Assessment of BTX Concentrations Near a Petrol Station Using Diffusive Samplers

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Abstract. A combined monitoring and dispersion modelling methodology was applied for assessing air quality related to concentration levels of benzene, toluene and xylenes (BTX) at three different levels of proximity to a petrol selected service station: (I) next to the fuel pumps, (II) in the surrounding environment, and (III) in the background. A Gaussian dispersion model (CALINE4) was used for assessing the road traffic contribution to the local concentrations under different meteorological conditions.
It was established that Stage 2 vapour recovery reduces BTX concentrations not only near the pumps but also in their surrounding environment. However, there is evidence that the efficiency of the system is wind speed dependent. The modelling simulation of the worst case wind scenario revealed the significance of local traffic emissions. It was shown that the traffic contribution to the local BTX levels even from a single road in the vicinity of the station can be, under certain conditions, higher than the contribution of the station itself. Finally, after comparison with previous studies, the concentrations measured near the service station (which was situated in a rural environment) appear to be lower than those observed in busy street canyons in city centres.
It can be concluded that although Stage 2 recovery system effectively reduces working VOC losses in service stations, it will only have a limited positive impact on local air quality if the service station is located in a heavily polluted area.

Keywords: Air quality, population exposure, benzene, service station, petrol, vapour recovery, Stage 1 & 2 control, displacement loss, spillage loss, wind conditions, dispersion modelling.

1 Introduction

From a toxicological point of view benzene is the most notorious petrol component. It has been classified in the group 1 of IARC [1]. Furthermore, according to the World Health Organisation (WHO) [2], there is no single threshold value for benzene below which there is no danger for human health. WHO proposes a unit risk excess of 6 x 10^{-6} per $\mu g/m^3$ for leukaemia based on a linear extrapolation model without threshold. From a regulatory point of view a limit value of 5 $\mu g/m^3$ has been proposed for benzene by the European Commission (EC) [3]. For France the Loi sur l'Air [4] determines an air quality objective value of 2 $\mu g/m^3$.
Fuel storage and delivery activities in service stations have also been subject of EC regulation [5]. Tanks containing petrol can emit VOC vapours due to filling and emptying activities (displacement losses) as well as changes in temperature and atmospheric pressure (breathing losses). Every time an empty tank is filled, the corresponding air volume saturated with petrol

vapour is displaced into the atmosphere. Displacement losses can increase both occupational exposure to VOC in the immediate proximity of the pumps (for people working in the station, car drivers and passengers), and population exposure in the surroundings of the station [6,7]. For the reduction of these emissions vapour recovery devices can be put in place. These systems return the VOC saturated volume of air which has been displaced from the tank being filled to the tank being emptied during the delivery of the fuel. The equipment used for vapour recovery during the loading of a storage tank is called Stage 1 control, while the system used for the same purpose during the refuelling of a vehicle tank is called Stage 2 control.
A two week monitoring campaign was carried out in a modern service station by the RN 10 motorway near the small town of Prunay in the south of Rambouillet (Yvelines, France) in November 1999. During the first week the vapour recovery system of the station was operating, while during the second week it was disconnected. The adopted methodology, presented below, was based on real measurements and model simulations.

2 Methods

2.1 Site description

The specific service station was selected for the campaign because of the availability of modern refuelling facilities and vapour recovery systems (which could be switched on and off), the flat topography of the site (which increases confidence in modelling results), the good natural ventilation of the area (which makes simple Gaussian models applicable), the existence of only one traffic axis (RN 10, a good linear source), the easily measured background contribution, and the relatively constant quantities of petrol sold in the station.

2.2 Sampling methodology

The concentration of a pollutant at a given location and time is the summation of the contributions from different emission sources. The major factor determining the dispersion of gaseous pollutants in the atmosphere is the wind (speed and direction) and its related turbulent effects. Considering the case of the service station the concentration C_i of a pollutant at a given location can be expressed in the following way:

$$C_i = C_o + C_s + C_r \qquad (1)$$

where
C_o is the background concentration of the pollutant
C_s is the concentration due to emissions released within the station
C_r is the contribution from vehicle traffic in the proximity of the station.

C_r and C_s are expected to vary with time and distance from the source. The total concentration C_i of the pollutant as well as the background contribution C_o can be measured using adequate equipment. By contrast, the other two independent contributions C_s and C_r need to be calculated. In order to study the efficiency of the vapour recovery system, the variation of VOC releases within the station needs to be quantified and attributed to different factors (vapour recovery, traffic volume, accidental spillage, weather conditions, composition of the fuel, etc.) In addition, the variations of C_s should be significant compared to C_o and C_r values.

A mobile monitoring unit (trailer-lab) and diffusive samplers were used for taking measurements at 20 sampling locations (Fig. 1), which can be classified in three different "levels" of proximity to the source: (I) next to the fuel pumps, (II) within their surrounding environment, and (III) in the background. The samplers placed nearer the source (level I) were located in pairs at two different heights (h_1 = 0.2 m, h_2 = 2.0 m).

2.3 Measurement techniques

Two anemometers, one 3-D ultrasonic (WindMaster, Gill Instruments, Hampshire, UK) and one mechanical (microvane and three-cup), were used for monitoring local wind speed and direction. This equipment was sheltered in the weather-proof trailer-lab parked next to the service station. Perkin Elmer (PE) diffusive samplers (adsorbent: Carbotrap B) were used for the multisite BTX measurements. The PE tubes were sheltered in specially designed aluminium boxes, and regularly replaced.
Field notes were taken for traffic volume and vehicle speed. The quantity of petrol sold in the station was controlled by the fuel pump meters.

2.4 Analysis of the samples

BTX samples were analysed using thermal desorption and gas chromatography / flame ionisation detection. A quality assurance (QA/QC) programme, including sampling duplicates, blanks and instrument calibration with standard gases was followed during the sampling and analytical work. Ambient BTX concentrations were calculated from the relationship:

$$C = \left(\frac{L}{S}\right)\frac{1}{D}\frac{m}{t} \qquad (2)$$

Where C is the ambient concentration of the gas, L/S is a constant depending on the dimensions of the sampling tube, D is the diffusion coefficient of the gas in ambient air, m is the mass of the pollutant sampled, and t the time of exposure [8]

2.5 Cartography and modelling

The cartography of the pollutants (i.e. the plotting of iso-concentration lines on a site map) is an efficient means of visualising sampling results and interpolated values. Amongst the different interpolation methods applicable to this case, kriging was considered as the most appropriate because of the irregular distribution of the sampling points and the possibility of using variogram models [9]. Carbon monoxide and benzene concentrations were modelled using CALINE4, the last version of the Gaussian dispersion model developed by the California Department of Transportation [10]. Model input requirements include emission factors, description of the site topography, meteorological and traffic data. CALINE4 calculates the pollutant concentrations for multiple receptors at distances up to 500 m from the source (see Fig. 1).

3 Results and discussion

Measurements were taken for two different time periods. During the first period the Stage 2 recovery system was operating, during the second period it was disconnected. General meteorological, traffic and fuel data were averaged during the different periods.

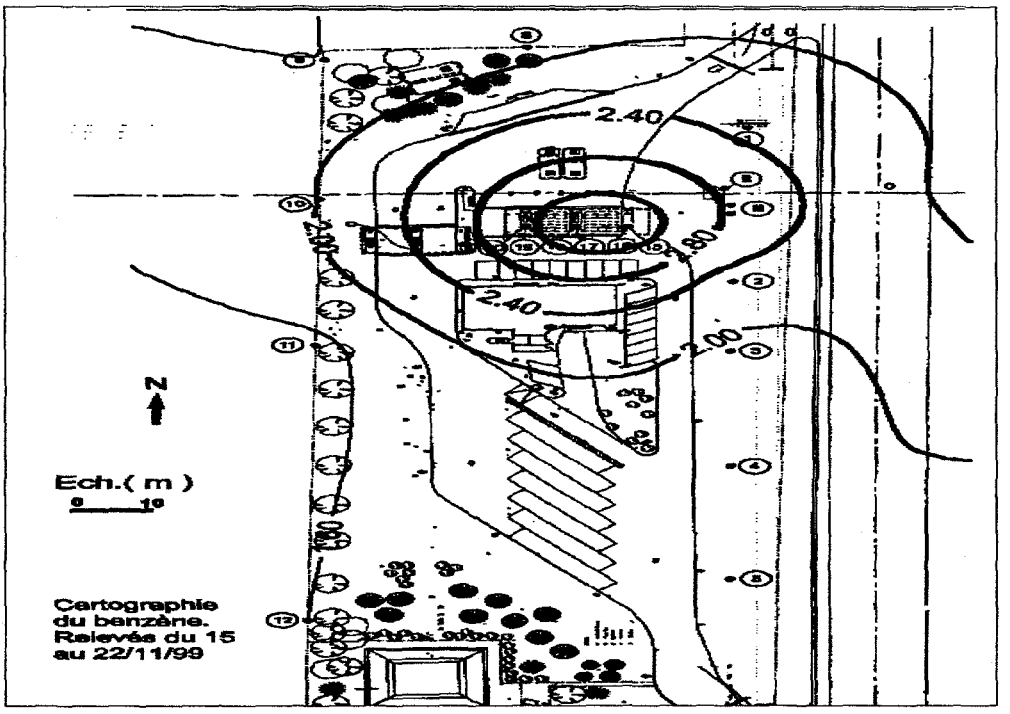


Fig.1. Concentration mapping using the kriging method with a linear variogram model.

Weekly mean BTX concentrations for all locations were measured (with and without vapour recovery) are given in Fig. 2 (stage 2 desconnected). The concentrations detected nearer the ground (at 0.2 m height) at proximity level I were significantly higher than the others and were considered separately

3.1 Displacement and spillage losses

The regular profile of the BTX concentrations measured in all sampling locations (with and without Stage 2 control) reveals the common origin (i.e. petrol combustion and evaporation) of VOC emissions. The background BTX concentrations, which were (as expected) much lower than those measured near the station or the motorway, were approximately the same for all level III locations. Near the fuel pumps (level I), concentrations are up to a factor 4 higher than the background values (see Fig 1). Large differences in BTX concentrations were detected between the sampling locations of different height near the pumps (level I). The concentrations observed

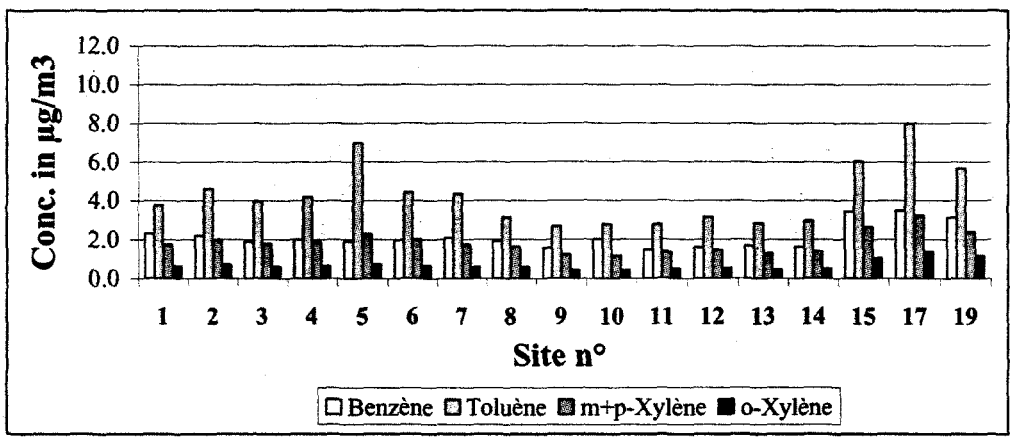


Fig. 2 Example of BTX concentrations profiles for sites 1 to 19

close to the ground were significantly higher than those measured at 2 m height. This could be explained by the short distance between samplers and car exhausts, as well as by the occurrence of accidental spillage losses of fuel on the ground.

3.2 Dispersion conditions

In order to establish the influence of wind speed on the ambient pollution levels, BTX concentrations were plotted against the reciprocal of the wind speed (see fig. 3 below) for the two different periods of the campaign. Only the measurements of higher temporal resolution were used.

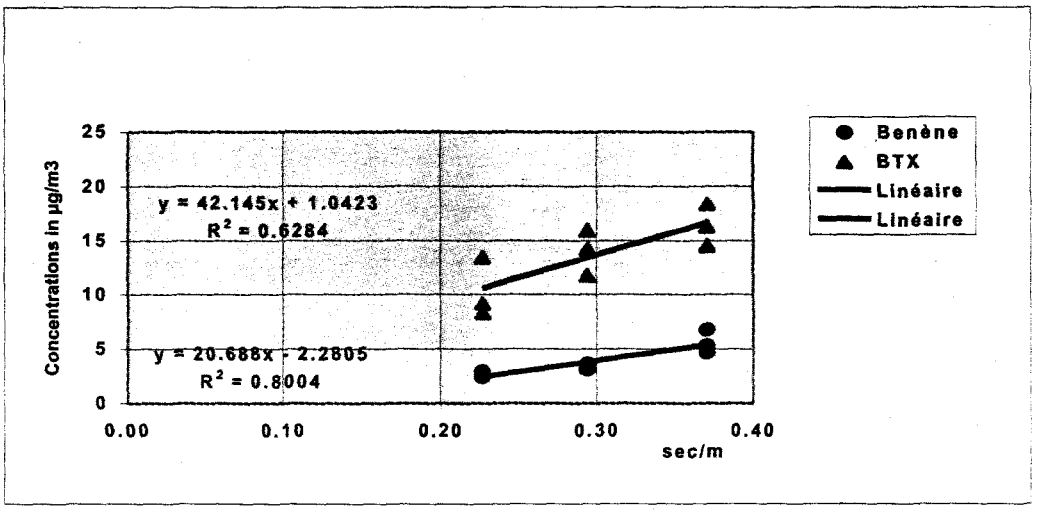


Fig. 3. Concentrations plotted versus wind speed

These corresponded to the sampling points near the pumps (level I), where diffusive tubes were replaced every 48 hours, thus covering a wider range of meteorological conditions. The observed concentration variations could be attributed mainly to the changes in wind speed since the station was constantly upwind with respect to the RN 10 and the quantity of fuel sold remained almost constant. It can be seen that for a given wind speed benzene as well as total BTX concentrations were lower when the Stage 2 control was operating, suggesting that the system works efficiently. The efficiency of the system, however, varies with the wind speed, as it is shown in Table 2. Furthermore, it appears that there is a critical wind speed value above which the system is no longer effective.

Table 2: Impact of Stage 2 control on BTX concentrations for different wind conditions

Wind speed (m/s)	Concentrations (µg/m3)				Reduction (%) = (1- Co/C)x100	
	Stage 2 control OFF		Stage 2 control ON			
	Benzene	BTX	Benzene	BTX	Benzene	BTX
3.5	3.6	13	2.56	13.1	29	0
3.3	4	13.8	2.6	13.4	35	3
2	8.06 *	22.1 *	3.5	17.2	56	22

* extrapolated value

While vapour recovery is taking place, benzene reduction is generally higher than total BTX reduction, possibly due to the higher volatility of benzene. Nevertheless, it should be remembered that measurements are not only affected by evaporative emissions, but also by combustion releases from vehicles using the station.

3.3 Road traffic contribution

CALINE4 was used to estimate the possible contribution from road traffic (RN 10) to the BTX levels occurring at the level II sampling locations. The meteorological input parameters were: wind speed = 2.5 m/s, ambient temperature = 7°C. The model was run for the most unfavourable wind conditions (i.e. worst case mode). CO emission factors were taken from the literature [11] and were adapted to the site specific car fleet composition before being introduced into the model. The outcome of the simulation was used to calculate benzene concentrations by applying an empirically established CO/benzene relationship [14]. This approach was adopted in order to avoid the use of benzene emission factors, which would have introduced a higher uncertainty component in the calculations. The results are presented in Table 3.

Table 3: Road traffic contribution to the CO and benzene levels in the surroundings of the service station (under worst case wind conditions)

Site n°	Wind Dir (deg)	CO (ppm)	Benz. (µg/m3)
1	169	0.4	4.8
2	12	0.4	4.8
3	12	0.4	4.8
4	11	0.4	4.8
5	11	0.4	4.8
9	19	0.2	2.4
10	161	0.2	2.4
11	161	0.2	2.4
12	161	0.2	2.4

As expected, NNE and SSE wind directions represented the worst case meteorological scenario. Under these conditions, winds blowing almost parallel to the road axis accumulate the pollutants emitted along the upwind segments of what can be considered as a linear source (i.e. RN 10). As far as the receptors of level II are concerned, under worst case wind conditions the emissions from RN 10 contribute more strongly than the petrol station itself to the total benzene levels. Finally, comparing the benzene concentrations observed during this study with levels usually occurring in urban environments, it can be concluded that the average benzene concentrations to which pedestrians may be exposed in busy street canyons are generally higher than those occurring in the surroundings (level II) of a Stage 1& 2 implemented service station located in a rural area [14,15].

4 Conclusions

The adopted methodology of using multisite diffusive sampling combined with dispersion modelling allowed a first evaluation of the benefits of Stage 2 control in a motorway service station. This deterministic approach gave reliable results without requiring excessive measurements or calculations. It has been demonstrated that Stage 2 vapour recovery reduces BTX

and especially benzene levels near the fuel pumps and in the surrounding environment of the service station. Consequently, population exposure to these substances is expected to be reduced during the operation of the system. Although vapour recovery reduces VOC emissions due to displacement losses, the effectiveness of the control device is proved to be inversely proportional to the local wind speed.

Fuel spillage losses in a service station should be taken into consideration when evaporative emissions are calculated in personal exposure studies. Under unfavourable wind conditions, the contribution from vehicle traffic in adjacent streets to the pollution levels near the station can be very significant and even higher than the contribution of the station itself. More detailed information of these campaigns can be found on [16]

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