Research Article

Benzene and Toluene in Urban Air in Malta

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Summary: *This is the first published report on the presence of benzene and toluene in street air in Malta. The data refers to one hour average concentrations obtained from active samplers positioned at 1.5 m height in urban, suburban and rural sites and in a road tunnel. Two sampling time periods were chosen, one just before and the other after the morning rush hour traffic. Both benzene, a known carcinogen, and toluene are found to be present in higher concentrations in street air from urban sites than from suburban sites and are not detectable in rural areas unless these sites are visited by motor traffic as on weekends. In general, concentrations of these hydrocarbons increase after the passage of morning traffic. Benzene concentrations ranged from 7 to 84 μg m^{-3} and toluene from 26 to 306 μg m^{-3}. It is suggested that the air quality in Malta with respect to the presence of benzene and toluene is probably poor for sites where automotive traffic is prevalent but is generally good for rural areas. Air quality can be improved with the phase-out of leaded petrol which will allow the introduction of catalytic converters in petrol-powered vehicles.*

Keywords: benzene, toluene, air pollution, Malta.

Introduction

Although there is much public concern regarding the quality of air in Malta, very little data on air quality have been published and the work has dealt with pollution from inorganic species, principally sulphur dioxide and combustion-derived particles (Vella et al 1993; Vella et al 1996) and airborne lead (Sammut and Savona-Ventura, 1996).

This is the first published report on the presence of volatile organic compounds (VOCs) in urban air in Malta and concerns the aromatic hydrocarbons benzene and toluene. It is based on a pilot study performed by one of the authors (OG) as a dissertation project conducted during 1996-7 (Gaerty, 1997).

VOCs are released in vehicle exhaust gases either as unburned fuels or as combustion products and are also emitted by the evaporation of motor fuels and solvents. Benzene and toluene are constituents of leaded and unleaded petrol and toluene is also employed as a solvent ("thinner") in automotive and other paints. Benzene is of particular concern because it is a human carcinogen. No EC or WHO guideline value currently exists for benzene concentration in air although the UK government is considering adopting a value of 5 parts per billion (ppb) by volume (16.6 μg m^{-3}) as an air quality objective with a target value of 1 ppb. Chronic low-level exposure to benzene has been shown to cause bone marrow depression and leukaemia; benzene also depresses the immune system; exposure to levels of 10 parts per million (ppm) or less for one year has been found to cause a 560-fold increase in cancer risk (US EPA, 1994). Long term exposure to toluene at ppm levels causes kidney, liver and respiratory tract damage but there is insufficient evidence to classify toluene as a human carcinogen.

In addition to the health risks posed by these hydrocarbons when present as primary air pollutants, they also contribute towards the formation of secondary air pollution including the photochemical generation of ozone, a process which is favoured by abundant sunlight.

Materials and Methods

The analytical method involved passing a known volume of air through a charcoal sorbent tube, eluting the analyte with carbon disulphide and analysing the eluate by capillary column gas chromatography using flame ionization detection.

Air was sampled using a battery operated SKC Universal Sampling Pump operated at a constant flow rate of 200 mL min-1: the pump was equipped with a low-flow adaptor (from SKC) which enabled accurate calibration in the low flow rate (< 500 mL min $^{-1}$) region. The flow rate was determined using a soap bubble calibrator supplied by the pump manufacturer.

Air sampling sites were chosen to represent urban, suburban and rural environments as well as a road tunnel. The locations are shown in Table 1.

Sampling was performed at approximately 1.5 m height and the sample tube was kept in a vertical position to minimise channelling (Lodge, 1988). Once the pump was switched off, the sorbent tube was removed from the sampling train, its open ends were sealed using plastic caps, placed in stoppered glass tubes and refrigerated pending analysis. The air temperature was recorded and wind speed was obtained from the Meteorological Office.

Commercially available charcoal sorbent tubes (SKC, ST226-01) containing two sections of 20/40 mesh charcoal (100 mg front section and 50 mg backup) were employed. Carbon disulphide was used as solvent to elute the sorbed hydrocarbons. The purity of several commercially-available brands of carbon disulphide with respect to benzene was found to be inadequate for this work and the solvent required purification prior to use. This consisted of heating the solvent (BDH, Analar Grade, 500 mL) with a mixture of concentrated sulphuric acid (BDH, GPR Grade; 10 mL) and concentrated nitric

Table 1. Benzene and Toluene concentrations in urban air in Malta.

Location	Location type & site number	Date & Time	Wind speed (knots) & direction	[Benzene] $\mu g\ m^{-3}$	[Toluene] $\mu g\ m^{-3}$
St Anne St., Floriana	urban, 1	25/3/97 5:50-6:50	10-15; WNW	72	132
"	"	25/3/97 7:45-8:45	15-20; WNW	63	79
Independence Ave., Mosta	urban, 2	9/4/97 5:45-6:45	15-20 E	24	29
"	"	9/4/97 7:52-8:52	18-25 E	29	63
Bisazza St., Sliema	urban, 3	10/4/97 6:00-6:50	14-20 NE	74	41
"	"	10/4/97 7:45-9:00	15-22 ENE	44	107
Birkirkara Rd., San Gwann	urban, 4	11/4/97 6:00-6:50	5-10 NE	80	170
"	"	11/4/97 7:45-8:35	10-15 NE	84	306
Naxxar Rd., Lija	urban, 5	14/4/97 5:58-6:58	4 SW	20	28
"	"	14/4/97 7:45-8:45	4-10 NE	43	79
Burmarrad Rd., Burmarrad	sub-urban 6	16/4/97 6:05-6:55	8-13 WNW	nd(*)	nd
"	"	16/4/97 7:45-8:45	8-15 NW	18	29
Saqqajja Hill, Rabat	urban, 7	17/4/97 6:23-7:03	5-10 SSW	7	26
"	"	17/4/97 7:30-8:30	5-10 S	58	122
Tan-Nadur, l/o Rabat	rural 8	18/4/97 5:30-6:40	20-30 NE	nd	nd
Howard Gardens Rabat	sub-urban 9	24/4/97 9:10-10:00	9-15 NW	31	38
"	"	24/4/97 17:10-18:00	8-12 N	nd	nd
National park, Ta' Qali	rural 10	27/4/97 9:10-10:00	10-15 WSW	13	nd
"	"	27/4/97 17:10-18:00	12-18 SW	12	nd
"	"	28/4/97 9:10-10:00	10-15 SW	nd	nd
"	"	28/4/97 17:10-18:00	10-15 WSW	nd	nd
Qammieh, Mellieha	rural 11	1/5/97 9:00-10:00	7-10 NE	nd	nd
"	"	1/5/97 16:30-17:30	3-8 SW	nd	nd
Regional Rd., St. Venera	Tunnel 12	30/4/97 5:50-6:20	20-30 WNW	507	nd
"	"	30/4/97 7:45-8:15	20-30 WNW	197	405

(*) nd = not detected

acid (BDH, GPR grade; 5 drops) under reflux for 3 hours with magnetic stirring. The solvent was then separated, washed and dried over sodium sulphate and re-distilled. The purity of the solvent was checked by blowing down under nitrogen a 1 mL portion to 50 (L and analysing the product by gas chromatography to check for the absence of a benzene peak.

Desorption of the hydrocarbons from charcoal was achieved using 0.50 mL purified carbon disulphide which had been chilled to about -5°C prior to use and the solution was spiked with internal standard (10 ppm isopropyl-benzene); even the charged sorbent was chilled before extraction with cold solvent to avoid loss of analyte. The desorption efficiency for benzene and toluene was determined by spiking the sorbent with standard amounts of analytes and using isopropylbenzene as internal standard. For benzene, the desorption efficiency was 87% while that for toluene was 82%.

A Perkin Elmer Model 8600 gas chromatograph fitted with a BP1 fused silica bonded phase capillary column (SGE) was employed; a Finnigan Matt ion-trap detector was used for mass spectrometric confirmation of chromatographic peaks. Analysis was performed within 48 hours of collection, each section of sorbent tube being analysed separately and in triplicate. Gas chromatographic conditions were as follows: 47°C for 0.3 minutes then to 55°C at 10°C min^{-1}, hold for 3 minutes, then to 300°C at 30°C min^{-1}; injector temperature 180°C; detector temperature 185°C, carrier gas (He) head pressure 10 psig; injection volume 3 µL, splitter ratio: 40. The instrumental detection limit for benzene and toluene in carbon disulphide solution was 1ppm.

Results and Discussion

The results are shown in Table 1. The values represent one-hour averages and the hydrocarbon concentrations in air clearly reflect the traffic density associated with the study area. Thus, for urban sites, benzene and toluene concentrations were generally higher than for sub-urban sites and are much higher than for rural sites, at which sites, concentrations are frequently below detection limits. In general,

both benzene and toluene were found to be more abundant in air during the sampling time corresponding to the morning traffic rush hour than earlier in the morning. Thus the post-7:30 am samples typically yielded higher concentrations of both hydrocarbons, but especially of toluene.

The benzene air concentration in urban sites found in the early morning measurements, which are presumably indicative of "background" levels, appear to be rather high in places. The values ranged from lower or very close to the UK environmental quality guideline concentration (e.g. sites 2, 5 ,6 and 7) to values as high as four times this guideline (sites 1, 3, 4). Just after the morning rush hour, at most of the sites, benzene concentrations increase and in places become four to five times higher than the guideline value.

Studies in Austria in 1995 showed that ambient levels of benzene in urban areas ranged from 5 to 28 $\mu g\ m^{-3}$ while for rural sites the values ranged from 2 to 5 $\mu g\ m^{-3}$ (Hanus-llnar and Hrabcik, 1995). These values, however, are not readily comparable to the Malta data because they refer to 14-day means obtained from passive samplers. Monitoring studies carried out in 1994 in North America (Montreal, Toronto and California) revealed a mean benzene concentration in air equal to about 4 $\mu g\ m^{-3}$ (Wallace, 1996) although again this value represents a 24-hour average rather than a 1-hour average.

In air pollution studies, concentrations of toluene usually correlate with those of benzene and this was found to be generally true for Malta air. Toluene is much more abundant in petrol than benzene as the gas chromatograms in Figure 1 for locally imported leaded and unleaded petrols demonstrate. However, the ambient air concentrations of these two hydrocarbons will be expected to be only partly determined by the abundance ratio in fuels; other factors which are expected to play a role include (a) the relative rate of oxidation of the two compounds in air and (b) the fate of these hydrocarbons during combustion in internal combustion engines. Vehicle exhaust gas contains benzene both as an unburned fuel but also as the dealkylation product of substituted aromatic hydrocarbons. In exhaust gas from unleaded petrol-powered internal combustion engines, the mass abundance ratio of toluene/benzene is approximately 2 (Butler, 1979). The mean abundance ratio in Malta air is 1.9 which is similar to 1.8 reported for Swedish air (Gustavsson, 1996). This strongly suggests that the

presence of these hydrocarbons in air is indeed mainly derived from pollution by petrol-powered engines.

It is interesting to note that at the National Park in Ta' Qali, benzene was detected in air on 27/4/97, which was a Sunday, but not on the next day. Benzene in air at this site is unlikely to have originated from traffic travelling on roads upwind from the study site: this is because, on both sampling days, wind direction and speed were similar and if the benzene detected on Sunday represented transported pollution from these roads, such pollution would probably have been present on Monday as well since this is a busier day for traffic. Rather, benzene air pollution at this site more likely reflects the influx of motor traffic into the picnic and leisure area of the park during the weekend break.

For site 1 in Floriana, the increase in abundance of both benzene and toluene in air after the morning rush hour did not occur but a reduction in values was actually measured. This result is possibly an analytical artifact, although it may also be related to the presence of a
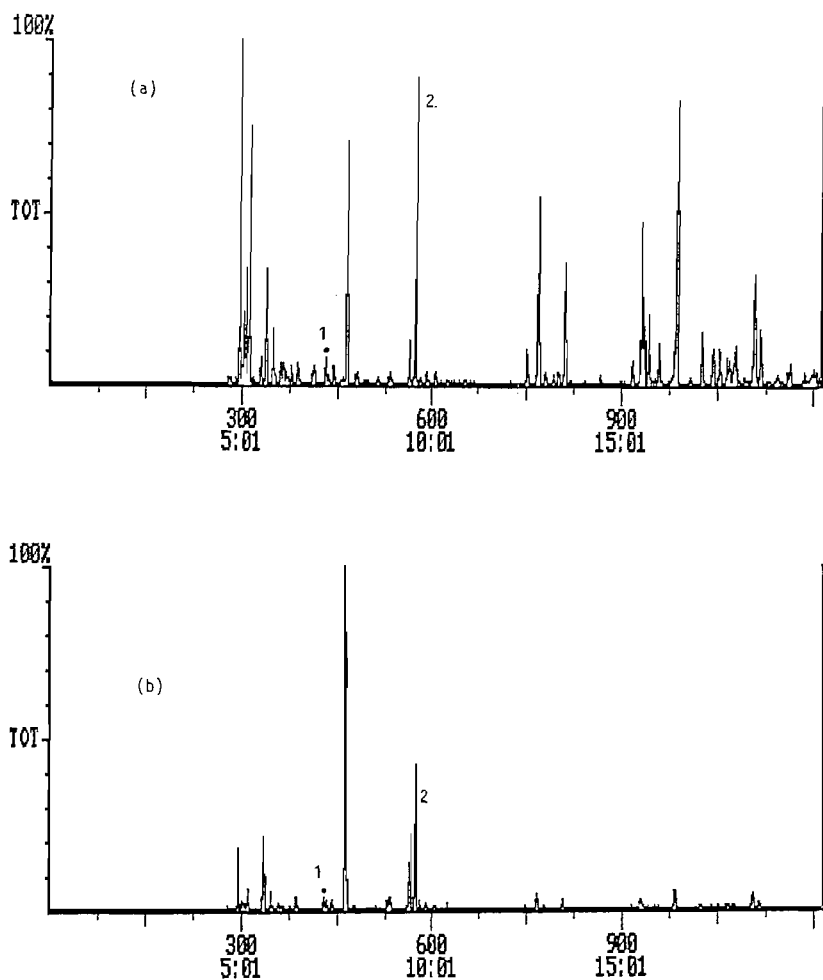

Figure 1. Gas chromatograms for leaded (a) and unleaded (b) petrol as imported in Malta. Peak 1 = benzene; peak 2 = toluene. Chromatographic conditions: analytical column: BP1, 50 m, narrow bore ; temperature programme: isothermal at 100°C for 5 minutes, ramp at 10°C min-1 to 275°C.

roadside service station sited about 300 m from the sampling site which may have received a fuel consignment during the early morning. Such deliveries are expected to introduce into street air a considerable quantity of petrol vapour from the displacement of head space air from underground reservoir tanks. The effect of roadside service stations on air quality is currently being investigated in our laboratory.

Finally, the situation obtaining inside the road tunnel in site 12 deserves comment. The very high concentration of benzene (507 μg m^{-3}) measured in the tunnel prior to the arrival of heavy morning traffic is noteworthy; the absence of toluene at this time is possibly the result of efficient degradation processes occurring by dark reactions (e.g. with nitrate radicals). The reduced benzene concentration measured during the period 7:45 to 8:15 after the passage of morning rush traffic could possibly result from ventilation effects caused by traffic traversing the tunnel. It is interesting to note that the toluene/benzene mass concentration ratio found at this time (= 2.1) is very close to the value in fresh car exhaust gas.

According to the Material Safety Data Sheet (Penn State Univ.) for benzene, the occupational threshold limit value is 3 mg m^{-3} and this is rather close to the concentration values measured in the tunnel. Clearly, applying the precautionary principle, it would appear sensible to consider protective measures for workers involved with repairs inside the tunnel.

Conclusions
The results of this pilot study suggest that the quality of Malta air with respect to benzene and toluene is probably poor for those areas where automotive traffic is very prevalent but appears to be generally good for rural sites. These are preliminary conclusions and require confirmation by additional work on a larger sample size. Also, for purposes of comparison with data from other countries, longer time period sampling using passive techniques is required. However, it is felt that the data as it stands does confirm the view that these hydrocarbons in Malta air do originate principally from petrol-powered vehicular exhaust. It is therefore clear that the air quality situation will continue to worsen if the current rate of increase of vehicular traffic on Malta's roads persists in future. In view of the toxicity of the hydrocarbons, and especially that of benzene, this situation is expected to exert a negative impact on the health of the population. Measures that reduce

hydrocarbon emissions from vehicular exhaust can address this problem but such measures, which require the introduction of catalytic converters for petrol engines, cannot be implemented until leaded petrol is phased out. Several countries in Northern Europe have phased out or are close to a phase out of leaded petrol and the use of catalytic converters is supported by EU requirements (COWI, 1998). It is hoped that similar measures be introduced to Malta as soon as is practically possible.

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