

Summary of UK Ambient Hydrocarbon Air Quality Network Operations During 2000

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Approved on behalf of Managing Director, NPL
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By

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INTRODUCTION

This report summarises the operation of the UK Ambient Hydrocarbon Air Quality Monitoring Network during 2000. NPL act as Central Management and Control Unit (CMCU) for this network on behalf of the Department of the Environment, Transport and Regions, under contract EPG 1/3/80.

1. BENZENE AND 1,3-BUTADIENE CONCENTRATIONS AND TRENDS

Table 1 gives the ratified annual average concentrations in molar ppb recorded at the network sites for 2000.

The figures for 1997, 1998 and 1999 are given for comparison. It is notable that the 2000 1,3 Butadiene concentrations at non-curb side sites (i.e. not Marylebone Road) are on average 16% lower than in 1999 and that the 2000 Benzene concentrations at non-curb side sites are on average 39% lower than in 1999. At Marylebone Road the 2000 1,3 Butadiene average concentration is 13% lower than in 1999 and the 2000 Benzene average concentration is 41% lower than in 1999.

Table 1: Annual average concentrations for 1,3 Butadiene and Benzene for 1997- 2000

	1,3 Butadiene (ppb)				Benzene (ppb)			
	1997	1998	1999	2000	1997	1998	1999	2000
Belfast	0.16	0.10	0.11	0.08	0.93	0.69	0.66	0.39
Birmingham	0.23	0.15	0.15	0.13	1.05	0.86	0.74	0.42
Bristol	0.22	0.16	0.12	0.12	1.42	0.94	0.80	0.44
Cardiff	0.27	0.20	0.16	0.13	1.34	0.98	0.99	0.52
Edinburgh	0.11	0.09	0.08	0.06	0.67	0.59	0.53	0.36
Eltham	0.21	0.17	0.15	0.12	1.00	0.82	0.78	0.49
Harwell	0.04	0.05	0.05	0.04	0.35	0.33	0.27	0.16
Leeds	0.23	0.17	0.14	0.11	1.11	0.85	0.89	
Liverpool	0.23	0.18	0.14	0.13	0.89	0.73	0.73	0.60
London-UCL	0.37	0.23	0.23	0.17	1.80	1.20	1.11	0.63
Middlesbrough	0.17	0.12	0.13	0.10	1.05	0.77	0.79	0.64
Southampton	0.33	0.25	0.23	0.23	1.83	1.57	1.31	0.75
Marylebone Road	-	1.02	0.83	0.72	-	4.27	3.31	1.94

Figures 1 to 6: (collected at the end of this report) present the Benzene and 1,3 Butadiene data for 2000 in a number of graphical representations, with some comparisons to earlier years.

2 CONCENTRATIONS OF OTHER HYDROCARBON SPECIES

The annual average concentrations of the other hydrocarbons measured by the Network are given in the following table. 2 and 3-methyl Pentanes are combined, as they appear on the National Archive.

Table 2: Annual average concentrations of hydrocarbons for 2000 (ppb)

	Belfast	Birmingham	Bristol	Cardiff	Edinburgh	Eltham	Harwell	Leeds	Liverpool	London - UCL	Middlesbrough	Southampton	Marylebone Road
Ethane	1.61	5.90	3.91	●	3.00	3.56	1.80	6.93	4.45	5.20	5.31	5.42	7.70
Ethene	1.12	1.95	1.90	2.64	1.04	1.96	0.51	2.23	1.95	3.06	3.69	3.15	12.44
Propane			1.96	3.11	2.14	1.50	0.82	2.76	2.64	2.13	3.93	2.07	3.04
Propene	0.53	0.79	1.02	1.33	1.11	0.86	0.22	1.45	1.29	1.64	3.05	1.63	4.11
i-Butane	1.22	1.88	2.56	2.82	1.24	1.38	◆	1.45	1.46	2.85	1.78	3.62	6.58
n-Butane	0.56	0.97	0.97	0.88	0.80	0.78	◆	0.93	1.04	1.48	1.30	1.80	3.98
Trans-2-Butene	1.38	2.31	1.85	2.87	1.61	1.99	0.51	2.78	2.38	2.43	2.33	2.63	8.16
1-Butene	0.07	0.32	0.36	0.18	0.49	0.17	0.02	0.23	0.32	0.24	0.13	0.26	0.66
cis-2-Butene	0.07	0.11	0.11	0.10	0.09	0.12	0.02	0.13	0.29	0.16	0.10	0.20	0.68
i-Pentane	0.05	0.15	0.13	0.09	0.17	0.10	0.02	0.13	0.19	0.13	0.08	0.17	0.52
n-Pentane	0.64	1.36	1.39	1.57	0.75	1.52	0.39	1.78	1.73	2.01	1.02	2.40	7.88
1,3 Butadiene	0.25	0.41	0.44	0.54	0.46	0.36	0.10	0.67	0.70	0.57	0.66	0.59	1.76
trans-2-Pentene	0.08	0.13	0.12	0.13	0.06	0.12	0.04	0.11	0.13	0.17	0.10	0.23	0.72
Cis-2-pentene	0.04	0.08	0.08	0.12	0.04	0.07	0.01	0.09	0.13	0.12	0.05	0.16	0.54
methyl-Pentane	0.02	0.04	0.04	0.06	0.02	0.04	0.01	0.05	0.06	0.06	0.02	0.09	0.30
Isoprene	0.36	0.51	0.47	0.62	0.29	0.59	0.13	0.59	0.66	0.98	0.47	1.08	3.35
n-Hexane	0.04	0.06	0.07	0.08	0.05	0.08	0.02	0.05	0.07	0.12	0.05	0.13	0.34
n-Heptane	0.13	0.19	0.13	0.20	0.10	0.10	0.03	0.59	0.30	0.25	0.20	0.21	0.56
Benzene	0.11	0.12	0.12	0.11	0.08	0.13	0.02	0.13	0.14	0.15	0.12	0.16	0.33
Toluene	0.39	0.42	0.44	0.52	0.36	0.49	0.16	0.48	0.60	0.63	0.64	0.75	1.94
Ethyl Benzene	1.00	1.42	1.35	1.31	1.20	1.38	0.34	1.44	1.47	1.99	1.04	2.40	7.49
m+p-Xylene	0.18	0.33	0.21	0.21	0.26	0.21	0.04	0.22	0.39	0.30	0.17	0.42	1.19
o-Xylene	0.62	1.11	0.67	0.66	0.89	0.68	0.11	0.74	0.94	0.95	0.59	1.26	4.15
	0.22	0.32	0.22	0.25	0.25	0.25	0.04	0.26	0.35	0.34	0.19	0.50	1.53

- Value not reported due to contamination by natural gas.
- ◆ Values not reported due to continuous coelution.

3 SPECIFIC HYDROCARBON EVENTS REPORTED

The following table summarises the events observed by the Hydrocarbon Network during 2000. All observed events were reported to the DETR press office. Figures 6a - e (collected at the end of this report) show time series plots for selected species during these events.

Table 3: Summary of reported events

Site	Date/Time of Event	Elevated Species	Peak Concs	Maximum Benzene concentrations	Max 1-3Butadiene concentrations
Middlesbrough	09/5/00 11:00 – 18:00	Ethane Ethene Propane Propene Ethyne n-Butane i-Pentane n-Pentane 1,3 Butadiene n-Hexane Benzene	94.6 ppb 60.8 ppb 317.6 ppb 53.9 ppb 332.3 ppb 308.9 ppb 115.8 ppb 130.8 ppb 64.0 ppb 53.4 ppb 14.3 ppb	14.3 ppb	64.0 ppb
Southampton	14/05 14:00 – 15/05 03:00	13 Butadiene	8.6 ppb	1.0 ppb	8.6 ppb
Liverpool	24/5/00 04:00 – 10:00	Ethane Ethene n-Butane t-2-Butene 1-Butene c-2-Butene i-Pentane n-Pentane t-2-Pentene c-2-Pentene n-Hexane Benzene Toluene	24.9 ppb 25.8 ppb 54.8 ppb 60.6 ppb 58.3 ppb 69.4 ppb 282.5 ppb 41.4 ppb 53.3 ppb 28.9 ppb 24.6 ppb 29.1 ppb 20.1 ppb	29.1 ppb	1.6 ppb
Liverpool	17/8 22:00 - 18/8 10:00	Ethane Propane i-Butane i-Pentane n-Pentane Benzene	19.4 ppb 14.1 ppb 14.4 ppb 19.1 ppb 20.0 ppb 6.3 ppb	6.3 ppb	0.2 ppb
Middlesbrough	28/8/00 11:00 – 23:00	Ethene Propane Propene n-Butane i-Pentane n-Pentane	19.0 ppb 44.3 ppb 68.5 ppb 33.2 ppb 14.1 ppb 15.5 ppb	3.6 ppb	0.1 ppb

4. DATA CAPTURE SUMMARY

All data for 2000 has been ratified by NPL. A summary of the capture statistics for the key compounds is given in the following two Tables.

Table 4: Percentage Benzene data capture for 2000

	January	February	March	April	May	June	July
Belfast	99.5	98.9	96.7	99.4	98.1	91.8	²
Birmingham	91.4	90.8	98.9	91.9	80.5	99.4	99.9
Bristol	92.6	89.5	97.3	71.0	87.9	88.9	99.9
Cardiff	93.3	94.9	93.9	93.1	97.8	68.8	92.6
Edinburgh	100.0	93.2	100.0	98.9	96.9	100.0	81.7
Eltham	100.0	92.0	99.9	90.3	73.4	76.8	76.2
Harwell	89.0	95.0	74.5	97.6	99.8	99.9	99.9
Leeds	55.1	86.4	97.7	99.9	92.5	98.3	99.9
Liverpool	73.7	100.0	99.9	89.7	99.5	74.4	92.1
London-UCL	93.6	98.2	74.3	87.0	90.8	88.9	94.8
Middlesbrough	99.8	87.8	99.8	99.5	97.5	92.5	99.9
Southampton	99.5	99.8	94.4	99.9	99.8	91.8	67.6
Monthly mean	90.6	93.9	93.9	93.2	92.9	89.3	91.2
Marylebone Road	99.5	90.2	97.6	87.8	94.9	86.9	99.2

	August	September	October	November	December	Annual Mean ¹
Belfast	91.4	99.0	99.8	99.8	100.0	97.0
Birmingham	100.0	97.6	99.9	100.0	84.3	94.5
Bristol	97.0	99.9	97.6	84.9	96.0	92.0
Cardiff	90.2	81.9	98.5	97.9	96.9	91.7
Edinburgh	100.0	91.9	95.2	75.8	92.5	93.9
Eltham	98.9	82.9	77.7	99.3	99.9	88.9
Harwell	97.7	99.7	95.9	100.0	99.9	95.7
Leeds	100.0	100.0	95.4	92.8	96.4	92.8
Liverpool	99.6	87.4	99.7	65.1	99.3	90.1
London-UCL	76.2	85.0	90.1	82.4	87.0	87.3
Middlesbrough	94.0	70.8	65.2	100.0	100.0	92.3
Southampton	43.7	88.1	100.0	90.9	86.2	88.4
Monthly mean	90.7	90.4	92.9	90.7	94.9	92.1
Marylebone Road	93.4	99.1	75.8	94	91.5	94.0

¹ These figures represent data capture as a percentage of "available" time, i.e. excluding calibration and scheduled servicing.

² There is no Benzene data capture for Belfast in July due to a heating oil spillage next to the site influencing n-Heptane, Benzene, Toluene and the Xylenes. Consequently the mean was taken over eleven months.

Table 5: Percentage 1,3 Butadiene data capture for 2000

	January	February	March	April	May	June	July
Belfast	99.5	98.9	99.6	99.4	98.1	96.6	89
Birmingham	91.4	90.8	98.9	91.9	80.5	99.7	99.9
Bristol	92.6	89.5	97.3	71.3	87.9	88.9	99.9
Cardiff	95.2	94.8	93.9	93.1	97.8	69.3	92.6
Edinburgh	100.0	92.3	100.0	99.7	96.9	100.0	81.9
Eltham	100.0	92.0	99.9	90.3	73.4	76.8	76.3
Harwell	89.0	95.0	76.8	97.6	99.8	99.9	99.9
Leeds	89.0	86.9	97.7	99.0	92.5	98.3	99.9
Liverpool	73.7	99.7	96.9	89.7	99.5	73.9	90.2
London-UCL	93.6	98.2	74.3	86.8	90.8	88.9	94.8
Middlesbrough	99.6	87.8	99.8	99.5	97.5	92.5	99.9
Southampton	99.5	99.8	94.4	99.9	99.8	91.8	67.7
Monthly mean	93.6	93.8	94.1	93.2	92.9	89.7	91.0
Marylebone Road	99.6	90.2	97.6	87.8	94.8	86.9	99.8

	August	September	October	November	December	Annual Mean ¹
Belfast	91.4	99.0	99.8	99.8	100.0	97.6
Birmingham	100.0	97.6	99.9	100.0	84.3	94.6
Bristol	97.0	99.9	97.6	85.3	96.0	92.0
Cardiff	90.1	82.4	98.5	98.2	96.9	92.0
Edinburgh	100.0	91.8	95.2	75.8	92.3	93.9
Eltham	99.3	82.9	77.5	99.3	99.9	89.0
Harwell	97.6	99.7	95.9	100.0	99.9	95.9
Leeds	100.0	100.0	95.4	92.8	96.4	95.7
Liverpool	98.2	86.8	99.1	65.1	99.0	89.4
London-UCL	93.4	85.0	90.1	82.4	87.0	88.8
Middlesbrough	94.2	70.7	65.2	100.0	100.0	92.3
Southampton	43.8	88.1	100.0	90.9	86.3	88.4
Monthly mean	92.1	90.3	92.9	90.8	94.8	92.4
Marylebone Road	93.3	99.1	77.2	94	91.3	94.2

¹ These figures represent data capture as a percentage of “available” time i.e. excluding calibration and scheduled servicing.

5. CAUSES OF SIGNIFICANT DATA LOSS

All sites achieved greater than 87% data capture, significantly greater than the 75% needed to allow representative annual averages to be reported.

The four sites that failed to achieve 90% data capture were:

- (i) **Eltham (89.0% 1,3 Butadiene, 88.9% Benzene):** Most data loss occurred during the summer months with problems with the FID assembly. It was stripped and repaired on one occasion and the whole assembly replaced on another. Associated problems with various Hydrogen generators and pipe work further contributed to loss of data. The intermediate service in July resulted in service engineers being recalled twice to the site to investigate problems with chromatography. There were also some minor problems with the Liquid Nitrogen delivery system.

Liverpool (89.4% 1,3 Butadiene): In January, Liverpool suffered Y2K problems resulting in a lot of missing or irretrievable files. Carrier gas problems led to two visits by service engineers in June, because of poor chromatography associated with degrading trapping material. Service engineers were on site again in August, the trapping material was again replaced as well as the ATCT head. Insulators on the TCT oven were also replaced but an engineer was recalled in September when further problems with the oven arose requiring the heater to be replaced. Instability of calibrations in November also led to data loss.

London UCL (88.8% 1,3 Butadiene, 87.3% Benzene): Liquid Nitrogen delivery problems were a constant drain on data capture throughout the year. The Dewar was replaced in January but cooling problems remained. The auto-cal system was replaced in April after it began sticking in an open position; a service engineer removed the auto-system bringing it in line with the rest of the network using a manual calibration set-up. However a week's data was lost as the GC was found to be sampling room air.

- (iv) **Southampton (88.4% 1,3 Butadiene, 88.4% Benzene):** The entire loss of data at Southampton can be attributed to problems with the air conditioning unit. Numerous service engineer call outs resulted in the unit being replaced. The hut is shared with Phase I equipment and as a result the temperature in the cabin caused various instruments to trip out, resulting in the GC sitting for periods of time switched off to save putting components under stresses at which they may have failed.

Nb An incident at Belfast in July was also responsible for serious data loss. A heating oil tank close to the site was damaged while it was being refilled, spilling several hundred litres of the liquid. This resulted in 6 weeks data loss as the spill contaminated n-Heptane, Benzene, Toluene and the Xylenes.

6. SITE OPERATIONS

Varian engineers visited twelve network sites during the year to conduct annual services of the chromatographic instruments as a part of a preventative maintenance program. During this visit the machines were given a complete service and a number of components were routinely replaced.

In addition, Varian engineers carry out a second 6-month minor service. During this intermediate service a number of key components, which have lifetimes of less than 1 year of continuous use, are replaced.

The total number of visits by service engineers, and the number of 'special' visits by LSO's, are given in the following table. LSO 'special' visits are those requested by the CMCU.

NPL does not act at CMCU for the Marylebone Road site.

Table 6: Summary of service visits and LSO special visits

Site	Chrompack Visits	LSO Special visits	Annual Service 2000
Belfast	1	8	June
Birmingham	3	18	June
Bristol	4	18	February
Cardiff	12	15	August
Edinburgh	10	8	September *
Eltham	6	14	December
Harwell	5	9	February *
Leeds	12	26	March *
Liverpool	7	11	March
Middlesbrough	5	17	October *
Southampton	5	10	August
UCL London	4	8	March

* Annual service subsumed with general maintenance

The average number of Chrompack visits made to Hydrocarbon monitoring sites in 2000 was 6.2. In 1999, the average number of visits to a site was 6.6; in 1998 the average was 4. A very problematic Leeds machine skewed the average in 1999 and 2000. If that data is removed the average becomes 5.3 in 1999 and 5.5 in 2000. The difference in averages between 1998 and 1999 is explained by ageing hardware requiring an elevated level of

attention. Between 1999 and 2000 as part of the progressive maintenance program extra components such as the pump motors and assemblies were replaced.

In 2000 the average number of LSO special visits to sites was 13.5, which compares with an average number of 12 in 1999 and 11 in 1998. This trend again would suggest a problem with ageing hardware.

7. LSO DUTIES PERFORMED

The following table summarises the duties performed by the LSO's at the 12 network sites. LSO's are expected to perform a calibration every two weeks and fill in a check list on every weekly visit. The number of weekly visits has been calculated from the number of checklists received by the CMCU.

Table 7: Summary of LSO weekly visits and site calibrations

Site	Number of Calibrations 2000	Number of "Weekly" Visits 2000
Belfast	22	52
Birmingham	22	46
Bristol	26	50
Cardiff	27	49
Edinburgh	31	52
Eltham	27	50
Harwell	26	53
Leeds	24	44
Liverpool	29	45
Middlesbrough	22	54
Southampton	31	46
London-UCL	14 ¹	47

¹ Automated calibrations performed at London UCL up until 09/05/00

8. SUMMARY

The annual mean Benzene and 1,3 Butadiene concentrations recorded by all hydrocarbon monitoring sites including Marylebone Road are well below the current air quality limits set by the EC directive of 5ppb for Benzene and 1 ppb for 1,3 Butadiene.

Data capture was good for the majority of the sites, with a network average of 92.2% for Benzene and 92.6% for 1,3 Butadiene. These figures include the data capture averages for the affiliated Perkin Elmer Marylebone Road site, which improved considerably from a 1999 average of 82% to a value of 94% for 2000. Four sites fell marginally below 90% data capture for 1,3-Butadiene and three sites for Benzene. This was caused by various factors, which were all dealt with by the end of the year. All sites recorded greater than 75% data capture allowing annual averages to be calculated.

The network recorded elevated hydrocarbon events at three sites during 2000, those being Liverpool, Middlesbrough and Southampton. These events are not necessarily directly attributable to general atmospheric conditions but may be caused by local industry. That would appear to be the case at Middlesbrough and Liverpool and the exceedance at Southampton is explained by the location of the site, being as it is in the apex of two major roads.

The performance of the Chrompack engineers and the Local Site Operators has been good, especially with the news of the changing nature of the Hydrocarbon network. Their continued support and promptness in dealing with call out requests was much appreciated and helped keep good data capture right up until the end of operation of the current network.

FIGURES

- Figure 1a - Benzene monthly average concentrations in ppb for 2000
- Figure 1b - Benzene monthly average concentrations in ppb for 2000, excluding Marylebone Road
- Figure 2a - 1,3 Butadiene monthly average concentrations in ppb for 2000
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- Figure 3a - Benzene annual average trend in concentration from 1994 – 2000, excluding Marylebone Road
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- Figure 5a - Benzene / 1,3-Butadiene average monthly concentration ratios for 1999
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- Figure 6e – Concentrations of Hydrocarbons measured at Middlesbrough on the 28th August 2000

Figure 1a Benzene Monthly Average Concentrations in ppb for 2000

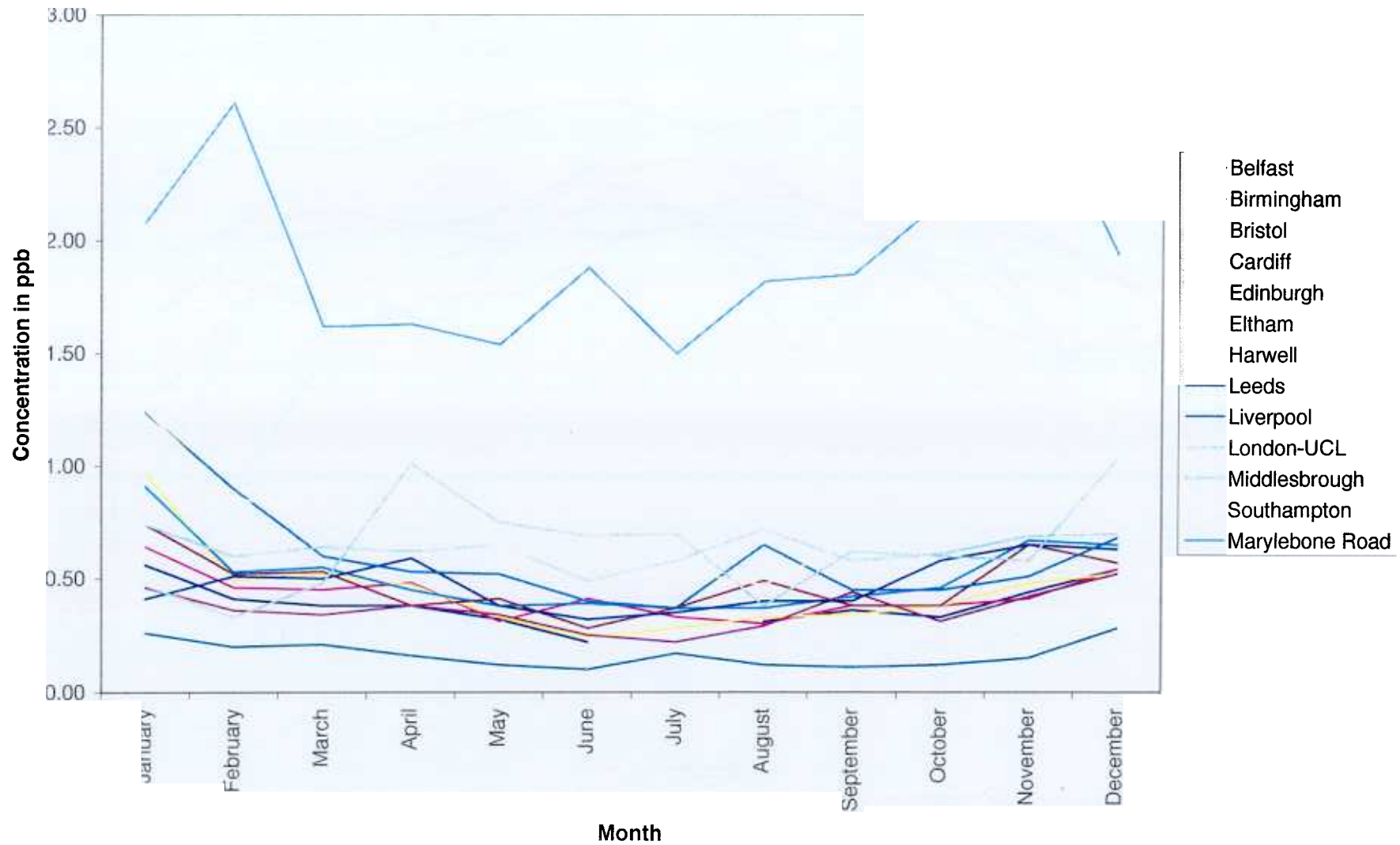


Figure 1b Benzene monthly average concentrations in ppb for 2000, excluding Marylebone Road

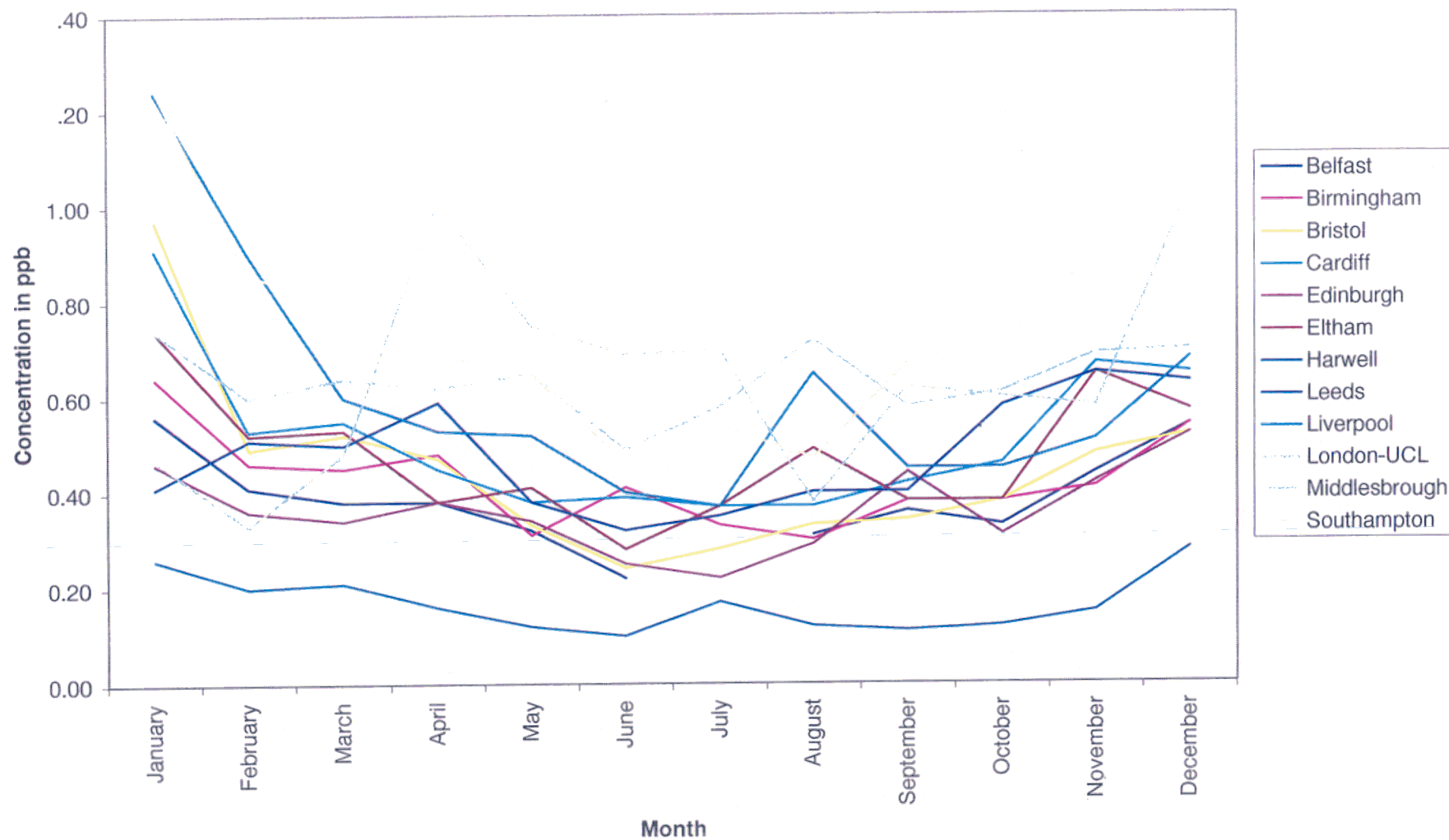


Figure 2a 1,3 Butadiene Monthly Average Concentrations in ppb for 2000

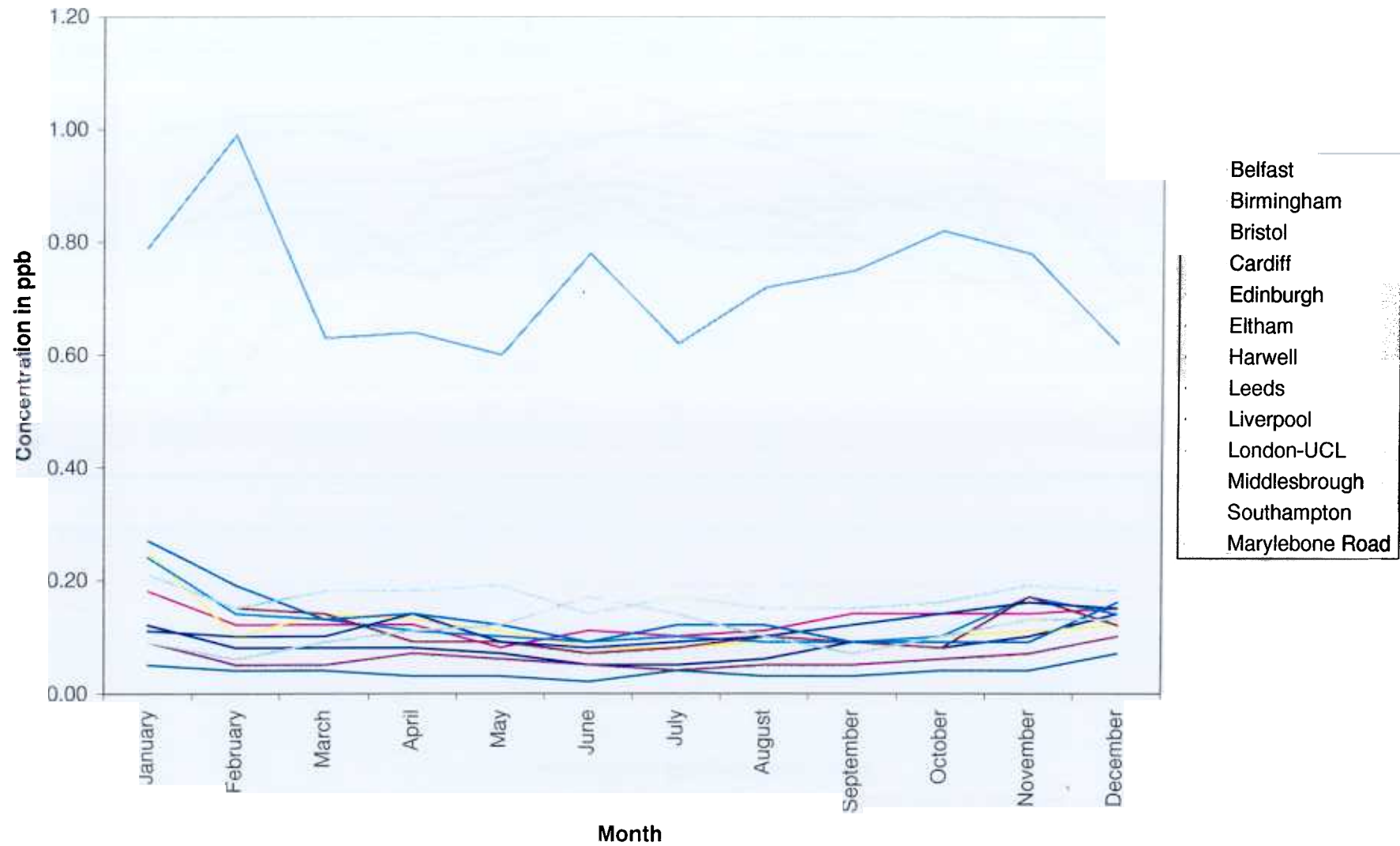


Figure 2b 1,3 Butadiene Monthly Average Concentrations in ppb for 2000, excluding Marylebone Road

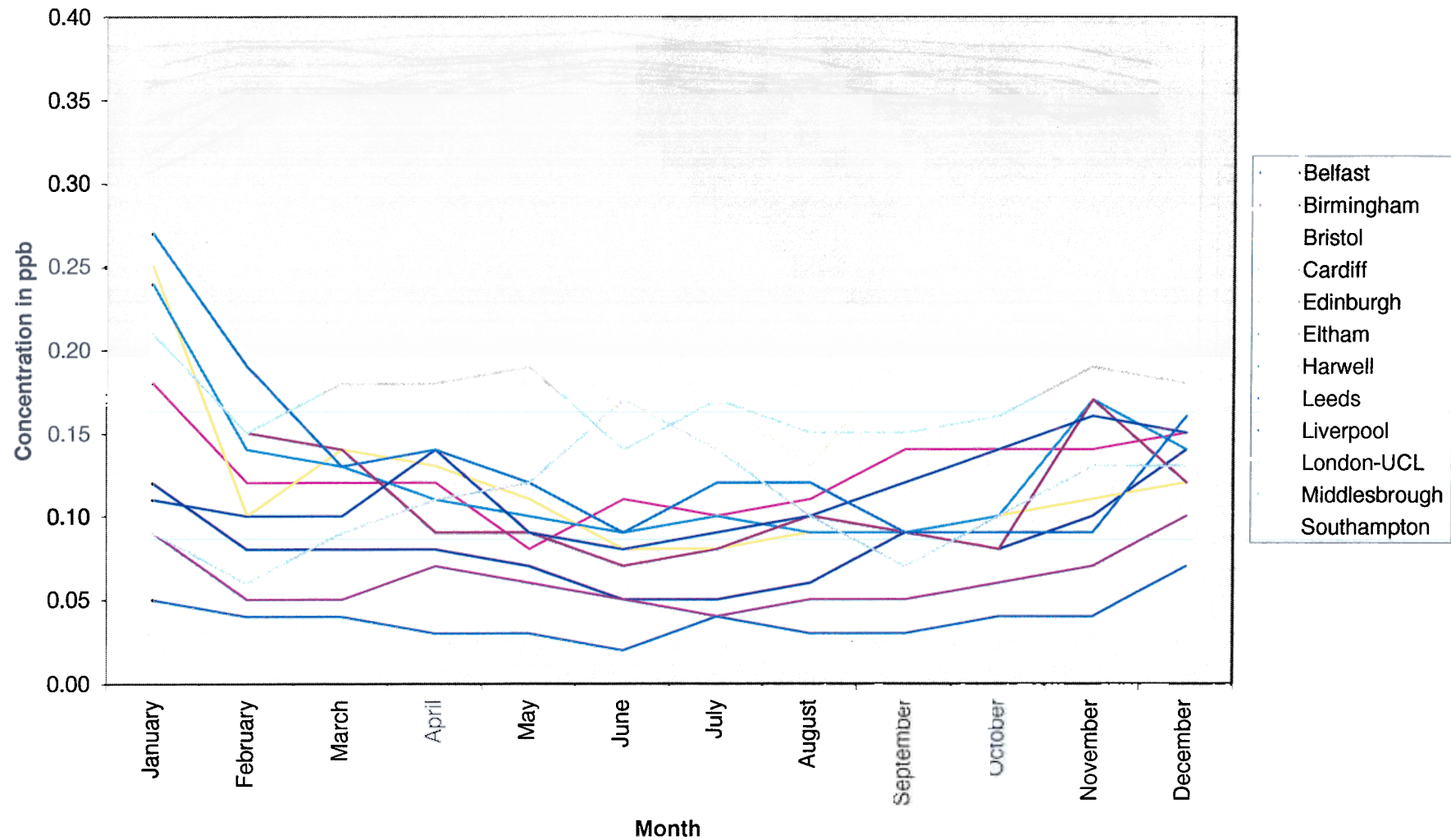


Figure 3a Benzene Annual Average Trend in Concentration From 1994-2000, excluding Marylebone Road

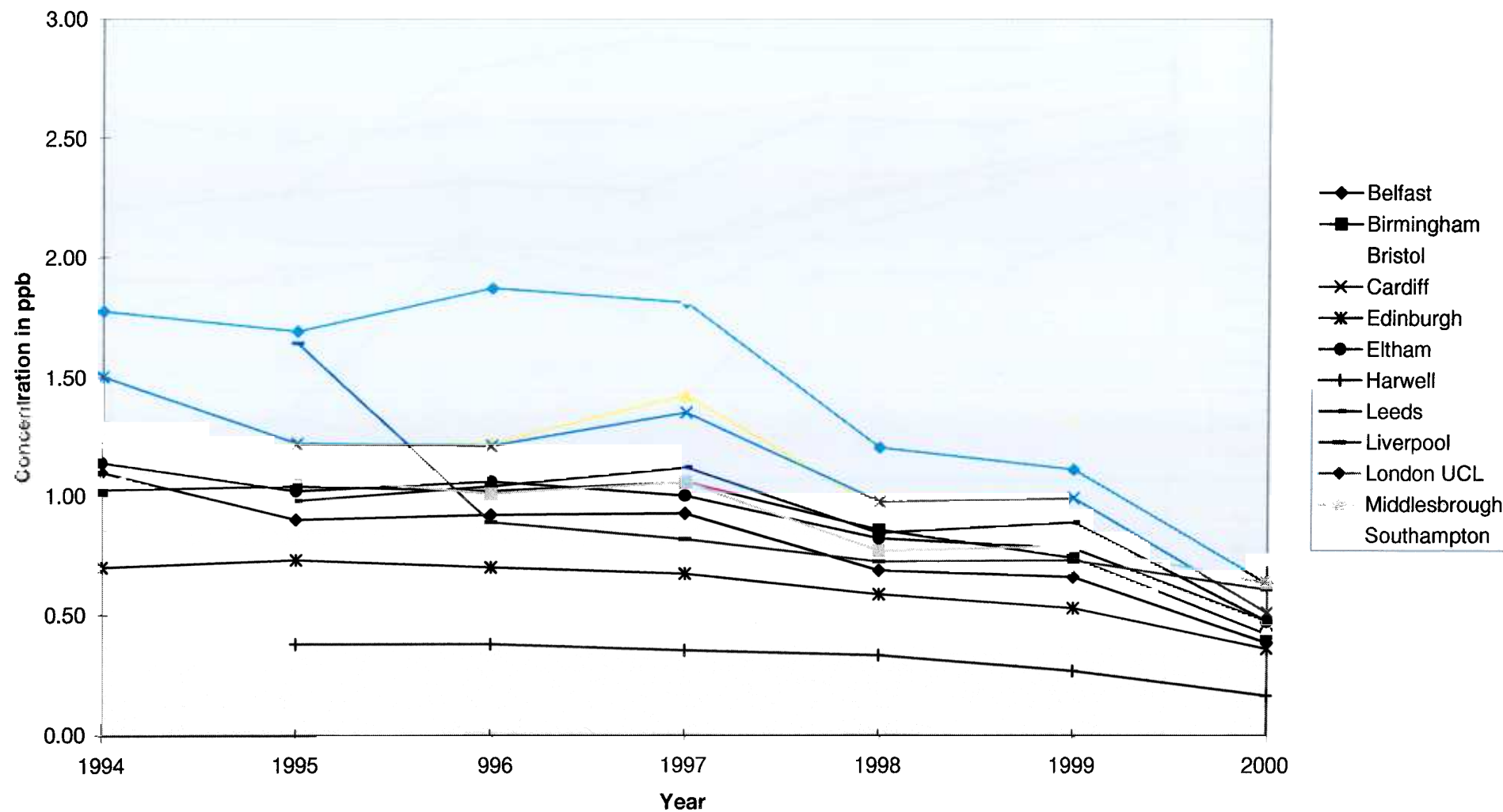


Figure 3b 1,3 Butadiene Annual Average Trend in Concentration for 1994-2000, excluding Marylebone Road

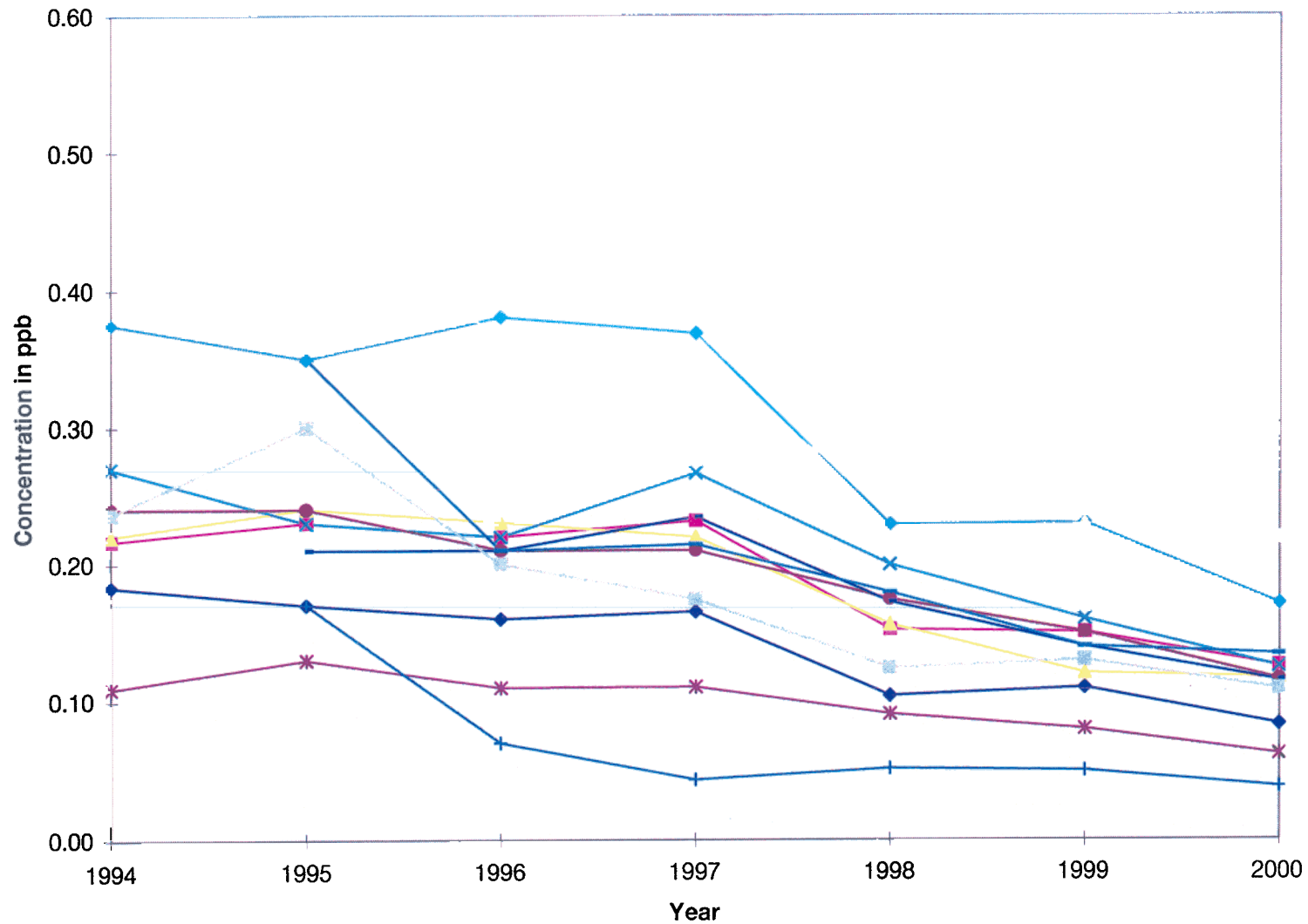


Figure 3c Network Annual Average Trend in Concentration for Benzene and 1,3 Butadiene from 1994 to 2000, excluding Marylebone Road

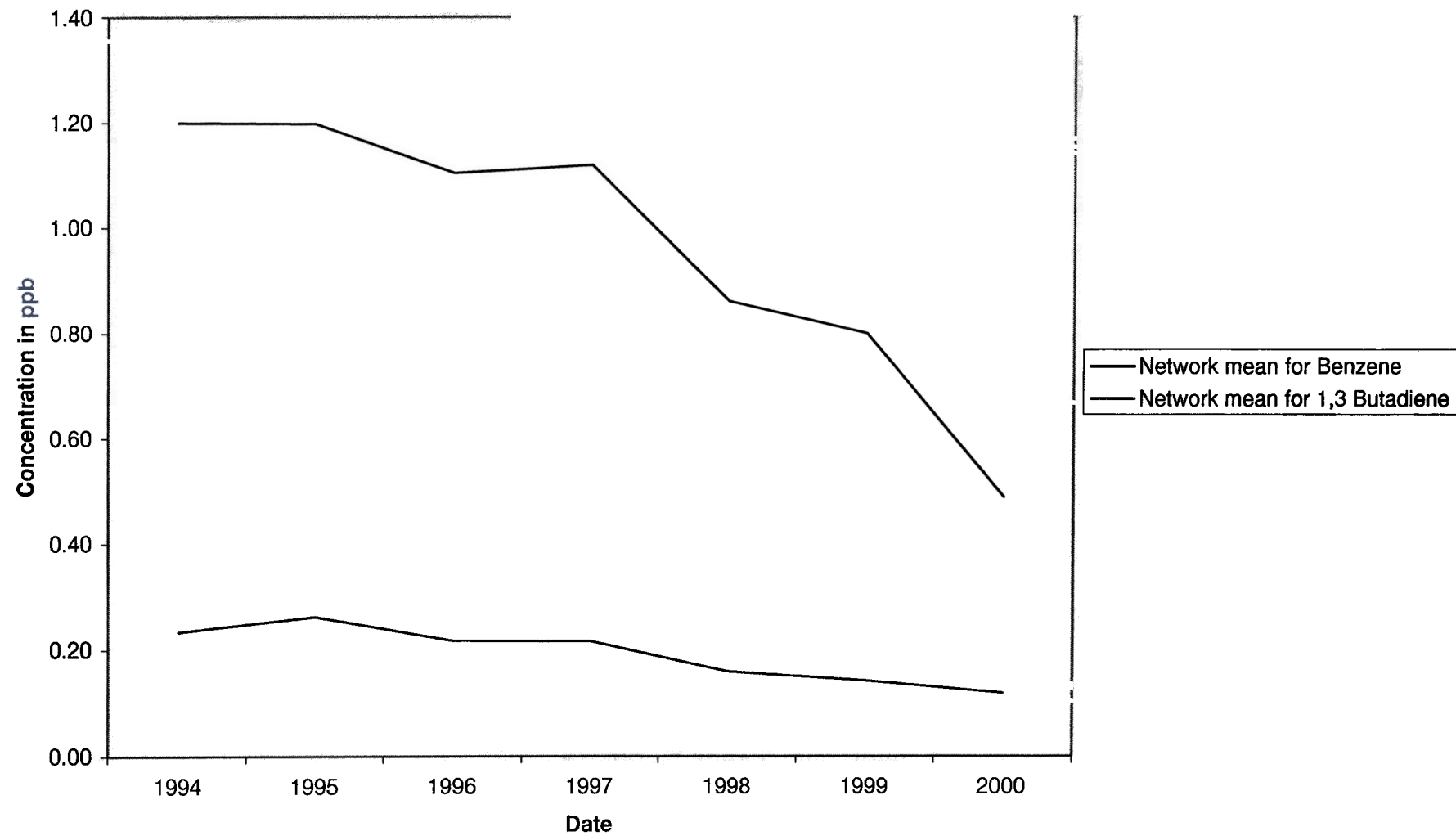


Figure 3d Benzene Monthly Average Concentrations in ppb for 1996 to 2000, excluding Marylebone Road

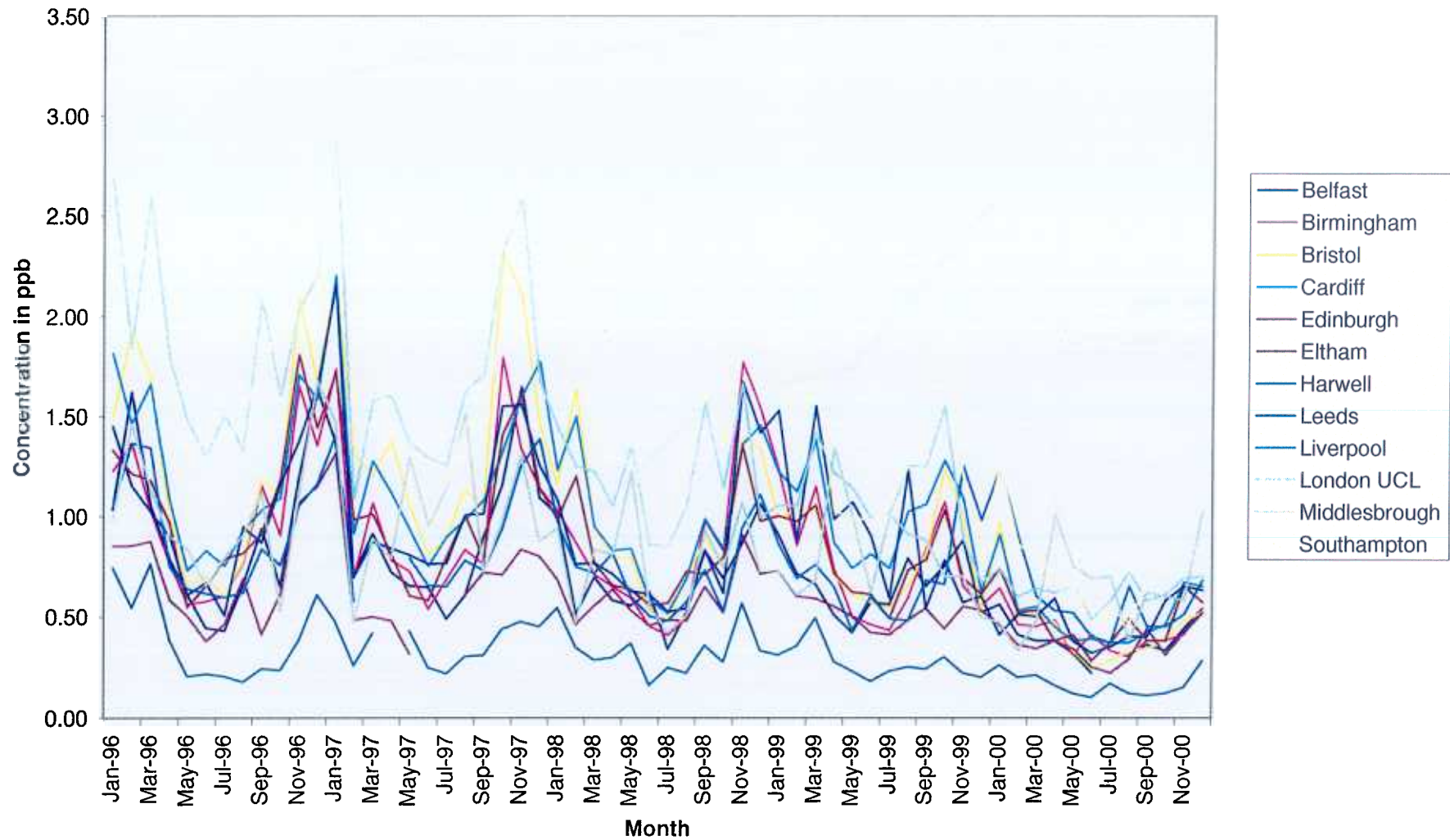


Figure 3e 1,3 Butadiene Monthly Average Concentrations in ppb for 1996-2000, excluding Marylebone Road

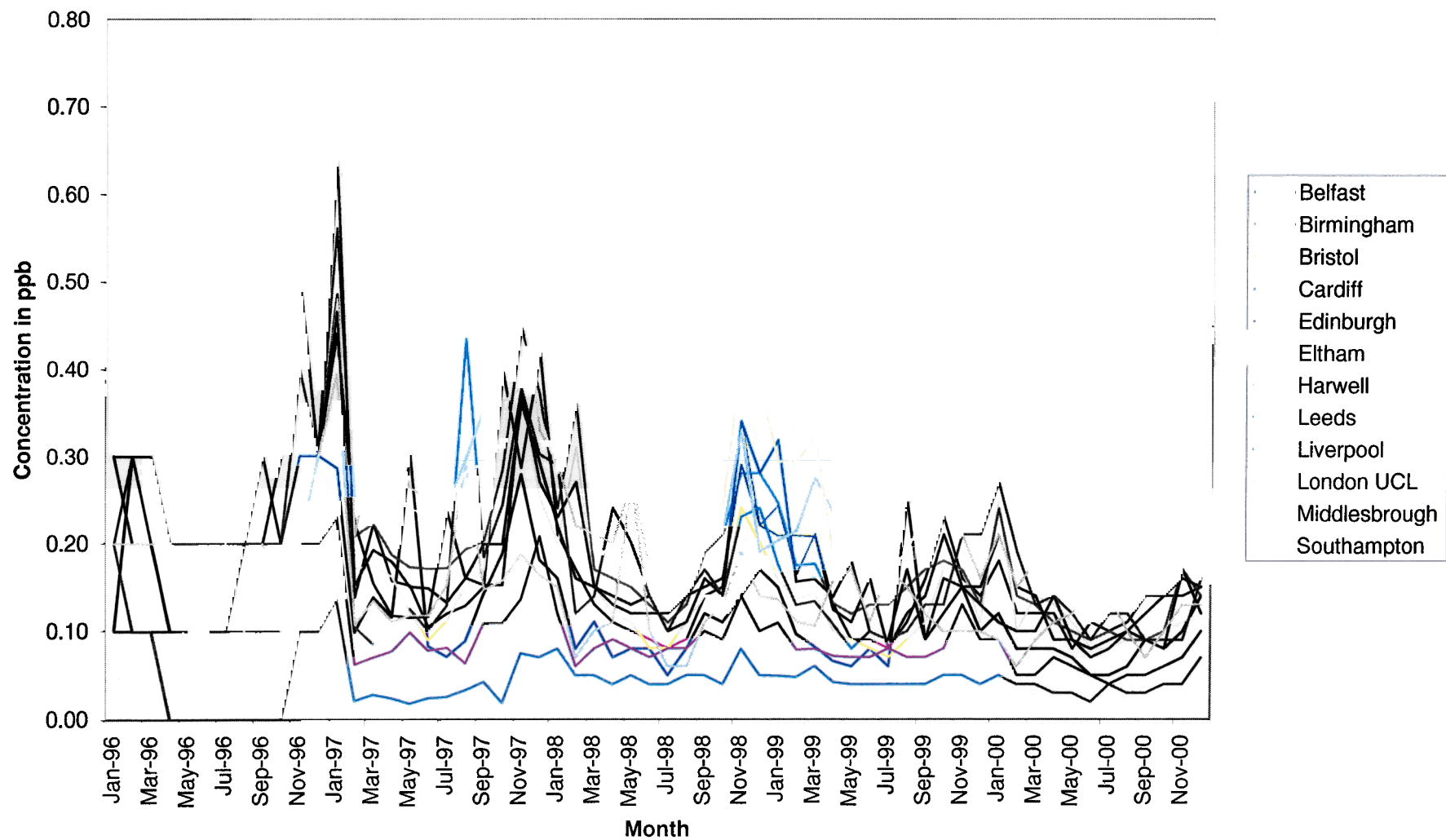


Figure 3f Benzene, 1,3 Butadiene and Carbon monoxide Monthly Average Concentrations in ppb for 1998 to 2000 at Marylebone Road

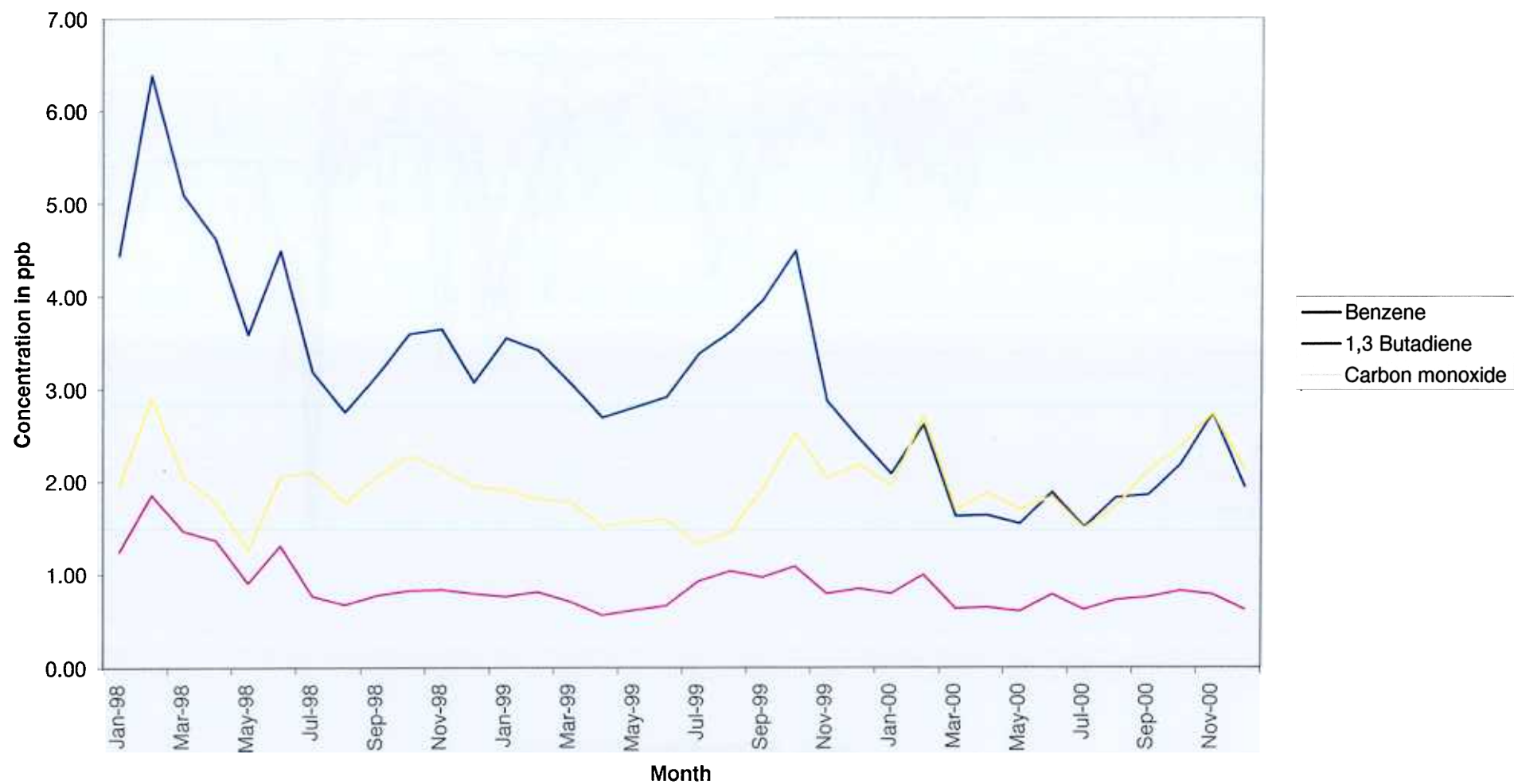


**Figure 3g Network Monthly Average Concentrations in ppb for Benzene and 1,3 Butadiene
form 1994 to 2000 , including Marylebone Road**

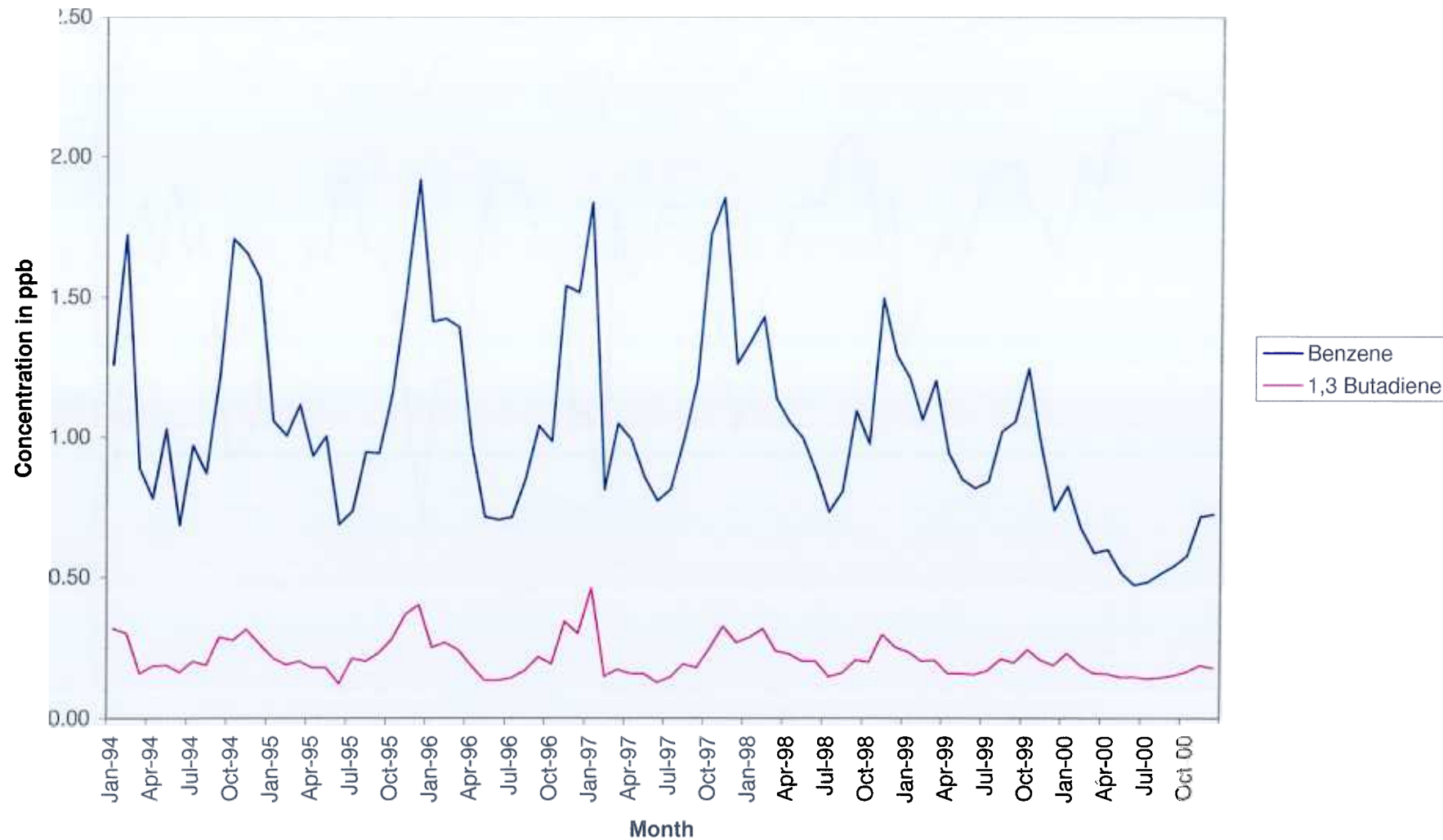


Figure 3h Network Monthly Average concentrations in ppb for Benzene and 1,3 Butadiene from 1994 to 2000, excluding Marylebone Road

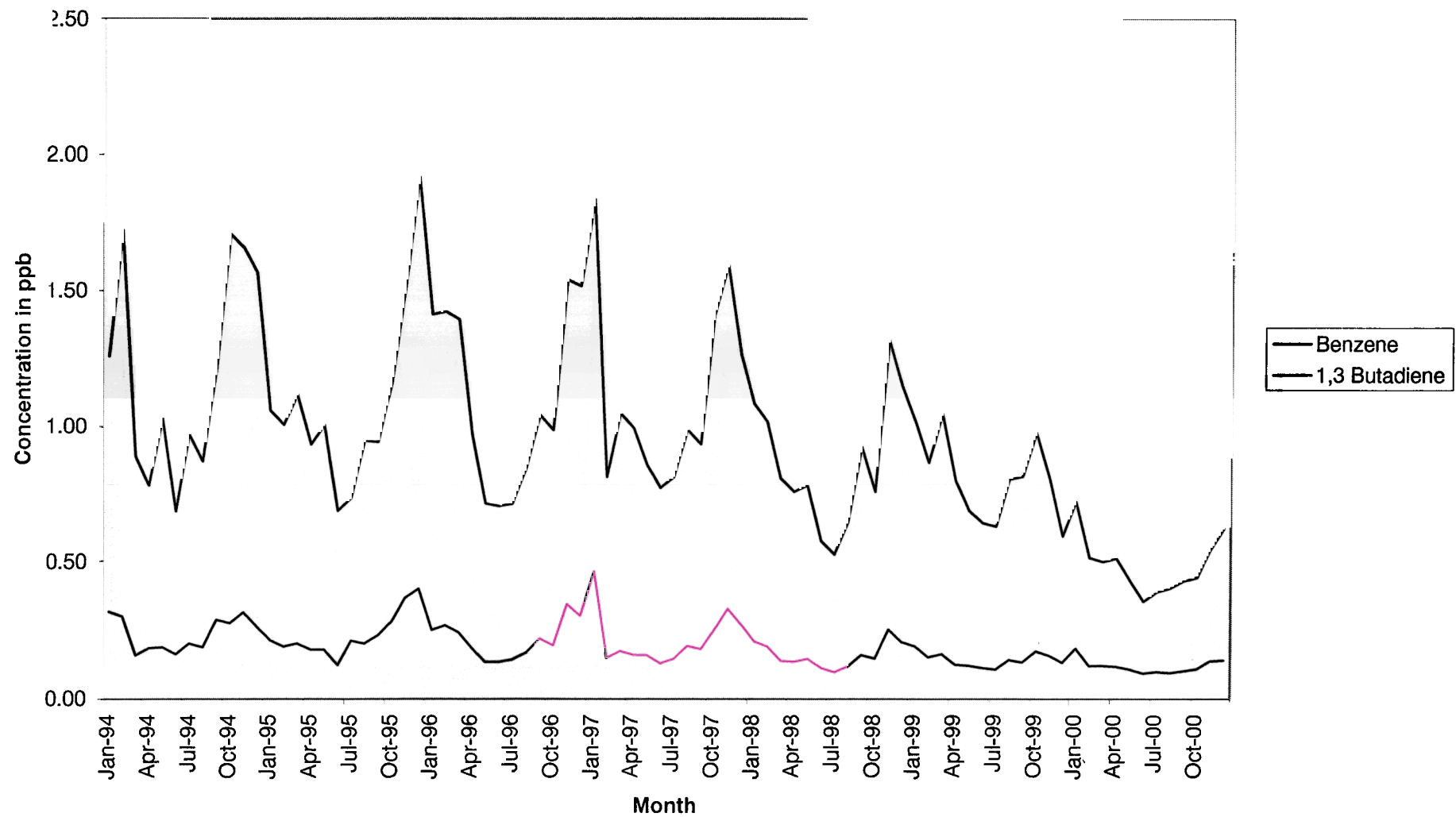


Figure 4a Benzene mean diurnal variation for 2000

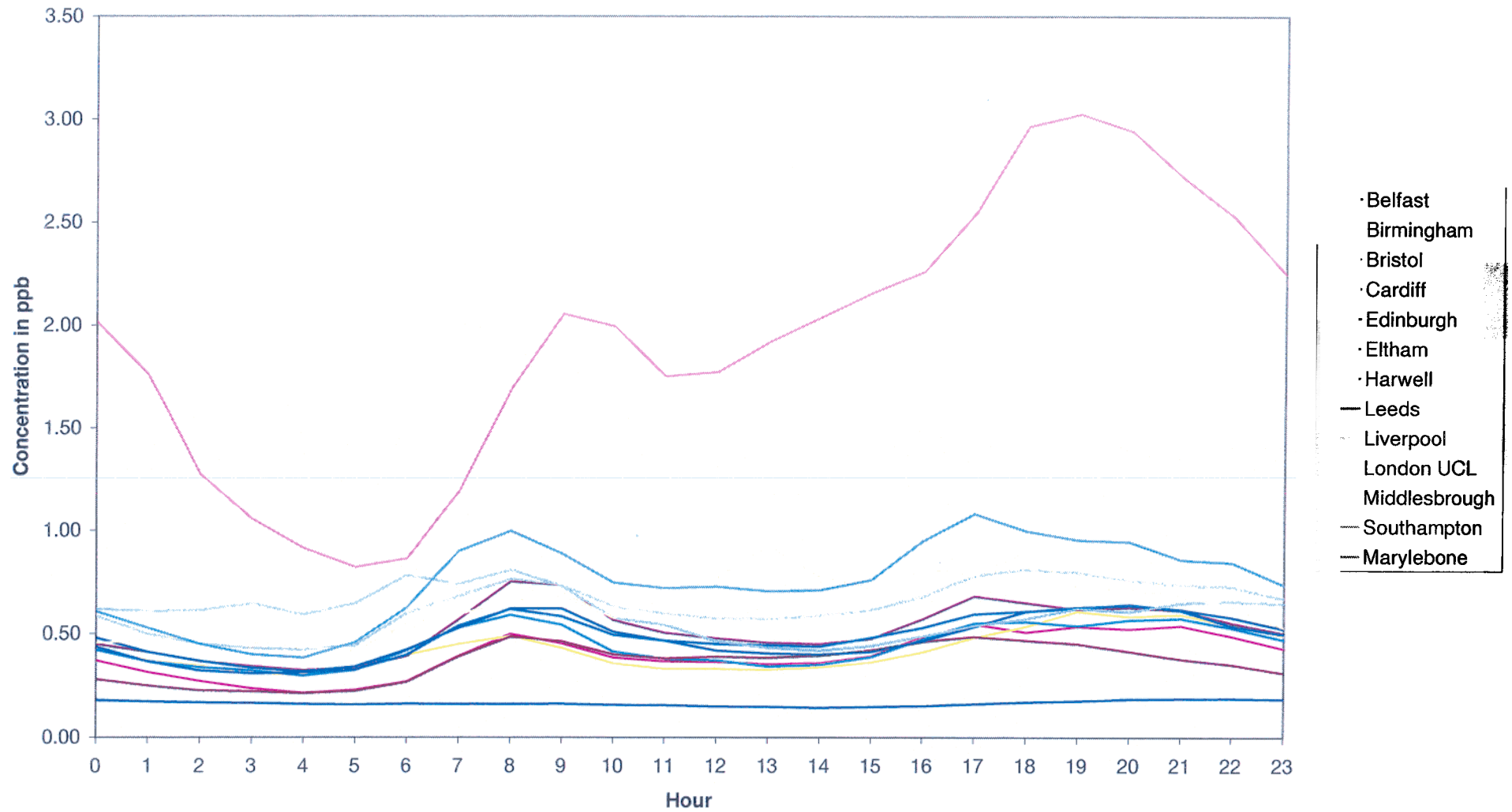


Figure 4b Benzene mean diurnal variation for 2000, excluding Marylebone Road

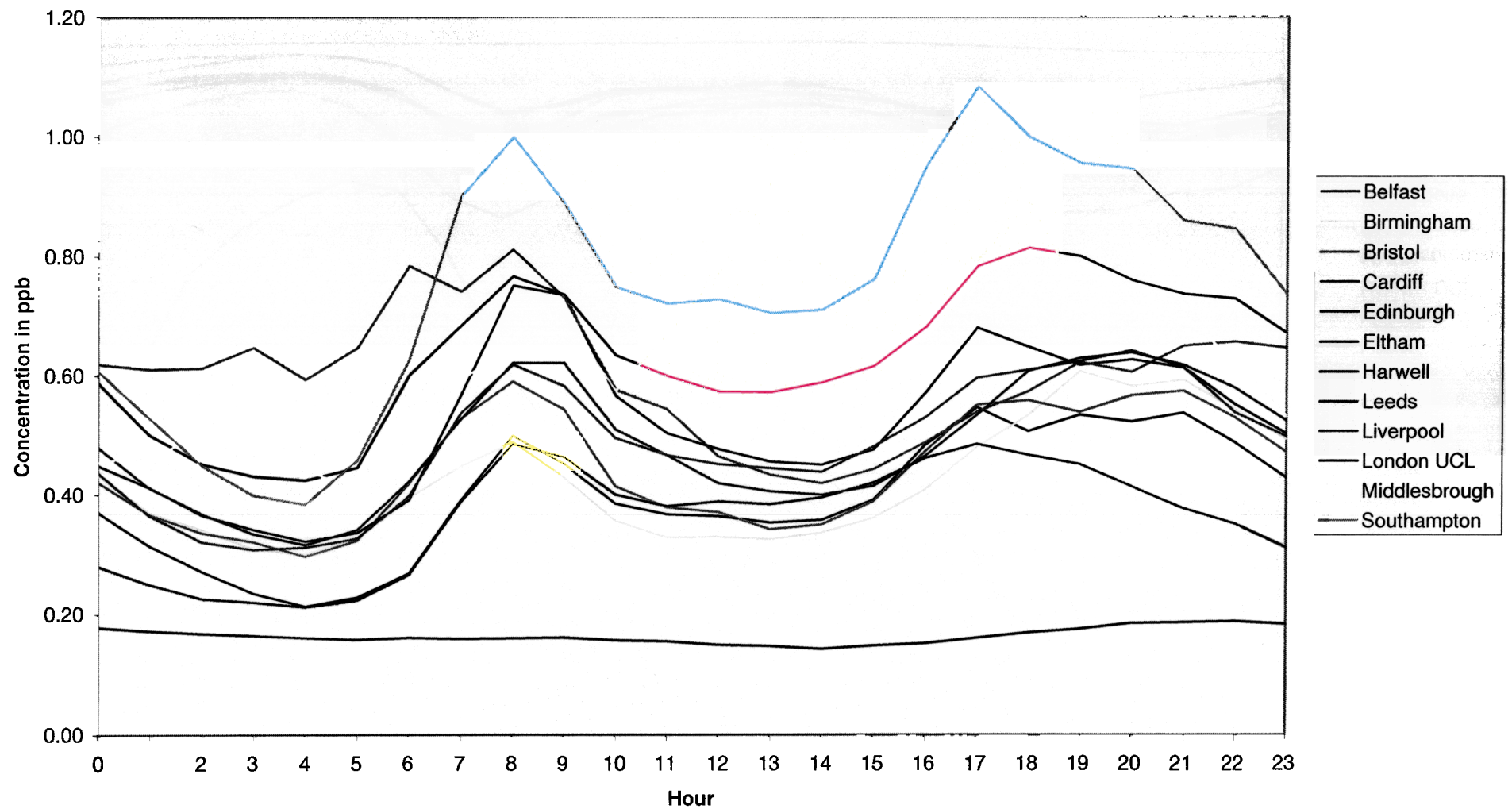


Figure 4c 1,3 Butadiene mean diurnal variation for 2000

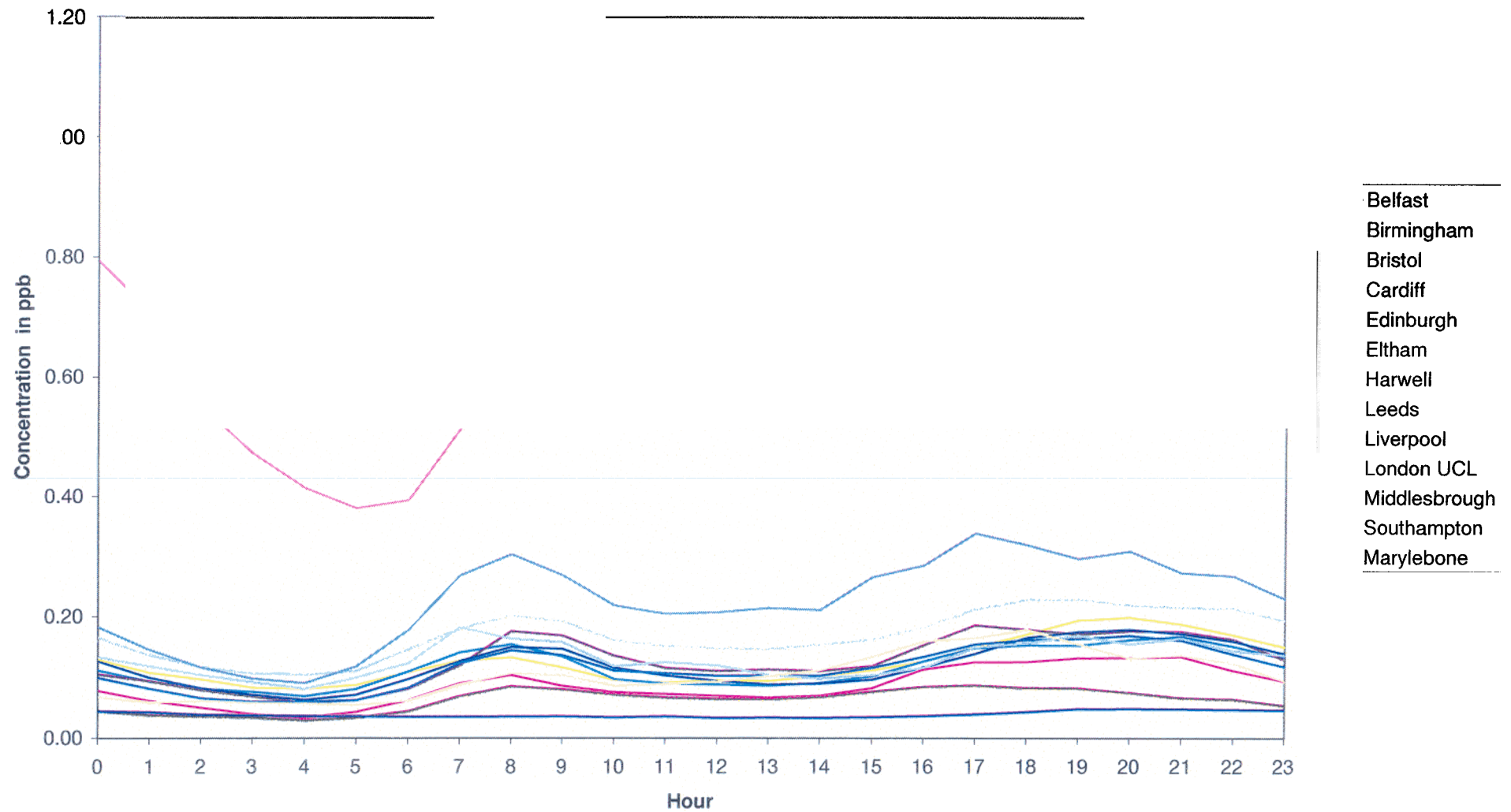


Figure 4d 1,3 Butadiene mean diurnal variation for 2000, excluding Marylebone Road

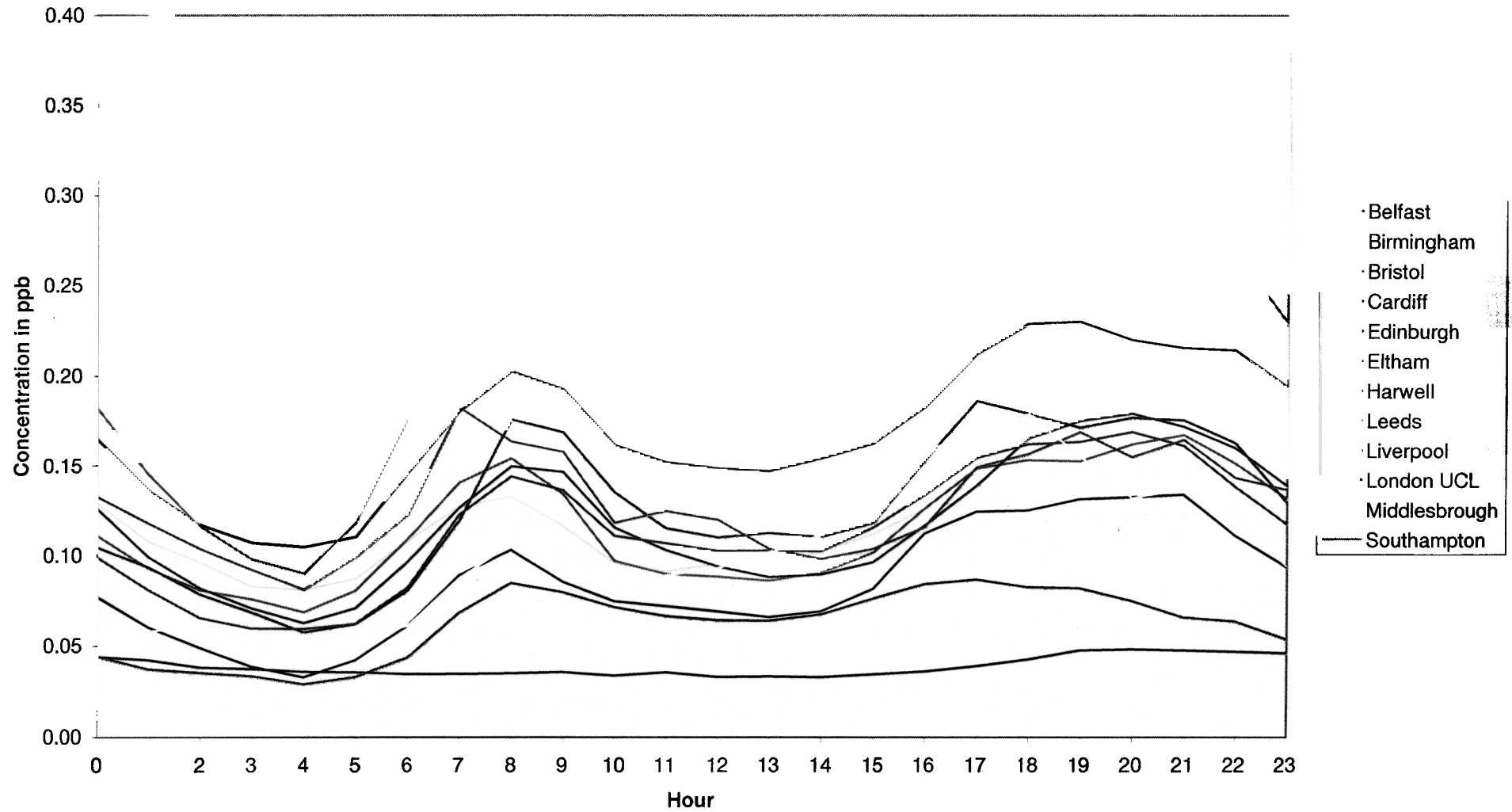


Figure 5a. Benzene/ 1,3-Butadiene Monthly average concentration ratios for 1999

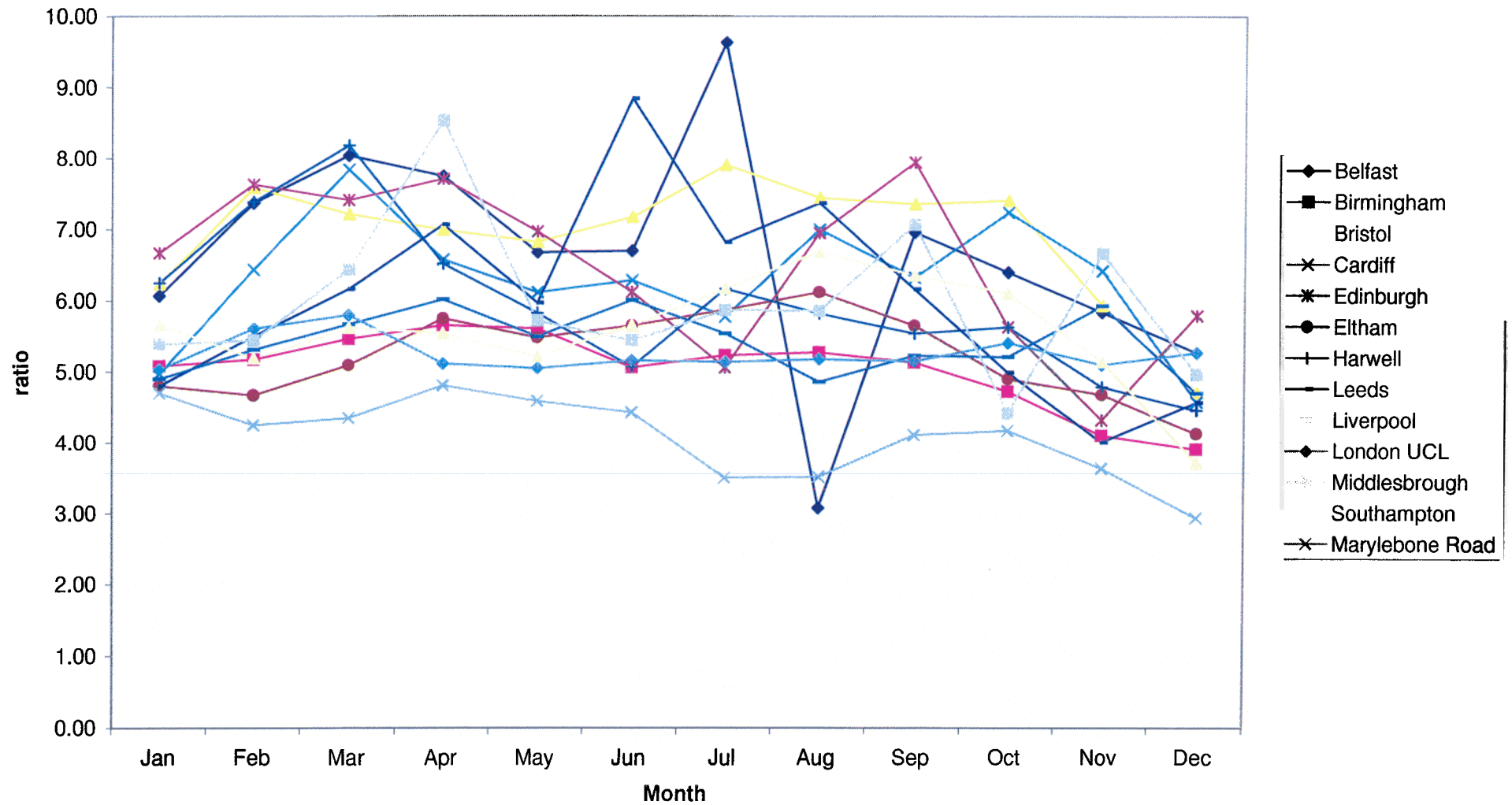


Figure 5b. Benzene/1,3 Butadiene Monthly Average Concentration ratios for 2000

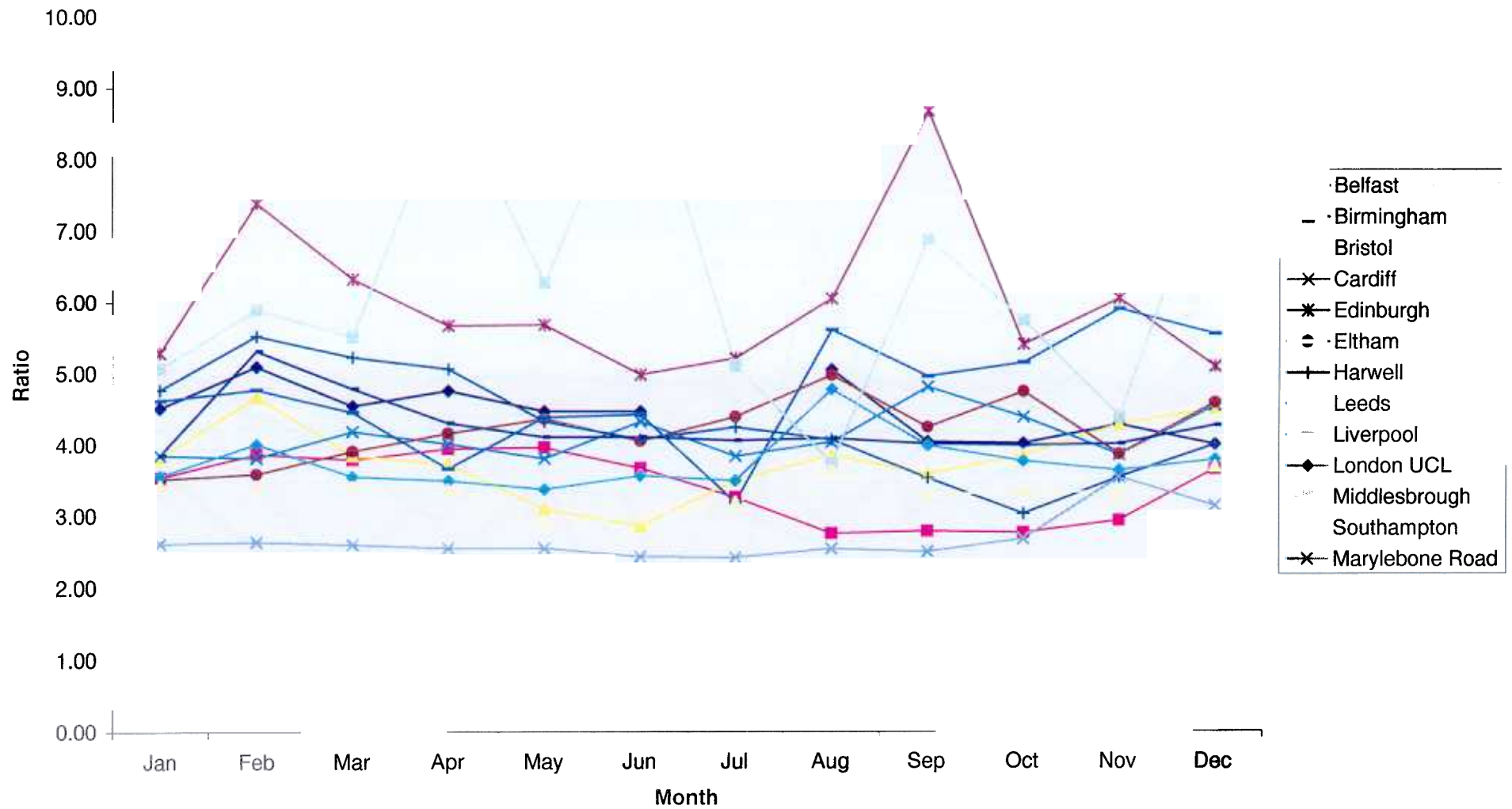


**Figure 5c Benzene/1,3 Butadiene Concentration Ratios: Mean Monthly Network Averages
in 1999 and 2000**

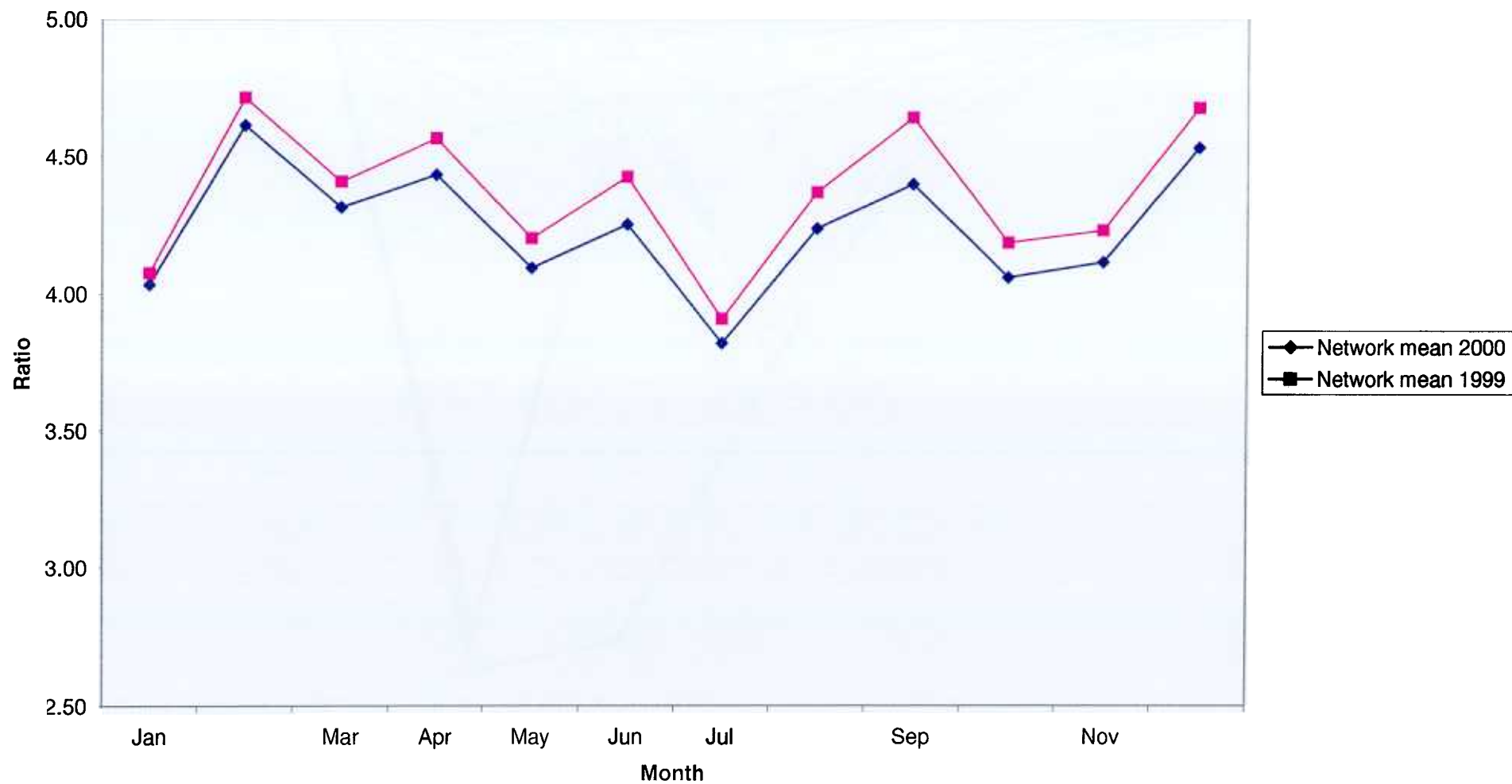


Figure 6a Concentrations of Hydrocarbons Measured at Middlesbrough on the 9th of May 2000

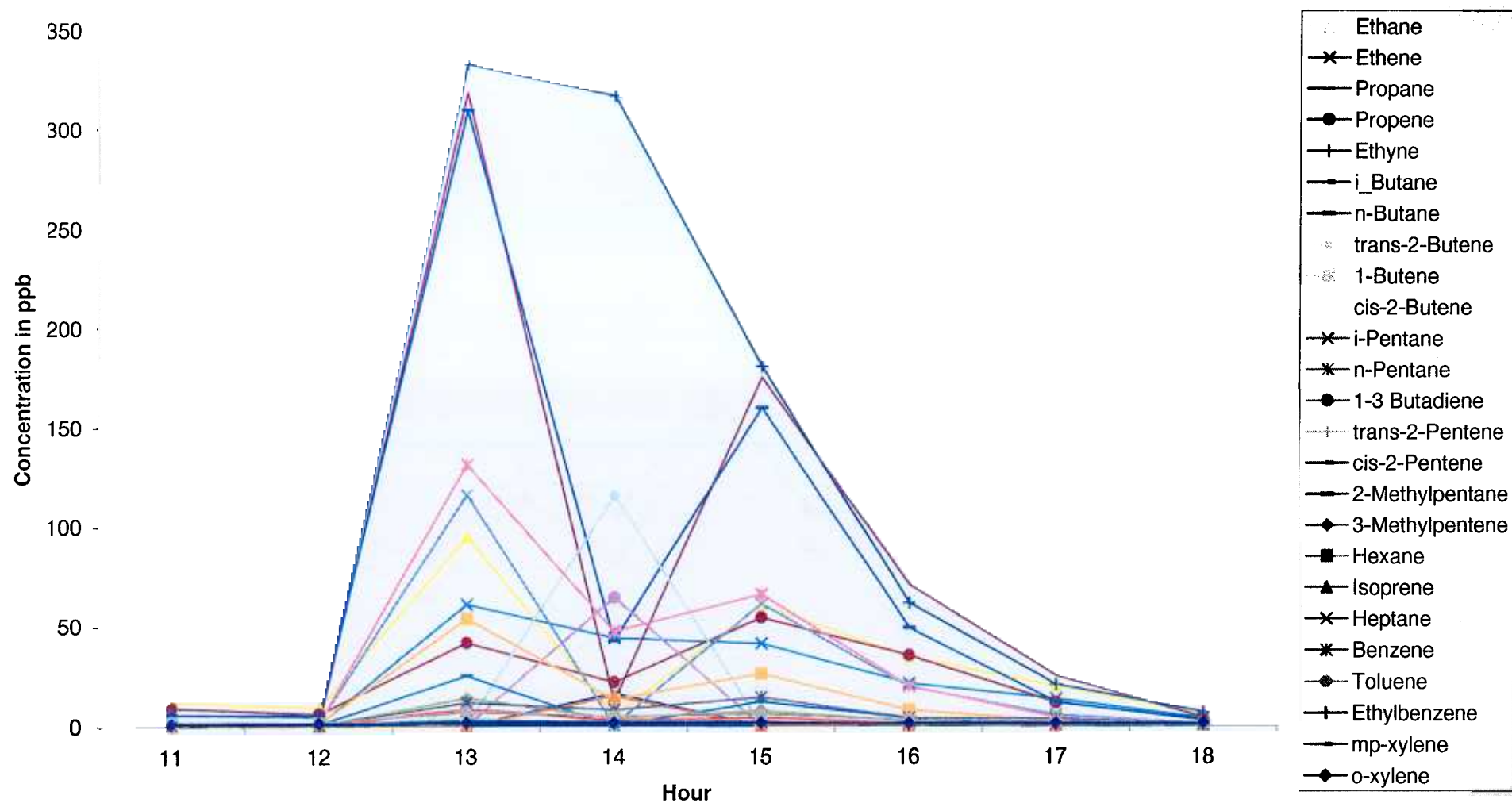


Figure 6b Concentrations of Hydrocarbons Measured at Southampton on 14th and 15th May 2000

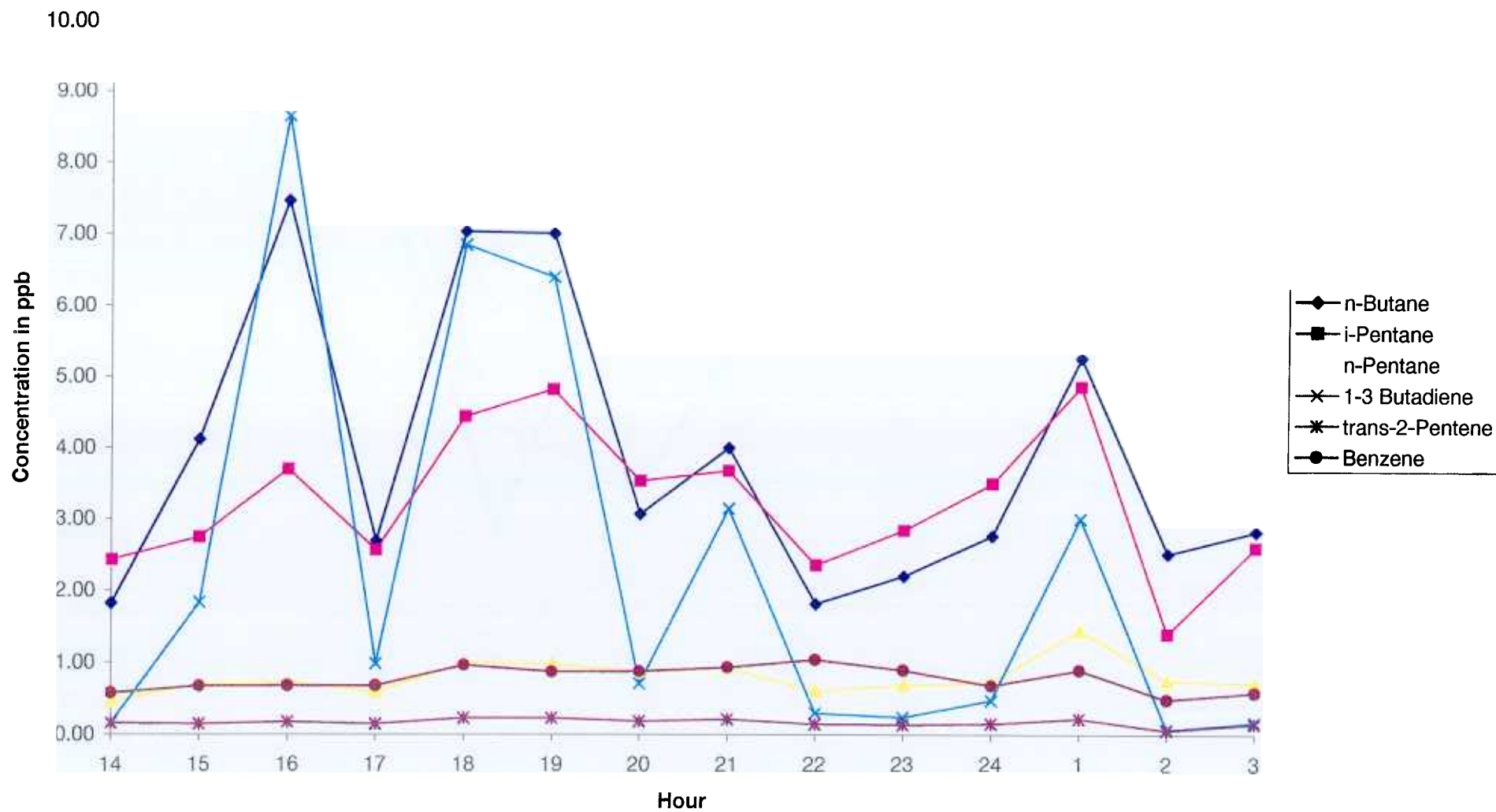


Figure 6c Concentrations of Hydrocarbons Measured at Liverpool on 24th May 2000

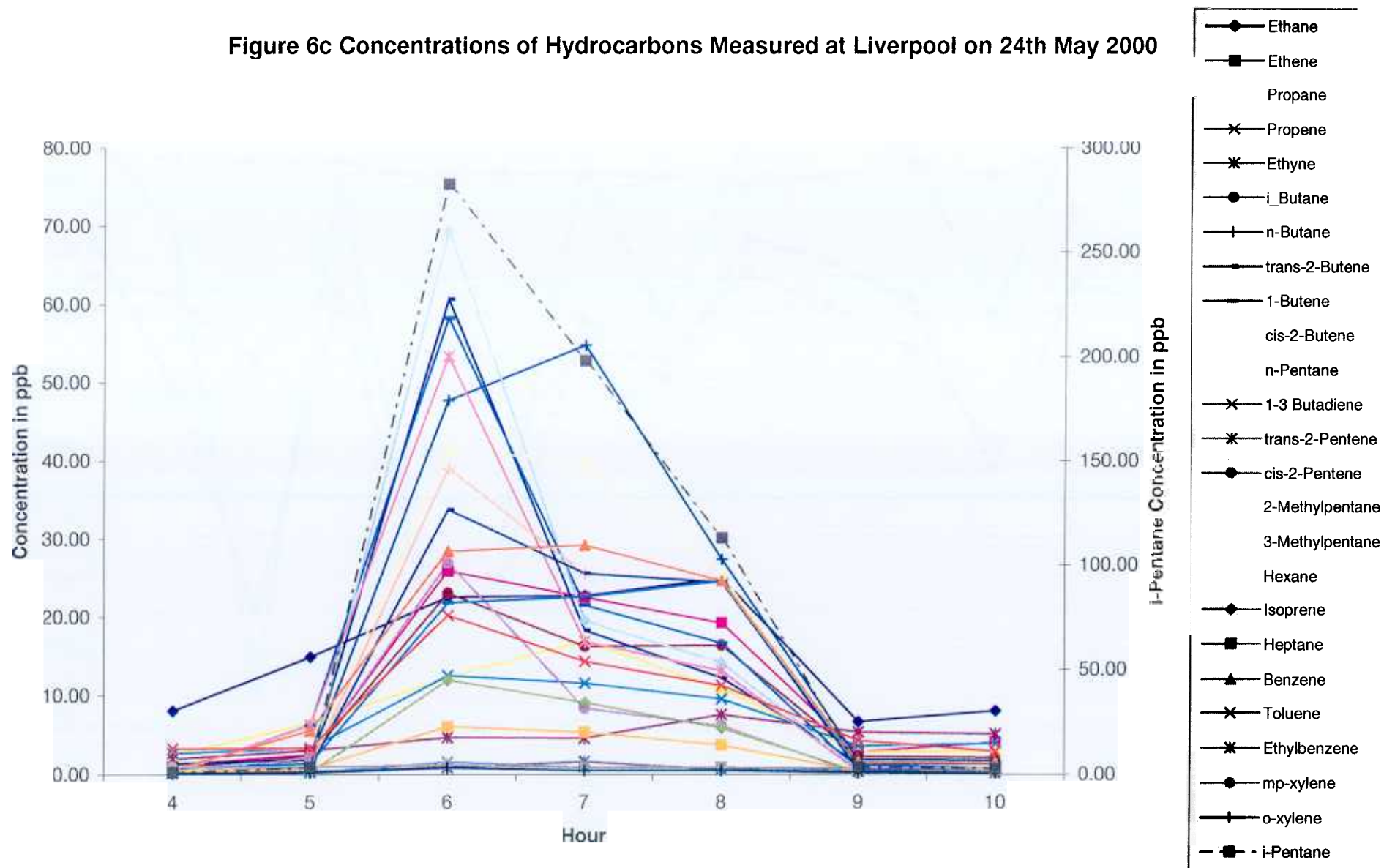


Figure 6d Concentrations of Hydrocarbons Measured at Liverpool on 17th - 18th August 2000

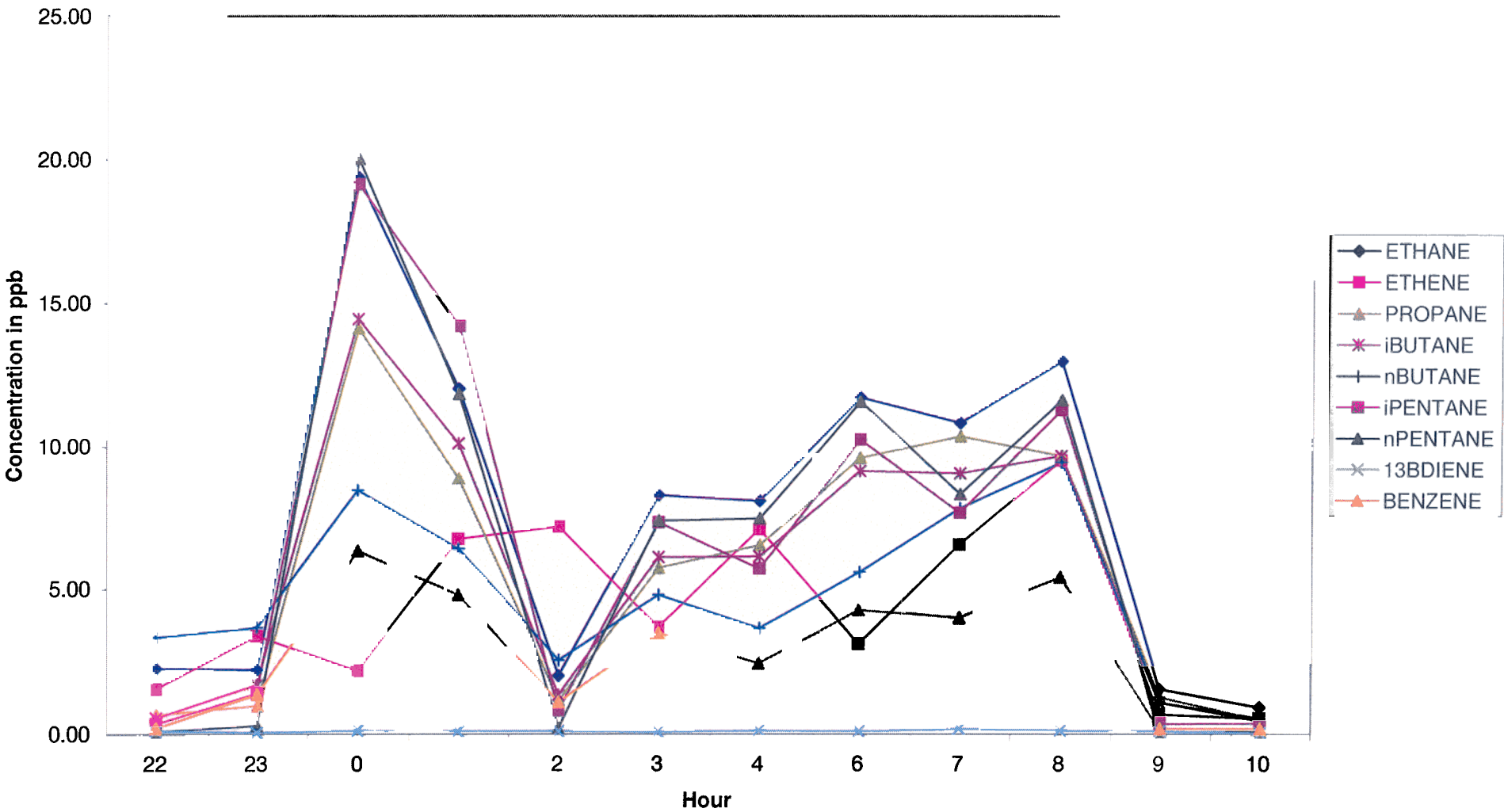


Figure 6e Concentrations of Hydrocarbons Measured at Middlesbrough on 28th August 2000

