The VOC in an urban area influenced by industrial emissions: characterization of their multi-origin and source contribution

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Abstract

Continuous hourly measurements of volatile organic compounds (VOC) from C₂ to C₁₀ were performed in Dunkerque, northern France from August 2002 to September 2003. The receptor site was chosen to be influenced by both urban and industrial VOC emissions. First the analysis of concentrations according to the wind direction has allowed us to prove this double influence for benzene and octane whereas seasonal and daily time series have only permitted us to formulate hypotheses. Secondly the scatter plots of compounds versus acetylene, a traffic exhaust tracer, have confirmed this double origin for the two compounds. Then a simple regression analysis has allowed us to reach the hydrocarbon/acetylene ratio characterizing the traffic exhaust source. Finally this traffic exhaust ratio has been used to achieve the traffic exhaust contribution to individual hydrocarbon levels. The industrial contribution in benzene and octane ambient levels could reach 80% for some wind directions, showing the role of meteorological conditions. This observation must be taken cautiously because of the weak frequency of the concerned wind directions.

Keywords: VOC sources, industrial emissions, wind direction, ratio, ambient level contribution.

1 Introduction

Our study is registered in a larger research program called CPER that results from a contract between the French state and the North region. The global aim is to develop a research program among different teams to describe the pollution in this industrialized region. Our work is included in a subroutine dedicated to the characterization of VOC behaviour. VOC play an important role in air quality
degradation due to their participation in the cycle leading to the formation of excess ozone in presence of NOx. Anthropic sources such as urban sources (vehicle exhaust or evaporation, domestic heating…) and industrial sources (combustion, use of solvents…) are well known to contribute to the presence of VOC in the atmosphere. Nowadays little information is available on the contribution of these two sources to individual VOC levels. Such an information is essential in the development of efficient pollution abatement strategies. The case study is a middle-sized city in northern France, Dunkerque that presents both large urban areas and multiple industrial activities. Through the localisation of the main VOC sources and the other teams' constraints, a receptor site has been chosen and instrumented. Continuous measurements of 53 VOC have been performed during more than one year. Our study will focus on 4 non-methane hydrocarbons (NMHC) which are expected to have different behaviours: acetylene, benzene, octane and 1,2,4-trimethylbenzene.

2 Methods

2.1 Location and site description

Dunkerque belongs to the urban community of Dunkerque (CUD) located in northern France with a total population of 200,000 inhabitants dispersed on a surface of 250 km². Dunkerque is the third French port and concentrates a large industrial activity with 225 factory constructions in the CUD [1]. Figure 1 shows a map of the CUD. Dunkerque, Saint Pol sur Mer, Grande-Synthe and Petite-Synthe constitute the major urban areas. The CUD is equipped with a network of roads and motorways that are represented on the map. The ten VOC larger industrial emitters have been identified thanks to the data of the DRIRE (regional direction of industry, research and environment) and are also located on the map. Chemistry and oil industries are the main industrial activity with six emitters and more than 75% of the total VOC emissions for the CUD (DRIRE data).

The receptor site is located in Grande-Synthe with an aim of being influenced by both urban and industrial sources. The chemistry and oil industries are gathered on two sites. The first one is located in Mardyck and is composed of a refinery, a hydrocarbon cracking industry and a storage area of hydrocarbons. Winds from the sector WNW-NW (more precisely 280°-320°) are able to transport industrial emissions from Mardyck to the receptor site. The second one is located in the port of Dunkerque in the NNE-NE wind sector (30°-50°) and is constituted of two storage areas and a refinery less important than the one quoted previously.

2.2 Material and data acquisition

The VOC samples were continuously analysed by a bidimensional GC/FID. The Turbo Matrix/Auto System provided by Perkin Elmer was used in its on-line mode. The optimisation of parameters, the quality procedure and the data acquisition were previously described in details [2]. This automated monitoring
system has allowed hourly measurements of 53 C$_2$-C$_{10}$ VOC in the way to characterize the VOC behaviour in this area as envisaged within the framework of the CPER. The measurements began in August 2002 and finished in October 2003 with 77% of the period covered by measurements. The detection limits (DL) were inferior to 0.05 ppb for most compounds and the DL for the compounds particularly studied in this work were 0.25 ppb for acetylene, 0.5 ppb for benzene and inferior to 0.15 ppb for octane and 1,2,4-trimethylbenzene. A recording of the meteorological parameters was performed in parallel. Temperature, wind direction and wind speed were measured by OPAL'AIR, the French air quality monitoring network in charge of the Dunkerque area. Their meteorological station was located in Saint Pol sur Mer, 4 km from our site. The data analysis that will be conducted here is limited to the September 2002-August 2003 data set to obtain a sequence of the four seasons. Autumn was defined from September to November, winter from December to February, spring from March to May, and June, July and August constitute summer.

**Figure 1:** The receptor site and the source localisation.

3 **Univariate analysis of the data set**

The univariate analysis of the data set began with the descriptive analysis of the four NMHC seasonal and daily time series.

The analysis of daily profiles revealed that the diurnal distribution of the four NMHC studied (acetylene, benzene, octane, 1,2,4-trimethylbenzene) was dominated by traffic emissions with two increases of concentrations at rush hours: 7 to 9 AM and 18 and 19 PM. This is typical urban site behaviour [3, 4]. Moreover, the seasonal variations of acetylene and benzene have shown a light
rise (very light for benzene) of concentrations during the winter. This trend corresponds to the general tendency described in the literature for urban sites [5, 6]. The enhancement of vertical mixing through increased convection during the summer months is currently attributed to this seasonal trend. Then acetylene and probably benzene (the seasonal trend is very weak) have urban behaviour through this seasonal analysis. On the contrary seasonal variations of octane and 1,2,4-trimethylbenzene concentrations cannot be detected; the work of Cheng et al. [5] interprets this trend by a domination of nearby sources. Consequently the octane and 1,2,4-trimethylbenzene seasonal variations could illustrate a potential nearby industrial influence at the receptor site.

Therefore a second type of univariate analysis has been undertaken to confirm and improve the understanding of the industrial source influence at the receptor site. Owing to the particular localisation (grouping together in two sites) of the industrial sources around the receptor site, an analysis of NMHC concentration variations according to the wind direction has been undertaken [7, 8]. Figure 2 shows the concentration variations with wind direction for acetylene, benzene, octane and 1,2,4-trimethylbenzene.

As shown on Fig.2 acetylene and 1,2,4-trimethylbenzene present a more uniform rose diagram than benzene and octane. The mean value for each wind direction depends essentially on the urban density: relatively high around 70° with the Dunkerque city and around 120° with the N225 traffic road. Urban density becomes smaller in the west and the north of the receptor site and the concentrations of acetylene and 1,2,4-trimethylbenzene decrease. For benzene and octane, the concentrations are nearly constant and particularly low for winds coming from the urban area defined as the 70°-220° sector and present strong and rapid increases when winds come from industrial areas (NW, N and NE). Both compounds present a concentration increase for winds coming from the industrial area of Mardyck (NW). Octane concentrations increase also for winds coming from the storage area of the port (50°), whereas benzene concentrations present a second increase for the north wind sector. A steel industry which used a coke oven is located in the north of the receptor site and could be a source of benzene. Indeed coke ovens are known to be benzene emitters [9].

Consequently our hypothesis of an industrial source of octane has been well confirmed, in the same way as the unique urban source of acetylene. But no industrial origin of 1,2,4-trimethylbenzene has been demonstrated. Its seasonal variation should have presented an increase during winter as a typical urban source compound, so another parameter controls concentration, perhaps the wind speed. Indeed concentration rises involved by wind speed decreases could mask a light seasonal variation. Besides the industrial source of benzene has not been established thanks to analysis of time series. The industrial influence is not so strong to mask typical urban seasonal variation.

The analysis of the data set through the wind direction has allowed to distinguish two typical behaviours of compounds: nearly uniform roses for compounds emitted by urban activities and roses with abrupt and strong increases for compounds which have an industrial source added with the urban sources.
4 Bivariate analysis of the data set

4.1 Method description

The bivariate analysis of the data set consisted in working with hourly concentrations and using simple linear regression inspired by Derwent and co-workers [10]. Acetylene has been chosen as a reference compound. Indeed, acetylene is thought to be wholly combustion derived and relatively unreactive, and often used as an indicator of vehicle exhaust emissions [11, 12]. Furthermore, our previous analysis according to the wind direction has confirmed this hypothesis in spite of the particular vicinity of our site constituted of several industrial plants.

4.2 Different behaviours

To illustrate our approach, Figure 3 shows the scatter plots of the simultaneous concentrations of acetylene versus individual NMHC with more than 6000 hourly data. The correlations vary from hydrocarbon to hydrocarbon and from wind direction to wind direction.

On the one hand, 1,2,4-trimethylbenzene (1,2,4-tmb), which has previously shown a uniform rose diagram and has consequently no identified industrial source, presents a good correlation with acetylene \((r = 0.75)\). The uniform scatter plot indicates that both hydrocarbons have a common source, probably traffic exhaust. On the other hand, octane and benzene clearly reveal multiform scatter plots with two main families of points. These multiform scatter plots indicate that both hydrocarbons pairs have two common sources. The first one is
presumably motor traffic whereas the second one could be an industrial source
because the univariate analysis has demonstrated the presence of an important
industrial source for benzene and octane, especially in the north wind sector
(270°-50°).

This last hypothesis has been confirmed by an original analysis of the scatter
plots with the wind direction (WD). The simultaneous hourly concentrations
have been distinguished in two groups: a first group corresponding to data
collected when wind brings industrial emissions at the receptor site (i.e. 270° to
19° for benzene and 270° to 69° for octane and 1,2,4-tmb) and a second group
for wind directions coming from urban areas. This separation of the data
according to the wind direction corresponds to the separation of the two families
of points on scatter plots. This analysis has permitted to clearly show two groups
of points and to highlight two main sources of benzene and octane: urban
activities (especially traffic exhaust thanks to the acetylene tracer) and industries.
The points corresponding to the traffic exhaust source design a slim shape
whereas the industrial family points is more diffuse. Indeed industrial activities
gathered many processes with different emission ratio whereas urban activities
are largely dominated by traffic exhaust that is characterizing by only one ratio.
For the 1,2,4-trimethylbenzene, the two groups of points are confused
confirming the single urban origin of this compound.

![Figure 3: Scatter plots of individual NMHC versus acetylene.](image)

4.3 Determination of traffic exhaust ratio

The last section has permitted to show a uniform and slim distribution of the
points representing the traffic exhaust source. A simple regression analysis
(SRA) was conducted to assess the individual NMHC/acetylene ratio that characterizes the traffic exhaust source.

First, a part of the data was selected because it represents particular conditions in which traffic exhaust is the major source of NMHC. The data measured for working days from 7 AM to 9 AM were selected because during these rush hours traffic source takes more importance as shown by daily time series [3, 4]. As the evaporation phenomena are limited in winter, the data collected in December, January and February were selected. Then the data corresponding to the wind directions bringing industrial emissions at receptor site were excluded. Figure 4 presents the benzene versus acetylene plot in the conditions quoted before in the way to determine the benzene/acetylene ratio of traffic exhaust emissions.

Table 1 resumes the SRA parameters, especially the slope that corresponding to the individual NMHC/acetylene ratio. Our results are compared to the other ratios found in the literature. The ratios determined by Fontaine and Galloo [13] are derived from emission factors determined thanks to measures on vehicles, whereas the ones determined by Borbon et al. [11] are deducted from ambient measurements.

The uncertainty associated with our result comes from the uncertainty on the slope calculated thanks to the SRA. The uncertainty on emission ratios determined by Fontaine and Galloo [13] comes from the variation coefficient of the successive measures. This comparison permits to prove a good agreement between literature data and our results. Thus our ratios and their uncertainty to acetylene could be used in the following of the study.

Table 1: Individual NMHC to acetylene ratio*.

<table>
<thead>
<tr>
<th></th>
<th>benzene</th>
<th>octane</th>
<th>1,2,4-tmb</th>
</tr>
</thead>
<tbody>
<tr>
<td>determination coefficient r (SRA)</td>
<td>0.92</td>
<td>0.95</td>
<td>0.97</td>
</tr>
<tr>
<td>Slope of SRA (this study)</td>
<td>0.360±0.018</td>
<td>0.030±0.002</td>
<td>0.119±0.008</td>
</tr>
<tr>
<td>emission ratio [13]</td>
<td>0.352±0.095</td>
<td>0.018±0.05</td>
<td>0.135±0.038</td>
</tr>
<tr>
<td>slope of SRA for traffic site [11]</td>
<td>0.334</td>
<td>0.020</td>
<td>nd</td>
</tr>
<tr>
<td>slope of SRA for urban site [11]</td>
<td>0.316</td>
<td>0.028</td>
<td>nd</td>
</tr>
</tbody>
</table>

nd: non determined; * unit is ppbv/ppbv

Figure 4: Benzene vs. acetylene.
5 Contribution of traffic exhaust in NMHC ambient levels

5.1 Method

Our method is based on the knowledge of the traffic exhaust ratio determined in the last section and inspired by Borbon et al. [11]. It consists in multiplying the traffic-exhaust ratio for a compound $i$ by the ambient concentrations of acetylene to calculate the concentrations of hydrocarbon $i$ due to traffic exhaust (i.e. modelled concentrations of compound $i$).

$$[\text{acetylene}]_{\text{ambient}} \times \text{ratio}_{(i/acetylene)} = [\text{NMHC}_{i-\text{traffic}}]_{\text{modelled}}$$

Then the modelled concentrations of the compound $i$ (due to traffic exhaust) is compared to ambient concentration measured for the compound $i$ at the same time, and the contribution of traffic exhaust in ambient levels for the compound $i$ is deducted. Moreover, the knowledge of the slope uncertainty permits to calculate a minimum and a maximum value for the term $[\text{NMHC}_{i-\text{traffic}}]_{\text{modelled}}$.

5.2 Traffic exhaust contribution variations with wind direction

As it has been shown through this study, the wind direction is a determining factor, consequently this analysis has to focus on the variation of the traffic exhaust contribution with wind direction. The traffic exhaust contribution for each hourly datum has been calculated and then the minimum and the maximum value for each wind direction has been determined. The results for octane, benzene and 1,2,4-trimethylbenzene are present in figure 5.

The 1,2,4-trimethylbenzene, which was expected to have no industrial source, shows a traffic exhaust contribution superior to 60% whatever the wind direction. These observations are consistent with the previous conclusions, which allotted only a traffic source to this compound. Nevertheless the traffic exhaust contribution decreases in some wind directions. The decreases recorded for the wind directions 300°, 320°, 0° and 50° could be due to industrial emissions not so important to clearly appear on the pollutant rose diagrams (Fig. 2). Indeed these wind directions correspond to identified NMHC industrial emitters (Fig. 1). The light decrease in the wind direction sector 120°-140° could be attributed to an increase of the relative importance of another source. This source could be evaporation phenomenon associated with traffic activities because the presence of the high traffic way N225, a potential NMHC emitter or light industrial emissions due the emitter located near Bierne (Fig. 1).

In the case of octane, the traffic exhaust contribution goes down to 20% for the industrial wind sectors: 290°-320° and 40°-50°. Consequently industrial emission contribution in octane ambient levels could reach 80% in some particular wind conditions. As for the 1,2,4-trimethylbenzene the light decrease in the wind direction sector 120°-140° could be attributed to the evaporation phenomenon associated with traffic activities or the industrial source quoted previously.

The last studied compound is benzene, the benzene traffic exhaust contribution to ambient levels can decrease to 20% for two wind sectors: 310°-
320° and north. In each case industrial emitters have been identified. Therefore industrial emission contribution can increase to 80%.

Figure 5: Traffic exhaust contribution to individual NMHC ambient levels.

The traffic exhaust contribution of benzene never exceeds 80% and this contribution exceeds 100% for octane and 1,2,4-trimethylbenzene in some wind directions. No explanation has been brought so far.

6 Conclusions

The univariate analysis of individual NMHC concentrations according to wind directions has allowed to highlight the double influence of industrial and urban emissions at the receptor site. The study of scatter plots of individual NMHC versus acetylene has confirmed this double influence and allowed to assess a hydrocarbon/acetylene ratio characterizing traffic exhaust emissions. This ratio was used to evaluate the traffic exhaust contribution to individual NMHC levels.

These analyses have demonstrated the impact of the wind direction on the traffic exhaust contribution to individual NMHC ambient levels. Thus we were interested in the wind direction frequency. The winds coming from the large 290° to 10° sector only represent 15% of the winds. The other wind sector concerned with industrial sources, 40°-50° correspond to 9% of the winds. The frequency of winds coming from the SW sector (180°-270°) is 38%. Consequently the impact of the industrial emissions in term of contribution to ambient level is limited thanks to meteorological conditions which are favourable. Such an observation could also explain the typical urban behaviour presented for these compounds through the time series analysis.

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References


