

Air pollution monitoring with two optical remote sensing techniques in Mexico City

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ABSTRACT

An open-path Fourier Transform Infrared (FTIR) and a Differential Optical Absorption Spectrometer (DOAS) were installed and simultaneously operated along a 426 m optical path in downtown Mexico City. O₃ and SO₂ were measured by both optical remote sensing techniques and the results from the comparison are presented. The instruments presented comparable sensitivities for O₃ and an excellent agreement ($R^2 > 0.99$) in their correlation. Although the sensitivity of the infrared technique for SO₂ was limited to concentrations > 20 ppb or so, the agreement of the FTIR response with the more sensitive DOAS technique during the high levels of this pollutant was favorable ($R^2 = 0.94$) and accurate to within experimental error. These episodes (>100 ppb) were found to occur several times per month. Benzene and toluene were measured by the DOAS technique and their concentrations are reported for a 3-month period during 11/2 – 12/5, 2003. The mean and highest concentration registered for benzene was 5.1 and 18.7 ppb, respectively, with an average of daily maxima at 11.5 ppb. Toluene's highest concentration during this period reached 97.3 ppb, with a mean and daily maximum average of 13.4 and 41.7 ppb, respectively. A benzene/toluene ratio of 2.6 was determined for the entire period of study and a decrease of $\sim 20\%$ in the daily ambient concentration of these aromatic hydrocarbons was observed on Sundays relative to weekdays.

Keywords: Optical remote sensing, FTIR, DOAS, air pollution, Mexico City.

1. INTRODUCTION

Optical remote sensors for monitoring air pollutants in urban sites present many advantages over point-sampling analyzers and laboratory determinations from collected samples. Among these is their capability to measure a wide range of gases simultaneously with a single instrument, they operate *in situ* eliminating contamination from sample handling, they provide continuous data in real-time, their calibration is often inherent by the spectroscopic data and through their long paths, they provide more representative values for ambient concentration than the conventional point samplers or monitors.¹⁻⁴

Fourier Transform Infrared (FTIR) and Differential Optical Absorption Spectroscopy (DOAS) are widely used techniques for studying the chemical composition of the atmosphere in an ample range of applications and platforms (i.e. ground, airplanes, satellites). The spectroscopic analysis is based on the characteristic absorptions which the molecules present in the IR and UV electromagnetic regions.

In this contribution, some results are presented from a study in which these two open-path instruments were operated simultaneously in downtown Mexico City during the cold-dry season of 2003. Some results from the open-path FTIR instrument have already been reported for CO, CH₄, acetylene, ethylene, ethane and propane.⁵ Other gases efficiently measured by this method are CO₂, HCHO, N₂O, NO and HN₃. The ammonia concentrations, for example, were found to have a regular diurnal cycle and levels exceeding 35 ppb almost every day.⁶ Here we present a comparison of O₃ and SO₂ acquired simultaneously by the FTIR and DOAS instruments, and report on the ambient concentrations of benzene and toluene during a 3-month period. Formaldehyde, which can also be concurrently measured by both techniques, presents average monthly values of daily maxima which range from 24 ppb in February to 13 ppb in October of 2003.⁷

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The measurements were performed along a 426 m optical path in downtown Mexico City. The transmitting and receiving telescopes were installed on top of two four-story buildings, allowing the beam trajectories to be 20 m or less above the surface. Figure 1 shows a sketch of the site ($19^{\circ}24'N$, $99^{\circ}7'W$) and the optical path of the measurements. The location is 2 km ESE from the main Plaza (Zocalo) of Mexico City and although it is surrounded by some green areas, it presents intense vehicular and commercial activity. The Mexico City International Airport is 3-6 km to the east, an important bus terminal (TAPO) is less than 1 km to the NE and several prominent markets are located west of the measuring site. The monitoring station “Merced”, located approx. 30 m from the west-end of the optical path, is one of more than 30 stations from the local network of atmospheric monitoring (RAMA) where the criteria pollutants and meteorological parameters are being routinely measured.

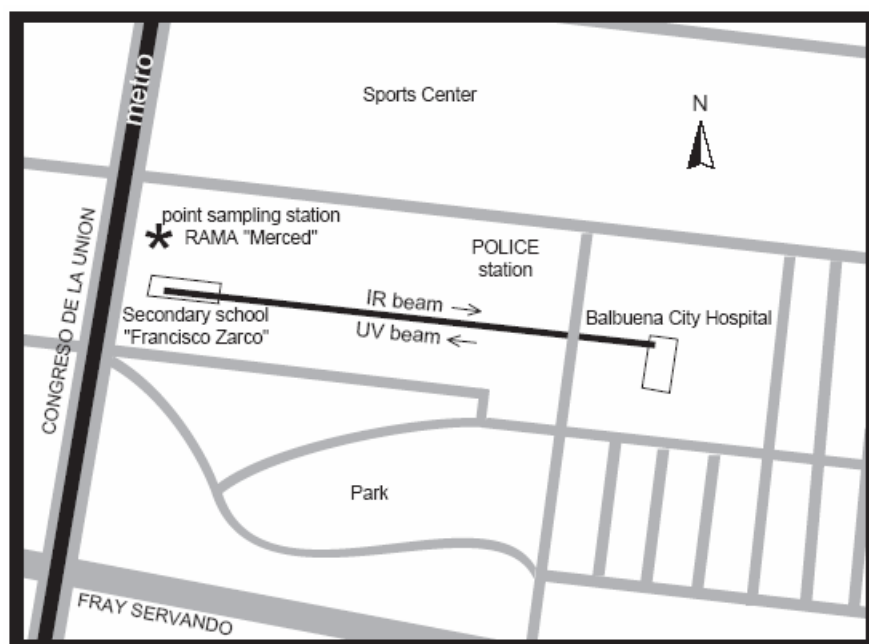


Figure 1. Measurement site in downtown Mexico City showing the 426 m optical trajectories of the open-path FTIR and DOAS instruments.

2. INSTRUMENTATION

Infrared spectra were collected in the 600 to 4000 cm^{-1} range with an open-path FTIR in a bistatic configuration. The spectrometer (Nicolet, Madison WI) was installed at the west-end of the 426 m trajectory and was equipped with an IR source and a ZnSe beamsplitter operating at a unapodized resolution of 0.5 cm^{-1} . A pair of 12" Cassegrain telescopes (polished aluminum) was used to send and receive the modulated beam across the atmosphere. The detector is a HgCdTe cooled at 77 K and connected to the spectrometer via a cable. The optical arrangement was constructed by IMACC (Austin TX) and described more in detail elsewhere.⁵ Concentration retrievals were done by means of a classical least-squares regression and HITRAN generated spectra⁸ as references.

DOAS measurements were simultaneously carried out with a commercial instrument (Opsis, Model AR500) along the same optical path. The collimated UV radiation from a xenon lamp (high pressure, 150 W), located at the east-end of the trajectory, was collected by a Newtonian telescope and sent through an optical fiber to the analyzer. This consists of a Czerny-Turner spectrometer and a refractive grating, which projects the dispersed light into a rotating slotted disc in front of a photomultiplier tube. The instrument was acquired to retrieve ozone, sulfur dioxide, nitrogen dioxide, benzene, toluene, p-xylene and formaldehyde concentrations using the internal evaluation software.⁹

A multipoint calibration was carried out for benzene, toluene and p-xylene prior to the installation of the instrument in the field. This procedure allows the response of the instrument for a specific gas to be calibrated with respect to a gas

sample of known concentration. A calibration curve was created by flowing a reference gas (0.5 l min^{-1}) through three cells of different lengths (14.99, 39.86 and 100.91 mm) and by changing the combination of these within the calibration bench (Opsis CB100, RE060 and CA150). Certified gases (Praxair, Mexico) were acquired at 90.5 ± 4.5 , 200 ± 2.0 and 50 ± 2.5 ppm for benzene, toluene and p-xylene, respectively. These concentrations were tested with the FTIR spectrometer in a multi-pass cell and fell within the errors specified by the provider. The corrections for the 8-point calibration were applied accordingly to the aromatic compounds measured and to all compounds the adjustment for real pressure and temperature conditions was performed.

Prior to the measurements reported here, a background spectrum was stored for every spectral region used in the analysis using the calibration bench mentioned above with no gas cells installed. A wavelength precision test was also successfully carried out using a low-pressure mercury lamp (CA004) and the acquisition times during the field measurements were set to 5 min.

3. RESULTS

1.1. Ozone and Sulfur Dioxide

The ozone time series during two days from both OP-FTIR and DOAS techniques are shown in Figure 2 (left). This plot shows the widely known afternoon-peak of this pollutant from its photochemical production which exceeds the 110 ppb 1-hr standard as maximum-allowed concentration on about 80% of the days.¹⁰ Both techniques present an excellent agreement as appreciated by the reproducibility in the fine structure of the curves and a correlation coefficient of >99%. The minimum detection limit of this gas is 2 ppb or better by either instrument in this particular configuration and optical set-up. FTIR determinations, which are calculated based on a HITRAN generated reference,⁸ present ~15% errors from the regression algorithm around the peaks. The ozone data from the DOAS is thus calibrated with respect to the FTIR according to the fit presented in Figure 2 (right).

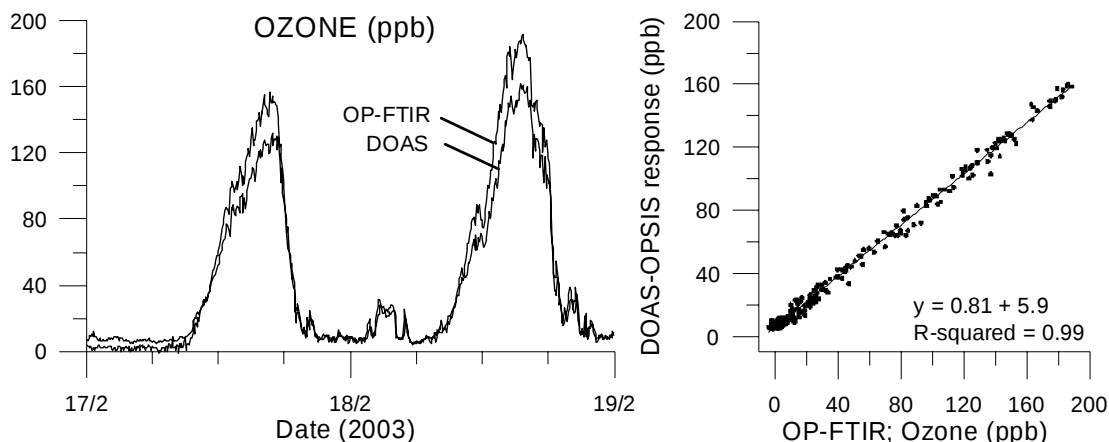


Figure 2. Five-minute concentration data of ozone (ppb) from both open-path FTIR and DOAS instruments during two days in February of 2003. The corresponding correlation plot and linear fit used for the calibration of the DOAS is shown to the right.

Similarly, a comparison between the SO_2 concentrations measured by these two optical remote sensors is presented in Figure 3. During the three-day period shown in the figure, an episode in which the ambient concentration of this gas reached approx. 230 ppb was monitored by both instruments. During the three-month period of this study (12/2/03 – 11/5/03), eight of these episodes with maxima larger than 100 ppb were registered. Since the origin of these events cannot be explained by local sources (traffic, commercial activities, etc.), the frequency in which these appear depends on the emission patterns of specific sources (i.e. industries) and the meteorological conditions.

One can distinguish from Figure 3 (left), that the sensitivity to measure SO_2 is much better with the DOAS than with the open-path FTIR technique. The minimum detection limit for SO_2 is about 2 ppb from the DOAS instrument, whereas

for the FTIR remote system it reaches 20 or 30 ppb with this optical configuration. This can also be observed in the low-concentration regime from the correlation plot in Figure 3 (right). For the higher concentrations, there is good agreement between these two methods and their differences fall within the experimental errors.

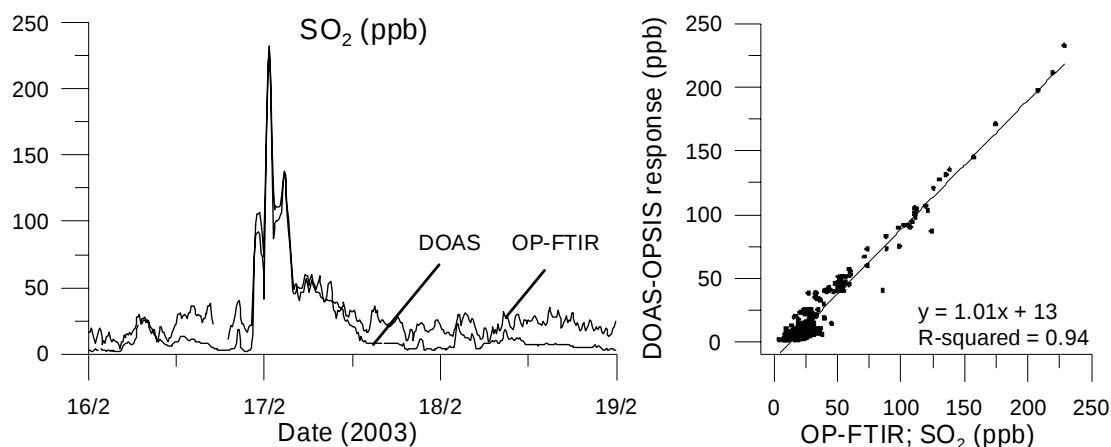


Figure 3. Five-minute concentration data of sulfur dioxide (ppb) from both open-path FTIR and DOAS instruments during three days in February of 2003. The curve with the low noise level in the time series corresponds to the more sensitive determination of SO_2 by the DOAS technique. The DOAS vs. FTIR correlation plot and linear regression for these three days of data are shown to the right.

1.2. Benzene and Toluene

The concentration curves of benzene and toluene for a 3-month period, as measured by the Opsis-DOAS instrument, are presented in Figures 4 and 5. The instrument's response was corrected based on a multipoint calibration performed in the laboratory as described in section 2 and adjusted for real temperature and pressure conditions. No humidity correction was applied. A reference spectrum (background) was measured once prior to the data shown in the figures. The errors reported by the instrument are the standard deviations during the evaluation procedure and ranged between 15 and 30 % from the reported concentrations around the peaks.

The mean concentrations for benzene and toluene during the period of study were 5.1 and 13.4 ppb, respectively. Benzene presented a highest concentration of 18.7 ppb and an average of all the daily maxima at 11.5 ppb. The highest concentration recorded for toluene was 97.3 ppb with 41.7 ppb as the average of all the maxima recorded every day. This information together with an evaluation of weekdays vs. Saturdays and Sundays is summarized in Table 1.

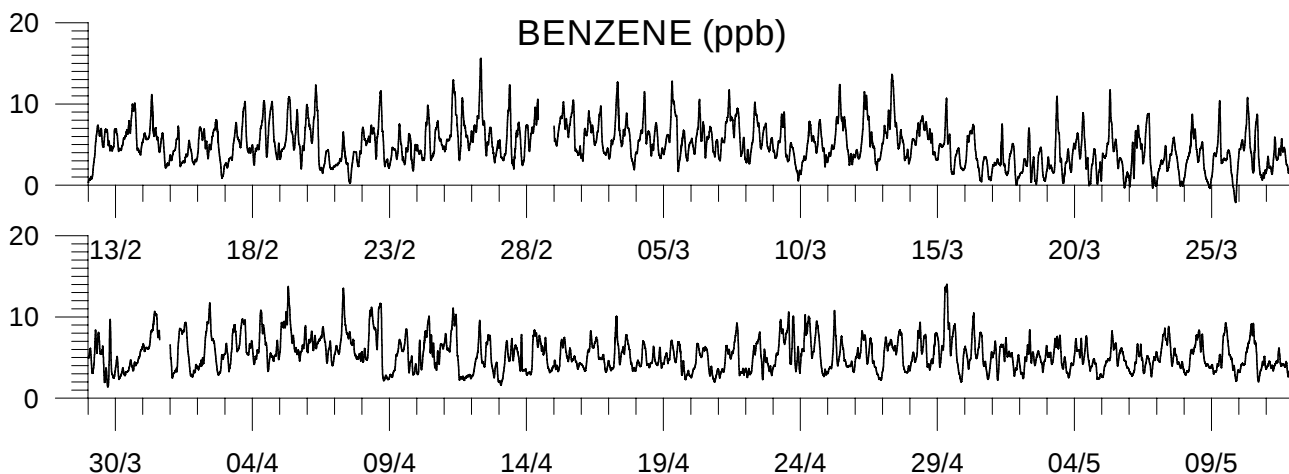


Figure 4. Concentration time series (ppb) of benzene for a 3-month period during February and May, 2003 obtained from the DOAS instrument along a 426 m path.

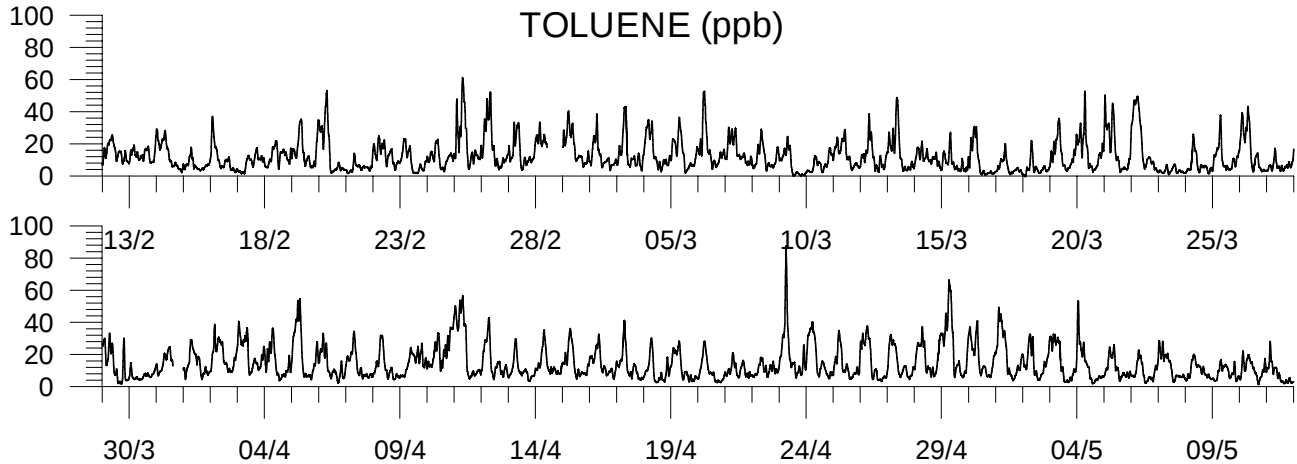


Figure 5. Concentration time series (ppb) of toluene for a 3-month period during February and May, 2003 from the DOAS instrument.

The histograms in Figure 6 present all the data collected for benzene and toluene during the 3-month period categorized by concentration range. Gaussian fits showing their distributions are included in the plots and the results are presented at the bottom of Table 1. The distribution for benzene is better represented by the Gaussian curve than in the case of toluene. This is evidenced by the larger standard deviation in toluene's distribution fit (see table) and the more erratic and less regular peaks presented in its time series (Figure 4). However, when the natural logarithm is applied to the concentration data of toluene (see inset), the gaussian curve centered at 2.31 (10.1 ppb) can fit the observed data better. This can be explained in the following terms: While benzene is known to be strongly related to both on- and off-road mobile sources and therefore presents regular daily patterns, the emissions of toluene to the atmosphere in urban environments are also primarily from vehicular sources but include important contributions from surface coating operations (paint, varnish, etc), solvent use (degreasing and commercial/consumer applications), etc.¹¹

The toluene/benzene ratio from all data during 3-month period was 2.6 as can be seen from the linear regression in Figure 5. This correlation considers only the daily averages during the time of study. However, the same ratio but with a lower correlation coefficient (0.77) results when all the individual 5-min data is included in the analysis.

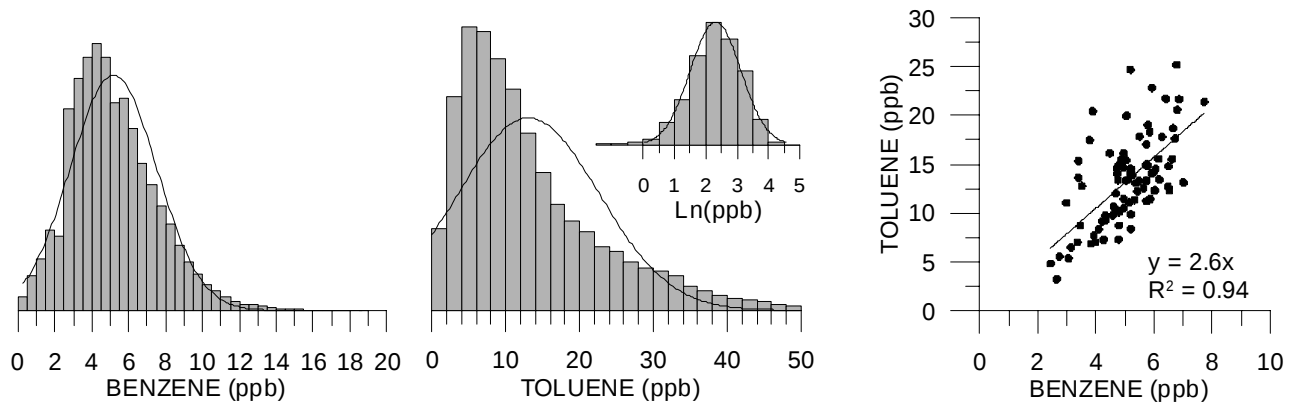


Figure 6. Histograms with Gaussian-distribution fits of all data acquired for benzene and toluene during the 3-month period (12/2/03 – 11/5/03). The correlation plot shown to the right corresponds to the daily average values of these gases during the entire period.

The determination of the other aromatic compound analyzed with the Opsis-DOAS instrument, p-xylene, did not offer a confident result and is thus not included in the present contribution. The concentration curves of p-xylene presented an unusual behavior with unreal correlations which has also been experienced by other groups using the same

instrument.^{12,13} It has been concluded by these previous studies that the problem can most probably be attributed to errors in the evaluation routine of this particular instrument.⁹ This and many other aromatic hydrocarbons, however, have been successfully measured in the field using more adequate evaluations.^{14,15}

Table 1. Summarized results for benzene and toluene monitored during a 3-month period (12/2/03 – 11/5/03) in downtown Mexico City with a DOAS remote sensor.

	BENZENE				TOLUENE			
	Weekday	Saturday	Sunday	Overall	Weekday	Saturday	Sunday	Overall
No. of data points				23635				23589
Maximum value	18.7	15.7	14.6	18.7	97.3	64.9	77.2	97.3
Avg. of daily maxima	12.0	11.5	9.2	11.5	42.9	41.8	35.7	41.7
Mean	5.2	5.2	4.6	5.1	14.0	14.1	9.7	13.4
Median				4.8				10.4
Gaussian distr. Avg.				5.2				13.1
Standard deviation				2.4				9.6

4. CONCLUSIONS

Two optical remote sensing techniques were installed and successfully operated to monitor a wide range of air pollutants in downtown of Mexico City. Ozone and sulfur dioxide were measured by both open-path FTIR and DOAS techniques and the results from the comparison are presented. The instruments showed comparable sensitivities for O₃ and an excellent agreement in their correlation. The infrared technique presented some limitations for detecting low concentrations of SO₂ (<30 ppb). Nevertheless, during an episode of high levels of this pollutant, which occurs a few times per month, the agreement of the FTIR response with the more sensitive DOAS technique was favorable ($R^2 = 0.94$) and accurate to within experimental error.

Benzene and toluene concentrations are reported for the 11/2 – 12/5/2003 period from the Opsis-DOAS instrument and summarized in Table 1. The mean and highest concentration registered for benzene was 5.1 and 18.7 ppb, respectively, with an average of daily maxima at 11.5 ppb. Toluene's highest concentration during the 3-month period reached 97.3 ppb, with a mean and daily maximum average of 13.4 and 41.7 ppb, respectively. A benzene/toluene ratio of 2.6 was determined for the entire period of study. The table also shows that there is a ~20% decrease in the average ambient concentrations of these aromatic hydrocarbons on Sundays relative to the weekdays. Only small reductions in the average ambient concentrations could be observed on Saturdays, indicating that there are no significant changes in the usage of vehicles during this day.

Generally, benzene presented a more regular behavior in its concentration levels while toluene seemed more erratic. This is evidenced by the larger standard deviation found in toluene's Gaussian distribution fit and the sporadic peaks observed in the time series. This is most probably due to that benzene, being closely related to mobile emission sources, remains fairly linked to the regular changes in traffic and wind patterns. Toluene's emissions are also dominated by vehicular activities, but include important sources such as paint applications, degreasing and solvents which affect casually on its ambient levels.

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