INTER METHOD COMPARISONS OF AMBIENT BTEX MEASUREMENTS

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1. INTRODUCTION

Arising from concern about possible impacts of petroleum vapours on the local community in a residential area of the south Durban industrial basin, ECOSERV were employed to develop and implement an air quality monitoring program. Benzene, toluene, ethylbenzene and xylene (BTEX) compounds were selected as the most appropriate indicator pollutants for such vapours. Passive (diffusive) measurements of these compounds therefore commenced at several residential locations to evaluate impacts.

Several inter method and inter laboratory quality assurance strategies were implemented to verify that reported concentrations were acceptable. One of these strategies was an intensive co location program to compare the reported passive sampler derived BTEX concentrations with those recorded using the NIOSH Method 1501 active sampling method. This paper provides an overview of the passive and active sampling methodologies and presents the results from three months of co located measurements. The objective is to quantify differences in concentrations recorded using the two different sampling methodologies.

2. METHODOLOGY

2.1 The Passive sampler

BTEX concentrations in the air can be determined using a cost effective passive (diffusive) sampling methodology that is widely used internationally and in South Africa. This method is used to measure medium to long term trends, mapping average spatial concentration profiles, and evaluating compliance with longer term guideline limits. The principle of gaseous diffusion onto an absorbing medium is used to trap the volatile organic components onto an absorbing medium. Due to the absorbing mechanism relying on natural diffusion, this method cannot be used for measuring short term concentrations such as hourly or daily averages. The sampler therefore needs to be exposed to the air for periods of one to two weeks. A distinct advantage of the passive sampler is that a pump or power supply is not required.

2.2 The Active Sampler

The NIOSH Method 1501 is a method for measuring aromatic hydrocarbons in the air. The principle of sample collection is distinctly different to that of the passive sampler in that the air sample is pumped through a small glass tube packed with a similar absorbing material such as charcoal. Security at the sampling location is an important requirement to minimise the chance of pumps being stolen. Due to the relatively large volume of air drawn through the absorbing material, sampling periods cannot be extended for weekly to two weekly periods because the absorbent would become saturated and organic compounds will eventually pass through without being absorbed. Such over saturation would result in an under estimation of concentrations. This method is therefore applied to shorter sampling durations than the passive sampler and is ideal where hourly or daily average concentrations are required.

2.3 Sample Analyses

Gas chromatography (GC) is used to analyse both passive and active samples. Using this method the sample is desorbed and forced into a long thin heated column packed with a special coating on the inner walls. The different organic compounds in the sample have different affinities for the coating material that means that some compounds pass through very rapidly whereas other compounds are retained for longer periods before being released. This forms the basis of compound separation within the chromatographic column. A small flame located at the end of the column causes electrons to be released as each compound passes through. The electrons are magnified using a photo multiplier tube and millivolt outputs are detected as individual peaks on the chromatogram as each compound exits the column. The size of each sample peak is then compared to the size of each peak recorded for a known standard mixture of organic compounds. Using a calibration factor or curve, the sample components can then be determined.

2.4 Sampling Strategy

Differences between the passive and active sampling methodologies have been described. In order that concentrations derived from these two methods can be compared to one another, concentrations from the same sampling periods must be established. Each pair of samplers must also be co located and be positioned adjacent to each other. Each pair of samplers can still be placed at different locations.

In this study, passive and active sampler pairs were co located simultaneously at five different locations. Due to the different sampling period requirements described for each method, active samplers were exchanged on a daily basis and passive samplers were exchanged every week to ten days. For every average concentration derived from one passive sampler, the corresponding active sampler average for each location was calculated by averaging the seven individual daily average concentrations. The co location review period covered 3 months of measurement data from March 2003 to June 2003 and comprised of approximately 50 passive samples and 400 active samples at five locations.

3. RESULTS

The first plot shows the average correlation for all compounds measured over the entire period under review. Individual co located concentrations are then presented as scatter plots for each compound. The ideal and perfect inter method correlation would show all points lying along the 45 degree line shown on each graph. Where points lie to the left hand side of this line, the active sampler produced a result that was higher than the passive sampler result. Where points lie to the right hand side of this line, the passive sampler produced a result that was higher than the active sampler result.

Figure 4.1 Three month average inter method comparison for all compounds

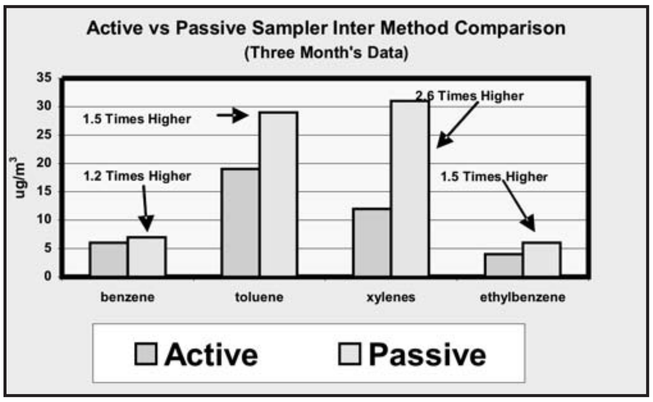


Figure 4.2 Benzene concentrations recorded by the passive and active samplers

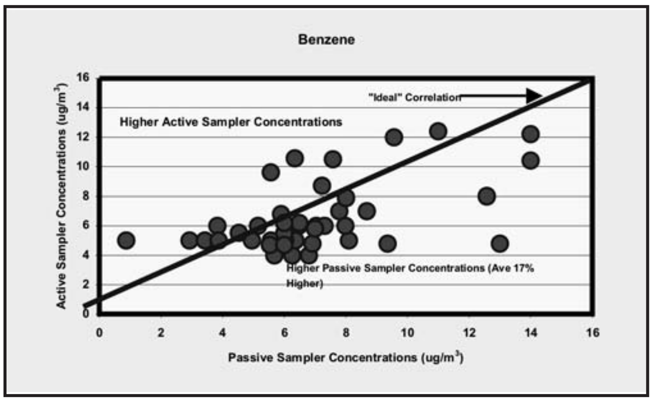


Figure 4.3 Toluene concentrations recorded by the passive and active samplers

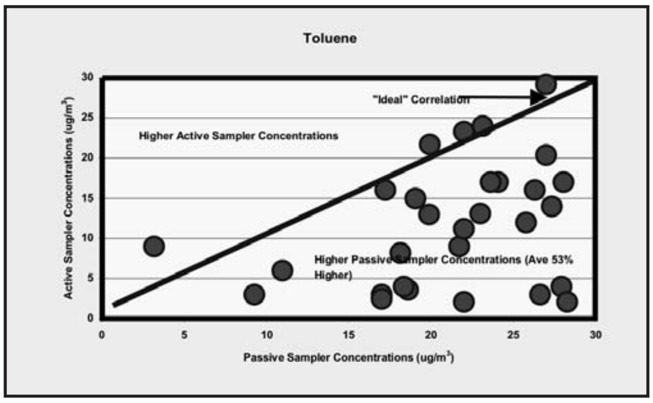


Figure 4.4 Ethylbenzene concentrations recorded by the passive and active samplers

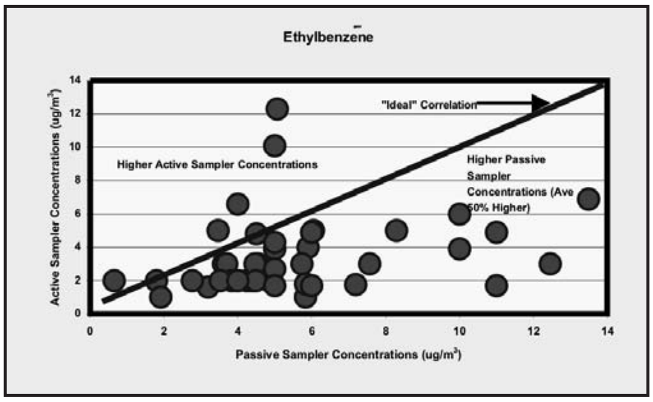
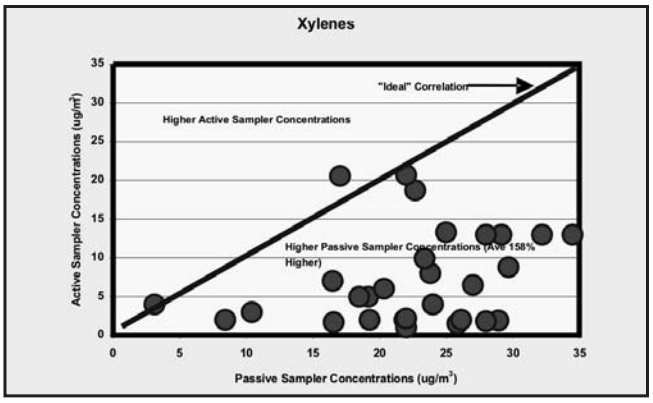


Figure 4.5 Xylene concentrations recorded by the passive and active samplers



4. CONCLUSIONS

Passive sampler concentrations recorded higher concentrations than those recorded from the NIOSH Method 1501 active sampling method. The extent of the inter method discrepancies differ for each compound.

Benzene recorded the best inter method correlation with the passive sampler concentrations being only 1.2 orders of magnitude higher. This was followed by toluene and ethylbenzene where passive sampler concentrations were found to be 1.5 orders of magnitude higher. The poorest inter method correlation was found for total xylene concentrations where the passive samplers recorded concentrations that were 2.6 orders of magnitude higher.

The scatter plots show that the poor correlations recorded were not solely associated with the higher or lower concentrations, but occurred throughout the entire concentration ranges for all of the BTEX components. Correlations with a third methodology such the UV open path method may indicate whether errors are most likely to originate from the active or the passive method. The discrepancies may be attributed to one or a combination of the following sources of errors that require further investigation:

- Analyses method errors thermal vs solvent desorption efficiencies
- Passive sampler diffusion rates too high
- Over saturation of active samplers if sample volumes are too high
- Under absorption by active samplers due to high sampling rates

This inter method review highlights the importance of quality control and inter method assessments that should be applied to all spheres of air quality measurements. Such assessments must not only evaluate precision but also accuracy, limits of detection and general levels of uncertainty. Reporting of such data quality statistics should be integrated with measurement data reporting mechanisms, and be integrated into the total cost of measurements instead of being viewed as an additional cost.

ECOSERV will continue to evaluate, improve and integrate a range of quality control assessments into all spheres of measurements performed. This strategy is not only applied to ambient air quality measurements but also to emission measurements.