

BENZENE AND TOLUENE IN NEW ZEALAND AIR

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Abstract:—Benzene concentrations in the New Zealand urban environment may be higher than in the past, and as a result of changes in urban sources we could expect increases in rural environments. Recent work in New Zealand gives typical concentration values for benzene in the urban, rural and marine environments in the ranges 300–6000, 0–900 and 0–100 parts per trillion, respectively. Seasonal variations above and below the mean concentrations of 10 ppt are evident in background levels and the measured concentrations at a non-urban site are very sensitive to wind direction. Corresponding measurements of toluene have been made at a clean site and the relationship between toluene and benzene has been used to identify the contributions to samples from background and from urban air.

Key word index: Aromatic hydrocarbons, clean air, Southern Hemisphere.

INTRODUCTION

The sources and behaviour of anthropogenic aromatic compounds in the atmosphere are of interest because of their association with human health problems and the use of fossil fuels (Merian and Zander, 1982; Field *et al.*, 1992). The major sources of benzene and toluene are from evaporative losses from petrol as well as the internal combustion process itself. The burning of biomass also results in a release of benzene and plant and animal matter may also emit small amounts. The only known important atmospheric loss process for benzene and toluene is by reaction with the OH radical with respect to which an atmospheric lifetime of about 10 days is typical for benzene, and about 1–2 days is typical for toluene (Atkinson, 1990).

Acute exposure to benzene causes central nervous system depression, the chemical is irritating to the skin and by defatting the xeratin layer may cause erythema vesiculation and dry and scaly dermatitis (WHO, 1987), and chronic exposure can cause leukemia. Benzene has been shown to cause chromosomal damage and it is considered to be a human carcinogen.

"Safe" levels of atmospheric benzene are not well established, but in several countries the regulatory limits for benzene are $10 \mu\text{g m}^{-3}$ (3000 ppt), sometimes less. Typical urban levels for benzene and toluene are several parts per billion (e.g. Nelson and Quigley, 1982), and both compounds should be identifiable in air that has had a recent trajectory over populated regions. Generally, in urban areas toluene concentrations exceed those of benzene (Field *et al.*, 1992).

In the remote marine troposphere, the levels of benzene are nearly always well below 100 ppt and toluene and other alkyl benzenes are on average much less abundant than benzene (e.g. Rudolph *et al.*, 1984; Nutmagul and Cronn, 1985). However, the number of studies of benzene and alkyl benzenes in the marine atmosphere is very limited, especially for the Southern Hemisphere and there is not sufficient information to establish a representative background concentration.

In this paper the results of automated quasi-continuous measurements of benzene and alkyl benzenes at a coastal site in New Zealand are presented. We present here data for a non-urban site with and without urban influence, together with some preliminary data for selected urban sites. These data are also used to derive "background" levels for benzene at mid-southern latitudes.

EXPERIMENT

Air samples have been taken at a coastal site at Baring Head near Wellington (41° 24'S, 174° 52'E). The Baring Head facility is at an unmanned lighthouse station, on the edge of an 80 m cliff, with the prospect of a clean air fetch from between SE and SW directions (see Fig. 1). This site is already proven as subject to clean air representative of large areas of the southern oceans (e.g. Lowe *et al.*, 1994) when the wind is from the south. However, when the wind is from the north the site is often within the plumes from the Wellington and Lower Hutt cities, 15–20 km away to the north and northwest. The total population of the Greater Wellington area is about 400,000.

From December 1991 to September 1992 an automatic gas chromatograph system operated at Baring Head for a study of light hydrocarbons in clean air (Clarkson *et al.*,

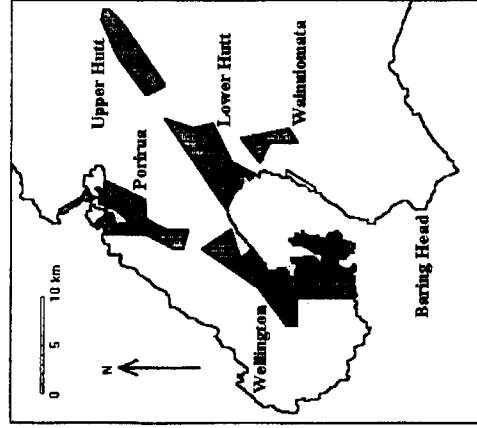


Fig. 1. Map of the Wellington region showing the relationship of the sampling site at Baring Head to the urban areas around Wellington.

1995). During routine operation the measurements were made at intervals of about 4 h and the total number of ambient air samples was 1196. For preconcentration of the hydrocarbons a sample of 2 l of ambient air was drawn through a 1 ml cryogenic trap containing glass beads at liquid nitrogen temperature over a period of 1 h. Then the sample was heated to about 80°C and injected onto a 30 m capillary column (GS-Q). Carrier gas was hydrogen at 10 ml min^{-1} and the temperature of the gas chromatograph was programmed from 40 to 200°C with a heating rate of 10 K min^{-1} after the C_3 compounds had passed through. This column has been effective for separating hydrocarbon compounds from C_2 to C_8 . With an FID detector, the separation was virtually identical to that described by Rudolph *et al.* (1990) for this column. In addition to the light alkanes and alkenes, the system was sensitive to benzene, toluene, xylenes and ethyl benzene. Detection limits were about 2 ppt (10^{-12}) for benzene and 3–4 ppt for the alkyl benzenes.

Calibration of benzene was made by weekly comparisons using reference gas mixtures containing a range of light hydrocarbons in concentrations of about 1 part per billion (ppb). The alkyl benzenes were quantified from the peak area of the FID signal assuming that their mass response factor is identical to that of benzene. During 1992 we participated successfully in an interlaboratory comparison of trace hydrocarbon analyses, including benzene, run by the National Center for Atmospheric Research, U.S.A. (Apel *et al.*, 1994). In Task 1 of this intercomparison our benzene analyses, based on a high-pressure reference mixture of hydrocarbons in air, including benzene, prepared and analysed at Kernforschungsanlage Jülich, gave a concentration about 5% higher than the benzene evaluation by NCAR in the same mixture.

Wind speed and direction at Baring Head were logged as 10 min averages and 4-day back-trajectories were routinely calculated from Meteorological Service of New Zealand numerical weather prediction analyses. Baring Head is subject to frequent storms from the south. An analysis of 4-day back-trajectories for southerly winds at Baring Head shows that air is descending and typically originates south of 50°S between Australia and Antarctica. Figure 2 shows a trajectory of this sort from a 3-day southerly event in January 1992. As a preliminary study of current levels of benzene in urban air and to determine the likely significance of benzene as an



Fig. 2. A typical southerly trajectory at Baring Head. This example shows the trajectory for the 4 days up to local noon, 3 January 1992. The air originated south of New Zealand; 24-h intervals on the trajectory are shown.

air pollutant in New Zealand, a small number of urban measurements were made in June 1994.

Fifteen separate samples were collected in Auckland (population approximately 800,000), with particular emphasis on areas with relatively high motor vehicle pollution levels. Samples were only taken in the 1 h time intervals from 0730, 0830, 1200 and 1630 which represent the peak times for motor vehicle activity. The morning and evening periods are also the most likely for calm weather, which leads to high levels of pollutants. The three sites used, which are all well established for routine air pollution monitoring, are Mt Eden, a typical urban site, about 2 m from the side of Mt Eden road; Queen Street, the main street in the central business district of Auckland, at first floor level, directly above the footpath; Penrose, a typical industrial area, about 2 m from and above the southern motorway.

The samples were collected in conjunction with the routine Auckland air monitoring programme, so that the benzene results could be placed in perspective with regard to the normal daily, weekly and seasonal variations of other air pollutants such as NO_x . The samples of ambient air were obtained by drawing the air through tubes containing activated charcoal (coconut base, 100 and 50 mg) at a rate of about 350 ml min^{-1} for 1 h using battery-operated pumps. The compounds adsorbed onto the charcoal were then desorbed in 0.5 ml dichloromethane and analysed by GC-MS. The sampling method used is well established and in common use for a wide range of measurements of organic vapours in air. The detection limit, after optimising the method for benzene, was about 30 ppt for the 1 h samples.

RESULTS AND DISCUSSION

Benzene and toluene levels were frequently above the lower limit of detection in the Baring Head

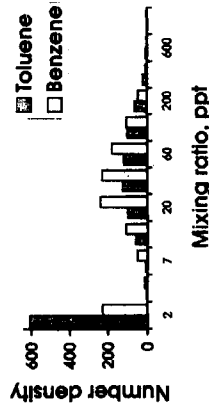


Fig. 3. Frequency distributions of the toluene and benzene mixing ratios observed at Baring Head. The concentration axis has a logarithmic scale.

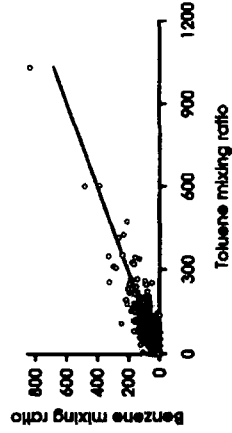


Fig. 4. Plot of benzene vs. toluene mixing ratios. The solid line shows the result of the linear regression.

samples but higher benzene derivatives were not observed. Measurements of concentrations below the detection limit are reported as zero. For the 1196 samples the mean benzene and toluene mixing ratios were 33 ppt (S.D. 49 ppt) and 32 ppt (S.D. 67 ppt). The median values were significantly lower, with 19 and 5 ppt, respectively. These large differences suggest that the probability distributions of benzene and toluene are highly skewed. For toluene this indicates that at

least half of the measurements gave results close to or even below the detection limit of 3–4 ppt. The frequency distributions for both compounds are shown in Fig. 3. Indeed, both substances seem to obey a log-normal distribution for the values above the detection limit. Moreover, there are numerous measurements with benzene and toluene below the detection limit (leftmost bars in Fig. 3). In spite of this scatter of the mixing ratios, the benzene and toluene mixing ratios show a strong linear correlation (see Fig. 4). The slope of the regression line is 0.651 ± 0.009 (1.4%), with an intercept of 11.4 ± 0.7 ppt (6%). The correlation coefficient of 0.8966 shows that this linear dependence is highly significant and that about 80% of the benzene variations can be statistically described by the toluene concentrations. This high degree of correlation and the significant benzene axis intercept of 11.4 ± 0.7 suggests that the observations may be described by some background benzene concentration of about 10 ppt and an extremely variable amount of mixing with polluted air containing benzene and toluene with a concentration ratio of about 0.6. One of the factors which will strongly influence the amount of mixing with polluted air is the origin of the air mass and the extent of contact with pollution sources. An example for the effect of the wind direction on the observed levels of benzene is given in Fig. 5. This illustrates the way in which the benzene concentrations drop below the detection limit of about 2 ppt during such a period of southerly winds. In most of these events the highest concentrations of both benzene and toluene in southerly air occurred in the first measurements after a wind change, similar to the pattern in Fig. 5. This is attributable in most cases to the return of northerly air over the site soon after a southerly wind change.

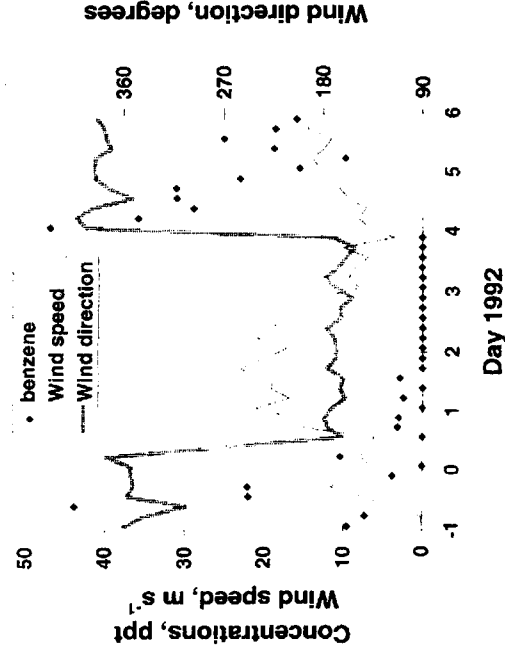


Fig. 5. The concentration of benzene relative to wind speed and direction at Baring Head, New Year 1992.



Fig. 6. Dependence of the (a) benzene and (b) toluene mixing ratios on the wind direction. The horizontal bars indicate the average for a 15° wind direction bin, the boxes the mean \pm the error of the mean. The squares represent the median values.

There is a systematic dependence of the mean benzene mixing ratio from the wind direction. In Fig. 6 the average benzene and toluene mixing ratios for 15° wind bins are shown as a function of wind direction. There are several wind directions for which the trace gas concentrations are similar and we combined the data from these wind directions into 5 wind sectors. The five sectors are:

1. 0–60°: For this sector the air masses reaching Baring Head have often passed over Waiuimomata (population 20,000, see Fig. 1) and been channelled down the Waiuimomata Valley exiting close to Baring Head, and so may have been subject to recent contact with significant pollution sources.
2. 60–135°: Air masses from this sector may partly be from the ocean, and may also have had contact with coastal and rural regions of the North Island of New Zealand.

3. 135–180°: Apart from occasional extremely curved trajectories no air masses from this wind direction sector had contact with land for several hundred or even thousand kilometers (such as in Fig. 2).
4. 180–255°: Air from this sector had no recent contact with strong pollution sources but may have passed over the South Island of New Zealand within a few hundred kilometers upwind.
5. 255–360°: Air from this sector has most probably passed recently over densely populated and industrialized areas of Wellington and Lower Hutt.

In Table 1 the trace gas concentrations observed in air from these five sectors are listed. It can be clearly seen that the observed levels of benzene and toluene reflect the different levels of pollution which are to be expected. We observe that the air from Sector 4 shows on average significantly higher benzene values than air from Sector 3, the "clean marine air" sector. On average, the impact of the South Island is sufficient to more than double the background benzene levels, although this area is neither densely populated nor heavily industrialized. The highest concentrations in the southerly sectors (3 and 4) occur during the rare occurrences of very light winds, i.e. $< 5 \text{ m s}^{-1}$. The measurements cover a period of nearly 10 months. Although this is not sufficient to derive representative average annual cycles, it seems worthwhile to look for systematic seasonal changes. The data sets for Sectors 1, 3, 4, and 5 contain enough data to allow the calculation of meaningful bimonthly mean concentrations. The results are shown in Fig. 7 for benzene and Fig. 8 for toluene. Apart from Sector 5, which seems to be most strongly influenced by local pollution sources, the results for benzene indicate that the average mixing ratios between July and September are higher than in December and January. Since the main removal mechanism for atmospheric benzene is the reaction with OH-radicals, this can be explained by

Table 1. Mixing ratios of (a) benzene and (b) toluene observed for the five different sectors of wind direction

	Sector 1 0–60°	Sector 2 60–135°	Sector 3 135–180°	Sector 4 180–255°	Sector 5 255–360°
(a) Benzene					
Median (ppt)	35	10	0	13	24
Mean (ppt)	46	25	6	14	44
Standard deviation (ppt)	44	45	11	12	80
Error of mean (ppt)	1.9	6.2	0.7	1.0	5.7
Number of data points	545	52	241	159	199
Relative error (%)	4	25	11	7	13
Lowest value	0	0	0	0	0
Highest value	386	263	127	72	834
(b) Toluene					
Median (ppt)	30	0	0	0	11
Mean (ppt)	49	22	4	4	45
Standard deviation (ppt)	64	64	19	11	108
Error of mean (ppt)	2.8	8.9	1.3	0.9	7.6
Number of data points	545	52	241	159	199
Relative error (%)	6	41	29	24	17
Lowest value	0	0	0	0	0
Highest value	604	416	144	94	1033

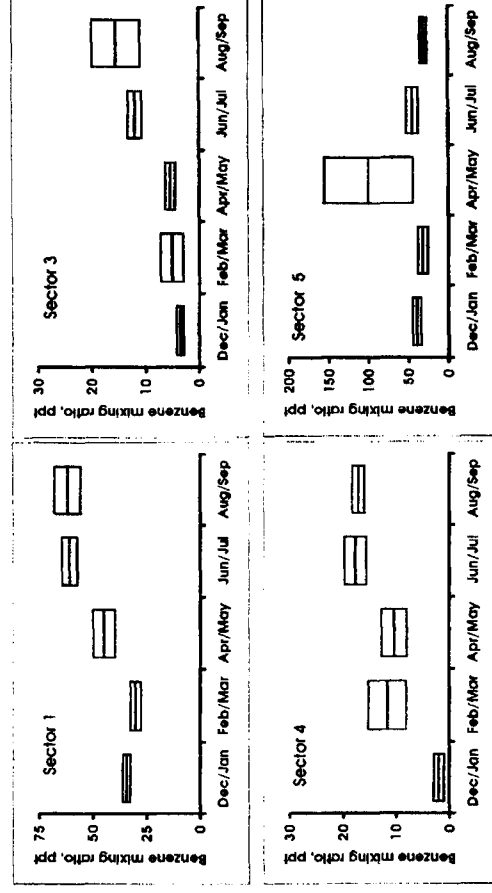


Fig. 7. Variation of the bimonthly mean benzene mixing ratios for different sectors of wind direction. The horizontal bars indicate the mean values, the boxes the mean values \pm the error of the mean.

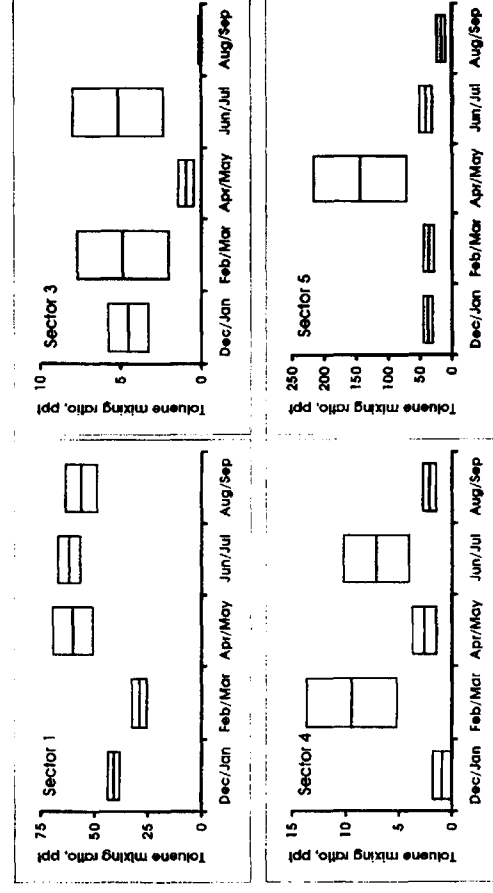


Fig. 8. Variation of the bimonthly mean toluene mixing ratios for different sectors of wind direction. The horizontal bars indicate the mean values, the boxes the mean values \pm the error of the mean.

a faster removal of benzene in summer due to higher OH-radical concentrations. However, for toluene no systematic seasonality can be seen. This supports the assumption that some of the data may be significantly influenced by an unsystematic contribution from local or regional pollution sources.

Based on this assumption and the good correlation between benzene and toluene, we can use the toluene mixing ratios to filter out those measurements which may have been influenced by local emissions. In Fig. 9

the seasonal variations of benzene derived from only those measurements with toluene below the detection limit are shown. Two major effects can be seen in comparison to the unfiltered data sets. The mean mixing ratios for the Sectors 1 and 5 are now significantly lower and the shape of the seasonal pattern for the four sectors are now very similar. The largest changes are observed for Sectors 1 and 5, those with potentially the largest impact from regional and local emissions. For Sector 4 and especially Sector 3, the

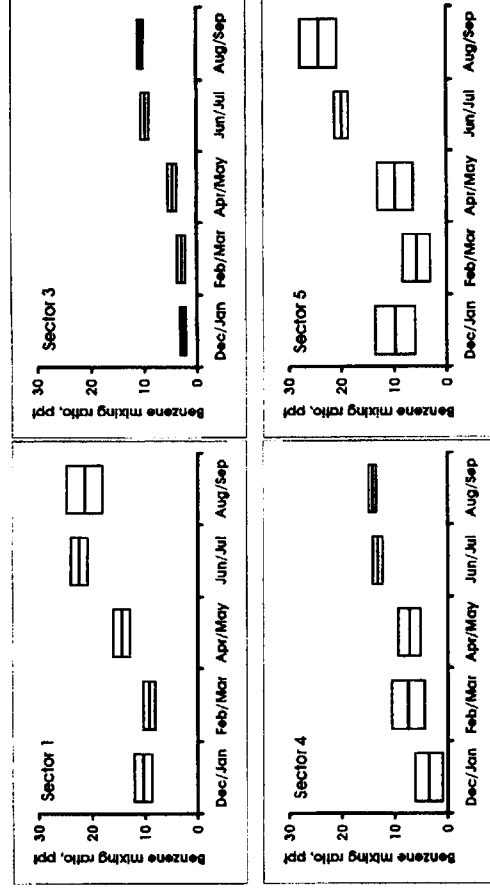


Fig. 9. Variation of the bimonthly mean benzene mixing ratios for different sectors of wind direction. Only measurements for which the toluene mixing ratios were below the detection limit are considered. The horizontal bars indicate the mean values, the boxes the mean values \pm the error of the mean.

Table 2. Correlation between benzene and toluene for different sectors

	Slope	Error of slope	Intercept (ppt)	Error of intercept (ppt)	Correlation coefficient
Sector 1	0.55	0.02	21	1.8	0.81
Sector 2	0.65	0.03	10	2.2	0.95
Sector 4	0.43	0.13	23	4.5	0.53
Sector 5	0.72	0.02	9	3.3	0.96
Sector 1	0.57	0.02	18	1.3	0.83
Sector 1	0.55	0.04	14	1.9	0.81
Sector 1	0.49	0.02	16	2.0	0.91
Sector 1	0.55	0.04	26	3.2	0.79
Sector 1	0.69	0.05	22	4.1	0.83

changes in the average mixing ratios are relatively small, but the random variability is significantly reduced. This supports our assumption that the trace gas concentrations at Baring Head are mainly determined by a certain background level on which is superimposed a highly variable, wind-direction-dependent, local component. To test this further, we look at the toluene-benzene relation in some more detail. Table 2 shows the results from linear regressions of the benzene vs the toluene mixing ratios for the different sectors. The data set for Sector 3 contains only a few measurements with toluene above the lower limit of detection; therefore, the calculation of a meaningful regression line is not possible. For the other sectors the data sets are sufficient and for Sector 1 even the calculation of bimonthly regression lines is justified. For nearly all these cases the correlation coefficient indicates a very high degree of correlation, with more than two-thirds of the variability of the

benzene concentrations being statistically connected to the toluene concentrations. The only exception is found for Sector 4. This may be the result of the rather low average toluene concentration of 3.5 ppt observed for this sector. This means that many of the toluene measurements are close to the detection limit which adds a substantial random variability to the toluene values. In general, the slopes of the regression are around 0.5, suggesting that the regional pollution sources contributing to the benzene and toluene concentrations at Baring Head have an average benzene/toluene ratio of 0.5. This is compatible with the observed benzene/toluene ratio in cities (e.g. Nelson and Quigley (1982) who observed a ratio of about 0.3 in Sydney).

The results from the benzene measurements in Auckland city are shown in Table 3 and Fig. 10. The corresponding NO_x concentrations are also included as well as some general observations of weather conditions.

Table 3. Benzene concentrations at sites in Auckland, June 1994. Sampling was through 1 h following the time listed

Site	Date time (June 1994)	Benzene (ppt)	NO _x (ppb)	Weather conditions
Penrose	13 1200	300	18	Cloudy, dry, W/NW, < 5 kt
	13 1630	3500	274	Cloudy, dry, S/SE, < 5 kt
	14 0730	2900	177	Clear, SW, ~ 15 kt
	14 0830	2500	154	Clear, SW, ~ 15 kt
	15 0730	5600	660	Clear/cloudy, S, < 5 kt
	15 0830	4400	460	Clear/showers, S, < 5 kt
	16 0730	1200	34	Cloudy/showers, NE, < 5 kt
	16 0830	1100	44	Cloudy, NE, < 5 kt
Mt Eden	13 0830	5800	133	Foggy, NE, < 5 kt
	13 1630	2900	70	Cloudy, S/SE, < 5 kt
	14 0730	1400	11	Clear, S, 5 kt
	14 0830	940	8	Clear, S/SW, ~ 15 kt
Queen St	13 1200	2200		Fog cleared, NE, < 5 kt
	14 0830	2100		Clear, S/SW, ~ 5 kt
	14 1200	2100		Clear, SW, ~ 5 kt

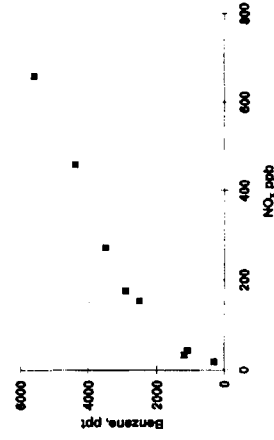


Fig. 10. Both benzene and NO_x at Penrose are closely associated with density of motor vehicles. High values of both occur at times of peak traffic flows.

For the case of the Penrose site in particular, on the edge of a busy motorway with up to 100,000 vehicles per day, there is a clear relationship between higher benzene concentrations and high NO_x, both attributable to motor vehicles as the principal source.

From the relationship between NO_x and benzene we can make a preliminary estimate of the annual average levels of benzene in the air. At the Penrose site the annual average levels of NO_x are in the range 15–20 ppb (Graham and Narsey, 1993). This implies an annual benzene concentration of a few hundred parts per trillion, possibly as much as 1000 ppt, and comparison with the results at other sites suggests that such levels may be widespread through the inner areas of the city at least. This estimation of the urban annual average above gives a concentration at least two orders of magnitude higher than the clean air concentration and about 10–20 times higher than the Baring Head north-erlies mean concentration (representing a rural level).

COMPARISON WITH OTHER OBSERVATIONS

Few measurements of aromatic hydrocarbons have been made in remote continental or marine areas, and

most of these have been in the Northern Hemisphere. Those most comparable to the New Zealand marine environment were made in 1983 in the South Atlantic by Rudolph *et al.* (1984) and in the eastern Pacific in 1983 by Nutmagul and Cronn (1985). Unpublished measurements for benzene and other aromatics from the Stratoz III flights in 1984 and Antarctica between 1982 and 1989 covered most latitudes of the Southern Hemisphere.

Rudolph *et al.* (1984) on an Atlantic ship cruise in February–April 1983 found benzene mixing ratios of 10–15 ppt between 30° and 60°S and 14 ± 6 close to Antarctica. Toluene was in most cases below the detection limit of 5 ppt. Unpublished measurements from the same group from Antarctica (von Neumeyer Station) in 1988 and 1990 gave annual mean values of 9 ± 4 for benzene and in most cases less than 1 ppt for toluene. Further results for 20–50°S from airborne measurements (Rudolph, 1984) were 8–18 ppt for benzene and 2.5 ± 3.5 ppt for toluene. The same data sets indicated that the concentrations of higher alkylbenzenes such as ethyl benzene and xylenes are below the detection limits.

Nutmagul and Cronn reported several aromatic compounds between 40°N and 30°S from a ship cruise in the Pacific in November 1983. At the northernmost latitudes benzene concentrations consistently exceeded 50 ppt, whereas south of the equator concentrations were generally close to 10 ppt. These observations are consistent with the measurements at Baring Head. The clean air concentrations of benzene measured in New Zealand have mean values of about 5 ppt in summer and 10–15 ppt in winter. There have been many more studies of aromatic hydrocarbons in urban air, and of particular interest is the work of Nelson and Quigley (1982), who reported hydrocarbon concentrations from Sydney. The concentration of benzene averaged over several sites during 1979 and 1980 was 2600 ppt. They comment that the composition of Sydney air is consistent with that found

in cities of Europe and North America. A study of aromatic hydrocarbons in 12 U.S. cities by Singh *et al.* (1985) showed benzene average concentrations between 1000 and 9000 ppt and an average for the ratio benzene/toluene of 0.6.

More recent data from urban sampling (e.g. OECD, 1993) remains consistent with this. The OECD study quotes a median daily concentration of benzene in 10 major cities in the United States as ranging between 1300 and 5900 ppt. In Germany, typical benzene concentration in rural areas is 300–1500 ppt while the typical concentration in urban areas is 1500–10,000 ppt.

SUMMARY AND CONCLUSIONS

The measurements of benzene at Baring Head can be explained by the existence of a low background with mixing ratios around 10 ppt with mixing ratios in winter being about a factor of two higher than in summer. Superimposed on this background is recent pollution of local or regional origin. This is in good agreement with the high degree of correlation between toluene and benzene. The slope of the benzene–toluene regression is about 0.5, which agrees very well with the ratio observed generally in cities. Since the atmospheric lifetime of toluene (1–2 days) is much shorter than that of benzene (10 days), the toluene mixing ratios are determined by local and regional emissions. Thus, the toluene measurements provide a simple and efficient filter to eliminate air samples subject to local and regional influences from the data set. For benzene we estimate from the toluene detection limit of 3–4 ppt and the slope of the benzene–toluene correlation, that the remaining regional impact is less than 2 ppt. For the “background air” wind direction sector (Sector 3, 135–180°) the filtering has only a minor influence which demonstrates that air from this sector indeed represents background air at mid-southern latitudes. This also agrees with the finding that the benzene mixing ratios in air from this sector are, on average, a factor of two lower than the background (filtered) values from most other sectors.

The only exception is the south to southwest sector (Sector 4, 180–255°). In this case the filtering seems to be sufficiently effective to remove all regional impact and the observed mean background concentrations of benzene are basically identical to those from the “background air” sector.

The shape of the seasonal variation of the filtered benzene mixing ratios is very similar for all wind directions. The lowest mixing ratios are found in December/January and February/March, the highest in June/July and August/September. This can be explained by the faster photochemical removal of benzene during summer and is similar to the pattern found in the Southern Hemisphere for other non-methane hydrocarbons (Rudolph *et al.*, 1992).

We have only small numbers of measurements from urban areas, but the urban concentrations ranging from 300 to 5800 ppt are quite similar to concentrations reported from large cities elsewhere in the world, although direct comparisons are difficult as there is generally insufficient information on sampling times and conditions for results from other studies. The benzene concentrations show a correlation with the NO_x data collected simultaneously and can thus be used to obtain a first estimate of the benzene levels to be expected in urban areas of New Zealand. The exact nature of the benzene/NO_x relationship is likely to be dependent on other factors such as distance from roads and the nature of vehicle movements. Nevertheless, the few available benzene measurements in urban air and the extrapolation based on NO_x concentrations indicates that the levels of benzene at Baring Head are orders of magnitude lower than the levels in urban areas.

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