The impact of reduction in the benzene limit value in gasoline on airborne benzene, toluene and xylenes levels

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Abstract

Background benzene, toluene, xylenes (BTX) average concentrations have been measured over the urban agglomeration of Toulouse, France, during both springtime and summer periods of 1999 and 2001.

The benzene average amount over the two Toulouse campaigns in 1999 is equal to 2.2 $\mu g/m^3$, very close to the French air quality standard and well under the average value of 5 $\mu g/m^3$ recommended by European Economic Community countries, recognising that those regulations are given for a whole year. BTX pollution over Toulouse has, in particular, been produced by motor vehicle exhaust gases.

For the study conducted during the same periods of 2001, benzene concentrations were within the French quality value in the whole area. This is because the benzene limit value contained in gasoline went from 5% to 1 % since 2000 January 1.

It will be important to measure benzene over annual periods in order to know its exact values over such a period and to observe its potential seasonal variations.

Keywords: Benzene; Toluene; Xylene; Passive dosimeter; Urban area; BTX; Volatile organic compound (VOC)

1. Introduction

Volatile organic compounds (VOCs) play an important role in atmospheric chemistry. This is especially true for substituted aromatic VOC such as toluene and xylenes which have a high photochemical ozone creation potential. They take part in photochemical reactions and are major sources of radicals which can oxidise NO to NO_2, the precursor of ozone (Finlayson-Pitts and Pitts, 2000; Reis et al., 2000). Exposure to benzene has the potential for adverse health effects as it is a genotoxic carcinogen (Snyder and Kalf, 1994; Zhang et al., 1996; Lovern et al., 1997).

The regulation of major indicators for atmospheric pollution (ozone, nitrogen dioxide and sulphur dioxide) has been updated in recent years to include additional compounds like benzene. The ORAMIP, in partnership with the "Chemistry Energy and Environment" laboratory of the ENSIACET, has undertaken a background benzene, to-

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luene, xylene (BTX) average concentration measurement over the urban agglomeration of Toulouse during both springtime and summer periods of 1999 (May 5th to May 26th and June 14th to July 2nd) and 2001 (May 2nd to May 22nd and June 13th to July 4th).

The objective of our work was to evaluate *BTX average background concentrations* over a period of several weeks and to compare the BTX concentrations between 1999 and 2001. Samplers of passive type were selected for that purpose and were proved accurate tools under our experimental conditions. Due to their low cost and the simplicity of their positioning, it was possible to multiply the number of measurement points and hence to obtain a more precise pollution map of the area.

2. Methodology

2.1. BTX sampling and analysis

BTX sampling can be carried out by various methods using Tedlar or Teflon bags, canisters or adsorbents, respectively. The latter allow a sampling in either dynamic or passive mode. The advantage of a passive sampling mode is to provide a direct estimate of the average pollutant concentration corresponding to an acquisition period varying between few hours and few days (Brown, 1993; Begerow et al., 1995; Kozdron-Zabiegala et al., 1995; Baldan et al., 1999; Zabiegala et al., 2002).

Radial diffusive samplers Radiello models were used (Fig. 1). The diffusive surface is a synthesized polyethylene cylinder. The adsorbent was activated charcoal (530 mg). The adsorbed compounds were analysed by gas chromatography (GC/FID, GC/MS) after a CS_2 extraction (Cocheo et al., 1996). The gas chromatographic column was a DB1 (Alltech; 60 m, 0.32 mm and 0.25 μm). An internal standard 2-fluorotoluene was used for quantitative analysis (Meybeck et al., 2000).

The average concentration (C, $\mu g/m^3$) relative to the sampling period is given by the following expression: $C = m\ 10^6/(Qt)$, where m (μg) is the mass collected over a period t (minutes) and Q (cm^3/min) is the uptake rate (evaluated from laboratory experiments).

Blank values were determined on preconditioned tubes which were carried with sample tubes during the sampling process. Sampling capacity and extraction efficiency of the tubes as well as stability of the compounds in the tubes were tested in earlier studies (Meybeck et al., 2000). Repeatability for benzene, toluene and xylenes was very good. The standard deviation of triplicate samples collected at same sites during both campaigns was below 10% for all compounds.

2.2. Geographical zone and site selection

Toulouse is the fifth urban area in France with 351 822 inhabitants (INSEE census, 1999). The study area affects around 380 000 inhabitants.

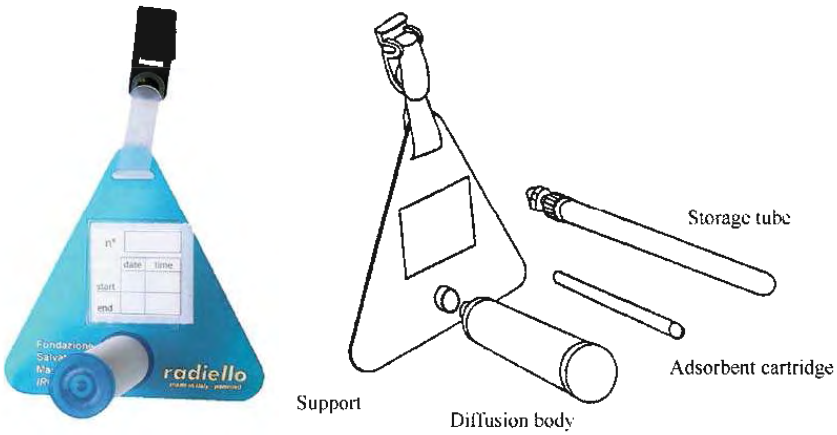

Fig. 1. Radiello diffusive sampler.

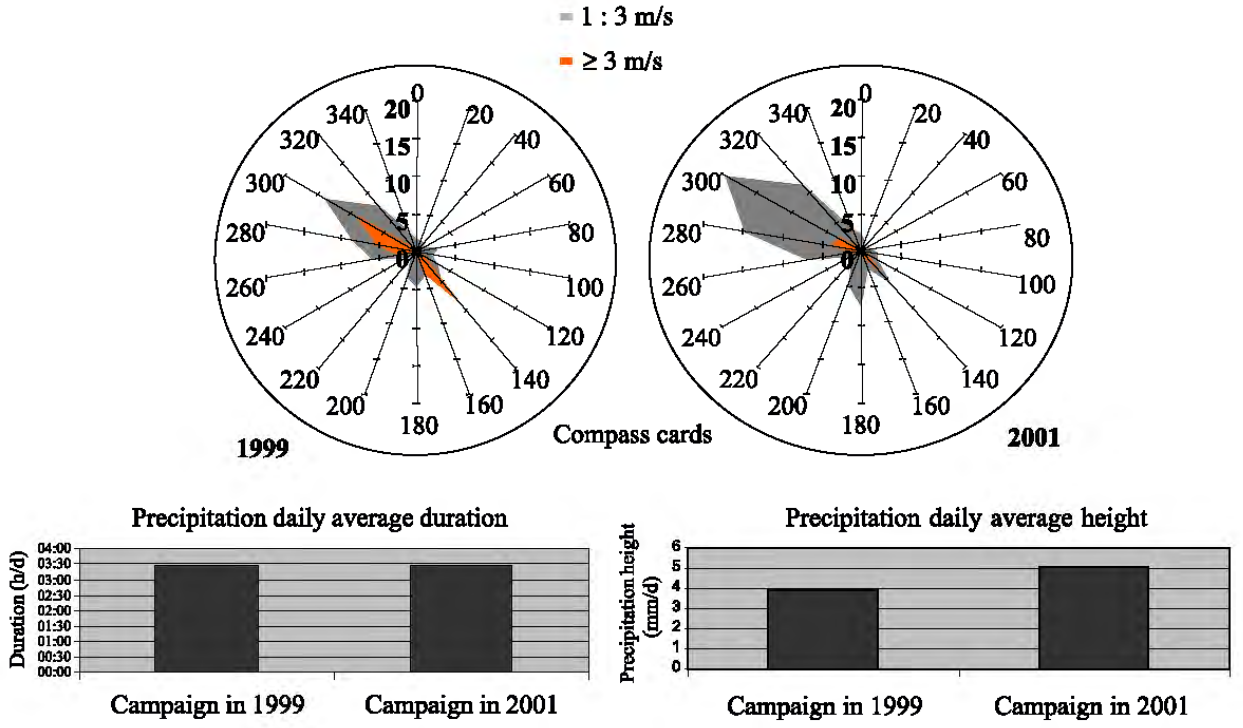

Fig. 2. Meteorological conditions for both global campaigns: 1999 (left; May 5th to 26th and June 14th to July 2nd) and 2001 (right; May 2nd to 22nd and June 13th to July 4th).

We have selected about 60 sites spread over an area of about 250 km^2. They were chosen among those previously used in 1991/92 and 1996/97 NO_2 measurement campaigns (ORAMIP, 1997). The number of selected sites is a good compromise between the cost of the study and the time available for collecting and analysing a representative data set. Sampling points were arranged over a regular grid of the urban

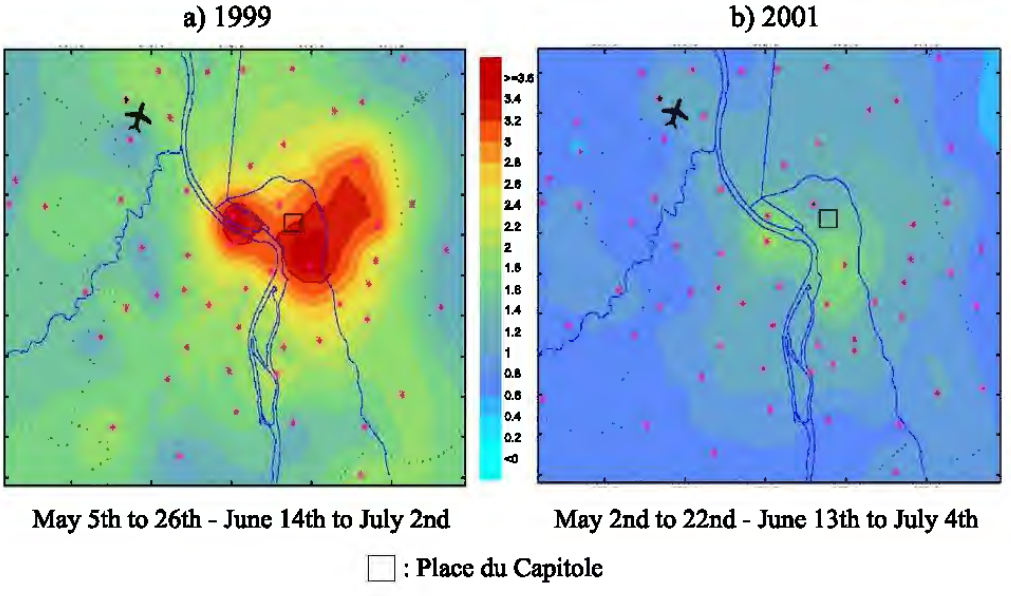

Fig. 3. Isoconcentration plots for benzene for both global campaign. (a) 1999; (b) 2001.

Table 1
Average concentration in BTX over Toulouse in 1999 (May 5th to 26th and June 14th to July 2nd)

($\mu g/m^3$)	Benzene	Toluene	*m,p*-Xylene	*o*-Xylene	All xylenes	All BTX
Average concentration	2.0	6.6	3.7	1.2	4.9	11.0
Standard deviation	0.7	2.5	1.5	0.5	1.9	4.1
Maximum value	3.8	14.1	8.0	2.7	10.6	23.1
Minimum value	1.1	3.0	1.6	0.6	2.2	5.1

area and were taken sufficiently far away from pollution sources to be representative of the background pollution level. The dosimeters were thus generally installed on poles, at 2-m high, in such a way to avoid any wall-screening effect. They were placed in polyethylene boxes in order to ensure protection against rain and solar radiation and to minimize disturbances due to the wind velocity.

2.3. Isoconcentration plots

Cartographic representations were made with the geostatistic computer program ISATIS which provides a set of statistical tools for incorporating the spatial coordinates of observations in data processing, allowing for description and modelling of spatial patterns, prediction at unsampled locations and assessment of the associated uncertainty.

We provide here representative plots corresponding to benzene, toluene and xylenes for both global campaigns.

3. Results and discussion

3.1. Meteorological conditions

Fig. 2 summarizes the mean meteorological conditions for both years. Precipitations did not allow a more important atmosphere washing for one or another campaign. For both periods, main wind directions followed a northwest to southeast line: it is the usual wind configuration in Toulouse. The 1999 period was marked by a wind speed more important.

3.2. BTX concentrations in 1999

Atmospheric average concentrations in benzene reach maximum values of 3.8 $\mu g/m^3$ in the town center (Fig. 3a), whereas toluene and xylenes are characterized by maximum concentrations being respectively of the order of 14 and 11 $\mu g/m^3$ (Table 1; Figs. 4a and 5a), corresponding to a maximum concentration in BTX at a given site of about 23 $\mu g/m^3$.

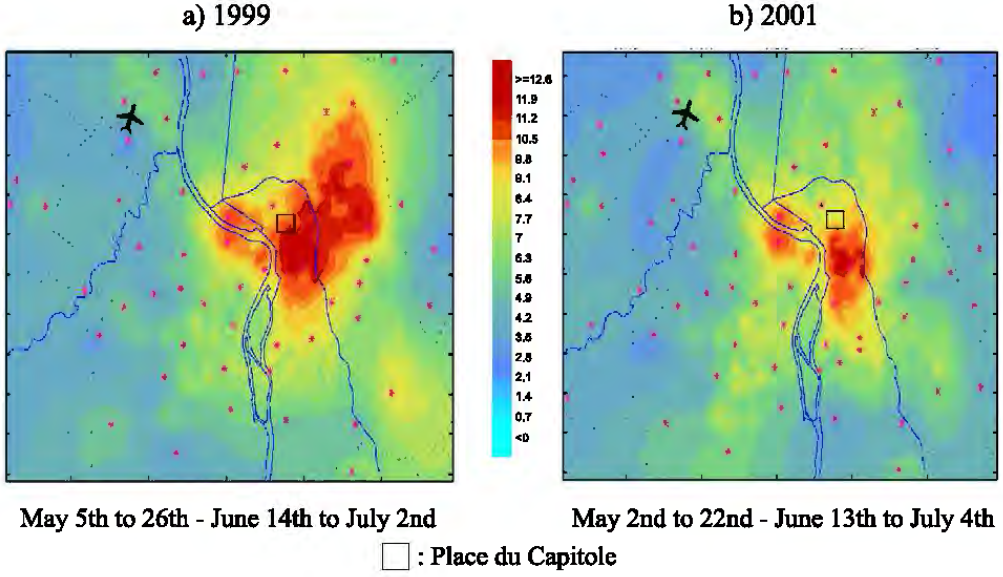

Fig. 4. Isoconcentration plots for toluene for both global campaign. (a) 1999; (b) 2001.

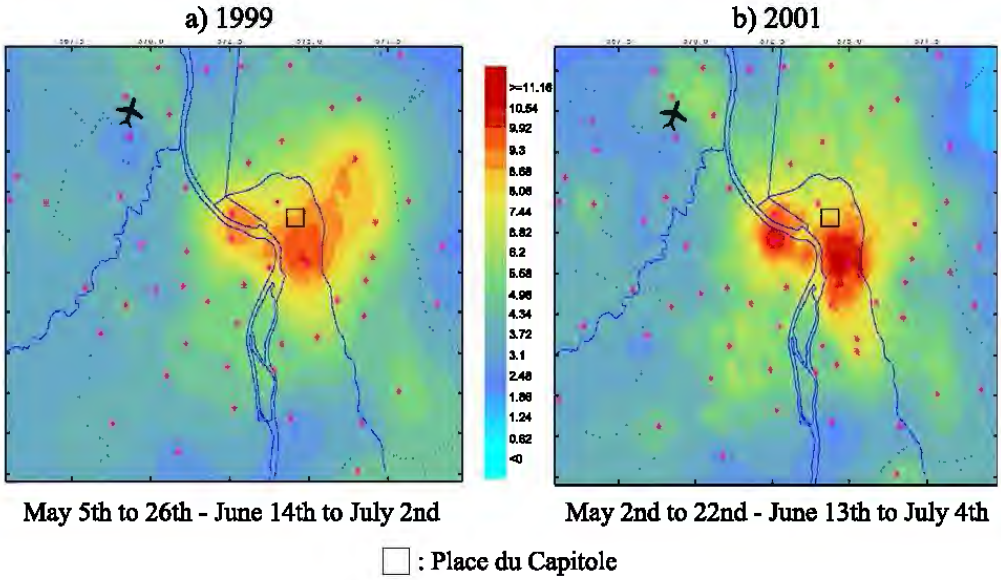

Fig. 5. Isoconcentration plots for xylenes for both global campaign. (a) 1999; (b) 2001.

Let us note that the benzene concentrations recorded here are only representative of the sampling period of the experiment and remain slightly below the upper tolerated value of 5 $\mu g/m^3$ imposed by the European regulation project.

It is noteworthy that the concentrations reach a maximum within the downtown center and are seen to decrease progressively toward the periphery. The zones exhibiting the highest concentrations are shifted towards the east, which can be understood because of the prevailing eastbound wind effectively recorded during the sampling period.

An evaluation of toluene/benzene and xylene/benzene concentration ratios is useful for characterizing the distance of vehicular emission sources (Derwent et al., 2000). Here, the average recorded concentrations led to toluene/benzene ratios close to 3 (ranged between 2.9 and 3.7), whereas the *m,p*-xylenes/benzene and *o*-xylene/benzene ratios were respectively of the order of 2 and 0.7 (Table 2). These ratios are of the same magnitude as those obtained from automotive exhausts, thereby confirming an origin of the pollution by BTX over Toulouse. In addition, the minimum toluene/benzene concentration ratios are observed on remote sites of the urban area, whereas the maximum ones are detected close to areas where an intense traffic exists. This is in agreement with an earlier observation by Gelencser et al. (1997) that the toluene/benzene ratio decreases as the distance from the pollution source increases.

3.3. BTX concentrations in 2001. Comparison

Atmospheric concentrations in benzene reach maximum values of 2 $\mu g/m^3$ in the town center (Fig. 3b), whereas toluene and xylenes are characterized by maximum concentrations being respectively of the order of 11.9 and 11 $\mu g/m^3$ (Table 3; Figs. 4b, 5b), corresponding to a maximum concentration in BTX at a given site of about 20 $\mu g/m^3$.

For both campaigns, VOC concentrations are maximum in downtown Toulouse and decrease progressively toward the periphery. The highest concentration zones seem to follow a northwest to southeast line corresponding to wind axis. The wind speed more

Table 2
Ratio between toluene/benzene, *m,p*-xylene/benzene, *o*-xylene/benzene concentrations in 1999

	Campaign 1999	Automotive exhaust
Toluene/benzene	3.3	2.7 (Brocco et al.,1997; Guicherit, 1997)
m,p-Xylene/benzene	1.9	1.8 (Stevenson et al., 1997)
o-Xylene/Benzene	0.7	0.9 (Guicherit, 1997)

Table 3
Average concentration in BTX over Toulouse in 2001 (May 2nd to 22nd and June 13th to July 4th)

($\mu g/m^3$)	Benzene	Toluene	*m,p*-Xylene	*o*-Xylene	All xylenes	All BTX
Average concentration	1.1	6.1	4.0	1.3	5.3	10.0
Standard deviation	0.3	2.1	1.5	0.5	2.0	3.4
Maximum value	2.0	11.9	8.4	2.7	11.0	19.7
Minimum value	0.7	3.0	1.6	0.6	2.1	5.0

important in 1999 does not seem to have favoured a better pollutant dispersion.

The average concentrations in BTX over Toulouse corresponding to the two campaigns are displayed in Table 3.

For the 2001 period, benzene average concentrations have been divided by two compared to 1999, whereas toluene and xylene concentrations are statistically the same. Meteorological conditions are almost identical. Thus, for the 2001 study period, the benzene allowable rate decrease from 5% to 1% in gasoline has had a significant effect on benzene concentrations in ambient air in Toulouse. Such decrease of ambient benzene concentrations have also been observed between 1999 and 2000 in Paris (AIRPARIF network), around 42% (http://www.airparif.asso.fr).

For the 1999 period, benzene concentrations in most of the study area exceeded 2 $\mu g/m^3$ (French quality focus) but they remained below 5 $\mu g/m^3$ (European limit value), whereas for the 2001 period, benzene concentrations were within the French quality value in the whole area. However, those regimentations are given for a whole year. Accordingly, it will be important to measure benzene over annual periods in order to know its concentration over such a period and to observe its seasonal variations.

4. Conclusion

BTX, pollutants directly resulting from automotive exhausts and also from evaporative emissions, are notably toxic to human health and can also generate secondary pollutants like ozone, aldehydes and acids whose impact can be at least as deleterious toward man, ecosystems, monuments...

In this context, our goal was to evaluate average atmospheric background concentrations in BTX over the urban area of Toulouse over a period of several weeks.

We were led to adopt a passive sampling technique which appeared particularly appropriate for that purpose. About 60 sites were selected among the most representative of the Toulouse urban area. A mapping of concentrations reveals that maximum concentrations in BTX are recorded in the downtown area, with a progressive decrease toward the periphery. The areas exhibiting the maximum pollution level are slightly shifted toward east relative to the town center as a consequence of prevailing eastbound winds recorded during the time of the experiment.

Upon consideration of toluene/benzene and xylene/benzene ratios, we conclude that BTX pollution over Toulouse is in particular linked to the motor vehicle exhaust gases.

Benzene average concentrations have been divided by two in 2001 compared to 1999, whereas toluene and xylene concentrations are approximately the same. For the 2001 study period, the benzene allowable rate decrease from 5% to 1% in gasoline has had a significant effect on benzene concentrations in ambient air in Toulouse.

The benzene average amount in 2001 remain below 2 $\mu g/m^3$, the French quality standard and well under the average value of 5 $\mu g/m^3$, to which is tending European regulation, knowing that those regimentations are fixed for a whole year. Accordingly, it will be important to measure benzene over annual periods in order to know its exact amount over such a period and to observe its potential seasonal variations.

References

Baldan A, Pérez Ballesta P, Cancelinha J, De Saeger E. Laboratory test for the validation of the Radiello diffusive sampler. In: Cocheo V, De Saeger E, Kotzias D, editors. Proceedings of

International Conference Air Quality in Europe Challenges for the 2000s. Venice 19–21 May 1999. p. 212.

Begerow J, Jermann E, Keles T, et al. Passive sampling for volatile organic compounds in air at environmentally relevant concentration levels. Fresenius J Anal Chem 1995;351:549–54.

Brocco D, Fratarcangeli R, Lepore L, Petricca M, Ventrone I. Determination of aromatic hydrocarbons in urban air of Rome. Chemosphere 1997;31:557–66.

Brown RH. The use of diffusive samplers for monitoring of ambient air. Pure Appl Chem 1993;65:1859–74.

Cocheo V, Boaretto C, Sacco P. High uptake rate radial diffusive sampler suitable for both solvent and thermal desorption. AIHA J 1996;57:897–904.

Derwent RG, Davies TJ, Delaney M, Dollard GJ, Field RA, Dumitrean P, et al. Analysis and interpretation of the continuous hourly monitoring data for 26 C_2–C_8 hydrocarbons at 12 United Kingdom sites during 1996. Atmos Environ 2000;34:297–312.

Finlayson-Pitts BJ, Pitts JN. Chemistry of the upper and lower atmosphere. USA: Academic Press; 2000. 969 pp.

Gelencser A, Siszler K, Hlavay J. Toluene-Benzene concentration ratio as a tool for characterizing the distance from vehicular emission sources. Environ Sci Technol 1997;31:2869–72.

Guicherit R. Traffic as a source of volatile hydrocarbons in ambient air. Sci Total Environ. 1997:201–13.

Kozdron-Zabiegala B, Namiesnik N, Przyjazny A. Use of passive dosimeters for evaluation of the quality of indoor and outdoor air. Indoor Environ 1995;4:189–203.

Lovern MR, Turner MJ, Meyer M, Kedderis GL, Bechtold WE, Schlosser PM. Identification of benzene oxide as a product of benzene metabolism by mouses, rats and human liver microsomes. Carcinogenesis 1997;18:1695–700.

Meybeck M, Della Massa JP, Simon V, Grasset E, Torres L. Etude de la distribution atmosphérique de Composés Organiques Volatils (COV) monoaromatiques: Benzène, Toluène, Xylènes (BTX) et du dioxyde d'azote sur l'agglomération toulousaine. Pollut Atmos 2000;168:569–82.

ORAMIP. Etude de la distribution du dioxyde d'azote sur l'agglomération Toulousaine par la méthode des échantillonneurs passifs-Eté 1996—Hiver 1996/1997—Evolution sur 5 ans: 1991/92–1996/97, Rapport d'étude; 1997.

Reis S, Simpson D, Friedrich R, Jonson JE, Unger S, Obermeier A. Road traffic emissions—predictions of future contributions to regional ozone levels in Europe. Atmos Environ 2000;34:4701–10.

Snyder R, Kalf GF. A perspective on benzene leukemogenesis. Crit Rev Toxicol 1994;24(3):177–209.

Stevenson, KJ, Stacey, B, Willis, PG. Air quality at Heathrow Airport Annual Report for 1996, AEA Technology; 1997.

Zabiegala B, Gorecki T, Przyk E, Namiesnik J. Permeation passive sampling as a tool for the evaluation of indoor air quality. Atmos Environ 2002;36:2907–16.

Zhang L, Rothman N, Wang Y, Hayes RB, Bechtold W, Venkatesh P, et al. Interphase cytogenetics of workers exposed to benzene. Environ Health Perspect 1996;104:1325–9.