0.25	0.09	0.41
47*	Ethylbenzene	3.90	< DL	0.37	0.24	0.37
48*	*m&p*-xylene	15.03	0.05	1.22	0.78	1.27
49	Styrene	1.53	< DL	0.13	0.08	0.14
50*	*o*-xylene	3.29	< DL	0.33	0.22	0.31
51	*n*-nonane	0.60	< DL	0.09	0.07	0.06
52	*i*-Propylbenzene	0.25	< DL	0.01	0.01	0.02
53	*n*-Propylbenzene	1.12	< DL	0.06	0.04	0.06
54	*m*-ethyltoluene	4.23	< DL	0.29	0.19	0.27
55	*p*-ethyltoluene	1.96	< DL	0.11	0.07	0.10
56*	1,3,5-trimethylbenzene	2.28	< DL	0.13	0.09	0.13
57	*o*-ethyltoluene	1.35	< DL	0.08	0.05	0.08
58*	1,2,4-trimethylbenzene	5.90	0.03	0.40	0.27	0.38
59	*n*-decane	1.57	< DL	0.21	0.16	0.16

(*continued*)

TABLE I Continued

No	*Compound*	*Max*	*Min*	*Mean*	*Median*	*S.D.*
60	1,2,3-trimethylbenzene	1.73	< DL	0.28	0.19	0.22
61	*m*-diethylbenzene	0.09	< DL	0.01	0.01	0.01
62	*p*-diethylbenzene	0.47	< DL	0.08	0.06	0.08
63	NMHC (in ppbC)	850.79	16.19	147.68	112.62	105.53

*Compounds contained in the NPL calibration standard mixture; DL = Detection Limit.

(α-pinene and β-pinene) but have no effect on the recovery of isoprene [14]. This system is able to perform an automatic on-line sampling and sample pre-concentration, using a small pump, a mass flow-meter and a cold trap at −30°C with Peltier cells. Liquid nitrogen is not required. (2) Gas Chromatograph (GC). Separation of the target components is achieved through the use of a dual-column system with column switching. The sample enters first into the BP1 column. The first compounds to elute out from this column are switched to the PLOT column. The system includes two FIDs (one for each column) for signal detection.

Operating conditions for the GC are as follows: carrier gas, helium; FID temperature, 250°C; chromatographic columns, BP1 (50 m x 0.22 mm ID with layer thickness of 1 μm) and PLOT $A1_2O_3/Na_2SO_4$ (50 m x 0.32 mm ID with layer thickness of 5 μm); and oven temperature program: 45°C (15 min), 5°C/min up to 170°C, 15°C/min up to 200°C (6 min).

The analyser is fitted with ancillary equipment for automated data acquisition and data processing being the results stored on a data base [11]. The whole system can be operated and monitored remotely, using radio, phone or Internet links, allowing the unattended operation along several weeks without 'direct' intervention.

VOCs in samples were later identified and quantified weekly using a certified standard mixture with 27 compounds (see Table I) prepared by the U.K. National Physical Laboratory (NPL) by gravimetric methods. Compounds chosen for the standard were selected for reactivity reasons, their abundance in ambient air, and also for being typical pollutants in urban areas [15]. In addition, other compounds not included in this standard were identified by means of individual standards and calibrated by response factors for these compounds [16].

Since September 1997, a routine operation has measured ambient air pollutants hourly, using aspirated air through a sampling stainless steel manifold. Sampling flow of 15 mL/min is collected by the ATD400 for 40 min. VOCs are collected in a cryogenic trap, at −30°C, with solid adsorbents able to accumulate C_2–C_{10} VOCs. Later on, the trap is heated and carrier gas pushes the hydrocarbons to the chromatographic columns.

As an example, it can be seen on Fig. 1 the plots of two chromatograms, one for each column, including peak assignation, obtained when sampling ambient air at the SEB of Bilbao.

DATA VALIDATION

The intensive measurement of VOCs over a relatively long period of time, using automatic chromatography techniques, generates a large amount of data. In the measurement campaigns, the sampling of ambient air and its analysis took place

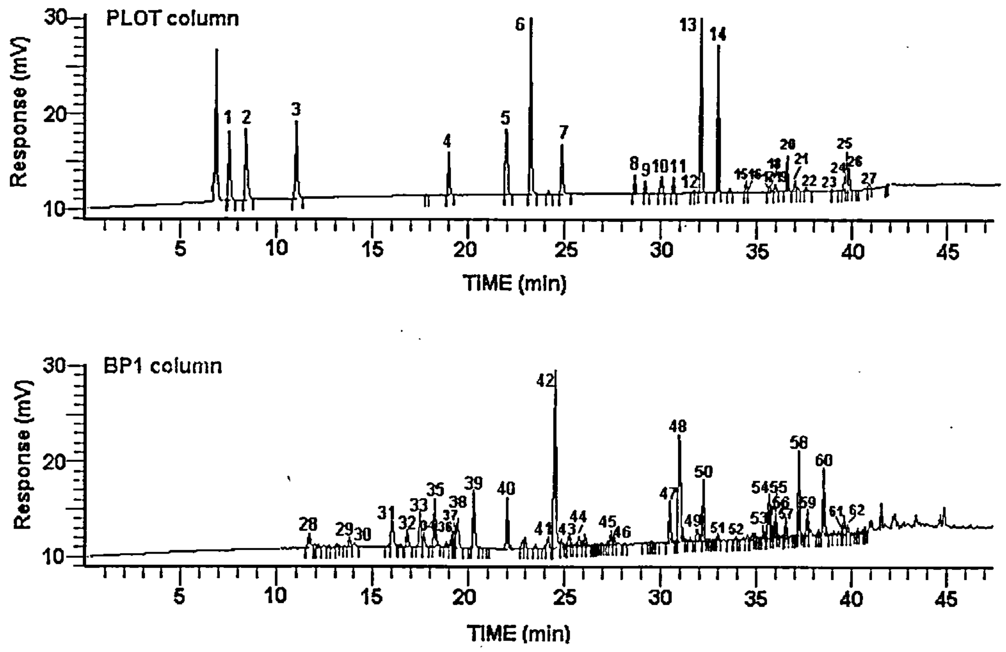

FIGURE 1 Example of chromatograms corresponding to an ambient air sample: Plot column (upper) and BP 1 (lower) columns. Peak numbers correspond to the numbering of the compounds in Table I.

every hour throughout the 24 h of the day, which amounts to 1488 pieces of data on average hourly concentrations of 62 VOCs.

Results have been processed using an in-house developed, strict validation procedure which allows the quantification of 62 different VOCs, and presents them as hourly averages. The validation process consists of four consecutive steps: routine checks, deterministic relationships, time series analysis and scattergrams (essentially for isomer analysis). The data validation scheme refers to the process undertaken with data stored in the chromatographic archives before introducing them into the final database.

The protocol of routine checks is followed daily: the information with which the results archives are stored (date, hour, type of sample, and name) is checked, and the chromatograms from the previous day are visually reviewed. This visual inspection begins with the appearance of the chromatogram, the shape and resolution of the peaks and baseline, and then proceeds to a more thorough examination of the identification and quantification correctness for the 62 VOCs. Any problem detected during this review is duly recorded, and then corrective actions in the method of control, acquisition, storage, detection, identification, quantification or data generation of the system are taken [17].

After this first validation level, the data are imported to a spreadsheet which checks out their internal consistency and identifies those values which are unrepresentative of the ambient air conditions when they are compared with the overall data. The internal consistency test includes the verification of the compliance with the lower limits set for the concentration of compounds [1] and of the specific limits of the monitoring site, based on the relationship between compounds observed historically and graphics

TABLE II Number of data in the validated database after quality control

Year	*1997*	*1998*	*1999*	*2000*	*2001*
Total collected data	2184	4752	4536	4032	4872
Percent of valid data (%)	76.7	95.2	91.6	95.4	98.2

of the data [18]. The time series are laid out graphically to identify atypical values, excessive differences between adjacent values, and incorrect identifications of peaks or long periods with unusually high or low concentrations. Scattergrams among pairs of compounds with habitually close ($r > 0.98$) correlation were also drawn, in order to identify atypical figures. After this thorough validation, the data are introduced into the historic database for statistical studies that are then also checked. This second level of validation means that the database is more robust, as any analytical errors would have been corrected [19], and the behaviour patterns of each VOC, which have to be established to monitor and manage air quality in urban and industrial areas, are properly established.

The total collected data and the percent of valid data in the validated database for the 1997–2001 campaigns are summarised in Table II. Taking out 1997, the initial year, which was mainly dedicated to setting up the system, valid data percentages were higher than 92%. The principal reasons of invalid (in this term we include 'no data') or suspect data were: maintenance of equipment, chromatographic problems, computer problems and different tests tailored to assess the technical limits of the system.

RESULTS AND DISCUSSION

Table I summarises the statistics of the 62 target compounds valid data on the last campaign (year 2001), lasting from April until October, with a grand total of 4775 hourly average concentrations, expressed in parts per billion in volume (nL/L). Total non-methane hydrocarbons (TNMVOC) are also included as the integral of all chromatographic peaks registered, individually identified or not. Concentration is, thus, calculated from the integrated area by using response factors, being propane, on channel A, and benzene, on channel B, the reference compounds. TNMVOC has been included on our reports for it is a good indication of the intensity of the impact caused by urban and/or industrial pollution sources at the monitoring site [19–21].

Many of the 62 species quantified are frequently present at concentrations near the detection limit with standard deviations very similar to the average values, which indicate a high variability of such compounds. The following compounds can be singled out for their relevance on urban air VOC studies [22]: Acetylene and ethylene, as motor vehicle exhaust tracers; *i*-butane, because it has replaced CFCs in most consumer aerosol products; *n*-butane, that accounts for roughly 35% of motor vehicle evaporative emissions; isoprene, highly reactive but most frequently used for tracing biogenic emissions [23]; benzene, also present in evaporative emissions and numerous combustion and industrial processes, and the first VOC included into the European Union Air Quality Directives; Toluene, one of the most abundant VOC in urban air, present in characteristic ratios in motor vehicle exhaust and emitted also by surface coating processes and printing; and internal olefines and xylenes, for they are important species due to their high reactivity. Those species which can only be associated to a single source can be used as 'opportunity tracers', i.e., in 2001, isobutene was always found (4775 valid sampling hours) with an average concentration of 0.6 ppbv (1.5% w/w). It has been included on the routine measurement protocol for it is a product of combustion of methyl tertiary-butyl ether (MTBE) [19], and presents a very good correlation with the remaining exhaust gases on vehicles.

The average concentration of isoprene (0.19 ppbv) is quite low when compared with values collated from the literature [24] but due to its reactivity has to be considered as an important ozone precursor. Also, among the quantified compounds it is the only one which can be used to trace down biogenic emissions.

The list of most abundant compounds in Bilbao (see Table I) is very similar to other lists already published [25–41] with the exception of acetylene and *n*-heptane. No other references have been found where *n*-heptane was among the most abundant compounds, whereas other lists include *n*-pentane or *i*-butene.

In Table III the fractional contribution of different classes of compounds is presented, including percentages calculated by weight and by volume. It can be seen that the proportion of every class of compounds do not show big deviations from year to year, and ratios among classes remain similar. It is important to point out that olefines and aromatics proportions do change when measurements made by weight or by volume are used (by a factor bigger than 2), due to the fact that olefines are much lighter than aromatics, i.e., in 2001, when measured by weight, olefines (16.5%) are less abundant than aromatics (38.5%), but percentages by volume are different, 29% vs. 23%, respectively.

In 1997 and 1998 only 27 VOCs were identified, which represented 65% of TNMVOCs. Later, with 62 compounds identified, 88% of TNMVOCs are accounted for. Those results are a bit higher than the ones obtained in the Photochemical Assessment Monitoring Network from Fresno, San Diego and Los Angeles, where 55 species are measured [21], accounting for 50%, 70%, and 75% of the TNMVOC, respectively [1]. In our case, non-identified fraction includes polar compounds, mainly oxygenated ones, such as carbonyls.

From the point of view of potential ozone formation, it is important to tie, for each VOC, concentration and reactivity, described, i.e., as photochemical ozone formation capacity. As a classification criteria for reactivity, in order to pinpoint the more reactive species, the concentration of each VOC has been multiplied by their correspondent Maximum Incremental Reactivity (MIR = mol O_3/mol VOC) [19,42,43]. *m&p*-xylene,

TABLE III Fractional contribution of various classes of VOC expressed by weight (% w/w) or by volume (% v/v)

Family	*Annual averages*							
	*1998**		*1999*		*2000*		*2001*	
	% w/w	*% v/v*	*% w/w*	*% v/v*	*% w/w*	*% v/v*	*% w/w*	*% v/v*
Parafines	42.3	50.0	43.7	48.1	47.5	50.1	44.4	46.3
Olefines	13.4	23.9	13.8	24.4	13.9	24.9	16.3	29.0
Aromatics	44.3	26.1	41.9	26.0	37.8	23.3	38.5	23.0
Chlorinated compounds**	–	–	0.7	1.6	0.7	1.6	0.7	1.6

*With 27 compounds identified; **trichloroethene + tetrachloroethene.

toluene, ethene, propene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, *o*-xylene, *m*-ethyltoluene, *i*-butene and 2-methyl-2-butene are the ten most reactive species. Results shows that, in general, olefins and aromatic compounds are very important as precursors of ozone, being *i*-pentane (9th on the 1998 reactivity list) the only exception. The analysis of the evolution of the concentration averages along the years shows that there are no dramatic changes, so a 'digital fingerprint' can be defined. Only two significant divergences can be found (Fig. 2), an increase of acetylene concentration

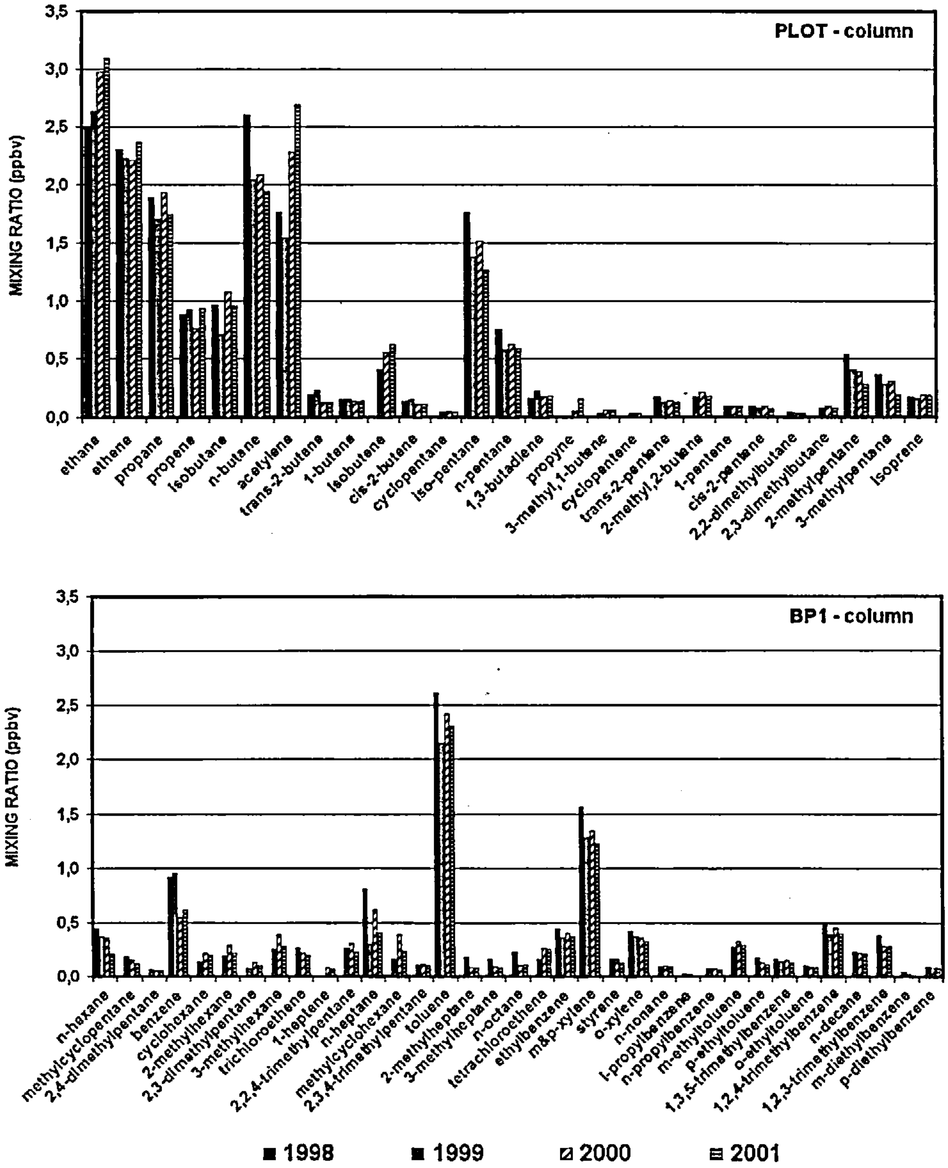

FIGURE 2 Light (upper) and C_6–C_{10} (lower) mean VOC concentration trends from 1998 to 2001 at SEB (Spain).

during years 2000 and 2001, and the reduction by 50% of the benzene concentration during the two last years with respect to the average values from 1998 and 1999. Those variations may be related to changes in fuel compositions, although a longer time series is required to verify such hypothesis.

Statistical Analysis

An enormous amount of data was obtained in this study. In order to further investigate the source composition of hydrocarbons, the correlation coefficient between individual compounds and multivariate techniques such as principal component analysis (varimax rotation) and cluster analysis (Pearson correlation) were applied. These methods are useful for inferring the mixed organic compound sources impacting a receptor location [44].

It was possible to identify groups of compounds highly correlated with $r > 0.800$ and $n > 4000$ data. To illustrate this, year 2001 results (with $n = 4754$ valid data for each compound) are presented. Similar results were obtained during the remaining campaigns.

The Founded Groups are

(1) *Aromatics Compounds:* toluene, ethylbenzene, *m&p*-xylene, *o*-xylene, *p*-ethyltoluene, 1,3,5-trimethylbenzene, *o*-ethyltoluene, 1,2,4-trimethylbenzene, *m*-ethyltoluene and *n*-propylbenzene. Correlation coefficients are shown in Table IV, and in Fig. 3, as an example, a scatter plot for *m&p*-xylene against ethylbenzene with 4872 points is presented, where it can be seen a linear relationship.

Also correlated with these compounds, but with lower correlation, are: isopropylbenzene, 1,2,3-trimethylbenzene, *m*-diethylbenzene and *p*-diethylbenzene. Emissions from motor vehicles were the dominant source of aromatic hydrocarbons in our area.

(2) *Olefins and Hydrocarbons Derived of* C_4–C_5: *trans*-2-butene, 3-methyl-1-butene, *trans*-2-pentene, 2-methyl-2-butene, 1-pentene, *cis*-2-pentene, 2,2,4-trimethylpentane, 2,3,4-trimethylpentane and isopentane. Other compounds correlated with these, but with lower coefficients, are: *n*-butane, *cis*-2-butene, cyclopentane, *n*-pentane, 2,3-dimethylbutane and 2,4-dimethylpentane. The source of these compounds were mainly motor vehicles emissions.

TABLE IV Correlation coefficients for aromatic compounds included in Group 1

	Toluene	*Ethyl benzene*	*m & p-xylene*	*o-xylene*	*n-propyl benzene*	*m-ethyl toluene*	*p-ethyl toluene*	*1,3,5-trimethyl benzene*	*o-ethyl toluene*
ethylbenzene	0.892	1.000							
m & p-xylene	0.895	0.995	1.000						
o-xylene	0.917	0.972	0.983	1.000					
n-propylbenzene	0.779	0.825	0.820	0.816	1.000				
m-ethyltoluene	0.780	0.850	0.847	0.837	0.964	1.000			
p-ethyltoluene	0.779	0.828	0.823	0.820	0.986	0.964	1.000		
1,3,5-trimethyl-benzene	0.784	0.825	0.825	0.824	0.976	0.963	0.987	1.000	
o-ethyl toluene	0.783	0.839	0.835	0.831	0.980	0.974	0.990	0.982	1.000
1,2,4-trimethylbenzene	0.793	0.847	0.847	0.843	0.975	0.977	0.984	0.981	0.992

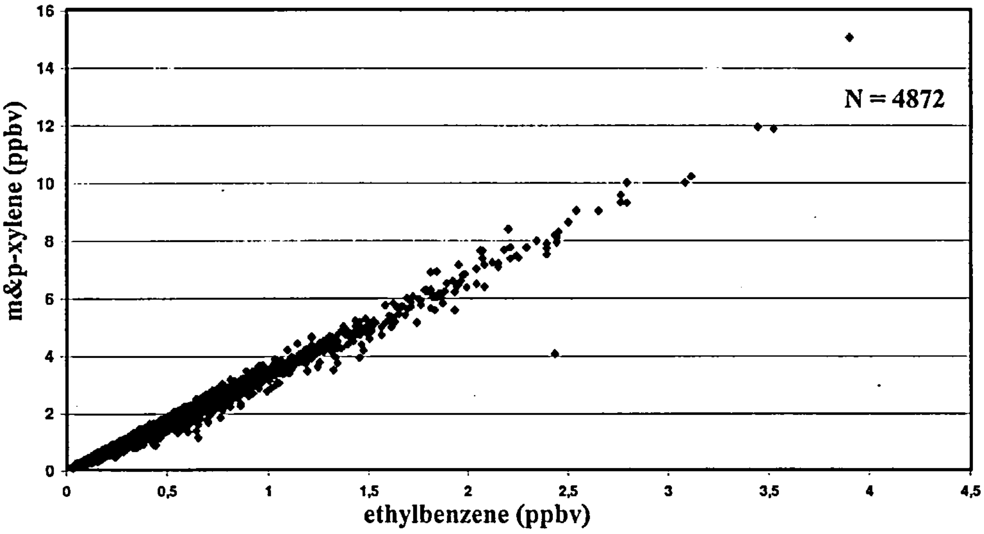

FIGURE 3 Scatter plot for ethylbenzene against *m&p*-xylene concentrations at the SEB for April–October 2001.

(3) *Light Olefins:* ethylene, propylene, propyne, 1-butene, isobutene and 1,3-butadiene. Acetylene appears correlated to propyne and with lower coefficients to ethylene and propylene. These compounds are related to combustion processes.

(4) *C_7 Hydrocarbons:* 2-methylhexane, 2,3-dimethylpentane, 3-methylhexane and *n*-heptane. Also correlated with these compounds but with lower coefficient are 1-heptene and methylcyclohexane.

(5) *C_8 Hydrocarbons:* 2-methylheptane, 3-methylheptane and *n*-octane.

(6) *C_6 Hydrocarbons:* 2-methylpentane, 3-methylpentane, *n*-hexane and methylcyclopentane.

(7) *Ethane and Propane:* correlated with $r = 0.804$. These compounds are related to the domestic, commercial, and industrial use of natural gas and generally show a different diurnal pattern from those shown by the other hydrocarbons. This behaviour is probably due to an accumulation of these compounds during the night under any low level inversion layers [25].

(8) *Nonane and Decane:* The high correlation coefficients ($r = 0.881$) indicate that both compounds came from the same sources.

(9) *Compounds with Lower Correlations:* Finally, some compounds show lower correlations: isobutane, 2,2-dimethylbutane, isoprene, benzene, cyclohexane, trichloroethene, tetrachloroethene and styrene. Those low correlation coefficients can be related to their different origin; some are of industrial or commercial origin (trichloroethene, tetrachloroethene and styrene), some others are mainly of natural origin (isoprene), but we have found that quite a number of compounds are equally emitted by traffic sources and by industrial sources [45,46] such as coke ovens, refineries or thermal power plants (isobutane, 2,2-dimethylbutane, benzene, and cyclohexane, among others).

On Fig. 4 can be seen the scatter plot for benzene against toluene. In this case a linear relationship such as the one shown on Fig. 3 does not appear. There are two different

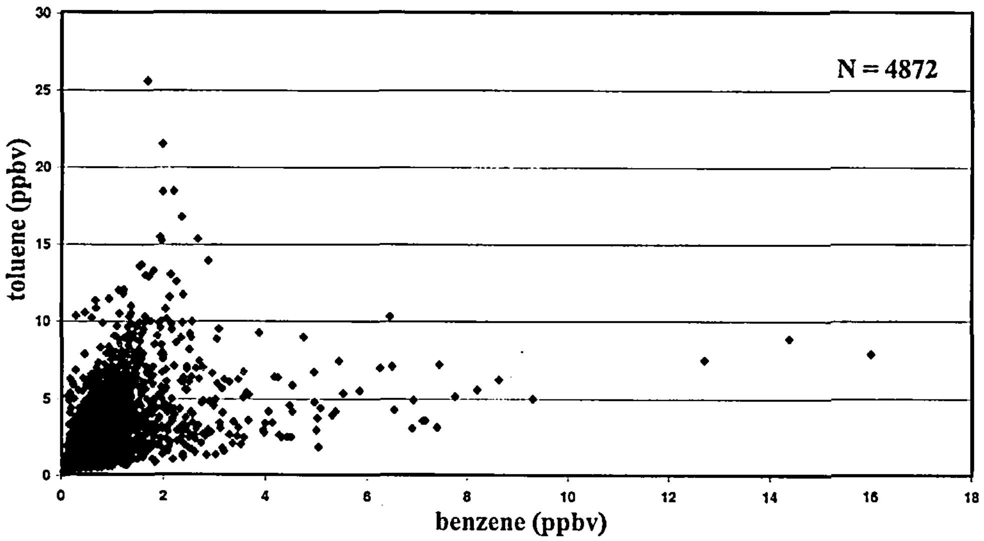

FIGURE 4 Scatter plot for benzene against toluene concentrations at the SEB for April-October 2001.

relationships, and we will need the input of the meteorological characterization of the area in order to study the benzene–toluene relation.

METEOROLOGICAL INFLUENCE ON ORIGIN AND CONCENTRATION OF SELECTED COMPOUNDS

In our area, the atmospheric pollutants dispersion patterns are well-known [47–50]. Some of the most frequent situations are associated with land and sea breezes regimes along the Bilbao estuary (SW and NW winds, respectively).

Meteorological parameters recorded at the ‘Feria’ monitoring station, located at a distance of around 300 m from the VOCs sampling site, were validated with the outputs from other sea-level meteorological stations located along the Bilbao estuary. Finally, the wind speed and wind direction data from ‘Feria’, were integrated in the NMHC database to analyze them simultaneously. Meteorological data cover all the measuring period and 98% of the survey period was covered by NMHC measurements.

We arbitrarily consider a calm period when the wind speed is lower than $0.5\,\mathrm{ms}^{-1}$; consequently, when the wind speed is higher than $0.5\,\mathrm{ms}^{-1}$, hourly mean pollutant concentrations were assigned to the corresponding wind direction. The wind rose diagram, excluding calms, during measuring period from April to October 2001 is presented in Fig. 5. The prevailing wind direction was SE–NW, strongly associated with sea breezes cycles developed on the scale of the Bilbao estuary, in SE–NW direction [51]. Figure 5 shows that the wind speed range for NW directions is relatively stronger than recorded for SE directions, mainly indicating that at the sampling point, located 16 km inland, the valley drainage flows and land-breeze regimes are characterised by light winds from the SE, and the day-time valley winds and sea-to-land airflow present winds of greater intensity.

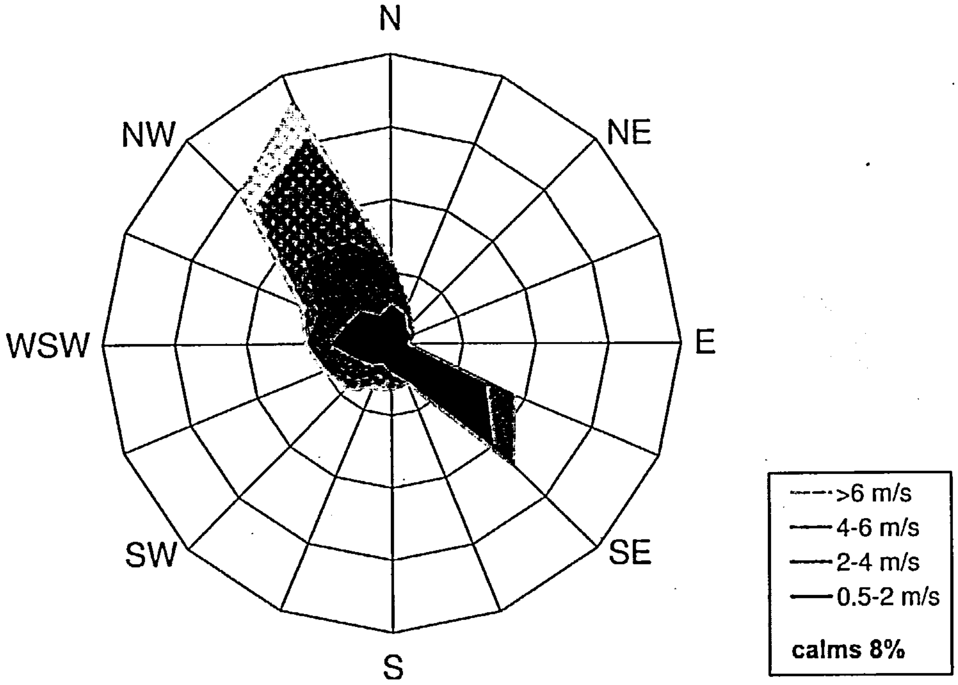

FIGURE 5 Wind rose diagram. Frequency (%) of wind directions sorted by speed range, observed during 2001 measuring period.

In addition, we have investigated the frequency of the wind directions associated with each pollutant daily maximum concentration. This frequency on the direction of the daily maximum, is illustrated on the pollution roses of several hydrocarbons (Figs 6 and 7). All of them have been plotted with data associated to wind speeds higher than 0.5 ms^{-1}, and calm periods have been calculated numerically. The relatively high percentage of maximum concentrations occurrence on calms periods, vary from 10% for trichloroethene data to 18% for ethene data.

As expected at an urban site, species related to traffic sources, such as CO, 1,3-butadiene, *n*-butane, *o*-xylene or ethylbenzene present a typical pattern with a high frequency of maximum concentration on SE–ESE direction, corresponding to the valley drainage flow (Fig. 6). Valley drainage flows, characterised by low wind speed, allow for a short time span between emission and sampling; hence, the air composition and traffic source composition at peak traffic times should be similar. However, different characteristics were noted for species, such as ethene, benzene, isoprene, trichloroethene and tetrachloroethene, that are both related with traffic and other sources (Fig. 7). Ethene is mainly emitted from vehicle exhaust [52], but its pollution rose suggest the contribution of non-traffic source on West quadrant. Benzene is present in vehicle fuel and exhaust emissions [53] but its pollution rose is quite different to aromatic compounds, implying that traffic source is not the main source of benzene. Isoprene, as expected from its biogenic origin [54], presents a curve following the wind rose diagram, and the anthropogenic origin of trichloroethene is characterised by a pollution rose with a marked prevalence of frequency on NW direction.

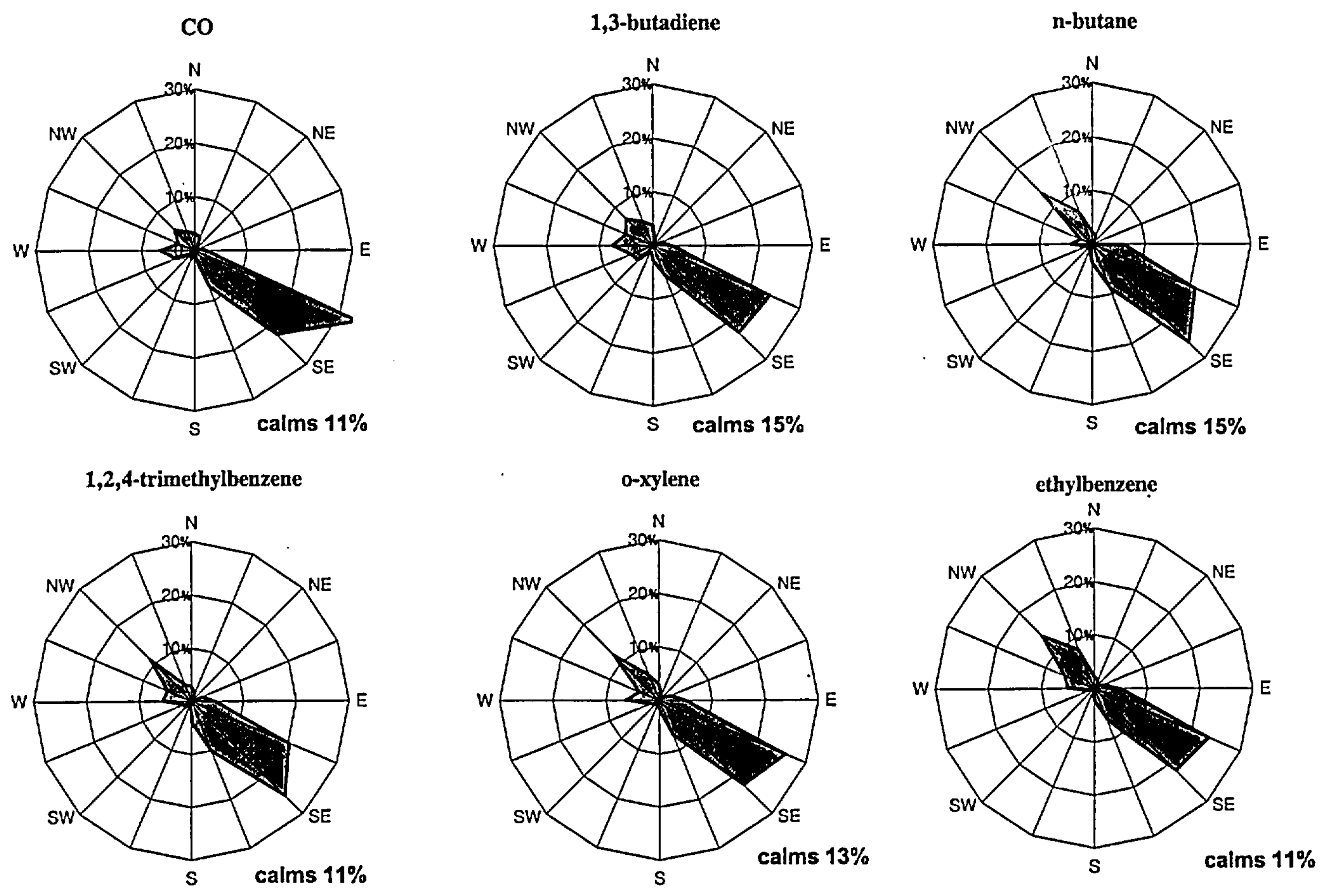

FIGURE 6 Pollution roses. Frequency (%) of wind directions associated with traffic related pollutant daily maximum concentration. Bilbao, April–October 2001.

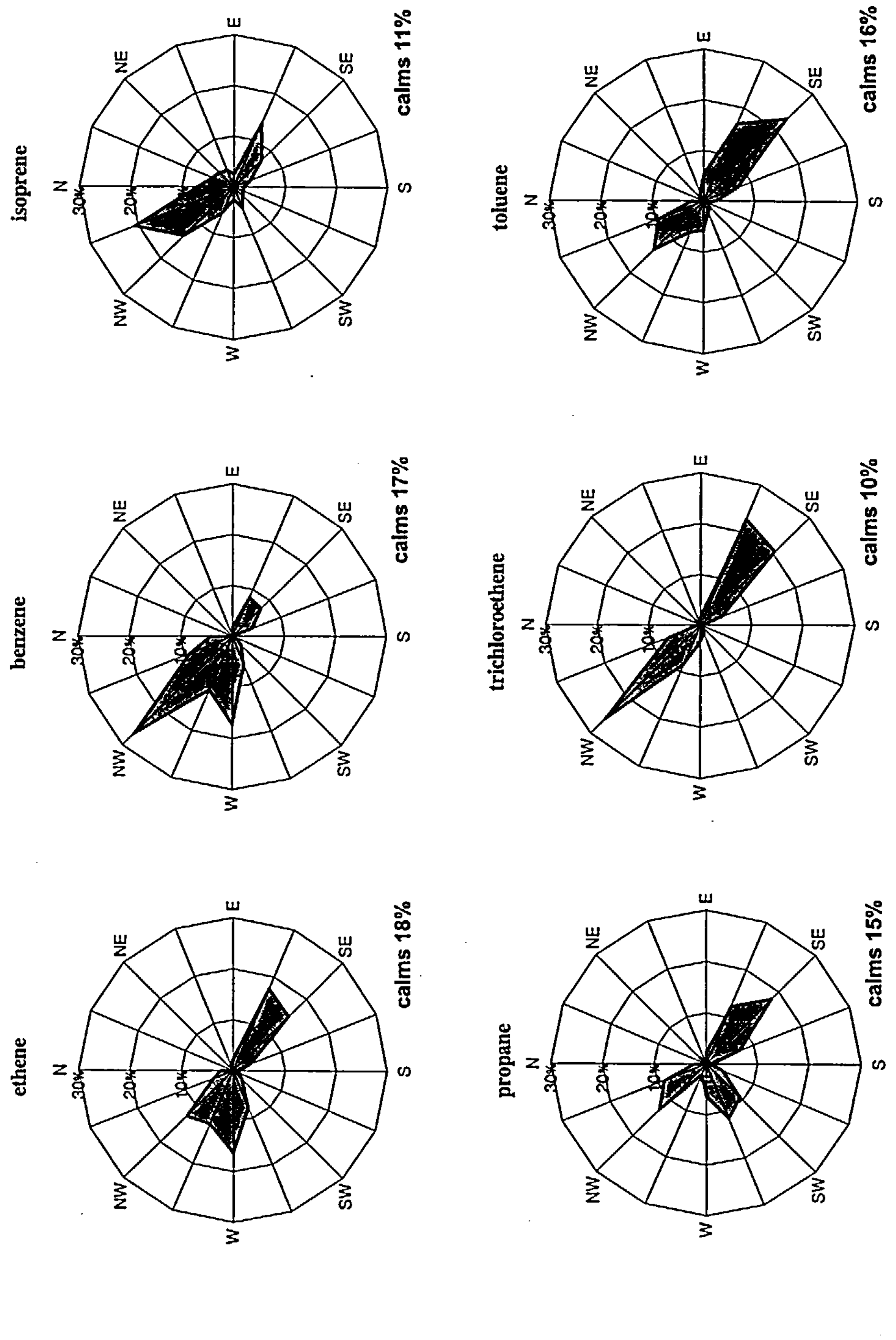

FIGURE 7. Pollution roses. Frequency (%) of wind directions associated with combined sources related pollutant daily maximum concentration. Bilbao, April–October 2001.

ANNUAL AVERAGES OF SELECTED RATIOS

Using the data gathered between 1997 and 2001, some commonly used VOC ratios have been studied: toluene/benzene, xylenes/benzene, propene/ethene, benzene/acetylene and ethene/acetylene [1,21]. The ratios between reactive and inert species concentrations are very useful as indicators of the relative changes in species composition and age of air masses. For example, as it is commonly accepted that toluene is more reactive than benzene, a lower toluene/benzene ratio can be indicative of a more aged air mass. In our area, however, this ratio is not directly applicable due to the habitual co-existence of fresh and aged air masses and the presence of industrial emissions containing benzene and other VOCs. Table V summarises the evolution of the annual mean ratios, showing significant differences among the ratios by year. This can indicate that there are other factors which contribute to this differences, as recent changes in the composition of some European gasoline or the fleet age, and the urban ratios toluene/benzene (3:1) typically founded in the literature are different than our results after year 1999. Moreover, acetylene is commonly used as indicator of the proportion of cars with/without catalytic converter [22]. We have detected a gradual increase, year by year, in the annual mean of the atmospheric acetylene concentrations that modifies the ratios including this compound.

During photochemical smog episodes, total VOC/NO_x ratio (where $NO_x = NO + NO_2$) during the early hours of the morning have been used as diagnostic parameters [55–59]. This ratio provides useful information about the probable efficiency of ozone formation from the existing mixture air–NO_x–VOC although sometimes it is difficult to assess the effectiveness of regulatory programs in improving ozone air quality in the presence of meteorological fluctuations [60]. Low ratios (lower than 5 ppbC/ppbNO_x) indicate a very low formation rate, for it is VOC limited. If NO_x concentration decrease it may lead to ozone formation. When ratios are high (above 20 ppbC/ppbNO_x) ozone formation is limited by NO_x availability. In this case, a decreases in NO_x concentration may effectively diminish the formation of ozone, but a reduction of VOCs will have no effect. When ratios have intermediate values (between 5 and 15), it is needed to call for a simultaneous reduction of both pollutants. Those ratios may change from place to place in the same urban area.

As an example, Fig. 8 is a scatter plot of total VOC concentration versus NO_x during September 1999 in Bilbao, measured at the same spot.

Some of the control strategies for ozone reduction call for a substitution of VOC for other less reactive compounds. Those strategies require the knowledge about the limiting factor, either NO_x or VOC. One of the most important components of a control strategy is the determination of reactivity – or ozone formation potential – based on

TABLE V Annual mean variation of selected VOC ratios

Ratio	*1997*	*1998*	*1999*	*2000*	*2001*
Propene/ethene	0.4	0.5	0.5	0.4	0.6
Xylenes/benzene	1.9	2.2	1.9	3.5	4.1
Toluene/benzene	2.4	2.9	2.5	5.1	4.0
Benzene/acetylene	0.7	0.6	0.8	0.3	0.2
Ethene/acetylene	1.4	1.4	1.4	1.0	1.0

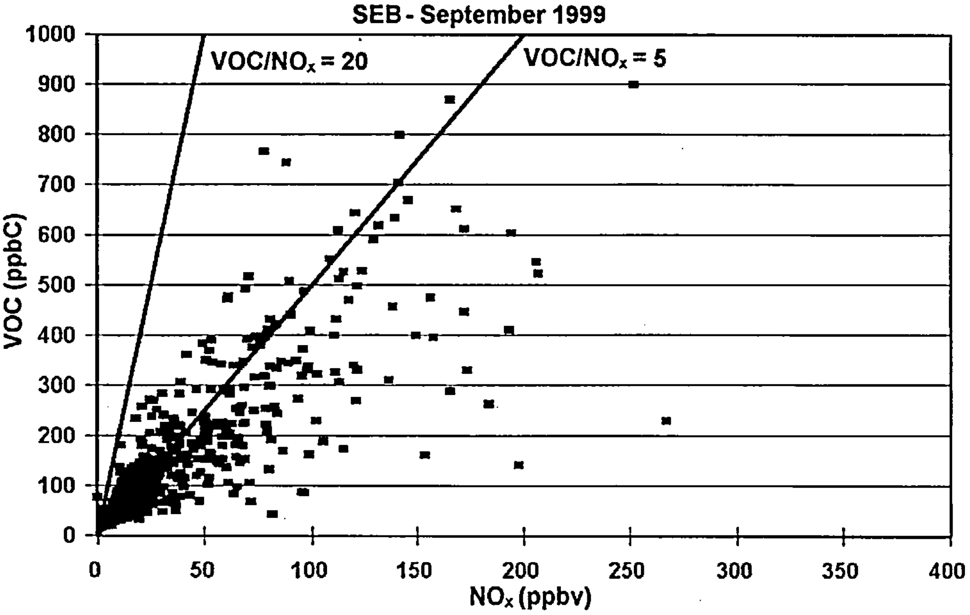

FIGURE 8 Plot of total VOC (ppbC) vs. NO_x (ppb) at the Bilbao station, during September 1999. It includes all hourly values.

experimental measurements of VOC mixtures as the ones included in this paper, or precursor emission inventories, when measurements are not available.

As it can be seen on Fig. 8, most of the values lie below the line which represents a Total VOC/NO_x ratio of 5, some cases are between ratios of 5 and 20, and almost none is over 20, which are mainly related to the fact that NO_x concentrations were very close to 0. Is it possible to say that, most of the time, ozone formation is VOC limited.

For comparison with values measured in other places [61], the usual 06:00–09:00 a.m. VOC/NO_x ratios, have been plotted. Figure 9 shows results for 25 days of September 1999. In this case, almost every value of the ratio lies below 5. Just with this information, and not having other contradictory information, is it possible to say that ozone formation, during the early hours of the morning is VOC limited, and that means that precursor control will have to focus on VOCs.

CONCLUSIONS

With a technique based on automatic on-line gas chromatography, evaluated and optimised in previous works, we have collected continuous hourly data for 62 C_2–C_{10} in ambient air during extended periods of 1997–2001. These systems generate a large amount of extremely complex data, whose handling, processing and validation require a huge effort before a consistent and reliable database can be achieved.

The 62 VOCs identified, i.e., paraffin, olefines, aromatics, and chlorinated compounds, make up for up to 88% of the total NMHC.

Statistical correlation analysis combined with multivariate techniques such as principal component analysis and cluster analysis were applied for inferring the

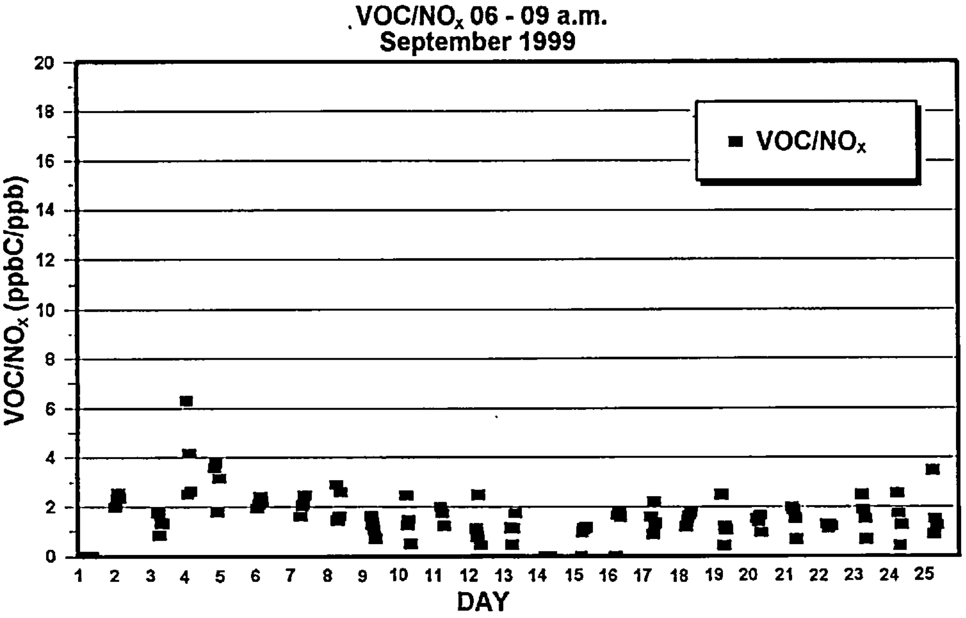

FIGURE 9 Total 06:00–09:00 a.m. VOC/NO$_x$ ratios from September 1999.

mixed organic compound sources impacting a receptor location. We found eight groups of compounds highly correlated (with $r > 0.800$ and $n > 4000$ data), corresponding to compounds with similar origin and/or similar chemical composition. There is a group of compounds with low correlation coefficients within them and with other groups. The reason lies on their origin, which is totally unconnected to traffic, or it is a mixture of sources: traffic, domestic, commercial and industrial.

The addition of a simple meteorological study for the characterisation of the prevailing winds in the area and using pollution roses has confirmed the classification previously done, allowing the differentiation, for each compound, of traffic or industrial origin. Results of these analyses have provided our regional air quality managers, who support the works, with valuable information on relative impact of ozone precursors transported into an air basin from upwind sources, recent trends in ozone precursor concentrations, efficacy of alternative control strategies and data to calculate the population exposures to some air toxics.

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