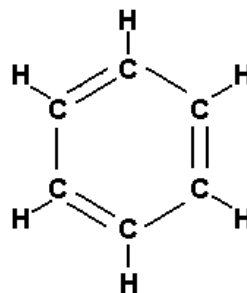Presentation of a research project:

Comparison of measurement methods for benzene in ambient air

U. Wideqvist, M. Hedman, V. Vesely and C. Johansson
ITM Stockholm university
A. Potter, E. Brorström-Lundén and K. Sjöberg
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SLB·analys

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INSTITUTET FÖR TILLÄMPAD MILJÖFORSKNING

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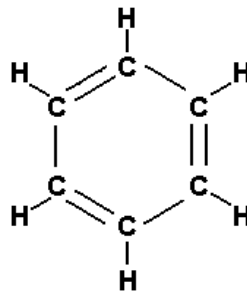**Institute of Applied Environmental Research**

IVL
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Presentation of a research project:

Comparison of measurement methods for benzene

By

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Contents

Summary

Field campaigns have been carried out to examine the uncertainty in the measurements of benzene and other volatile organic compounds (VOC's) in ambient air. Diffusive sampling, an indicative method, and active (pumped) sampling tubes filled with Tenax TA or Carbopack B were compared with an automatic BTX instrument (Chrompack, GC/FID). The measurements were made during differing pollution levels and different weather conditions. The project was financed by the Swedish Environmental Protection Agency and was carried out as a joint co-operation between ITM (Stockholm university), Swedish Environmental Research Institute (IVL) and SLB at the Environment and Health Protection Administration of Stockholm. The measurements and analysis presented in this report have been part of a master of science degree performed at ITM and presented at the Department of Analytical Chemistry (Stockholm university).

In this study we used the BTX instrument as the reference method for comparison with the other methods. Considering all data (66 values) from measurements at roof level (urban background) and in a densely trafficked street canyon the Perkin Elmer diffusive samplers showed about 30% higher benzene values compared to the BTX instrument. There seemed to be larger scatter in the data obtained at the street compared to the roof level. A 95% confidence interval of a linear least squares regression for all diffusive benzene measurements in the concentration range 0.7 to 9 $\mu g/m^3$ is between ±12% to more than ±100% at the lowest levels. For concentrations of 2.5 $\mu g/m^3$ the confidence interval is about ±30% of the mean predicted value and at the 5 $\mu g/m^3$ level the interval is around 15%. Based on a linear regression against the concentrations measured by the BTX, benzene concentrations as obtained using Perkin Elmer tubes for diffusive sampling with Tenax TA ($C_{diffusive}$) and an uptake rate of 0.406 cm^3/min, may be corrected by using the following:

$$C_{corrected} = \frac{C_{diffusive} - 0.53}{1.21} \ \mu g/m^3$$

Where 0.53 is the intercept ($\mu g/m^3$) and 1.21 is the slope. Concentrations are expressed in $\mu g/m^3$ at 1 atm and 20°C.

For toluene there was much better agreement between the two methods and no significant systematic difference was obtained. The mean concentrations and 95% confidence intervals of all toluene measurements (67 values) were 10.80±1.6 $\mu g/m^3$ for diffusive sampling and 11.3±1.6 $\mu g/m^3$ for the BTX instrument, respectively. The overall ratio between the concentrations obtained using diffusive sampling and the BTX instrument was 0.91±0.07 (95% confidence interval). At concentrations of around 3 µg/m3 the 95% confidence interval is about ±40% of the mean predicted value. At 10 µg/m3 the confidence interval is somewhat less than 10% of the predicted value.

Tenax TA was found to be equal to Carbopack B for measuring benzene and toluene in this concentration range, although it has been proposed not to be optimal for benzene. Other studies have shown that shorter sampling times may give higher concentrations due to higher uptake rates in the beginning of the sampling. But in our study this was only indicated at the roof level site where the concentrations were relatively low. According to the data from our study it is possible to sample up to ten days in the concentration range 1 – 10 $\mu g/m^3$. There was a good agreement between the active sampling method and the BTX instrument. The correlation between BTX data and data from both sorbents were high (>0.95) for both benzene and toluene. The slopes were close to one except for benzene on Carbopack, where it was slightly less than one. There was no significant intercept (at p=0.05).

Introduction

The use of diffusive samplers is a cost-effective way to measure atmospheric benzene and other volatile organic compounds. In Sweden, the Perkin Elmer tubes with Tenax TA have been used extensively for many years, for example in the Swedish Urban Air Quality Network (Persson et al 2001, Svanberg et al., 1998). Tenax TA is a suitable sorbent, because the compounds desorb completely when thermal desorption is applied in the analytical procedure. However, it does not retain benzene strongly enough to prevent some re-desorption during sampling under ambient conditions (Mowrer et al., 1996). This is partially compensated for by using a lower uptake rate than the theoretical one.

One of the reason for performing this study was that in a field study in Stockholm significant deviations in benzene concentrations were observed between diffusive sampling with Tenax TA as compared with a BTX monitor (Chrompack, GC/FID). Similar results have been reported in the literature.

An important question is weather Tenax is the most suitable adsorbent for benzene. Current, discussions within the EU may result in a recommendation of using Carbopack B as an adsorbent and therefore sampling with that sorbent was included in this study. In addition, Carbopack B is recommended by the US Environmental Protection Agency.

The measurements presented in this report has been part of a master of science degree performed at ITM and presented at the Department of Analytical Chemistry (Stockholm university) by Malin Hedman. Much of the material presented is based on her work that is published separately (Hedman, 2002).

Objective

The objective of the study was to:
1.   Review the existing knowledge of benzene measurements in the field.
2.   Quantify the accuracy and the agreement between the following sampling techniques for benzene in air in the 1-10 ug/m^3 concentration range
       a) Passive and active sampling on the sorbent Tenax TA.
       b) An automatic BTX-instrument.
3.   Examine differences between currently used methods and if they are constant and reproducible, determine operative factors between the methods.
4.   Quantify the range of measurements and the uncertainties of the methods.
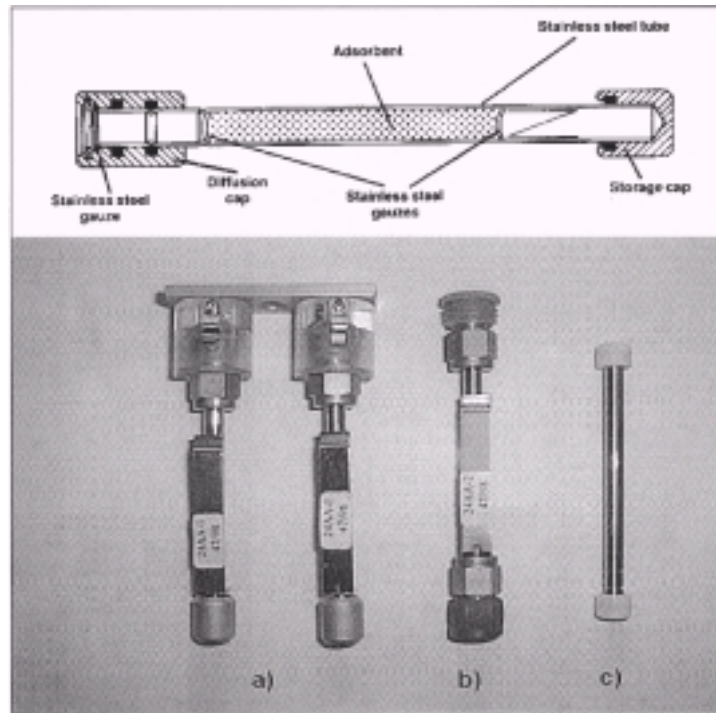
Figure 1. Sampling tubes for diffusive (passive) and pumped (active) monitoring of gases in ambient air. a) Duplicate holder contains 2 sampling tubes with end caps, b) Capped tube for storage and transport, c) sampling tube prior to automatic analysis.

Benzene in air in Sweden – previous investigations

IVL, the Swedish Environmental Research Institute, has performed measurements in urban areas in co-operation with the municipalities since 1992/1993. Mean benzene levels in 10 municipalities for the winter period (October to March) are shown in the Figure 2. The first year is 1992/93 and the last is 2000/01. The benzene levels have declined substantially between 1992/93 and 2000/01 more than a factor of 2, and in all cities irrespective of size, the mean level is around 2 µg/m^3. The measurements represents urban background air, i e not the highest levels in densely trafficked street canyons. In all these measurements diffusion sampling with Tenax as adsorbent (Perkin Elmer tubes) have been utilised (Figure 1).
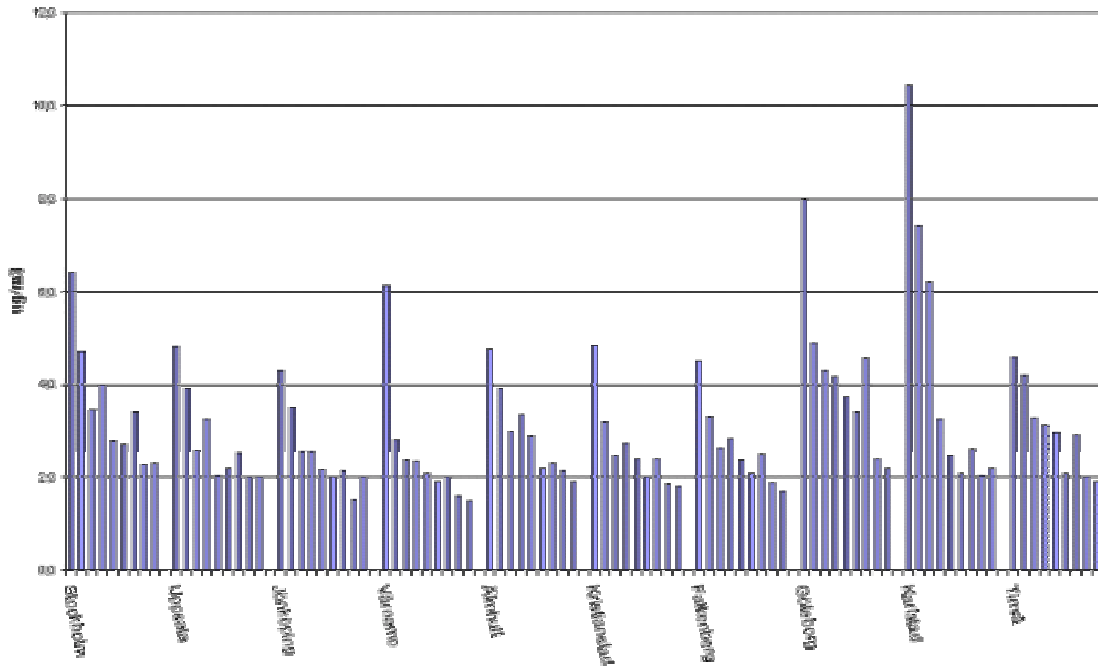
Figure 2. Mean (October – March 1992/93- 2000/01) levels of benzene in urban background air in 10 cities in Sweden (http://www.ivl.se).

Diffusive samplers with Tenax as adsorbent have also been used for measurements in of benzene, toluene and other VOC's in Stockholm since 1994 (Brydolf, 2001). These measurements were taken in a busy street canyon, Hornsgatan, 3 metres above the street. Unfortunately, the measurements have only been carried out during the spring, from April to June. The results from these measurements are shown in see Figure 3.

As can be seen in Figure 3 a systematic decrease of the toluene and xylene levels at Hornsgatan occurs, while the trend in the benzene levels in not quite as obvious, even though the last period (2000) shows the lowest level of all. Note that the benzene level in gasoline was reduced year 2000. Last year 2001, the average benzene level at Hornsgatan during April to December was 3.7 µg/m^3.
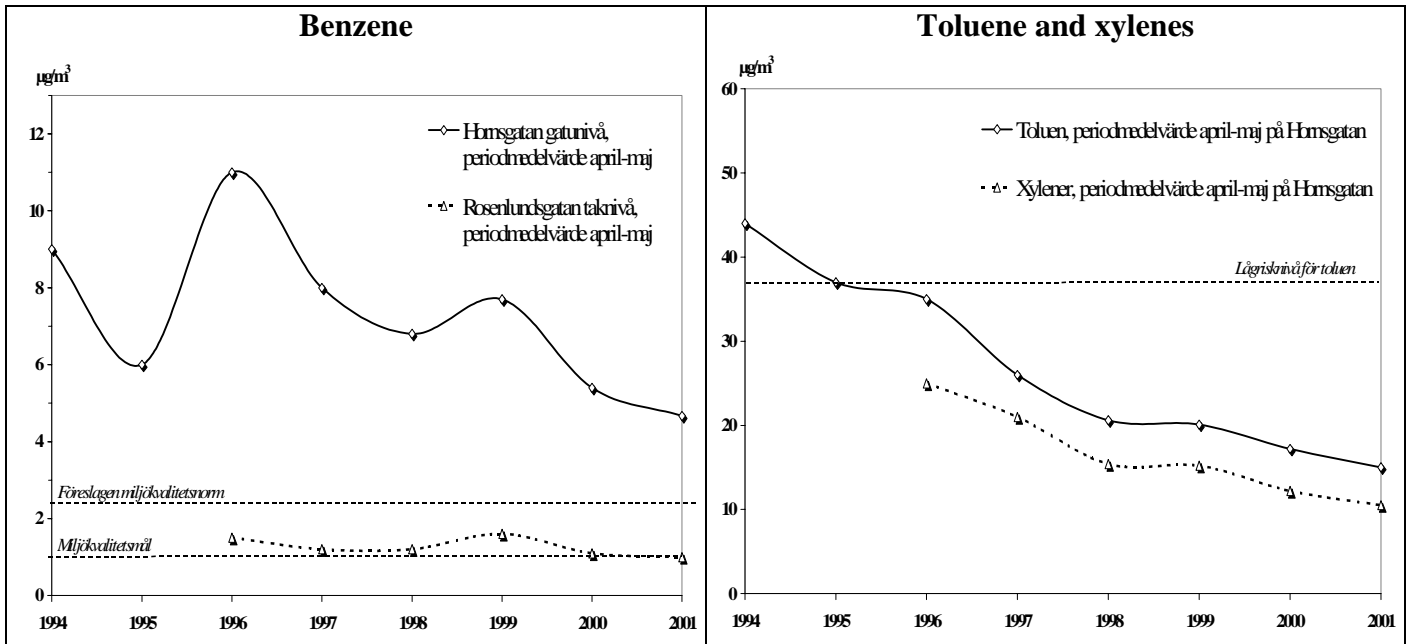
Figure 3. Measurements of benzene, toluene and xylenes in Stockholm April-May 1994 to 2001.

In the Greater Stockholm region there are more detailed measurements on the spatial variation for the year 2000 (Figure 4). Lowest levels are observed in June to August. There is about a factor of 3 higher levels at the most densely trafficked site (Järva Krog) as compared to a recreational area in the outer part of the city of Stockholm (Kanaan). The residential area of Enskede might to some degree be influenced by wood burning emissions but still the levels are similar to the other sites. Solberga is an industrial area and Rosenlundsgatan is a street in the centre of the city. At Rosenlundsgatan the measurements were performed at roof level.
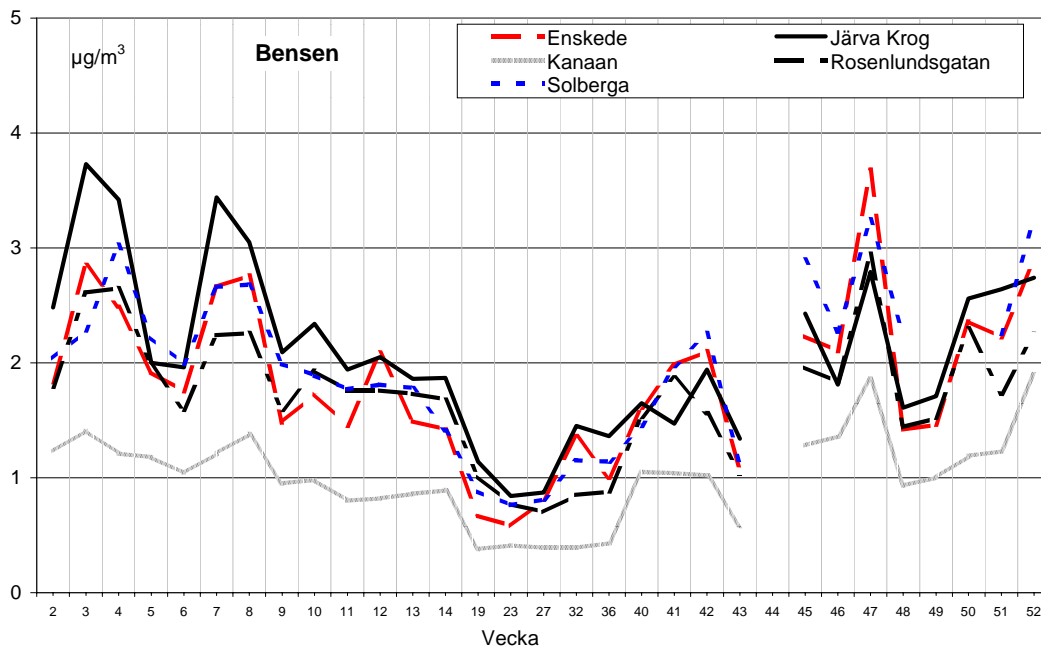

Figure 4. Measured Benzene levels at 5 sites in Stockholm during year 2000. Weekly averages taken using diffusion samplers with Tenax. Note that the weeknumbers on the x-axis is not consecutive. Data from Stockholms and Uppsala Läns Luftvårdsförbund (Luftvårdsförbundet, 1999).

The measurements included not only benzene, but also toluene, m-, o- and p-xylene, ethylbenzene and nonane. It is interesting to note that benzene shows relatively small spatial variation as compared to for example toluene and the xylenes (Figure 5). The quotient between the highest and lowest weekly average of all sites was 5 for benzene and 25 for toluene. That is, whereas benzene shows 5 times higher levels close to traffic sites as compared to background sites, toluene levels were 25 times higher. For m- and p-xylenes the levels were 35 times higher close to traffic. This shows that benzene is relatively inert as compared to the other compounds.

Figure 6 shows the quotient between toluene and benzene at the five sites shown in Figure 4. At the sites closest to traffic, the quotient is around 3 (g toluene per g benzene). In traffic exhaust the quotient has been measured to be around 3.5 (Johansson et al, 1997) and in rural air, far from direct emissions, it is around 0.6. The larger the distance from traffic the lower is the quotient. Other sources than traffic may have other toluene to benzene ratio. In wood combustion the quotient is lower than in traffic exhaust (Johansson et al., 2001a).
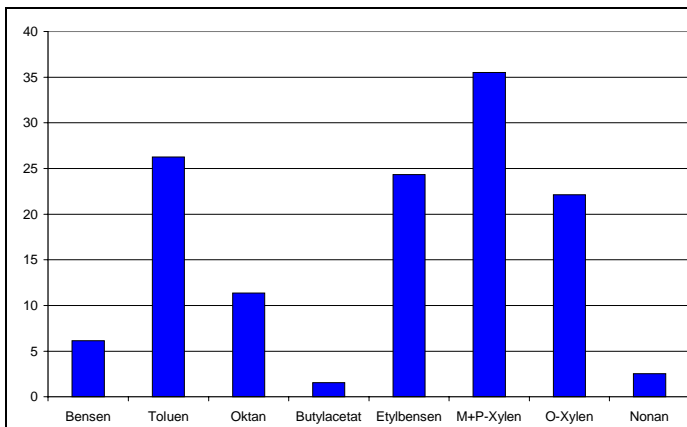

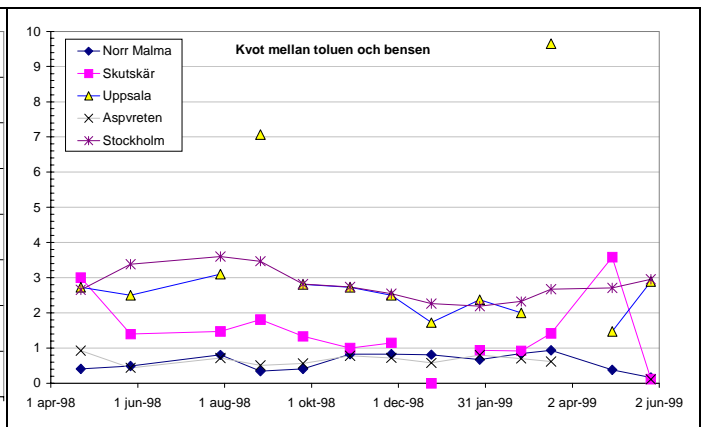Figure 5. Quotient between the highest and lowest levels at the different sites.

Figure 6. Quotient between the toluene and bensen levels at the sites (Unit: g/g).

Source apportionment of benzene — A study in Stockholm

In a study by Johansson and Burman (2001) the contribution of different sources (road traffic, energy production, industrial sources, ferries and background) was estimated for the Greater Stockholm area using a detailed emission database and a meteorological dispersion model.

Table 1 shows the calculated overall average contribution of different local sources to the concentration of benzene in Greater Stockholm area ("local" refers to the sources located within the Greater Stockholm area). According to these calculations the two main sources of benzene are local road traffic (32%) and background benzene (i. e. the sum of all sources outside the study area, 60%). Local residential heating contributes with about 7%, and this is mainly due to fossil fuel oil combustion. Industry, district heating and larger power plants contributes with less than 1% to the total benzene levels.

Table 1. Contribution of different local sources to the concentration of benzene in Greater Stockholm area (Unit: µg/m^3). Emission factors for road traffic were taken from the TCT model, which overestimates the emissions.

Source	Min	Max	Median	Mean	Standard deviation	Percent contribution to total concentration
Residential heating	0.013	1.352	0.115	0.188	0.199	7.1%[1]
Road traffic	0.075	8.373	0.535	0.902	0.966	32%
Industry and small district heating plants	0.001	0.036	0.004	0.004	0.003	0.06%
Energy power plants	0.003	0.032	0.007	0.008	0.004	0.37%
Ferries	0.000	0.005	0.000	0.000	0.001	0.01%
All including background	2.49	11.02	3.08	3.50	1.09	60%[2]

[1] Mean contribution for the area used in the dispersion calculations (Greater Stockholm).
[2] Mean contribution from background (i e from sources situated outside of Greater Stockholm).

The contribution from different source to the benzene level will vary depending on the location. Figure 7 shows calculated contribution from different sources to the total benzene concentration at three different sites located in the Greater Stockholm area. "Rosenlundsgatan" is located in the city centre, "Lidingö" is located in a suburban area east of the city and "Långsjön" is located in a residential area with relatively high density of houses using individual small scale furnaces. The main fuel is fossil fuel oil but there are some houses that partly use wood for heating. Several houses may use wood in small wood stoves or open fireplaces but the emissions from these have not been included in the emission database due to uncertain emission estimates. Note that concentrations refer to roof level, not street.

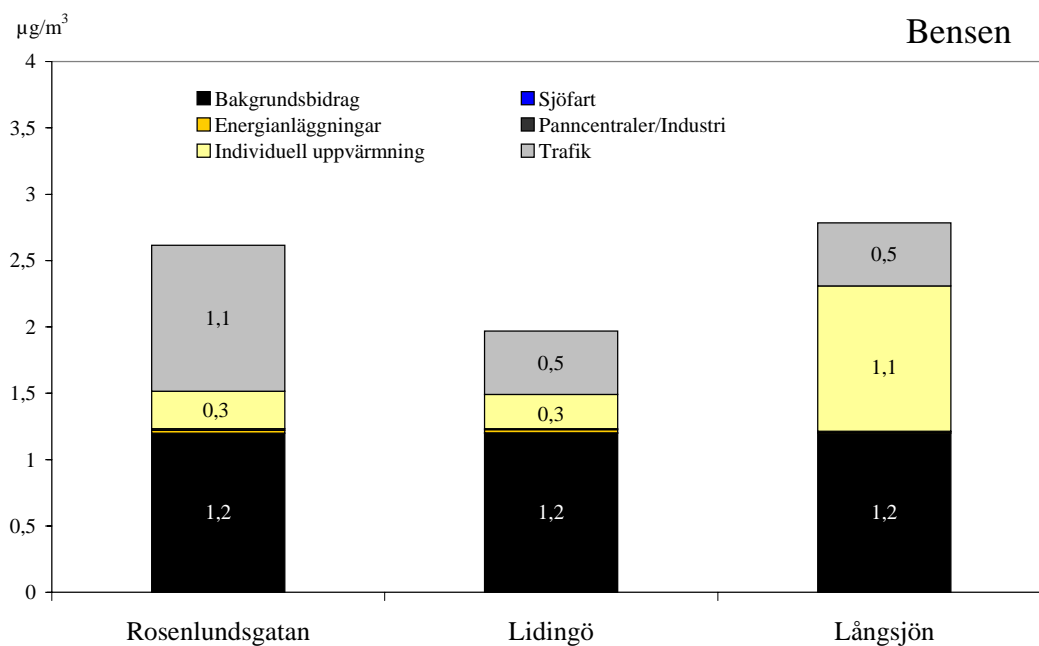Figure 7. Calculated contribution from different sources to the total benzene concentration at 3 sites located in Greater Stockholm. "Rosenlundsgatan" is in the city centre, "Lidingö" is a suburban area east of the city and "Långsjön" is located in a residential area with relatively high density of houses using individual small scale furnaces (mainly fossil fuel oil but also some wood combustion).

In the city centre (at "Rosenlundsgatan") the calculated yearly average is around 2.6 µg/m^3 which agrees well with the measured value. Local road traffic contributes with 1.1 µg/m^3, which is 42% of the total concentration (in this case we have used COPERT and Eva emission factors not the TCT factors which gives 3 times higher values). At the residential area ("Långsjön") the concentration is about the same as in the city centre but here the main sources are combustion of oil and wood (1.2 µg/m3) and background concentration due to sources outside the Greater Stockholm area (1.1 µg/m3). Local road traffic contributes with 0.5 µg/m^3 corresponding to 17% of the total concentration.

The study identified substantial uncertainties in road traffic emission factors for benzene. The TCT model for calculating road traffic emissions for carcinogenic compounds overestimate emissions of benzene. The calculated benzene concentrations due to road traffic emissions at roof level in the centre of the city using the TCT model was 3.3 µg/m3 and the measured <u>total</u> concentration was between 1 and 2.5 µg/m3. Since adding the background concentration to the calculated road traffic contribution gives 4.3 µg/m3 which is almost a factor 2 higher than the measured value.

Another way of obtaining emission factors for benzene is by using the fractions of benzene in VOC emissions according to the COPERT model (Ahlvik et al., 1997). Emission factors for VOC may be obtained from the EVA model of the Swedish National Road and Traffic Administration. This procedure gives a factor of 3 lower emissions compared to the TCT model.

Diffusive sampling — earlier method intercomparisons

Several studies have previously been performed to compare different types of passive (diffusion) samplers and/or diffusion samplers with automatic GC/FID instruments. Hafkenscheid och Mowrer (1996) compared diffusion samplers from 12 different laboratories. Four different adsorbents were used in the study. Five diffusion samplers from each laboratory were exposed in parallel during one week at a background and urban site. The precision obtained for concentrations less than 5 µg/m^3 was about 50%. The accuracy could not be determined since no independent method was employed.

Mowrer et al. (1996) compared three diffusive samples, using of Tenax TA as the adsorbent, with a BTX (GC/FID) at a densely trafficked site in Copenhagen. The samplers were exposed during one week. The benzene levels were around 15 µg/m^3 and the agreement between the Tenax diffusion samplers and the BTX analyser was within 3% (relative standard deviation). The overall mean value of the diffusion samplers was within 2.5% of the BTX instrument.

Recently Skov et al. (2001) presented a comparison between an automatic BTX instrument and adsorbtion tubes both pumped sampling and diffusion sampling using Tenax TA as adsorbent. There was a linear correlation (R^2=0.80) with a slope of 1.20±0.13, i. e. the Tenax sampler gives 20% higher values as compared to the BTX monitor. The intercept (0.45 µg/m^3) is not significantly different from zero at 95% confidence level.
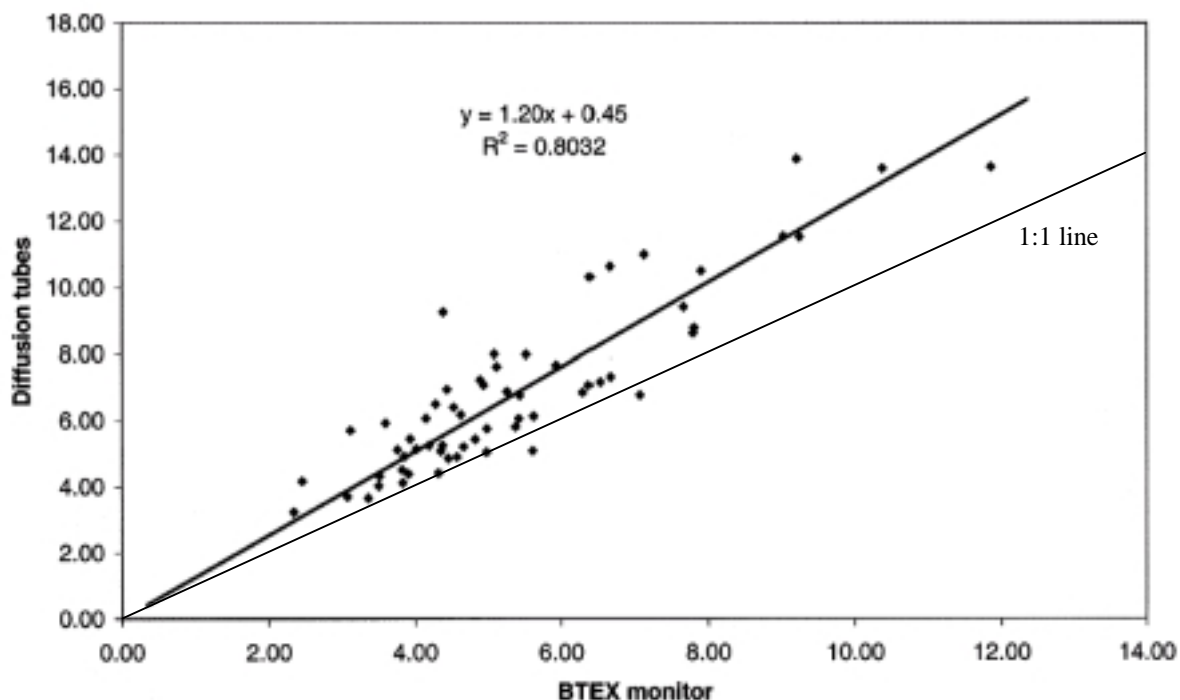
Figure 8. Comparison between benzene measured with a Chrompack BTX monitor and diffusive sampling using Perkin Elmer tubes with Tenax TA cartridge. Units µg/m3 at 1 atm, 295 K (Modified from Skov et al., 2001).

Brown et al. (1999) exposed diffusion samplers with different adsorbents (e. g. Chromosorb 106) at different locations in Great Britain and compared the results with automatic GC/FID measurements. The benzene levels were in the range 1 to 5 µg/m^3. The uptake rate in the diffusion samplers was obtained using an active (pumped) sampling on the same adsorbents. The uncertainty of the measurements, calculated as the sum of systematic and random errors were found to be around 20% for an exposure period of 2 to 3 weeks. For 1-week exposure the uncertainty increased to 30% to 40%. The benzene concentrations from the diffusion samplers were 30% lower compared to the automatic GC/FID.

Ballach et al. (1999) used diffusion samplers with Serdolit® AD-4 (former XAD-4) to study the applicability for cost-effective weekly benzene measurements during varying pollution and meteorological conditions. Their data indicate that neither ambient relative humidity or wind speed affect uptake rates for this sampler. The uptake rates were determined from active sampling using the same samplers. They found a small effect of uptake rate — after 20 days of sampling the uptake rate was 20% lower compared to 1-week sampling.

Roche et al. (1999) studied benzene uptake rates of Perkin Elmer diffusion samplers with Tenax TA as adsorbent. They found a time dependent uptake rate, with an exponential decrease for low exposure doses (<40 ppm min). No relative humidity effect was observed.

In a study carried out in Stockholm four different techniques for measurements of benzene and toluene concentrations in ambient air were intercompared (Johansson et al., 2001b). The measurements were performed at Rosenlundsgatan and Hornsgatan in the city centre of Stockholm. The techniques employed were:

- Automatic Gas-Chromatography with flame ionisation detection (BTX)

- Differential Optical Absorption Spectrometer (DOAS)
- Tenax Diffusive sampler
- Active Charcoal Diffusive sampler

The BTX instrument was taken as the reference method. At benzene concentrations normally encountered in urban background air in Swedish cities (0.5 µg/m^3 to 3 µg/m^3), the diffusion sampler with Tenax showed 60% higher mean values (Figure 9). For toluene the Tenax samplers agreed fairly well with the BTX.
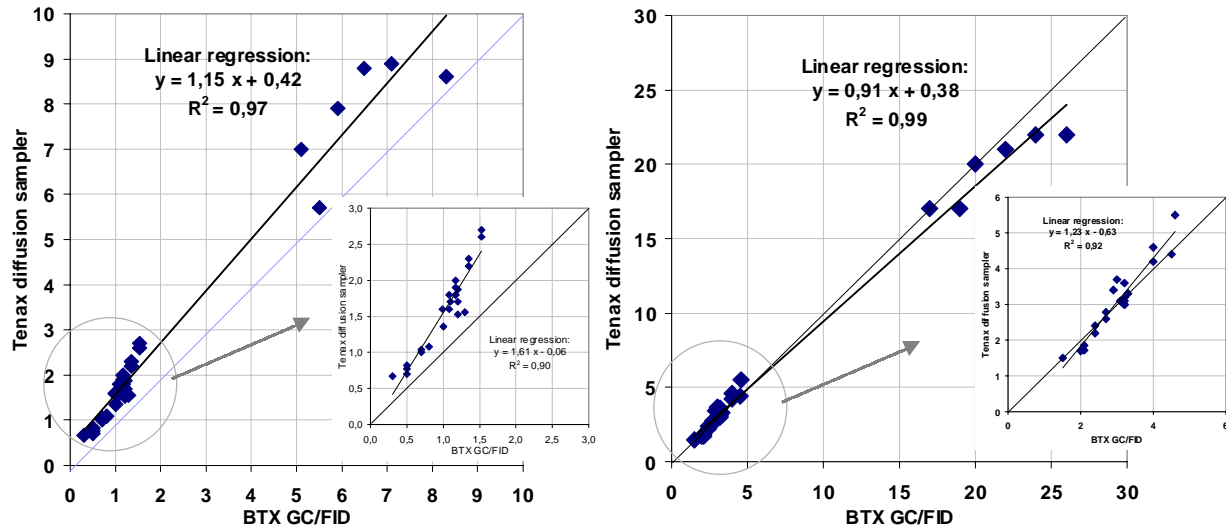

Figure 9. Comparison of benzene (left) and toluene (right) measurements using the Tenax diffusion method and an automatic GC/FID instrument. The values above 5 µg benzene/m^3 and 6 µg toluene/m^3 were obtained at a densely trafficked street location (Hornsgatan) and the lower values were obtained at roof level (Rosenlundsgatan). Units µg/m^3.

The diffusion samplers with Tenax gave 18% higher benzene concentrations compared to the BTX-instrument in a street canyon, where the concentrations ranged from 5 to 10 µg/m^3.

The correlation between the concentrations obtained from BTX and DOAS (roof level) was less than 0.4 and negative concentrations were frequently encountered using the DOAS. For toluene the agreement between DOAS and the BTX analyser was reasonable; the correlation coefficient was 0.7 and the average values agreed within 20%.

Thus, according our knowledge there has only been one comparison between diffusion samplers with Tenax and automatic GC/FID at the low levels normally encountered in urban background air in Sweden, i. e. less than 2 µg/m^3 (which corresponds to the concentrations found in urban background air today Figure 2). Johansson et al. (2001b) found a systematic difference between the BTX, (GC/FID) automatic instrument and the diffusion samplers at benzene levels normally encountered in urban background air in Sweden. It was hypothesised that the problem is related to the uptake rates for the diffusion samplers. As mentioned before, the study by Roche et al. (1999) showed time dependent uptake rates for of Perkin Elmer diffusion samplers with Tenax TA as adsorbent. The uptake rates of benzene may thus, be substantially higher during the beginning of the sampling. This would be particularly important for measurements taken at low concentrations. At higher concentrations (>5 µg/m^3), the results presented in Johansson et al. (2001b) for benzene is quite similar to that reported by Mowrer et al (1996) who also found good agreement between Tenax diffusion samplers and GC/FID measurements. The mean concentration in their study was 15 µg/m^3.

Skov et al. (2001) found fairly good agreement (R^2=0.80) between these two sampling techniques in the range 2-12 µg/m^3, the diffusion samplers giving about 20 % higher concentrations. They also found better agreement between the BTX and pumped sampling through a cartridge filled with Tenax TA and Carbopack B (compared to the BTX and the diffusion samplers).

Experimental

In this study three sampling techniques for benzene measurements were compared, one automatic, semi-continous BTX instrument and two based on trapping benzene on a sorbent. The two last were used both with active pumping and as passive samplers and with two different sorbents. Sampling was performed at two stations in the city centre of Stockholm, at the roof of the SLB building at Rosenlundsgatan and at street level at Hornsgatan, representing urban background and heavy traffic respectively. The BTX-instrument was placed at Hornsgatan. Two 10 day sampling campaigns were performed, one in September and the other in December. In addition, a shorter campaign was carried out at Hornsgatan, comparing only the active sampling with the BTX instrument.

The experimental design is shown in Table 1 and the instrument set up at Hornsgatan is shown in Figure 10. The samples were analysed for benzene, toluene, ethylbenzene, o-, m- and p-Xylene (BTEX-compounds). The passive samples were also analysed for octane and the active for 1,3,5-trimethyl-benzene, 1,2,4-trimethyl-benzene, 1,2,3-trimethylbenzene, naphthalene, 2-methylnaphthalene and 1-methylnaphthalene, but these results are not discussed in this report.

In the results presented below we have also included the diffusion sample data from the earlier study in Stockholm (Johansson et al., 2001b).

All mass concentration data have been calculated for 1 atm and 20 ^{o}C.

Table 2. Campaigns, sampling stations and instrumentation.

	Period 1	**Period 2**	**Period 3**
Sampling station	14-24 September 2001	6-9 November 2001	31 Nov - 10 Dec 2001
Hornsgatan, street level	BTX, Passive Tenax, Passive Carbopack Active Tenax, Active Carbopack	BTX Active Tenax Active Carbopack	BTX, Passive Tenax, Passive Carbopack Active Tenax, Active Carbopack
Rosenlundsgatan, roof level	Passive Tenax Passive Carbopack Active Tenax		Passive Tenax Passive Carbopack Active Tenax

Figure 10. Instrumental setup at Hornsgatan.

The BTX instrument

This instrument (Chrompack, CP 7001), run by SLB is a combined sampling and analytical system. Air is pumped through a cold trap filled with a sorbent (Tenax GR) to trap (VOCs). The trap is then heated and the VOCs are transferred by helium gas to a gas chromatograph with a flame ionization detector (FID) for analysis. The time resolution is one hour. The system was calibrated with certified gas mixtures (National Physical Laboratory, England)

Diffusive sampling on adsorbent

A cartridge filled with a sorbent and applied with a diffusion cap (Figure 1) is used and the up-take mechanism is mainly molecular diffusion. Two different sorbents were compared, Tenax TA and Carbopack B. Triplicate samples were collected with Tenax cartridges and duplicate samples with Carbopack B cartridges. Unexposed cartridges were set up and used as blank samples to control contamination during sampling and transportation etc. The cartridges were exposed for 3, 4, 7 and 10 days, according to the scheme in Table 2.

Active sampling on adsorbent

Air was pumped through the cartridges filled with Tenax TA or Carbopack B. An automatic carousel changed the cartridge every twelve hour. Tenax TA samples were collected at both stations and Carbopack B samples at Hornsgatan. Duplicate Carbopack B samples were collected during a few occasions and this sorbent was also checked for breakthrough by pumping air through two cartridges in series. Non-pumped cartridges were set up and used as blank samples.

Table 3. Diffusive sampling periods conducted during period 1 and 3 at the different stations.

Hornsgatan

Carbopack™

Period 1.

10 days		
7 days		3 days
4 days	3 days	

Period 3.

10 days	
7 days	
4 days	

Tenax TA

Period 1.

10 days	
7 days	
4 days	3 days

Period 3.

10 days		
7 days		3 days
4 days	3 days	

Rosenlundsgatan

Carbopack™ B

Period 1.

10 days	
7 days	
4 days	3 days

Period 3.

10 days	
7 days	
4 days	

Tenax TA

Period 1.

10 days	
7 days	
4 days	3 days

Period 3.

10 days		
7 days		3 days
4 days	3 days	

Analysis sorbent samples

The analyses of the passive samples were performed by IVL (and the active samples were analysed by ITM. The cartridges were desorbed thermally in an ATD 400-instrument (Perkin Elmer) at 250-350°C. Then VOCs were transferred to a cold-trap by helium gas, which in turn was heated and the VOCs further transferred to a gas chromatograph equipped with a mass spectrometer (in the case of ITM) or a flame ionization detector (in the case of IVL)

The IVL system was calibrated with cartridges to which a certified reference gas had been applied (Netherlands Meetinstitut, NMI). Up-take rates applied for benzene were 0.406 cm^3/min and 0.626 cm^3/min for Tenax and Carbopack, respectively. The uptake rate used for Tenax is recommended from the manufacturer, Perkin Elmer.

At ITM methanol solutions of different concentrations of the reference compounds were injected into the cartridges in a stream of nitrogen and they were used to calibrate the instrument. ITM cartridges were also pumped with the certified gas mixture used by SLB to compare the calibration procedures. The two methods for calibrating the analytical instruments (reference gas mixture and reference solutions) deviated. When a solution was injected into sorbent cartridges, about 30 % of the compounds were lost compared to cartridges prepared with the gas mixture. The comparison was performed only for one calibration point but here we have assumed it to be valid over the whole concentration range of interest. All results have been normalised to gas mixture reference.

Breakthrough was tested for the two sorbents in the laboratory by pumping the reference gas mixture through two cartridges in series. The amounts of BTEX compounds applied were 25-60 ng. Tenax TA had a breakthrough of 3 % of benzene and 8 % of toluene through the first

cartridge. The Carbopack cartridge showed no breakthrough. During field sampling, however a breakthrough of 7 % benzene and 3 % of toluene was observed for the Carbopack cartridges. Breakthrough on Tenax was not determined under ambient conditions in this study, but as this sorbent is weaker than Carbopack, a breakthrough of 15 % benzene and 7 % toluene was assumed. Data presented here have been corrected according to this assumption, but this need to be verified in a future study.

Blank concentration of benzene constituted < 5% of sample concentration on actively sampled Carbopack B cartridges. Corresponding blank values were 1-7% and 4-10 % of active Tenax TA samples collected at Hornsgatan and Rosenlundsgatan respectively. The higher percentage level for Rosenlundsgatan was due to the lower air concentration at that station.

Blank levels for passive samples were 0.4 ng benzene/sample for Tenax TA and 0.8 ng benzene/sample for Carbopack B. Duplicate and triplicates showed very good agreement with differences <10 % for active Carbopack B samples and passive Tenax TA and Carbopack B samples.

Results and discussion

The results of the sampling and analysis of benzene will be presented and discussed below and compared with some of the other VOC's. Measurements on active Carbopack B from period 1 were excluded, because the analytical parameters were not fully optimised.

Diffusive sampling with Tenax

Benzene

A comparison between benzene measurements using the diffusion samplers (Perkin Elmer tubes with Tenax Cartridge) and the automatic BTX monitor (Chrompack, GC/FID) is presented in Figure 11. This figure contains all available data from both Hornsgatan (obtained during year 2000 and 2001) and Rosenlundsgatan (obtained during 1999, 2000 and 2001). Data from 1999 and 2000 were obtained in the earlier study (Johansson et al., 2001b). Most of the diffusion samplers were exposed for 7 days, but there are also a few data from samplers that had been exposed for 3, 4 and 10 days. The linear regression for all data has a slope of 1.21±0.15 (95% confidence interval) and an offset of 0.53±0.55 µg/m^3 (95% confidence interval). There are thus systematically higher benzene levels as obtained using the diffusion samplers, even though the difference is only 21%. The offset is not significantly different from zero with a 95% confidence interval.

These results compare well with the results presented for Jagtvej in Copenhagen by Skov et al. (2001) (Figure 8). They found a slope of 1.20±0.15 (95% confidence interval) and an intercept of 0.40 µg/m^3. However, their data did not include any levels below 2 µg/m^3, which is commonly observed in urban background in Sweden (see Figure 2).
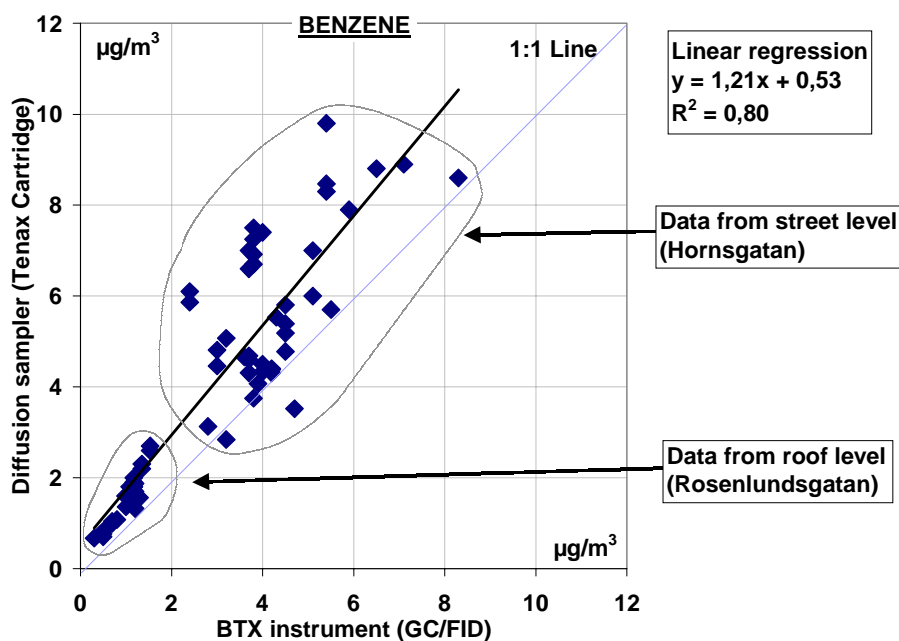
Figure 11. Comparison between benzene measurements using diffusion samplers (Perkin Elmer tubes with Tenax Cartridge) and an automatic BTX monitor (Chrompack, GC/FID). All data from Hornsgatan (street level) and Rosenlundsgatan (roof-top).

As can be seen in Figure 11 there seems to be a larger scatter in the data obtained at the street level site Hornsgatan were the concentrations are higher compared to the roof-top site. Figure 12 shows an enlarged plot with only the data from the roof-top site. The slope of these data is larger than including all data; 1.58±0.28 and the offset is –0.05±0.30. Thus, the slope is much larger for these data compared to if all data is considered.

We have not found any special reason to separate the two data series. Clearly the pollution environment is very different at street level as compared to the roof-top. The amplitude of the temporal variations in concentration of almost all pollutants is much larger at street level compared to roof level.

The concentrations of not only benzene and toluene but also other pollutants emitted in traffic exhaust is much higher at the street, increasing the risk for interference of other compounds in the analysis of benzene and toluene. The diffusion samplers and the BTX instrument employ the same principle of detection; separation on a column followed by flame ionization detection (FID). The FID responds to almost any hydrocarbon with similar response factors, but since both methods use a similar detection one would not expect different behaviour. If the GC columns are different it could explain the different response due interferences on the less specific FID detector.

A 95% confidence interval of the linear least squares regression for <u>all</u> diffusive benzene measurements in the concentration range 0.7 to 9 $\mu g/m^3$ is between ±12% to more than ±100% of the predicted value. For concentrations of 2.5 $\mu g/m^3$ the confidence interval is about ±30% of the mean predicted value and at the 5 $\mu g/m^3$ level the interval is around 15%.
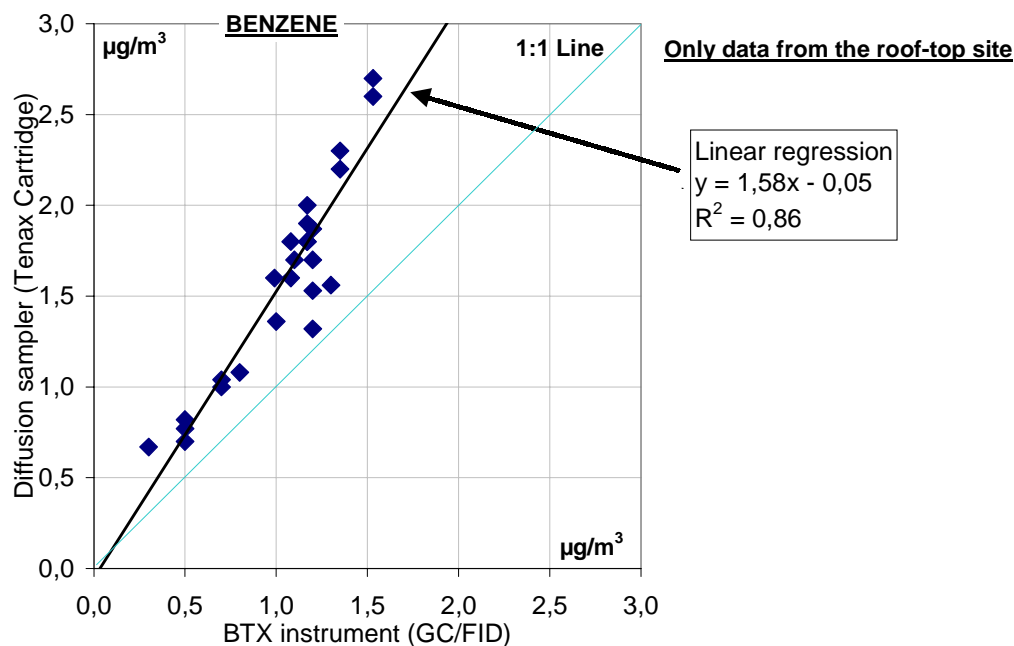
Figure 12. Comparison between benzene measurements using diffusion samplers (Perkin Elmer tubes with Tenax Cartridge) and an automatic BTX monitor (Chrompack, GC/FID). Only data from Rosenlundsgatan (roof-top).

Summary statistics for all diffusive samples taken 1999, 2000 and 2001 and corresponding BTX data for benzene is given in Table 4. The mean and 95% confidence interval for all diffusive samples is 4.22±0.61 µg/m3 and the corresponding value for BTX is 3.13±0.41 µg/m^3. The mean ratio of diffusive samples to BTX is 1.31±0.12. A two sided Students t-test (assuming unequal variances) indicates with more than 99.5% probability that the two data sets does not have the same frequency distribution and does not have the same mean.

Table 4. Summary statistics of all diffusive samples and corresponding BTX data for benzene. Units: µg/m^3.

	Diffusive Tenax	BTX	Ratio Diff/BTX	Difference Diff - BTX
Mean	4.22	3.13	1.31	1.16
Median	4.36	3.70	1.36	0.70
Max	9.80	8.30	2.54	4.40
Min	0.67	0.30	0.00	-1.18
Std dev	2.52	1.80	0.54	1.20
Upper 95% conf Limit	4.83	3.55	1.44	1.45
Lower 95% conf Limit	3.62	2.72	1.19	0.87

Toluene

A comparison between the toluene measurements using the diffusion samplers (Perkin Elmer tubes with Tenax Cartridge) and the automatic BTX monitor (Chrompack, GC/FID) is presented in Figure 13. This figure contains data from the same samples as for benzene presented above. The linear regression for all data has a slope of 0.90±0.07 (95% confidence

interval) and an offset of 0.72±0.87 µg/m³ (95% confidence interval). There is thus no difference between the two methods for toluene.
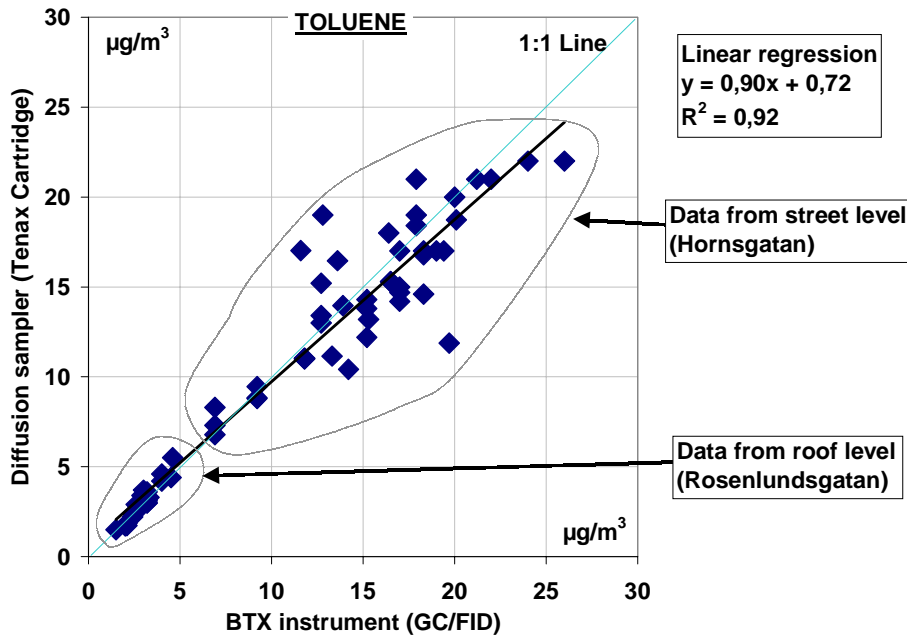

Figure 13. Comparison between toluene measurements using diffusion samplers (Perkin Elmer tubes with Tenax Cartridge) and an automatic BTX monitor (Chrompack, GC/FID). All data from Hornsgatan (street level) and Rosenlundsgatan (roof-top).

Also for toluene there seems to be somewhat larger scatter in the data from the densely trafficked street location as compared to the roof. Figure 14 shows the toluene data from the roof level, plotted with higher resolution. The slope is 1.22±0.18 and the intercept –0.58±0.55 (95% confidence intervals). Thus, for toluene the two methods seems to agree fairly well, especially for the urban background.
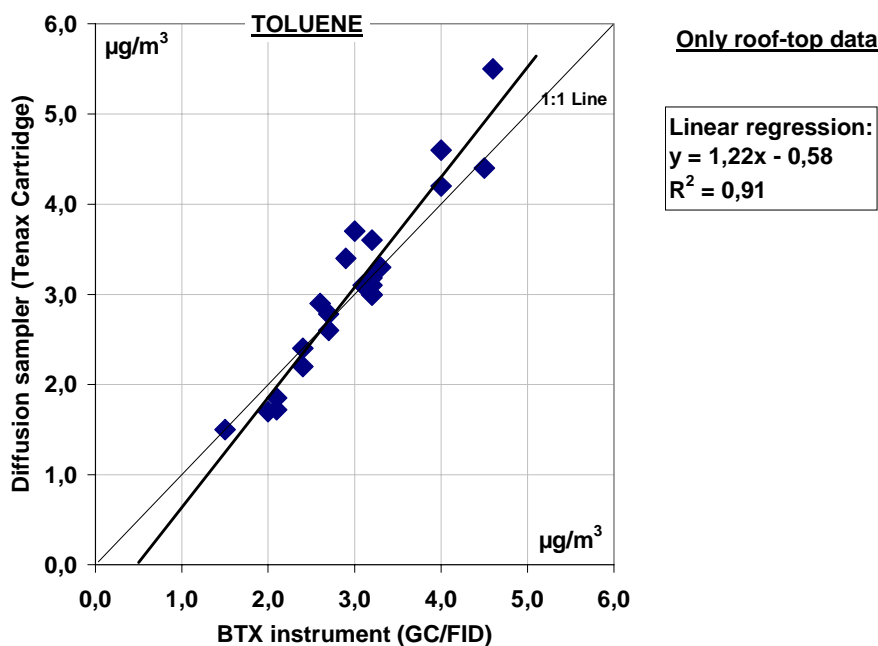
Figure 14. Comparison between toluene measurements using diffusion samplers (Perkin Elmer tubes with Tenax Cartridge) and an automatic BTX monitor (Chrompack, GC/FID). Only data from Rosenlundsgatan (roof-top).

Summary statistics for all diffusive samples and corresponding BTX data of toluene is given in Table 5. The mean values and 95% confidence intervals of all toluene measurements (67 values) were 10.8 ± 1.6 µg/m^3 for diffusive sampling and 11.3 ± 1.6 µg/m^3 for the BTX instrument, respectively. The overall ratio between the concentrations obtained using diffusive sampling and the BTX instrument was 0.91 ± 0.07 (95% confidence interval). At concentrations of around 3 µg/m^3 the 95% confidence interval is about $\pm40\%$ of the mean predicted value. At 10 µg/m^3 the confidence interval is somewhat less than 10% of the predicted value. A two-sided Students t-test (assuming unequal variances) indicates with 65% probability that the two data sets have the same frequency distribution and the same mean value.

Table 5. Summary statistics for all diffusive samples and corresponding BTX data of toluene. Units: µg/m^3.

	Diffusive Tenax	BTX	Ratio Diff/BTX	Difference Diff - BTX
Mean	10.8	11.3	0.91	-0.37
Median	11.2	12.7	0.96	-0.11
Max	22.0	26.0	1.48	6.20
Min	1.50	1.50	0.00	-7.82
Std dev	6.54	6.94	0.31	1.99
Upper 95% conf limit	12.4	12.9	0.98	0.10
Lower 95% conf limit	9.23	9.72	0.84	-0.85

Comparison between Carbopack versus Tenax

The correlation between the two sorbents used for passive sampling was high; 0.89 for benzene and 0.98 for toluene. Figure 15 shows the data obtained for benzene during different periods and at the two sites, roof and street level. The data scatter evenly round the 1-1 line.
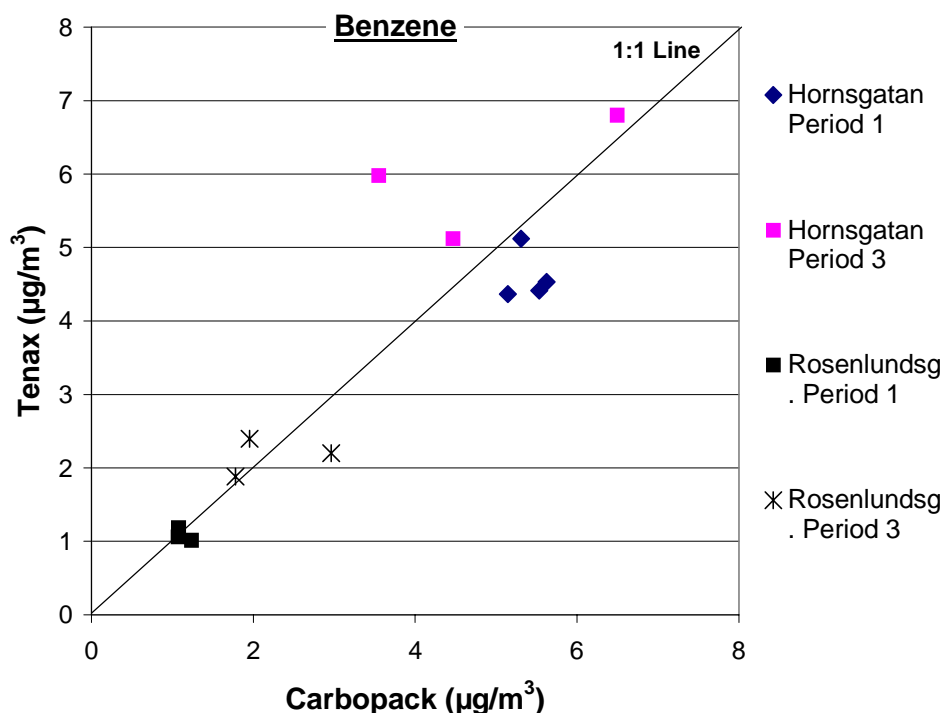

Figure 15. Comparison between benzene concentrations measured using diffusive sampling with Tenax TA and Carbopack B, respectively.

The averages and the 95 % confidence intervals are presented in Table 6. The confidence intervals overlap both for benzene and toluene, indicating that the methods are not significantly different. Tenax TA is thus found to be equal to Carbopack B for measuring benzene and toluene in this concentration range, although it proposed not to be optimal for benzene.

Table 6. Summary of the comparison between diffusive sampling using Tenax and Carbopack for toluene and benzene. Unit: $\mu g/m^3$.

	Tenax		Carbopack	
	Benzene	Toluene	Benzene	Toluene
Average	4.0	9.1	3.7	9.0
Standard dev.	2.5	6.0	2.0	6.2
95 % Confidence interval	0.77	1.8	0.72	2.3
Number of samples	40	43	28	28

Uptake rate as a function of sampling time

The mechanism for passive sampling is mainly based on molecular diffusion and the uptake rate should be constant, independent on sampling time or weather conditions.
It has been shown by Tolnai et al (2001) that the uptake rate of VOC on a sorbent is highest in the beginning of the sampling and then decreases to constant level. They found that the sum of the amount of VOC collected at several shorter sampling occasions was higher than the amount collected at a single longer sampling period. In their case the VOC's were collected on Carbopack during 4-28 days.

We have done a similar experiment and the results are presented below.

Benzene

The 4+3 day samples collected on Carbopack at Hornsgatan during Period 1 had equal amount as the 7-day sample and the 3+4+4 day samples and the 3+7 day samples had somewhat higher amounts than the single 10-day sample (Figure 16). The 3+4 day Tenax samples had 10 % higher amount than the single 7-day sample. At Rosenlundsgatan, where the ambient air concentration is about one fifth of that at Hornsgatan, 15 % higher amounts were found in the 4+3 day Carbopack samples compared to the 7-day sample. For Period 3 the 7-day Tenax sample was 25 % lower than the 4+3 day samples collected at Hornsgatan (Figure 17), but the 4+3+3 day samples had <10 % higher amount than the 10-day sample.

Even though the measurements at roof level seems to indicate that the sum of shorter sampling periods give slightly higher amounts of benzene than a longer sampling period, no clear conclusion can be made based on this study. In the study by Tolnai et al. (2001) much longer sampling periods were tested; up to 28 days were compared with several shorter sampling periods.
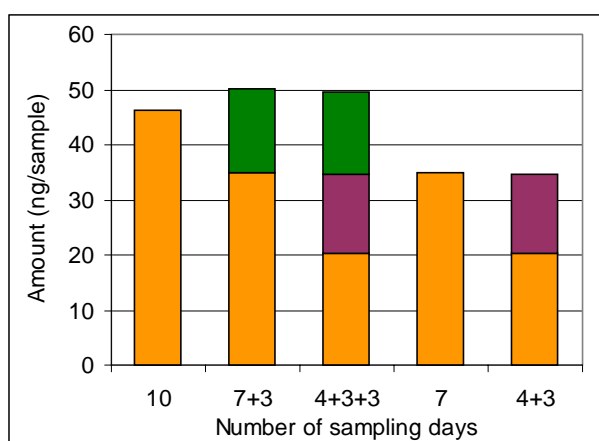

Figure 16. Total amount of benzene adsorbed on Carbopack exposed for different number of days. Samples taken at the street level during 2001.
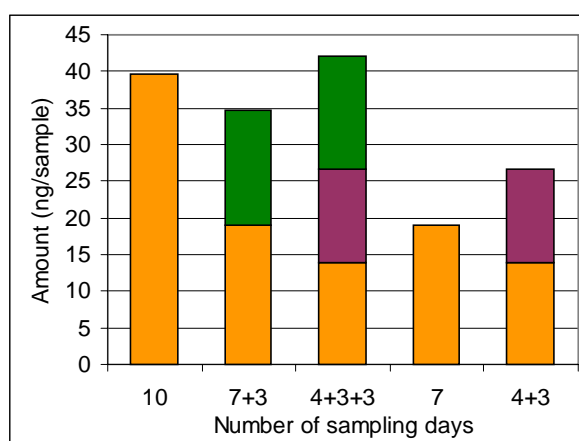
Figure 17. Total amount of benzene adsorbed on Tenax exposed for different number of days. Samples taken at the street level during 2001.

Toluene

Tenax data from Period 3 at Hornsgatan supported the hypothesis that shorter sampling time gives higher uptake, while Carbopack and Tenax data from Period 1 at Hornsgatan showed a mixed result (Figure 18, Figure 19).
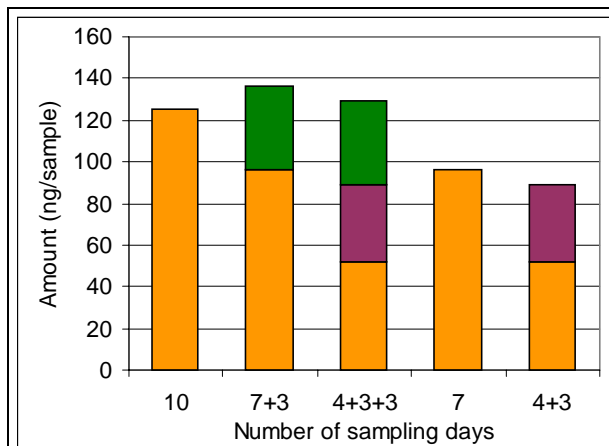

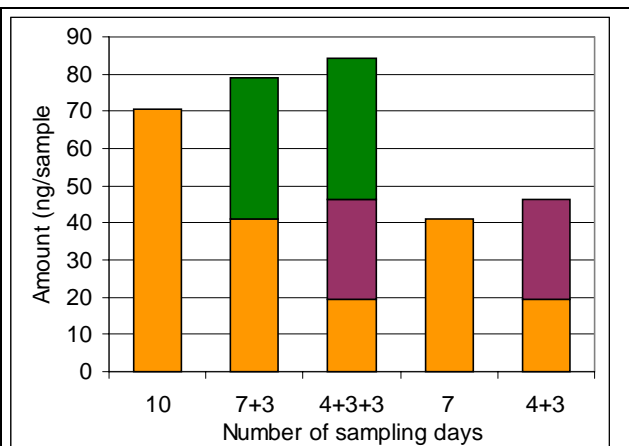| Figure 18. Total amount of toluene adsorbed on Carbopack exposed for different number of days. Samples taken at the street level during 2001. | Figure 19. Total amount of toluene adsorbed on Tenax exposed for different number of days. Samples taken at the street level during 2001. |

The results from this study show that it is possible to use the diffusive sampler up to ten days in the concentration range $1 - 10$ µg/m^3.

Active sampling

Tenax TA versus Carbopack B

A high correlation was found between the concentrations measured using the two sorbents. For benzene the concentration range was 2 to 9 µg/m^3 and the correlation coefficient was 0.99 and for toluene the range was 5 to 40 µg/m^3 and the correlation coefficient was 0.95 (Figure 20).

There was no significant (p=0.05) difference between the two sorbents. The mean concentration of benzene was 6.0 ± 1.4 µg/m^3 using Tenax TA and 5.7 ± 1.4 µg/m^3 using Carbopack B (95% confidence intervals). For toluene the mean values were 22 ± 7 µg/m^3 and 25 ± 7 µg/m^3 using Tenax and Carbopack respectively. But the ratio between toluene and benzene was actually significantly (p=0.05) higher using Carbopack as sorbent compared to Tenax; 3.4 ± 0.4 for Tenax and 4.4 ± 0.4 for Carbopack.

Table 7. Summary statistics for the comparison between simultaneous measurements of benzene and toluene using active sampling with Tenax and Carbopack as sorbents. Units: µg/m^3.

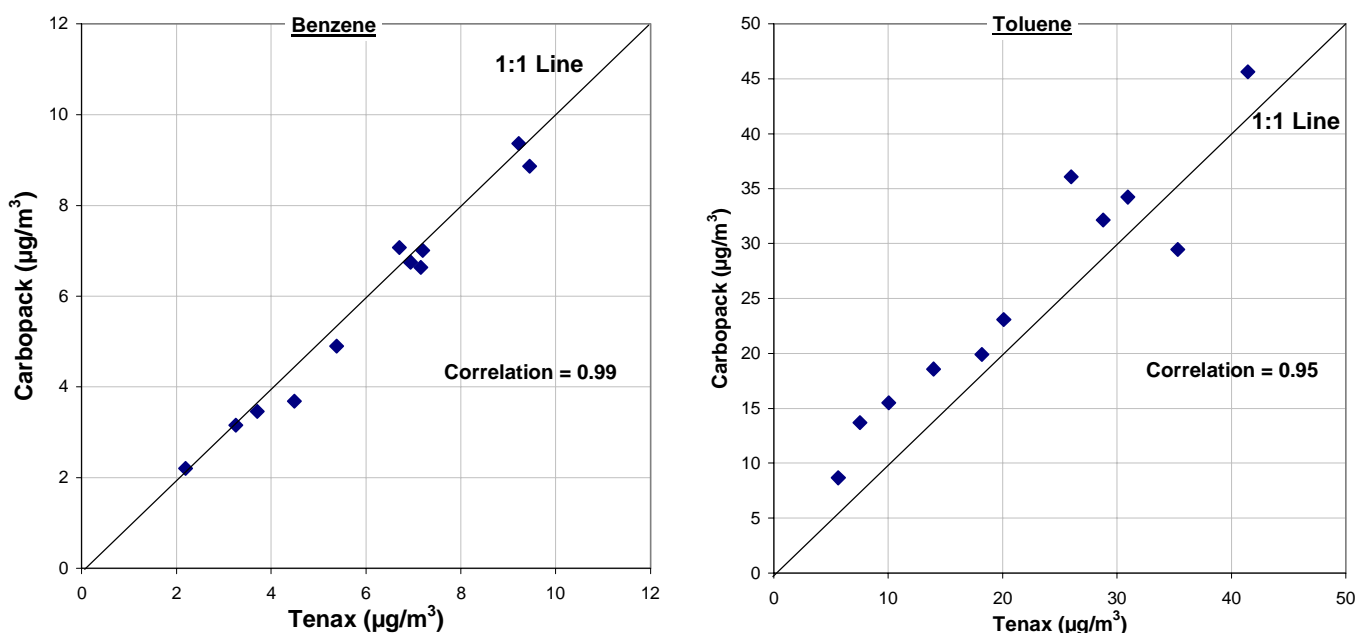|	Tenax TA			Carbopack B		
	Benzene	Toluene	Ratio Tol/Ben	Benzene	Toluene	Ratio Tol/Ben
Mean	6.0	21.6	3.4	5.7	25.2	4.4
Standard deviation	2.4	11.8	0.7	2.4	11.2	0.7
No values	11	11	11	11	11	11
95% confidence interval	1.4	7.0	0.4	1.4	6.6	0.4

Figure 20. Correlation between concentrations of toluene and benzene for sampling on Tenax and Carbopack respectively.

Active sampling versus BTX

The concentrations of benzene using the BTX instrument are plotted against Tenax and Carbopack in Figure 21 and Figure 22, respectively. Correlations between BTX data and data from both sorbents were high (>0.95) for both benzene and toluene. In Table 8 the confidence intervals for the slope and the intercept are shown for both sorbents for benzene and toluene.

The slopes are close to one except for benzene on Carbopack, where it is slightly less than one. None of the intercepts are significantly (p=0.05) different from zero.

Table 8. The confidence intervals for the slope and the intercept of the data plotted in Figure 21 and Figure 22. Slopes and intercepts with their 95% confidence intervals.

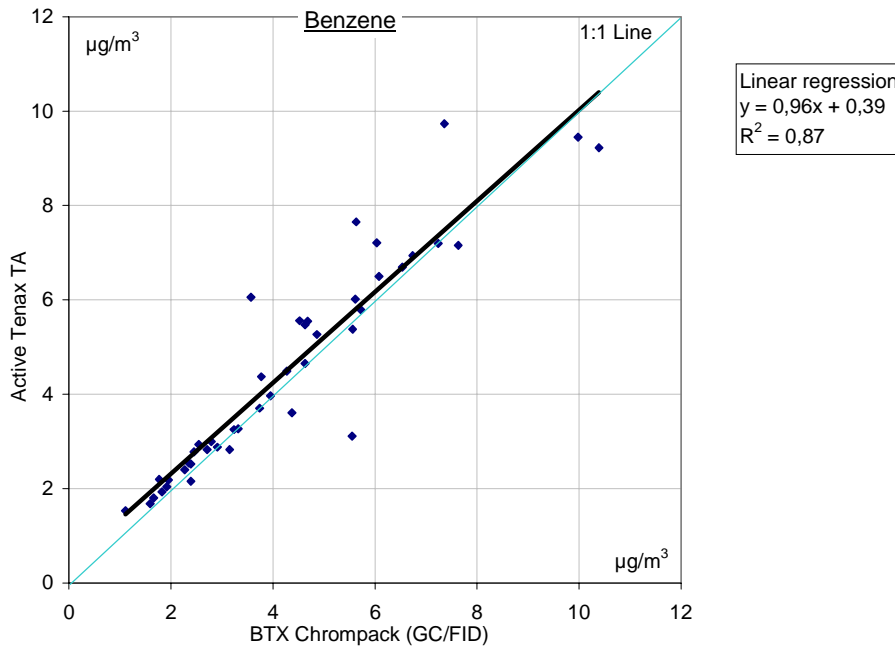|	Tenax TA		Carbopack B	
	Benzene	Toluene	Benzene	Toluene
Slope	0.96 ± 0.11	0.99 ± 0.10	0.84 ± 0.11	0.96 ± 0.16
Intercept, $\mu g/m^3$	0.38 ± 0.54	-0.74 ± 1.9	0.62 ± 0.64	3.2 ± 3.8

Figure 21. Comparison of benzene concentrations at Hornsgatan using active sampling on Tenax TA with the BTX instrument, respectively. The thick solid line is a linear regression.
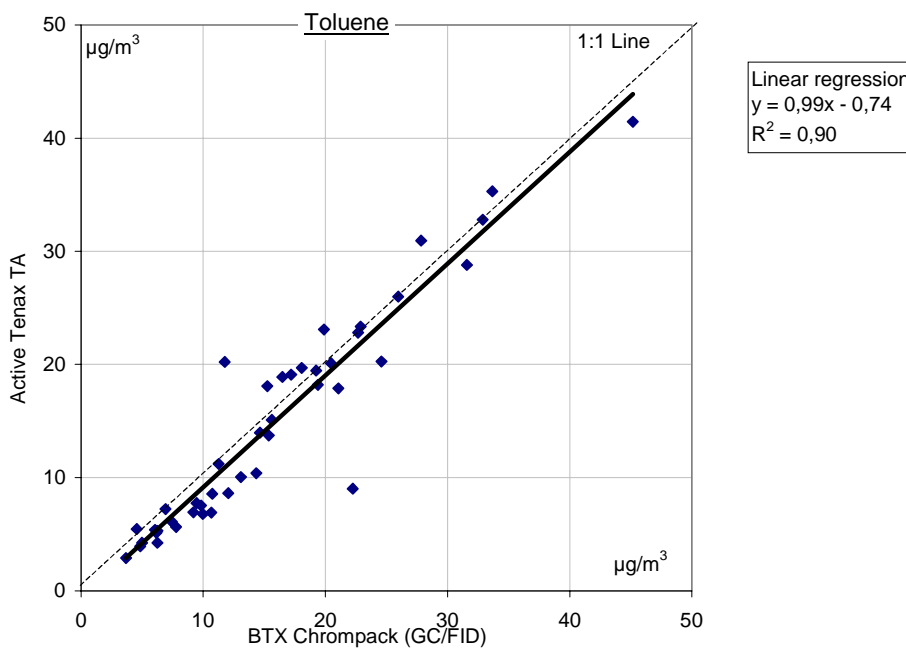

Figure 22. Scatterplot of Carbopack B data for benzene against BTX data. The thick solid line is a linear regression.

Discussion

This study has shown that there are differences between, diffusive samplers, active samplers and BTX-intrument, when measuring benzene. The results confirm earlier results that using the PerkinElmer tubes with Tenax as adsorbent overestimates the benzene concentrations by about 20% compared to BTX.

As the differences between the diffuse samplers and the BTX varied with the benzene concentrations a simple correction of the uptake rate of the diffusion samplers would not correct the error. Larger difference was found at lower concentrations, roof level, compared to higher concentrations, street level.

Important questions that remains to be answered are if the large scatter in the data as obtained at the densely trafficked street location Hornsgatan is due to some interfering compound(s) and if the absolute concentration affects the uptake rate in the diffusion samplers. Some further experiments will be made in Stockholm to examine weather the analytical quantification of benzene using FID (by IVL) differs from using MS (at ITM). But it is clear that before the remaining questions have been fully answered the uncertainty in benzene measurements using Tenax at concentrations less than a few $\mu g/m^3$ is at least 50% (after correcting for the systematic error of 20%).

An alternative to using Tenax for diffusive sampling of benzene would be to use Carbopack, as recommended by for example the US EPA. A few tests in our study using Carbopack B in the Perkin Elmer diffusion tubes indicate similar results as using Tenax TA (i.e. higher levels when compared with the reference instrument). Further studies at low concentrations (few $\mu g/m^3$) using Carbopack B are needed to verify this.

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