

Benzene in eThekweni

Concentrations in air
Monitoring and sampling

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Summary

The South Durban Basin in eThekweni has been troubled by poor air quality for a long time. Through the multi point plan and the engagement and support from the stakeholders the municipality have been able to create an atmosphere of will to improve the air quality in the area and the conditions have become substantially better over the last 10 years.

This report is a part of the abatement and implementation strategy from the eThekweni AQMP on air pollution in the municipality.

Benzene is one of the priority pollutants when assessing impacts on human health. Benzene is carcinogenic and therefore the long-term exposure is important. The long-term exposure is described by the yearly average concentrations. Passive samplers measurements undertaken in the period 2006-2008 show that the maximum measured concentrations in eThekweni are close to $5 \mu\text{g}/\text{m}^3$ of which the normal background concentration is $2-3 \mu\text{g}/\text{m}^3$. The maximum concentration was measured close to a service station. The South-African ambient air quality standard for benzene is set at $10 \mu\text{g}/\text{m}^3$ until 31 December 2014 and thereafter at $5 \mu\text{g}/\text{m}^3$. This means that the concentrations of benzene in eThekweni are below the current South African standard, but at some places concentrations above the standard for 2015 were measured.

To better understand the sources of BTEX and benzene in particular a monitor with a time resolution of 15 minutes was procured. The time resolution that the monitor delivers enables the benzene measurements to be correlated with other measurements and increase the understanding of sources. This report analyses measurements from the month of September 2009 at Settlers School station in the South Durban Basin (SDB).

The conclusions are based on regression analysis between measurements.

The analysis shows that there are several sources of benzene at Settlers School. The background concentration of benzene in the SDB is $2-3 \mu\text{g}/\text{m}^3$. The Engen refinery contributes $2-3 \mu\text{g}/\text{m}^3$ to the benzene hourly mean concentration with wind from Engen towards the station and in this way doubling the impact. The impact from the Engen refinery is from low level diffuse sources not connected to SO_2 emissions. The other source identified is traffic both tailpipe and non tailpipe. The tailpipe benzene emissions impact is associated with PM and NO_x .

More measurements should be included in a future study to give more convincing proof of the conclusions reached here. These measurements should be derived from a longer measurement period at Settlers School and from the newly acquired mobile monitoring station that is also equipped with a BTEX monitor. The recommendation on the future use of the GC monitor is that the monitors should be placed in the other monitoring stations in the network to carry out the same type of analysis and to determine if the sources can be distinguished. The reason for locating the GC monitors at the other stations is to be able to compare the

measurements with other primary pollutants measured here. The instruments should thereafter be moved to specific locations such as large parking lots and gas filling stations, which are considered as benzene hotspots. The other parameters measured in the mobile unit should be measured with the same resolution in time for a better interpretation of the data.

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1 Introduction

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2 Available data

There are several sources of data available for benzene with different averaging times. A survey with passive sampling was conducted between 2006-2008. A BTEX monitor has been in operation at Settlers School close to the Engen refinery since October 2008. The measurements have a time resolution of 15 minutes. The measurements were merged to 1 hour averages for further use. The meteorological measurements are from the Southern Works Station. (Appendix A)

3 Possible sources

Benzene is contained in the petrol sold in South Africa as part of the volatile fraction. The emissions of benzene are mainly dependent on evaporation from petrol, handling/production of petrol, and the tailpipe emissions from cars. There are international discussions on the sources of benzene and on the question of whether benzene can be produced by combustion processes. Possible sources of benzene have been assessed through literature and there are 3 possible main sources of benzene in the SDB. These are:

- Petrochemical refining
- Tail pipe emissions from cars
- Diffuse emissions from motor vehicle fuel tanks, filling stations etc.

The refining operations in the SDB handle large amounts of benzene and it is possible that the refining industry produces large emissions of benzene. This is reflected in the results of benzene monitoring at Settlers School which is close to the Engen refinery.

Cars using petrol will have tailpipe emissions when driving. Benzene that is not combusted or produced in the combustion process by the engine is emitted. These emissions are higher when the engine is cold or if the load is low.

Diffuse emissions occur from the production and transport of petrol. The filling stations are normally hotspots because the gasses that are released while filling the tank of cars are not recovered, but released into the atmosphere. If the filling of storage tanks at service stations is done in the absence of vapor recovering units, this will be a large point source. Benzene is also evaporated from the fuel tanks in cars and it is dependent on the content of volatiles in petrol and the ambient temperature.

4 Interpretation of data

The measurements using passive samplers have been carried out to establish the concentration levels of benzene in eThekweni. The South African ambient air quality standard for benzene is $10 \mu\text{g}/\text{m}^3$ as an annual average, and will be lowered to $5 \mu\text{g}/\text{m}^3$ in 2015. International limits are substantially lower (i.e. $2 \mu\text{g}/\text{m}^3$ as an annual average). The passive measurements show that the $10 \mu\text{g}/\text{m}^3$ level is not exceeded, but for several stations the concentrations are higher than $5 \mu\text{g}/\text{m}^3$, which will be the standard after 2015. To be able to find mitigation measures, it is important to understand the contribution to the concentrations from the different sources. This can, for instance, be done by evaluation of scatter plots and regression analysis of the measured data with other parameters that are measured in the area.

The BTEX monitor has been in operation at Settlers School since October 2008. The analysis done in this report will however be limited to the measurements in September 2009. The time resolution of the measurements used in the analysis is 1 hour.

Figure 1 shows the average concentration with wind direction for September 2009

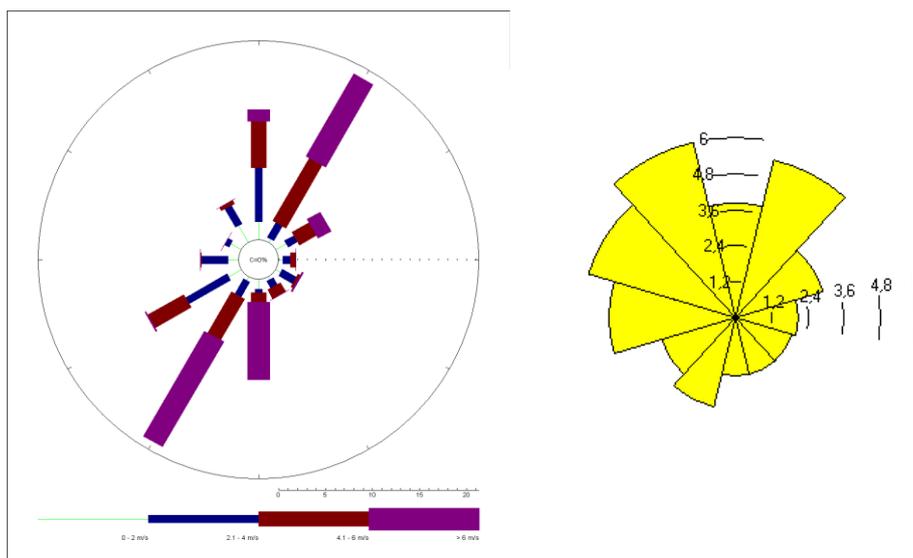


Figure 1: Concentration rose for benzene (right, units $\mu\text{g}/\text{m}^3$) at Settlers School. The wind rose/left, Length in occurrence (%) is from Southern Works for September 2009.

The concentration rose in Figure 1 shows that the highest concentrations come from the west to north east. This is the direction of the Engen refinery, but there are probably additional sources. When reading the graphs it is necessary to take into consideration the short time window that is included in the study.

Figure 2 shows the scatter plot of benzene concentrations and wind directions. It shows that with wind directions from north towards east, there are few low measured concentrations (shown by the red ellipsoids in the graph). From the high measured concentrations with these wind directions (340 through north to 75 degrees) it shows that there is a constant source in this direction. The average concentrations in these directions are approximately $5\text{-}6 \mu\text{g}/\text{m}^3$, while in the other sectors, they are $2\text{-}3 \mu\text{g}/\text{m}^3$. The source that is in this direction (west to north) is the Engen refinery. On average, the refinery contributed to the concentration at Settler School with $2\text{-}3 \mu\text{g}/\text{m}^3$, when the wind was blowing from the refinery for the month of September 2009. The two highest concentrations occurred with winds from the north (i.e. $\approx 25 \mu\text{g}/\text{m}^3$). When analyzing the connections with wind speed and atmospheric stability, it was observed that high concentrations are associated with wind speeds below 5 m/s and with neutral to stable conditions. The two highest concentrations occurred at low wind speed and stable conditions. This indicates that the benzene concentrations originate from low level sources. Figure 2 also indicates that there is a source to the south of the station. This could be the Sapref refinery. The reason for the low average concentration in this sector can be low number of measurements in this sector and that the dispersion conditions were favorable in September 2009.

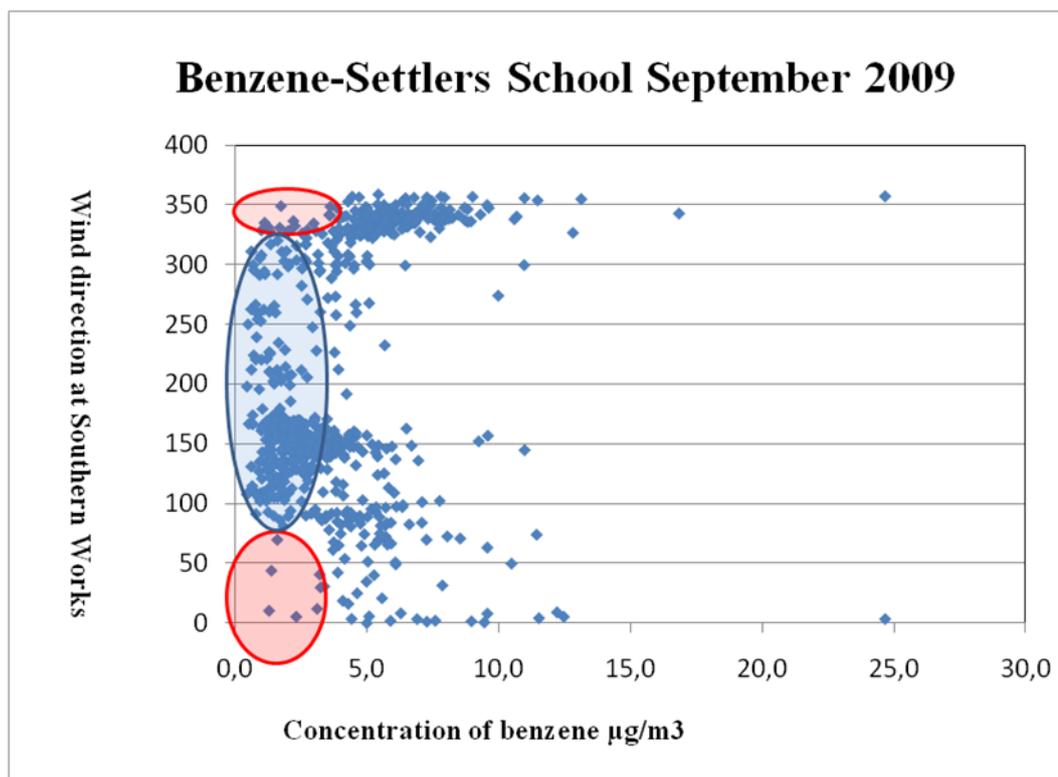


Figure 2: Scatter plot of hourly mean concentration of benzene with wind direction at Settlers School for September 2009. The red ellipsoids mark wind directions where low concentrations are rare and the blue ellipsoids where low concentrations are common.

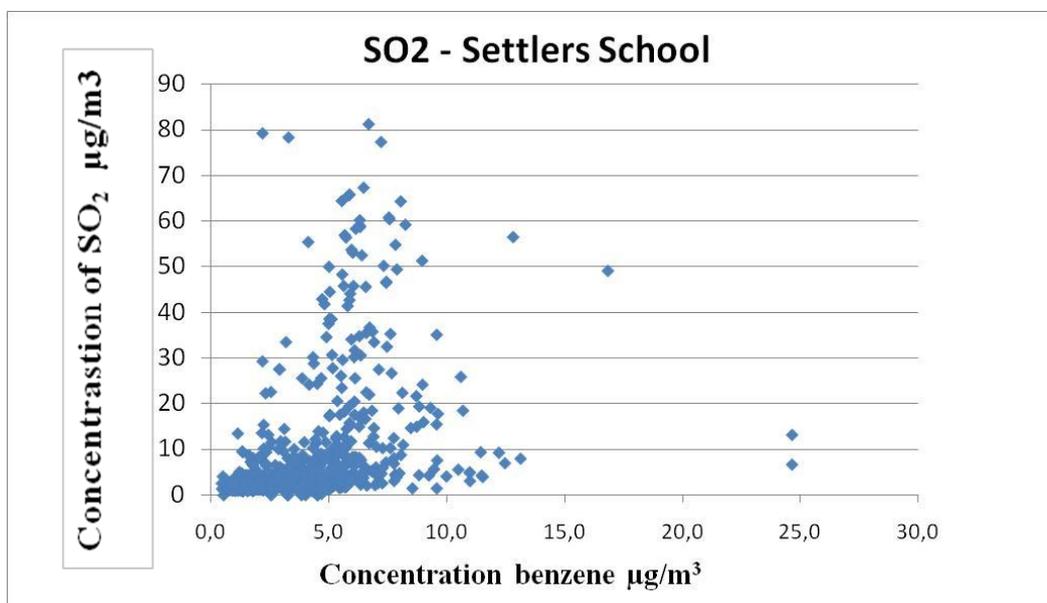


Figure 3: Scatter plot for SO_2 and benzene at Settlers School for September 2009.

Figure 3 shows the scatter plot of SO_2 and benzene at Settlers School. SO_2 concentrations are generally independent of benzene concentrations, and the high SO_2 concentrations are associated with moderate benzene concentrations (e.g. 5-10 $\mu\text{g}/\text{m}^3$). This indicates that there is an average of 2-7 $\mu\text{g}/\text{m}^3$ of benzene in the

concentration range of 20-80 $\mu\text{g}/\text{m}^3$ SO_2 . When the concentrations of SO_2 vary between medium to high (40-80 $\mu\text{g}/\text{m}^3$, when the wind is from Engen to Settlers School) the average concentration of benzene is approximately 5 $\mu\text{g}/\text{m}^3$. This is also independent of the SO_2 concentration seen in the vertical structure in the figure. This indicates that benzene and SO_2 do not come from the same source.

Figure 4 shows the relationships between the NO_x concentrations measured at the Southern Works station and benzene concentrations measured at Settlers School in September 2009. The Southern Works station and the Settlers School station are located close to each other. The plot indicates that there are three sources of benzene; one that is independent of NO_x seen on the data close to the y axis in Figure 4 and the other two of which one has a weak connection to NO_x and the other a stronger connection.

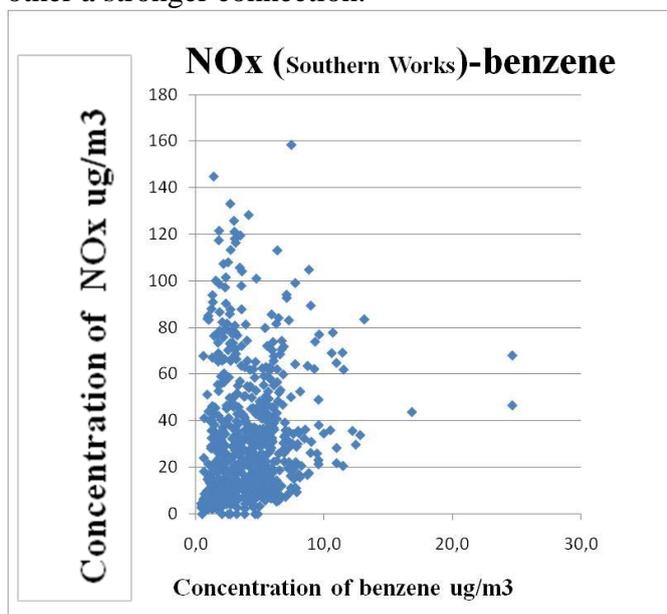


Figure 4: Scatter plot of NO_x concentrations at Southern Works and benzene concentrations at Settlers School in September 2009.

The dependencies of benzene and $\text{PM}_{2.5}$ are shown in Figure 5. The Figure shows the same pattern as for NO_x . The same is seen when PM_{10} from Wentworth is compared to benzene at Settlers School. This indicates that concentrations of benzene and PM_{10} , $\text{PM}_{2.5}$ and NO_x partly come from the same source category of which traffic emissions are a strong candidate. This however is highly influenced by the background influx of pollutants from outside of Durban that needs to be assessed.

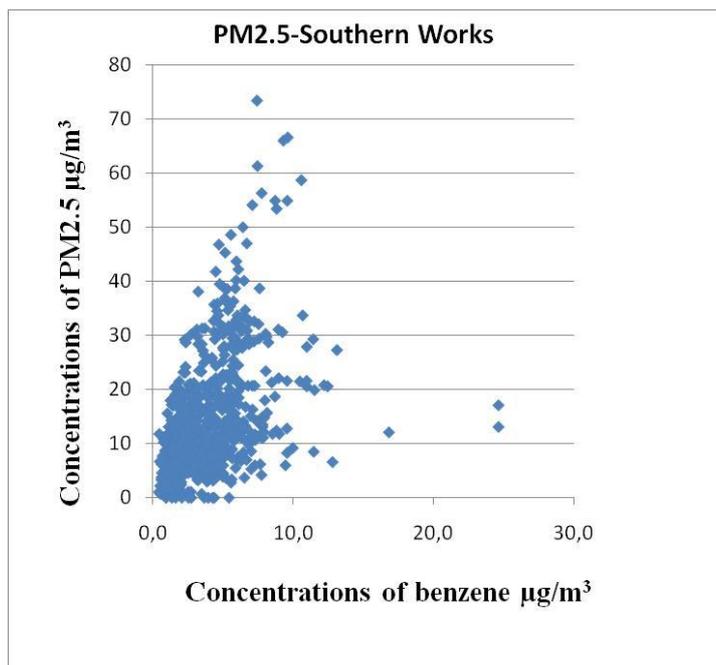


Figure 5: Scatter plot of $PM_{2.5}$ concentrations at Southern Works and benzene at Settlers School for September 2009.

5 Conclusion and way forward

The concentrations of benzene measured in eThekweni show that the proposed limit for 2010-2014 of $10 \mu\text{g}/\text{m}^3$ is not exceeded. The limit will be lowered in 2015 to $5 \mu\text{g}/\text{m}^3$. The highest measured yearly concentration was close to $5 \mu\text{g}/\text{m}^3$. To make sure that the concentration limit in 2015 is not exceeded it is necessary to understand the reasons for the concentrations of benzene, and a mitigation plan must be put in place to ensure compliance.

In order to evaluate benzene concentrations in ambient air a GC analyzer was included in the network to provide 15 minute averages of BTEX. Benzene is one of the components that this instrument analyses. To understand the sources of benzene from the measurements, it is important to obtain a time resolution where the meteorology is considered to be representative for the transport and the dispersion. The normal averaging time is 1 hour.

The measurements at Settlers School show that the wind direction from the Engen refinery towards the station lacks the low concentrations. The averages in these sectors were increased with a $2\text{-}3 \mu\text{g}/\text{m}^3$ which is a doubling in concentrations in these wind directions.

The measurements show that there is a low correlation between SO_2 and benzene concentrations, which indicates that the sources are different. For NO_x and benzene concentrations the analyses indicate that there are both common and independent sources of the two compounds. The same seems to be the case for benzene and PM. This indicates that there are at least two sources of benzene; one correlated with NO_x concentrations and one that is independent. The source that

produced NO_x concentrations but no benzene concentrations, also produce PM concentrations at Settlers School in September 2009.

To further investigate the benzene levels in eThekweni a mobile measurement station is included in the network. This mobile monitoring station should when not in use for other purposes, be located in benzene hot spots such as parking lots, near service stations and road side locations. Similar comparative exercises can then be performed on the different locations and the sources can be evaluated and mapped. The mobile station should sample in the same location for at least 2 months. This knowledge can then be used to assess the different sources and to plan mitigation measures to lower the impact towards 2015 to avoid exceeding the 5 µg/m³ limit in 2015. International practice concerning the levels states that the exposure should be kept as low as possible to avoid effects.

The study indicates that other sources make a more significant contribution to benzene concentrations in eThekweni than the emissions from the refineries. These sources are service stations as reflected in the concentrations measured at the Toti location (i.e. close to a service station) in the passive sampling survey with the maximum benzene concentration. The other major sources of benzene are the evaporation from tanks and tail pipe emissions from cars. This is seen from the different scatter plots and relationships between the priority pollutants. One way to lower the emissions of benzene from storage and use of petrol is to limit the amount of volatiles in the gasoline. This will decrease the concentrations in general in eThekweni, and if nationally implemented, it will improve the air quality in South Africa.

Appendix A

Monitoring of trace levels of benzene in eThekweni municipality –passive and continuous measurements

September 22, 2009

Pollution Control & Risk Management

**MONITORING OF TRACE LEVELS OF BENZENE IN ETHEKWINI
MUNICIPALITY - PASSIVE AND CONTINUOUS**

INTRODUCTION:

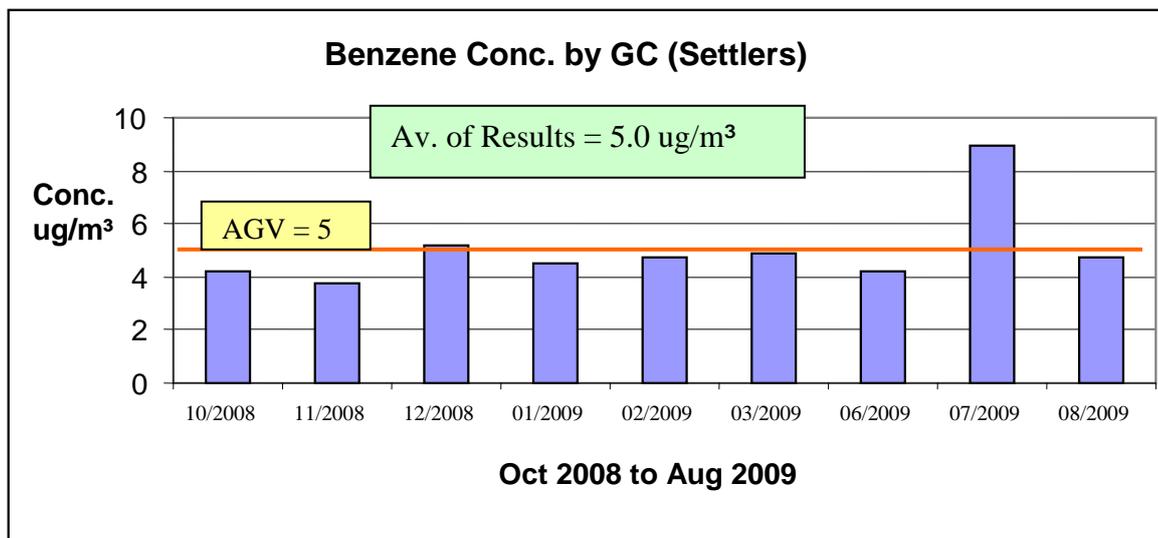
The air quality in Ethekewini is deteriorating due to industrial development and increased traffic densities, both of which are major contributors to rising levels of organic pollutants such as benzene, toluene, xylene, ethylbenzene and PAH's. Consequences of this include an increase in respiratory related illnesses and a degradation of both the quality of life and the environment. Comprehensive and reliable air monitoring data is key to the improvement of air quality, as without this information it is impossible to identify and apportion emission sources as is the case in the Durban South Basin and vehicular hotspots in and around the city.

The promulgation of the National Air Quality Act in 2004 necessitated the enforcement of national standards for permissible ambient concentrations of the organic air pollutant benzene i.e. an annual average of 5 µg/m³.

OVERVIEW OF SAMPLING AND RESULTS:

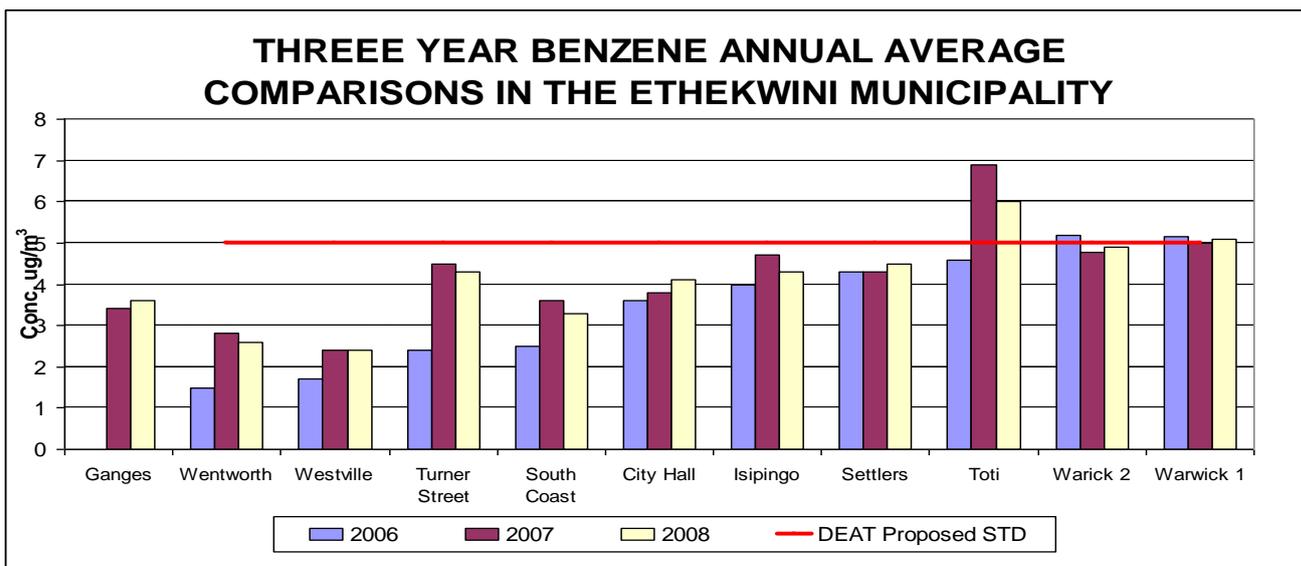
Methods which allow for pre-concentration of analytes are used in order to detect levels in the parts per billion range which are generally lower than emission levels. On-line continuous monitoring is being conducted at Settlers Primary School in the Durban South Basin using gas chromatography. Passive samplers employing organic-adsorbent material are positioned in 10 strategic sites in and around the city where high volumes of traffic and emissions are recorded. Sites being monitored for benzene, on a two-weekly basis, using the passive method are: Warwick Junction, Wentworth, Turner Street, Westville, South Coast, Ganges School, City Hall, Isipingo, Amanzimtoti and Settlers School.

CONTINUOUS MONITORING



PASSIVE MONITORING

Ganges	Wentworth	Westville	Turner Street	South Coast	City Hall	Isipingo	Settler	Toti	Warick 2	Warwick 1
0	1.5	1.7	2.4	2.5	3.6	4	4.3	4.6	5.2	5.1
3.4	2.8	2.4	4.5	3.6	3.8	4.7	4.3	6.9	4.8	5.0
3.6	2.6	2.4	4.3	3.3	4.1	4.3	4.5	6.0	4.9	5.1
	5	5	5	5	5	5	5	5	5	5
	10	10	10	10	10	10	10	10	10	10



WAY FORWARD:

The results obtained border on the maximum of the national limit of $5\mu\text{g}/\text{m}^3$ particularly in areas of high traffic volumes (Warwick and Amanzimtoti) and at Settlers School (Durban South Basin). Further consolidation of these results are necessary with respect to canister sampling and Tedlar bag techniques.



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ABSTRACT The report gives an example on how the continuous monitored data of benzene can be interpreted by the use of the other measured priority pollutants and meteorology. The results show that at the station located close to the refinery, the contribution from the refinery is only half of the total impact when the wind is blowing from the refinery towards the station. The study also indicates that the impact comes from traffic and evaporation from car tanks and filling stations. The report uses measurements from September 2009. The study needs to be expanded both upon longer time periods and geographical distribution.			
NORWEGIAN TITLE Målte konsentrasjoner av benzen.			
KEYWORDS Benzene	Monitors	Interpretation	
ABSTRACT (in Norwegian) Rapporten gir eksempler på hvordan kontinuerlige målinger av benzen med midlingstid en time kan tolkes ved bruk av andre målte forurensninger og meteorologi. Resultatene viser at selv på stasjonen som er mest belastet av benzen, bidrar raffineriet når det blåser fra raffineriet mot stasjonen med halve konsentrasjonen. Studien indikerer også at en hovedkilde er fordampning fra tanker og fylling av tanker (både bil og bensinstasjoner). Rapporten bruker målinger fra september 2009 på en stasjon. Studien trenger å utvides i tid og rom.			

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