

Summary of UK Ambient Hydrocarbon Air Quality Network Operations during 1999

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ISSN – 1369 6807

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INTRODUCTION

This report summarises the operation of the UK Ambient Hydrocarbon Air Quality Monitoring Network during 1999. 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.

Issues relating to data quality and the state of repair of individual sites are given in the separate 1999 Audit Report.

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 1999, with the figures for 1997 and 1998 given for comparison. Ratified data for Marylebone Road is only available from January 1998.

It is notable that the 1999 concentrations are significantly lower than in 1998, continuing the downward trend observed between 1997 and 1998.

Table 1: Annual average concentrations for 1,3 Butadiene and Benzene for 1997- 1999

	1,3-Butadiene (ppb)			Benzene (ppb)		
	1997	1998	1999	1997	1998	1999
Belfast	0.16	0.10	0.11	0.93	0.69	0.66
Birmingham	0.23	0.15	0.15	1.05	0.86	0.74
Bristol	0.22	0.16	0.12	1.42	0.94	0.80
Cardiff	0.27	0.20	0.16	1.34	0.98	0.99
Edinburgh	0.11	0.09	0.08	0.67	0.59	0.53
Eltham	0.21	0.17	0.15	1.00	0.82	0.78
Harwell	0.04	0.05	0.05	0.35	0.33	0.27
Leeds	0.23	0.17	0.14	1.11	0.85	0.89
Liverpool	0.23	0.18	0.14	0.89	0.73	0.73
London-UCL	0.37	0.23	0.23	1.80	1.20	1.11
Middlesbrough	0.17	0.12	0.13	1.05	0.77	0.79
Southampton	0.33	0.25	0.23	1.83	1.57	1.31
AVERAGE (12 sites)	0.21	0.16	0.14	1.12	0.86	0.80
Marylebone Road	-	1.02	0.83	-	4.27	3.31
AVERAGE (13 sites)	-	0.22	0.19	-	1.12	0.99

These concentrations can be expressed as $\mu\text{g}/\text{m}^3$ at standard conditions of 20°C and 1013mb by multiplying by a factor of 3.25 for benzene, and 2.25 for 1,3-butadiene.

Comparison to NAQS standards

No sites exceeded the NAQS standards for benzene or 1,3-butadiene in 1999.

Comparison to EC Daughter Directive

Comparing the 1999 results to the EC Daughter Directive for benzene:

The limit value of $5 \mu\text{g}/\text{m}^3$ (1.5 ppb) was exceeded at Marylebone Road;

The upper assessment threshold of $3.5 \mu\text{g}/\text{m}^3$ (1.1 ppb) was also exceeded at London-UCL and Southampton;

The lower assessment threshold of $2 \mu\text{g}/\text{m}^3$ (0.62 ppb) was exceeded at all sites except Harwell and Edinburgh.

Figures 1 to 6 (collected at the end of this report) present the benzene and 1,3 butadiene data for 1999 graphically, with some comparisons to earlier years.

Figures 1 & 2 show the 1999 monthly variations for benzene and 1,3 butadiene.

Figure 3 shows long term trends in annual and monthly averages.

Figure 4 shows diurnal variations.

Figures 5 & 6 show benzene/1,3 butadiene concentration ratios in 1998 and 1999.

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 pentane are combined, as they appear on the National Archive.

Table 2: Annual average concentrations of hydrocarbons for 1999 (ppb)

Species / Site	Belfast	Birmingham	Bristol	Cardiff	Edinburgh	Eltham	Harwell	Leeds	Liverpool	London - UCL	Middlesbrough	Southampton	Marylebone Road
Ethane	1.88	5.94	4.42	12.93	3.31	3.23	2.03	6.99	3.75	3.64	5.66	3.99	11.07
Ethene	1.37	2.04	2.19	2.16	1.05	1.94	0.69	2.29	1.60	2.35	3.16	2.56	12.77
Propane	2.46	3.13	2.30	3.88	2.52	1.70	0.97	2.95	3.09	2.55	5.33	2.32	3.94
Propene	0.74	1.00	1.41	1.36	1.13	1.15	0.28	1.79	1.31	1.57	3.19	1.66	4.12
Ethyne	1.55	3.35	3.45	3.01	1.63	2.13	0.46	2.59	1.50	3.79	-*	-*	7.34
I-butane	0.66	1.53	1.00	1.52	1.17	1.21	0.31	1.59	1.22	1.86	-*	-*	5.12
N-butane	1.51	2.82	2.31	3.46	2.06	2.31	0.65	3.87	2.62	3.18	2.87	2.96	8.89
Trans 2 butene	0.16	0.21	0.16	0.26	0.58	0.16	0.06	0.52	0.36	0.24	0.19	0.29	0.75
1 Butene	0.11	0.14	0.12	0.13	0.14	0.14	0.04	0.18	0.27	0.19	0.11	0.23	0.73
Cis 2 butene	0.08	0.13	0.10	0.15	0.21	0.11	0.03	0.26	0.20	0.16	0.10	0.20	0.57
I-pentane	0.76	1.70	1.63	1.90	0.91	2.02	0.72	2.02	1.89	2.78	1.34	2.47	8.95
N-pentane	0.34	0.51	0.53	0.84	0.63	0.46	0.16	0.73	0.90	0.61	0.80	0.71	1.74
1,3 butadiene	0.11	0.15	0.12	0.16	0.08	0.15	0.05	0.14	0.14	0.23	0.13	0.23	0.83
Trans 2 pentene	0.04	0.11	0.11	0.15	0.06	0.09	0.01	0.16	0.15	0.15	0.07	0.17	0.53
Cis 2 pentene	0.02	0.06	0.06	0.08	0.03	0.05	0.00	0.09	0.08	0.08	0.03	0.09	0.30
methyl pentane	0.33	0.65	0.57	0.85	0.35	0.75	0.16	0.95	0.84	1.20	0.61	1.18	3.56
N-hexane	0.06	0.10	0.09	0.11	0.06	0.13	0.02	0.09	0.07	0.17	0.09	0.16	0.47
Isoprene	0.15	0.17	0.19	0.27	0.14	0.15	0.05	0.41	0.31	0.23	0.26	0.35	0.65
N-heptane	0.14	0.14	0.11	0.14	0.09	0.13	0.03	0.22	0.15	0.21	0.16	0.19	0.50
Benzene	0.66	0.74	0.80	0.99	0.53	0.78	0.27	0.89	0.73	1.11	0.79	1.31	3.31
Toluene	1.27	1.64	1.47	1.70	1.30	1.61	0.51	1.89	1.59	2.41	1.11	2.60	7.60
Ethyl Benzene	0.28	0.50	0.24	0.26	0.19	0.32	0.05	0.34	0.45	0.38	0.23	0.41	1.20
m+p-xylene	0.91	1.73	0.79	0.82	0.69	1.01	0.14	1.15	1.22	1.21	0.77	1.26	4.12
o-xylene	0.31	0.57	0.27	0.27	0.23	0.37	0.05	0.39	0.39	0.44	0.24	0.46	1.55

* Value not present due to continuous co-elution.

3. SPECIFIC HYDROCARBON EVENTS REPORTED

The following table summarises the events observed by the Hydrocarbon Network during 1999. All observed events were reported to the DETR press office. Figures 7a - c 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
BIRMINGHAM	21-22/1/99 9:00	Ethane Ethene Propane Ethyne n-butane i-pentane Benzene	81.5 ppb 46.5 ppb 44.2 ppb 109.8 ppb 50.1 ppb 35.7 ppb 46.7 ppb	46.7 ppb	3.5 ppb
BIRMINGHAM	17-18/3/99 23:00	Ethane Ethene Ethyne Propane Propene 13Bdiene Benzene	80.4 ppb 32.0 ppb 42.0 ppb 32.9 ppb 13.3 ppb 2.8 ppb 12.4 ppb	12.4ppb	2.8ppb
MIDDLESBROUGH	2-3/7/99 22:00	Ethane Ethene Propane Propene Benzene	47.3 ppb 14.8 ppb 120.5 ppb 42.1 ppb 29.7 ppb	29.7ppb	3.6ppb

4. DATA CAPTURE SUMMARY

All data for 1999 have 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 1999

	Jan	Feb	Mar	Apr	May	Jun	Jul
Belfast	99.8	92.4	99.6	99.8	98.9	99.2	92.2
Birmingham	98.9	74.7	60.0	98.1	97.4	83.7	94.2
Bristol	99.9	99.9	90.3	92.9	96.9	86.0	91.9
Cardiff	99.3	96.3	98.0	94.9	86.4	90.5	91.3
Edinburgh	99.5	100.0	96.1	98.8	80.2	97.1	84.4
Eltham	99.8	93.9	91.3	91.4	97.7	98.6	91.3
Harwell	96.1	67.7	84.9	85.6	88.3	87.0	86.6
Leeds	23.0	84.3	96.2	96.5	82.9	97.5	82.1
Liverpool	87.5	96.4	99.4	86.1	70.6	91.4	35.5
London-UCL	99.8	92.1	97.9	99.6	99.3	97.4	90.8
Middlesborough	100.0	98.7	100.0	99.4	99.4	99.9	98.5
Southampton	99.8	99.9	98.5	80.7	100.0	98.6	99.9
Monthly Mean	92.0	91.4	92.7	93.7	91.5	93.9	86.6

Marylebone Road	77	87.2	74.9	61.7	50.4	87	79.6
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	Aug	Sep	Oct	Nov	Dec	Annual Mean ¹
Belfast	74.8	72.3	95.7	88.8	99.7	92.8
Birmingham	79.9	99.8	96.5	83.7	99.9	89.0
Bristol	97.7	92.2	89.1	98.2	99.7	94.5
Cardiff	47.1	83.9	79.6	97.5	96.4	88.3
Edinburgh	88.2	87.1	95.5	94.7	99.7	93.4
Eltham	98.5	99.9	100.0	82.6	99.6	95.4
Harwell	99.9	99.9	99.5	98.6	95.6	91.0
Leeds	46.5	98.1	87.7	66.3	89.1	79.0
Liverpool	68.9	89.2	99.8	91.0	94.4	84.0
London-UCL	99.4	99.7	78.9	91.5	97.3	95.3
Middlesborough	97.3	99.7	94.9	99.3	99.1	98.8
Southampton	99.6	99.4	88.7	99.7	98.9	97.0
Monthly Mean	83.2	93.4	92.2	91.0	97.5	91.6

Marylebone Road	92.6	89.2	99.3	79.8	96.1	82.8
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¹ These figures represent data capture as a percentage of “available” time, i.e excluding calibration and servicing.

Table 5: Percentage 1,3 Butadiene data capture for 1999

	Jan	Feb	Mar	Apr	May	Jun	Jul
Belfast	99.8	92.4	99.6	99.8	98.9	99.2	92.8
Birmingham	99.2	74.7	61.4	98.1	97.4	83.7	94.4
Bristol	99.9	99.9	90.3	93.2	96.9	86.0	92.9
Cardiff	99.3	96.3	98.1	94.9	86.4	90.5	93.0
Edinburgh	98.1	100.0	96.1	97.8	80.6	99.0	84.7
Eltham	99.8	98.2	96.6	94.3	97.7	98.4	90.1
Harwell	96.1	68.8	84.9	85.6	88.3	87.0	86.2
Leeds	23.0	84.8	90.7	97.6	83.3	97.5	82.8
Liverpool	88.7	96.2	99.4	83.9	70.2	67.9	33.5
London-UCL	99.6	92.1	98.1	99.5	99.3	97.4	90.8
Middlesbrough	100.0	98.7	99.5	99.6	99.4	99.9	98.5
Southampton	99.8	100.0	98.5	80.7	100.0	98.6	99.9
Monthly Mean	91.9	91.8	92.8	93.8	91.5	92.1	86.6

Marylebone Road	77	87.4	74.9	62.1	50.4	87.3	84.4
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	Aug	Sep	Oct	Nov	Dec	Annual Mean¹
Belfast	76.3	72.3	95.7	88.8	99.7	93.0
Birmingham	79.9	99.8	96.5	83.7	99.9	89.2
Bristol	97.7	92.6	89.4	97.9	99.7	94.7
Cardiff	85.3	77.2	78.8	97.5	96.4	91.1
Edinburgh	88.1	87.1	95.3	93.8	99.6	93.3
Eltham	98.1	99.3	100.0	82.6	99.7	96.2
Harwell	99.9	99.9	99.9	98.6	95.7	91.1
Leeds	46.5	98.3	88.0	66.3	89.4	78.8
Liverpool	68.9	89.2	99.8	90.8	94.4	81.8
London-UCL	99.4	99.7	78.9	91.5	97.3	95.3
Middlesbrough	97.3	99.7	94.9	99.3	99.1	98.8
Southampton	99.6	99.4	89.7	99.7	99.7	97.1
Monthly mean	86.4	92.9	92.2	90.9	97.6	91.7

Marylebone Road	80.6	86.6	99.4	80	96.3	82.1
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¹ These figures represent data capture as a percentage of “available” time i.e excluding calibration and servicing.

The data capture figures of 91.6% and 91.7% for benzene and 1,3-butadiene compare with respective figures of 92.7% and 93.0% in 1998, mainly due to the problems at the Leeds and Liverpool sites described below.

5. CAUSES OF SIGNIFICANT DATA LOSS

All sites achieved greater than 75% data capture, allowing representative annual averages to be reported for all sites.

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

- (i) Birmingham (89.0% benzene, 89.2% 1,3-butadiene): Most data loss was caused in February and March by faulty cryo-valves leading to extensive damage to the automated TCT sampling head on two occasions. The varying specification for these valves was a cause of problems in 1998, and very careful attention is now paid to the version used, by both Chrompack and NPL. Data also had to be removed between two successive maintenance visits as there were no valid calibrations available.
- (ii) Cardiff (88.3% benzene, 91.1% 1,3-butadiene): Most data loss was caused by a long period (August to October) of successive problems including natural gas ingress, cryo-valve failures and compressor contamination problems. The natural gas problems have been reduced by work on the Cardiff site infrastructure and relocation of the compressed air intake, so that current data capture is satisfactory.
- (iii) Leeds (79.0% benzene, 78.8% 1,3-butadiene): This site had repeated problems throughout the year, which Chrompack engineers were not able to diagnose. After the entire chromatograph system was replaced with the NPL instrument, without solving the problem, the cause was eventually traced to contamination from within the site infrastructure. The contamination problem has now been entirely solved, and preventative action has been taken at all other sites. The manifold was vandalised in August causing 8 days lost data and has been rebuilt in a more robust fashion.
- (iv) Liverpool (84.0% benzene, 81.8% 1,3-butadiene): This site had repeated problems throughout the year, requiring many return visits by Chrompack engineers. This often resulted in unscalable data as there were no valid calibrations available. The site also suffered from cryo-valve and ancillary equipment failure. Data capture for more recent months has been very good.

6. SITE OPERATIONS

The twelve network sites were visited by Chrompack engineers 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 replaced.

In addition, a 6-month minor service is carried out by Chrompack engineers. During this visit a number of key components which have lifetimes of less than 1 year of continuous use are replaced.

The total number of non-service visits by Chrompack 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 apart from the regular weekly visits.

Table 6: Summary of service visits and LSO special visits

Site	Chrompack Visits	LSO Special visits	Annual Service 1999
Belfast	6	16	June
Birmingham	6	21	December
Bristol	6	14	March
Cardiff	6	27	February
Edinburgh	6	2	August
Eltham	6	5	November
Harwell	6	24	July
Leeds	22	13	(1)
Liverpool	12	7	April
Middlesbrough	1	9	October
Southampton	0	1	October
UCL London	3	6	March

¹ The Leeds annual service was subsumed into another Chrompack visit.

The average number of Chrompack visits made to monitoring sites increased in 1999. In 1998, the average number of visits to a site was 4; in 1999 the average was 6.6.

In 1999 the average number of LSO special visits to sites was 12, which compares with an average number of 11 in 1998.

7 LSO DUTIES PERFORMED

The following table summarises the duties performed by the LSOs at the 12 network sites. LSOs 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 1999	Number of "Weekly" Visits 1999
Belfast	20	50
Birmingham	17	45
Bristol	24	50
Cardiff	24	46
Edinburgh	27	50
Eltham	24	48
Harwell	21	47
Leeds	29	49
Liverpool	24	45
Middlesbrough	22	51
Southampton	25	53
London-UCL	- ¹	48

Automated calibrations are performed at London UCL every 47 hours.

8. SUMMARY

The annual mean benzene and 1,3 butadiene concentrations recorded by all hydrocarbon monitoring sites in 1999 were below the NAQS standards of 5 ppb for benzene and 1 ppb for 1,3 butadiene, and show a significant decrease from 1998 levels.

Data capture was generally good with an average of 91.7%, with four sites falling below 90%. These four cases were caused by various factors which were addressed by the end of the year. All sites recorded greater than 75% data capture allowing representative annual averages to be calculated for all sites.

The performance of the affiliated (Perkin Elmer based) Marylebone Road site was broadly similar to 1998, with data capture of over 82% for 1999.

The network recorded fewer elevated hydrocarbon events (not directly attributable to atmospheric conditions) during the year than in 1998. The three reported were in Birmingham and Middlesbrough.

The performance of Chrompack engineers and the LSOs has been generally good. However, as noted last year, comprehensive support for the Chrompack instrumentation is expected to cease beyond 2003, with major implications for the Network beyond that time.

Issues relating to data quality and the state of repair of individual sites are given in the separate 1999 Audit Report.

FIGURES

- Figure 1a - 1999 monthly average concentrations in ppb for benzene (all sites)
 Figure 1b - 1999 monthly average concentrations in ppb for benzene (all sites except Marylebone Road)
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Figure 1a. 1999 monthly average concentrations in ppb for benzene (all sites)

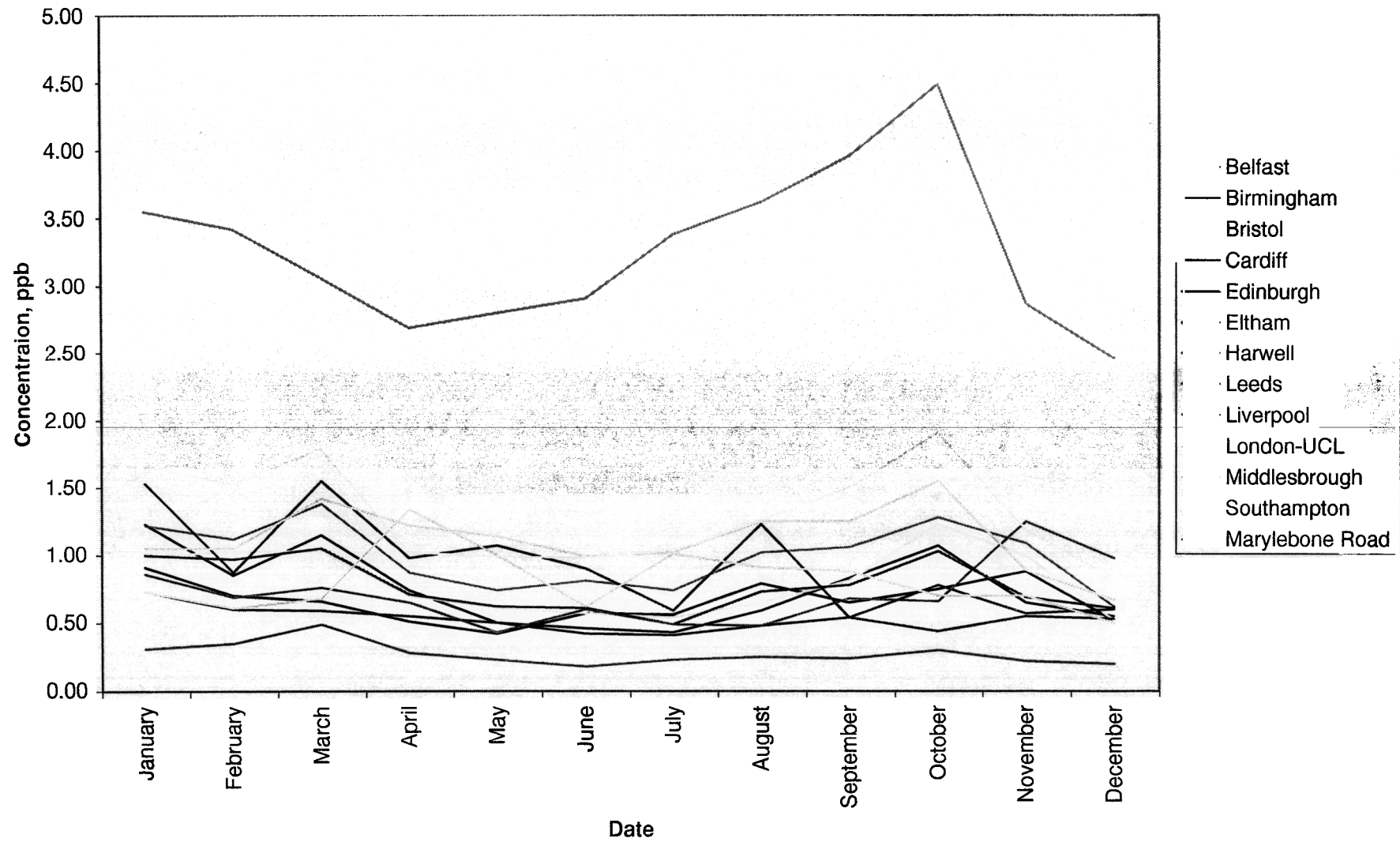


Figure 1b. 1999 monthly average concentrations in ppb for benzene (all sites except Marylebone Road)

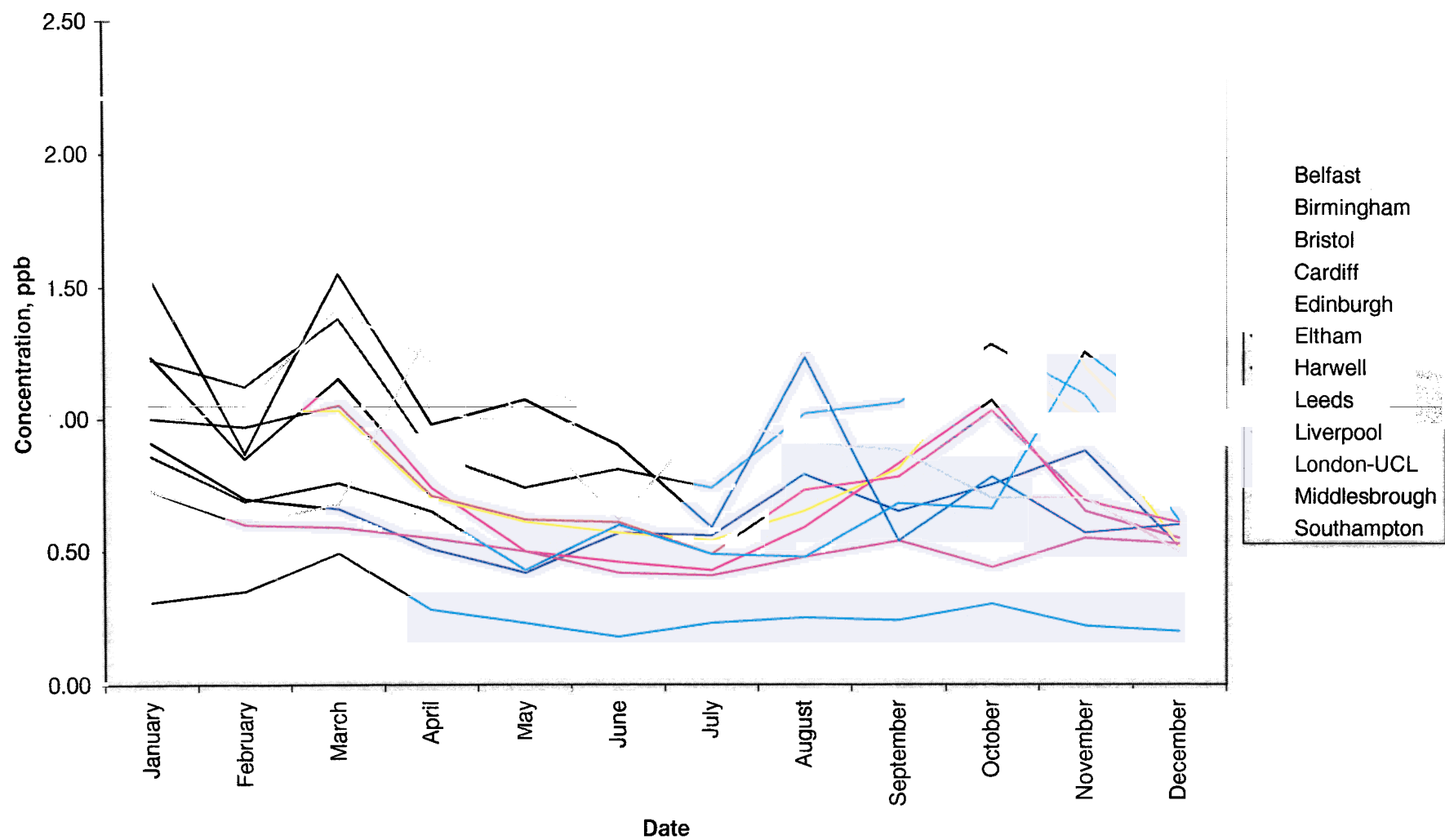


Figure 2a. 1999 monthly average concentrations in ppb for 1,3-butadiene (all sites)

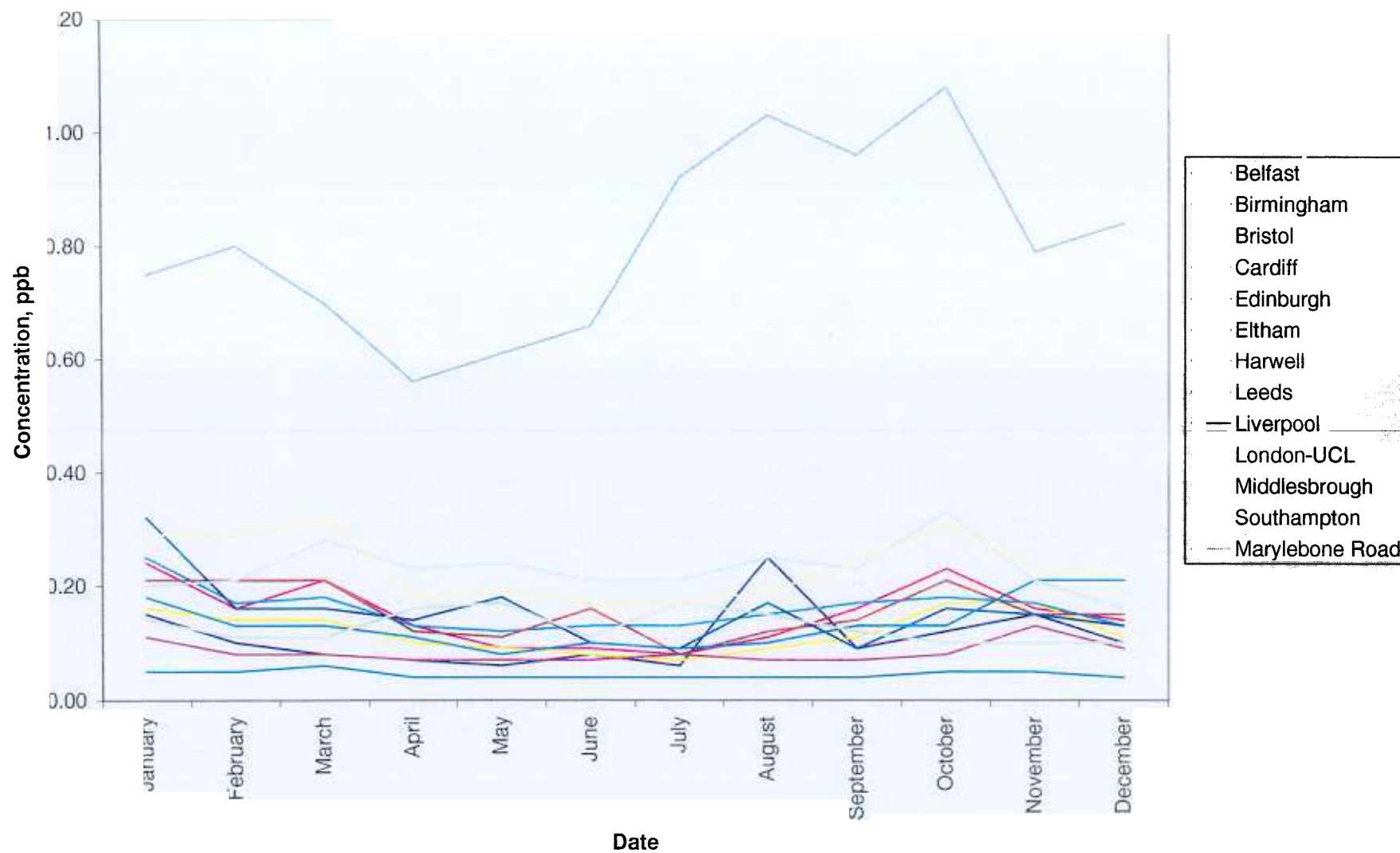


Figure 2b. 1999 monthly average concentrations in ppb for 1,3-butadiene (all sites except Marylebone Road)

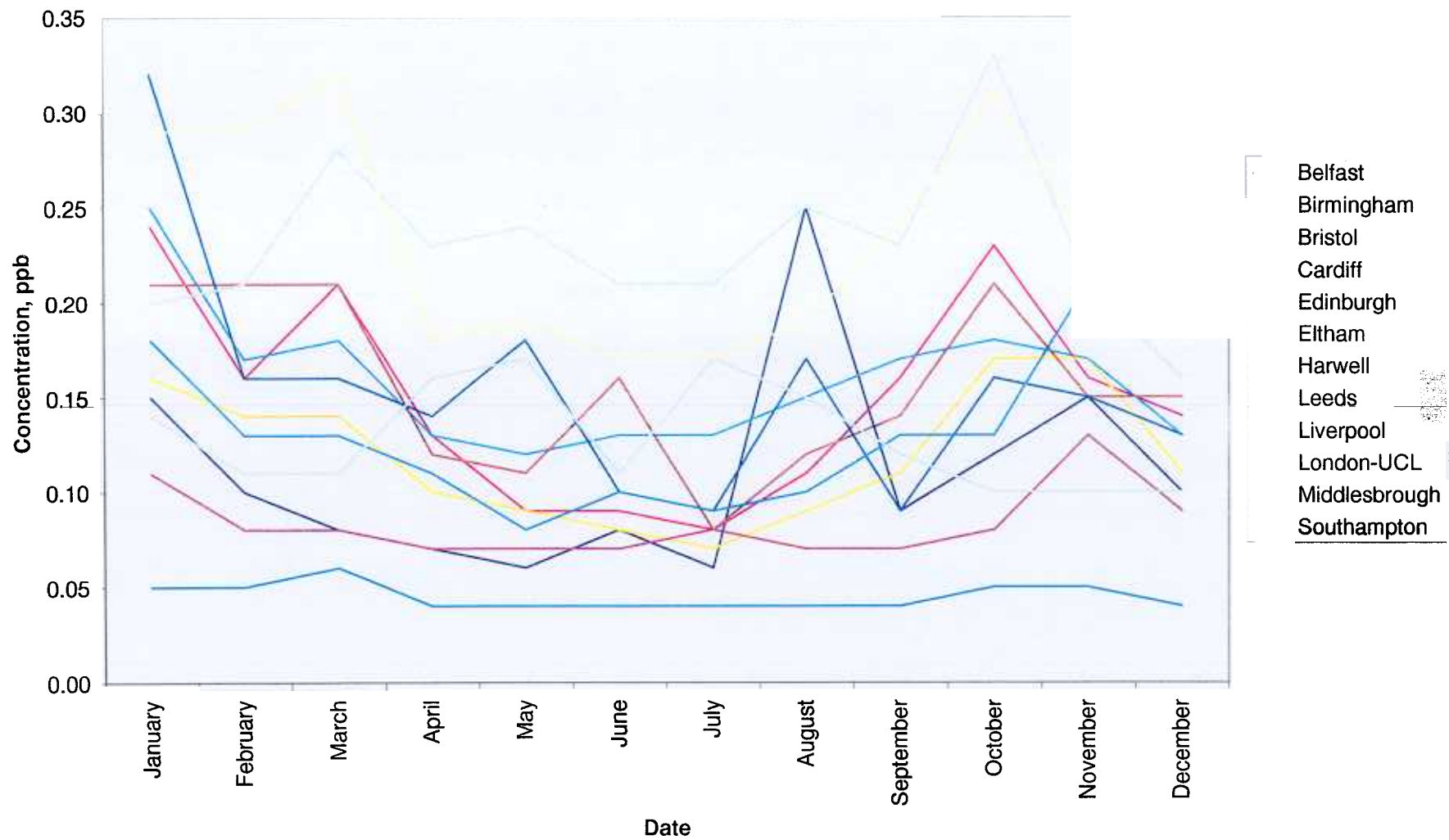


Figure 3a. Benzene annual average trend from 1994 to 1999

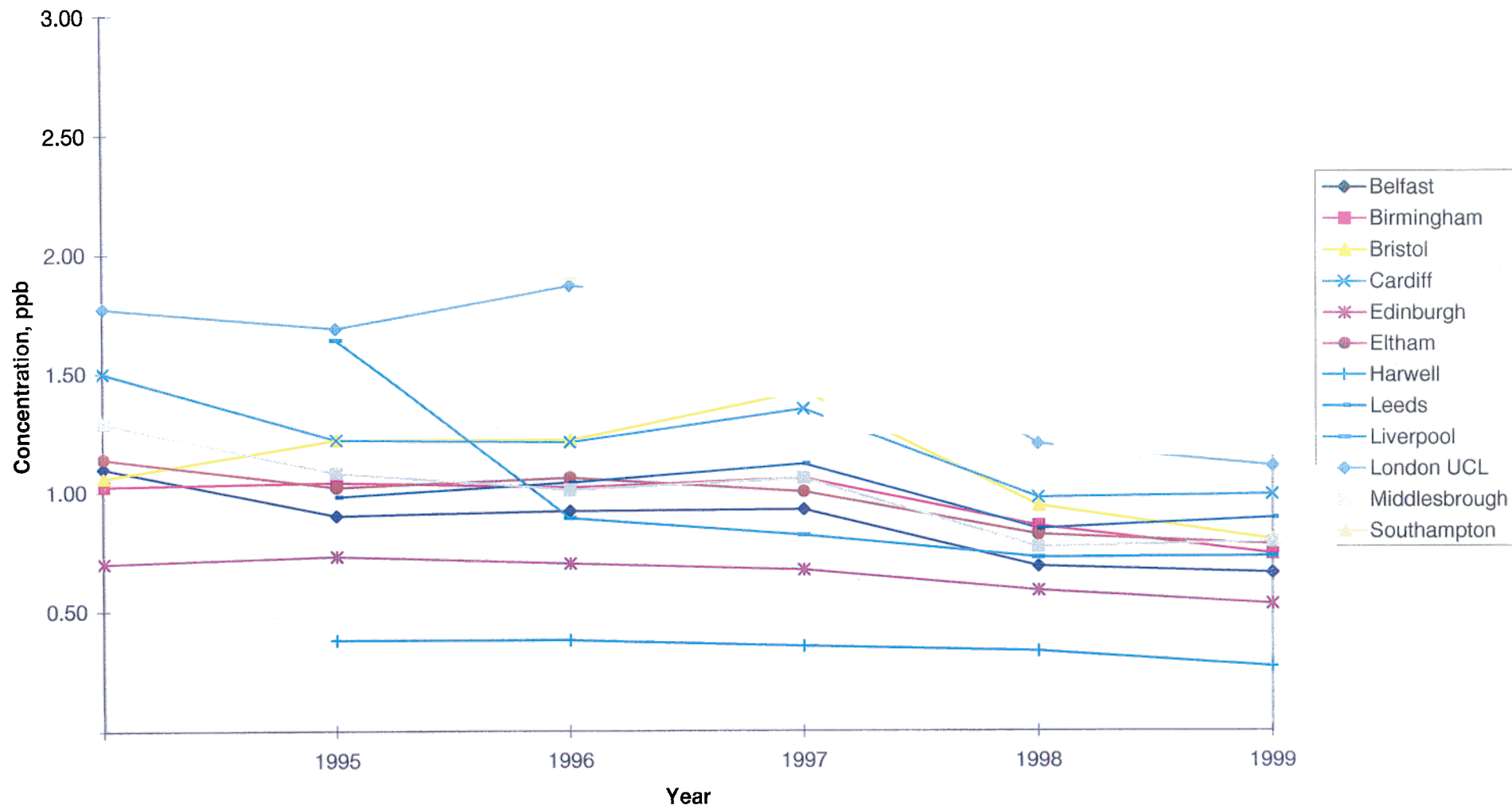


Figure 3b. 1,3-Butadiene annual average trend from 1994 - 1999

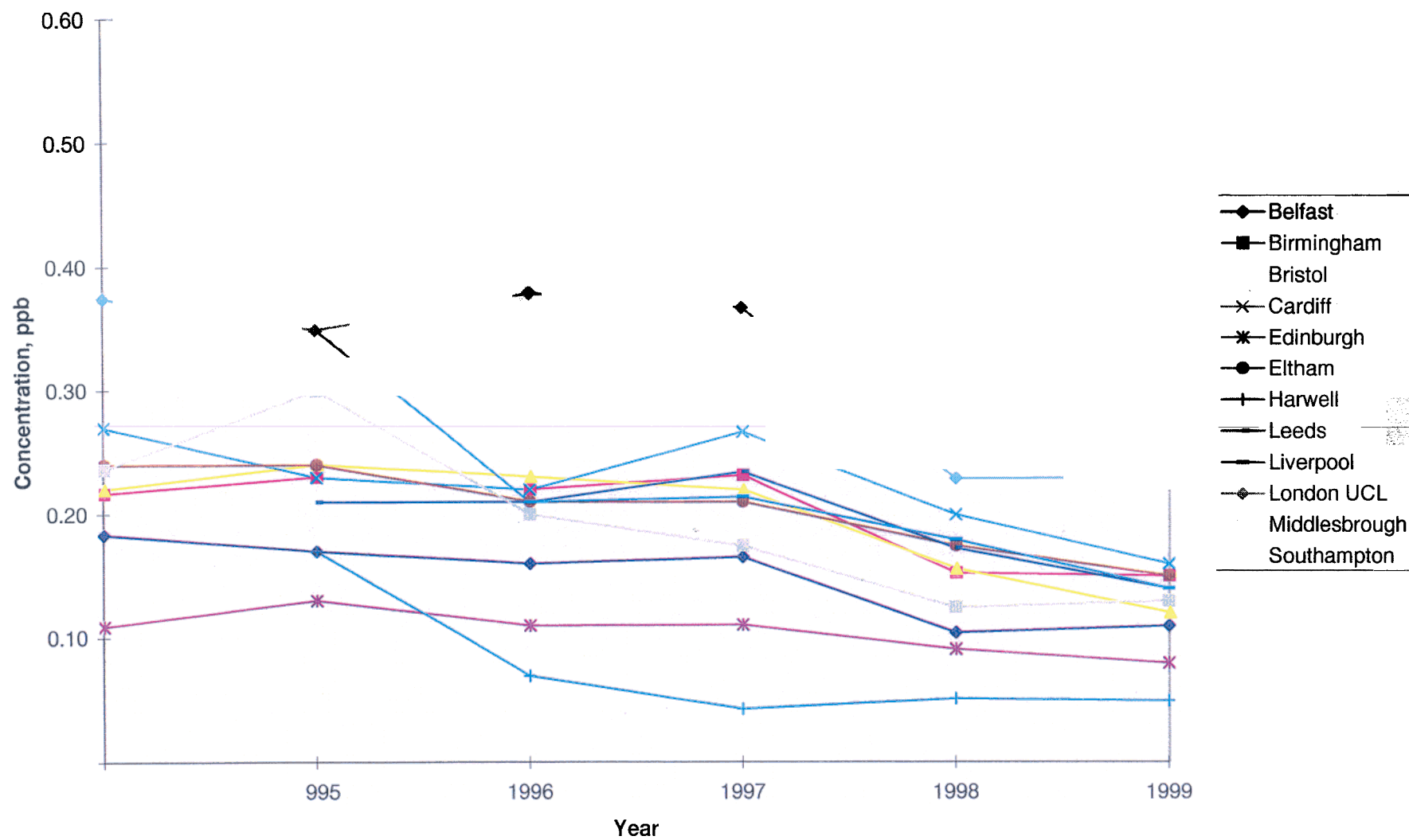


Figure 3c. Network average for Benzene and 1,3 Butadiene annual concentrations in ppb for 1994 to 1999, excluding Marylebone Road

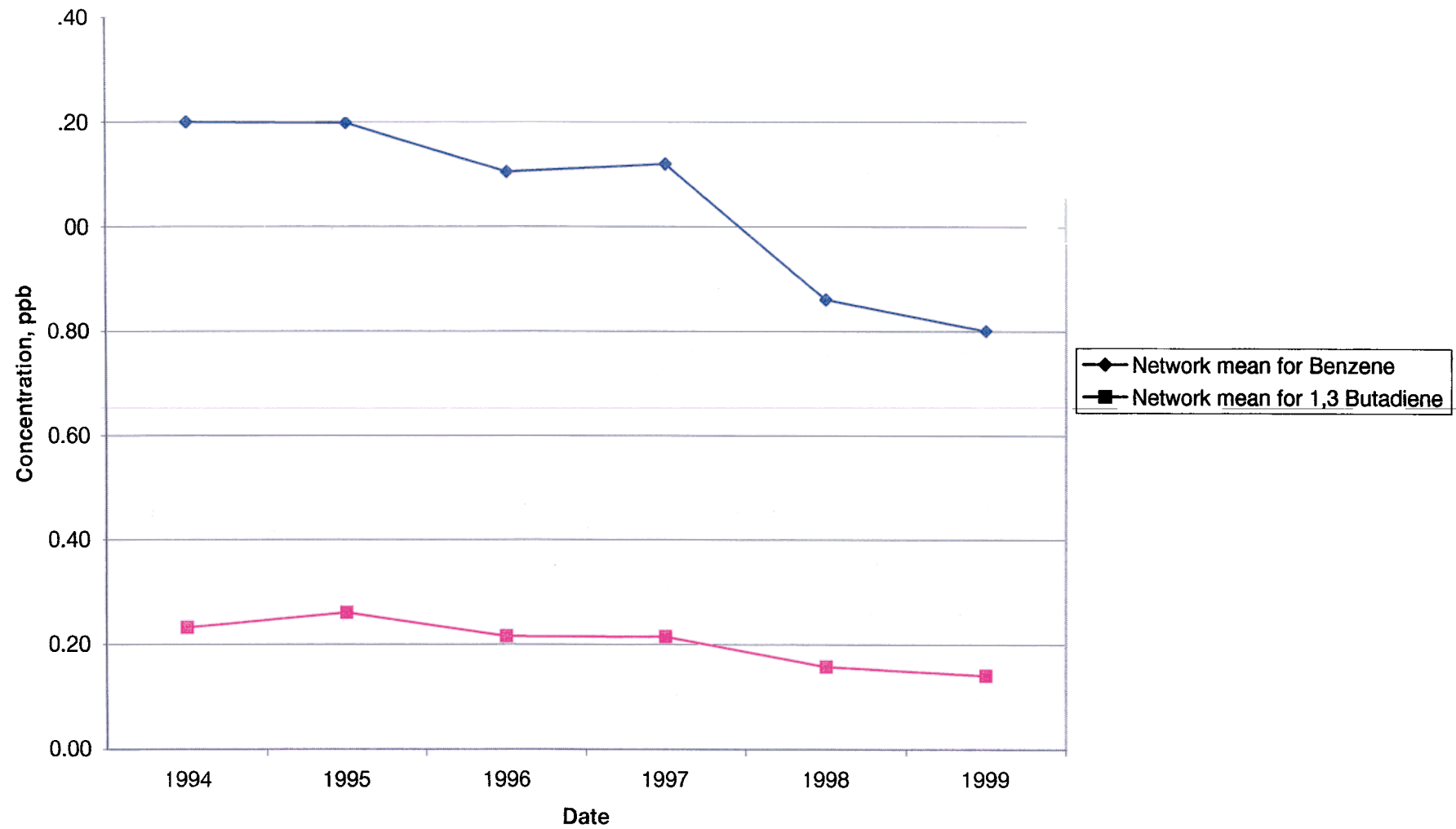


Figure 3d. Benzene monthly average concentrations in ppb for 1996 to 1999, excluding Marylebone Road

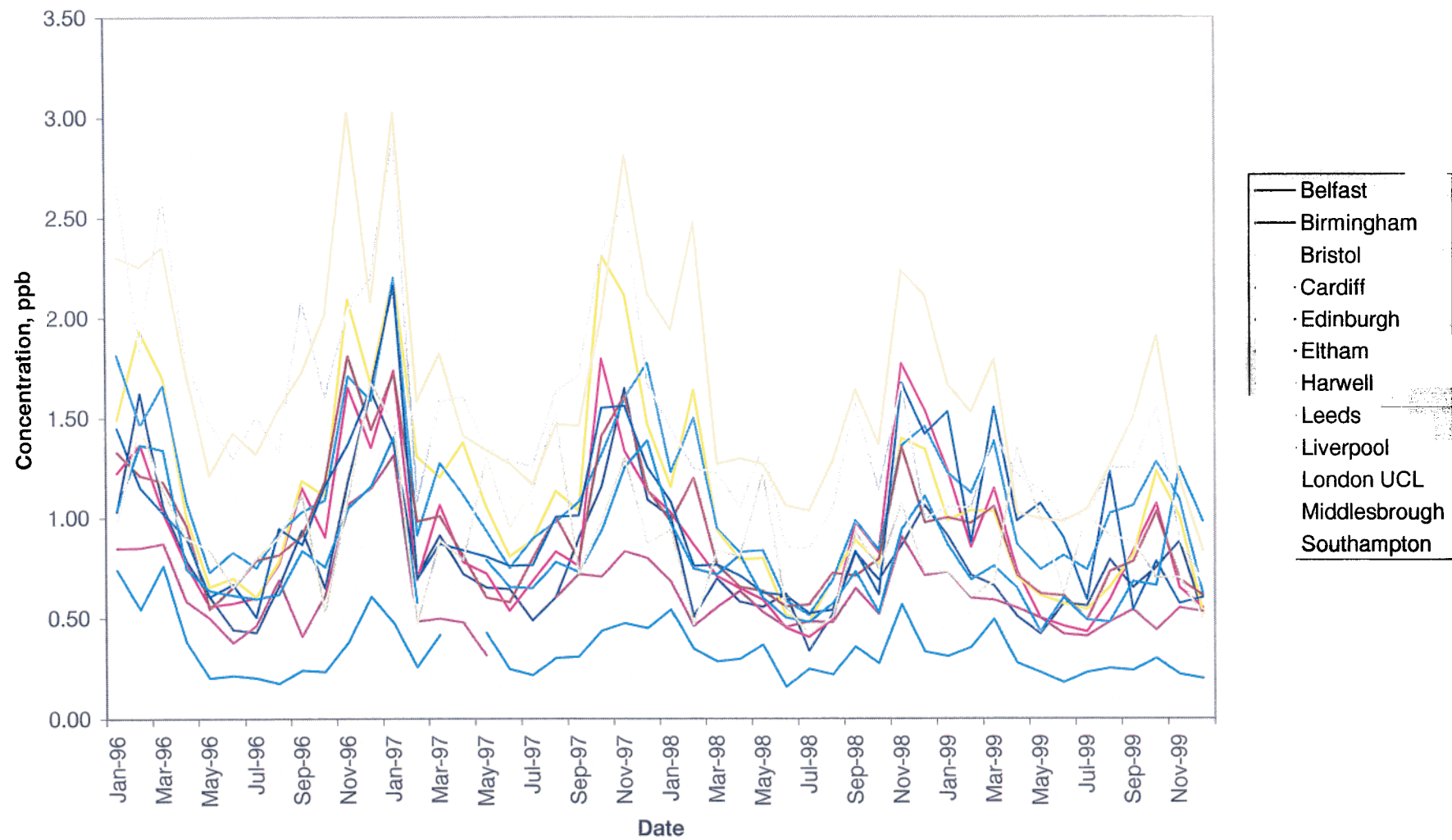


Figure 3e. 1,3-Butadiene monthly average concentrations in ppb for 1996-1999

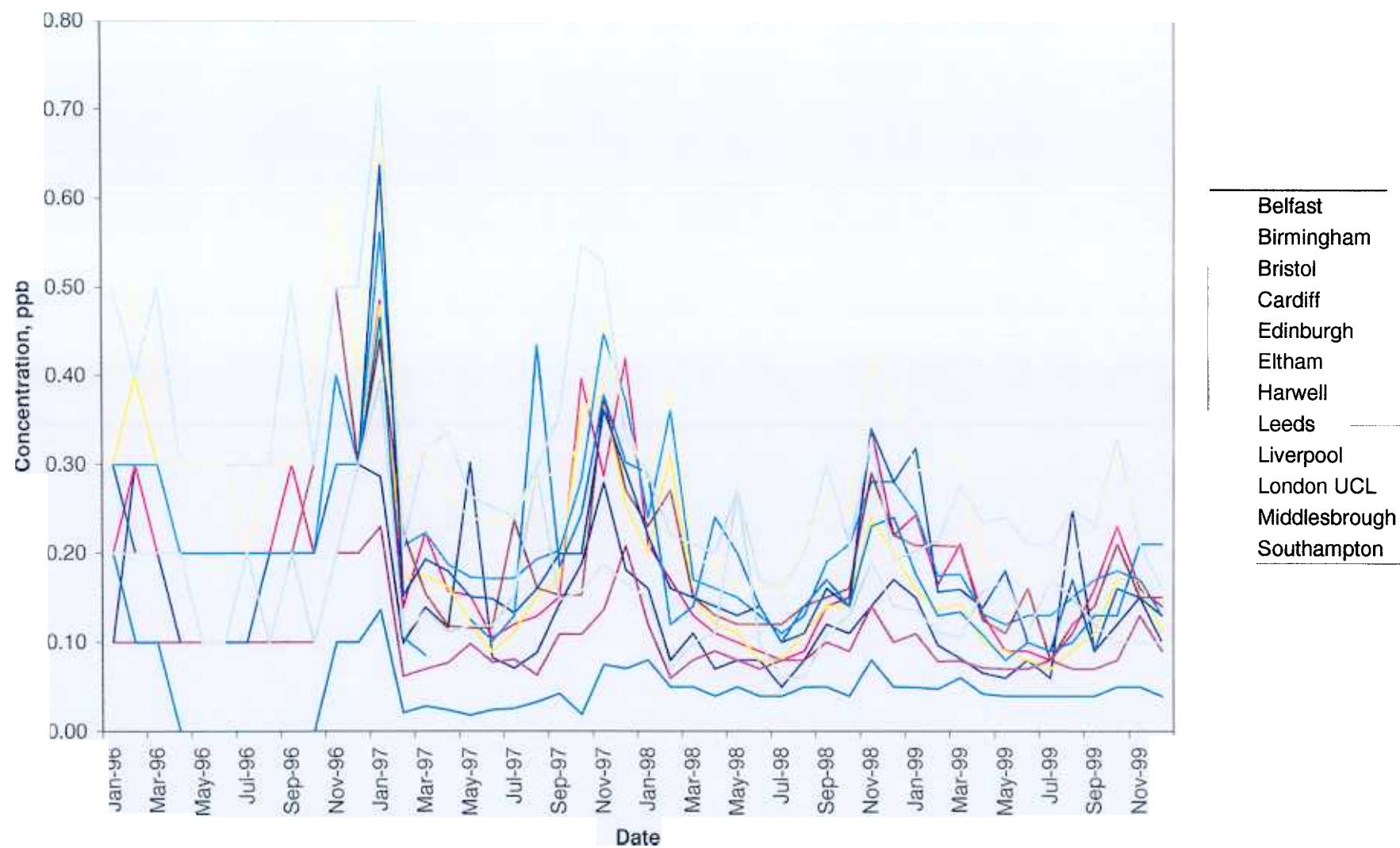


Figure 3f. Benzene, 1,3-Butadiene and CO concentrations at Marylebone Road 1998 -1999

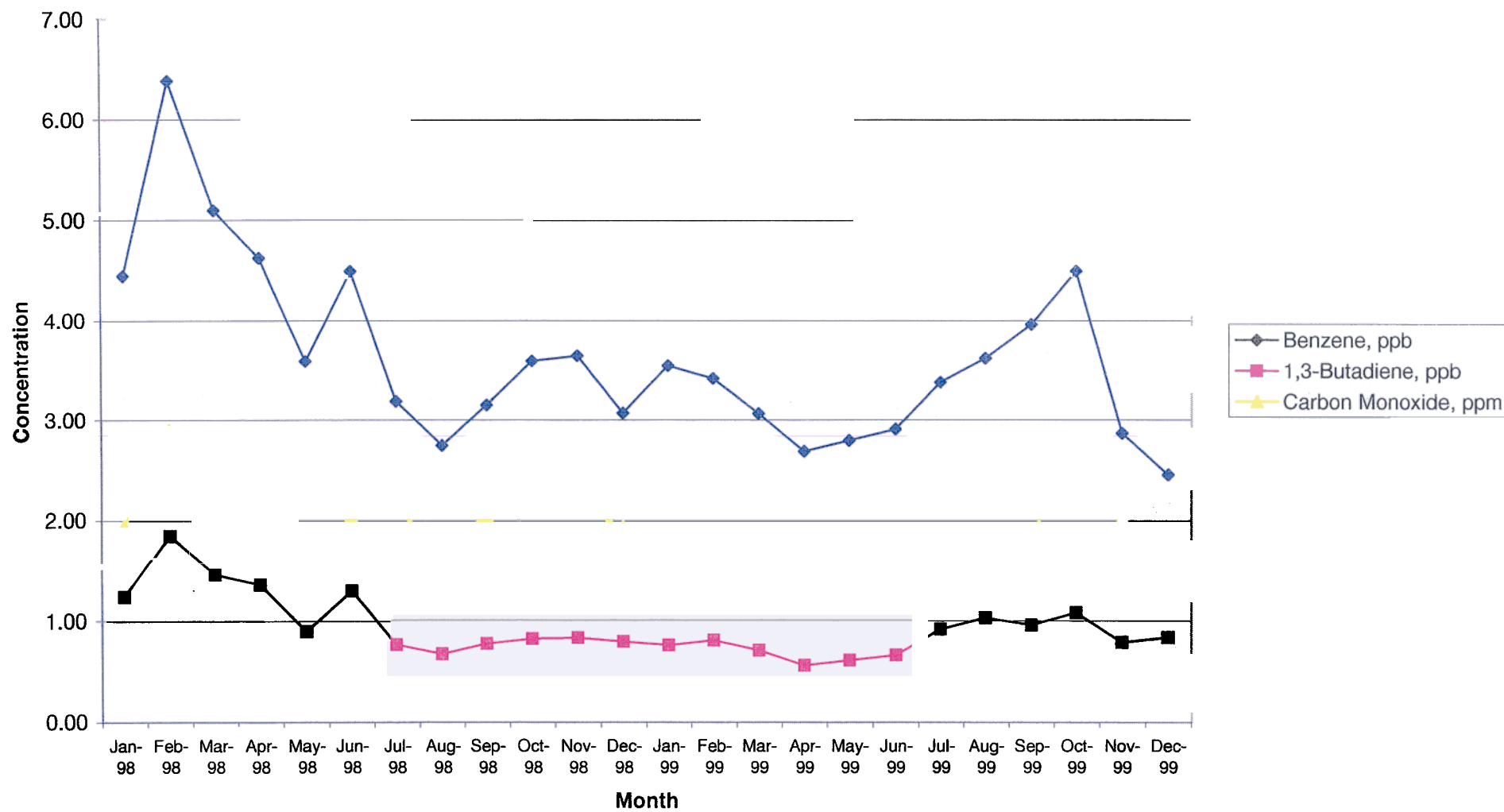


Figure 3g. Network average for Benzene and 1,3 Butadiene monthly concentrations in ppb for 1994 to 1999, excluding Marylebone Road site

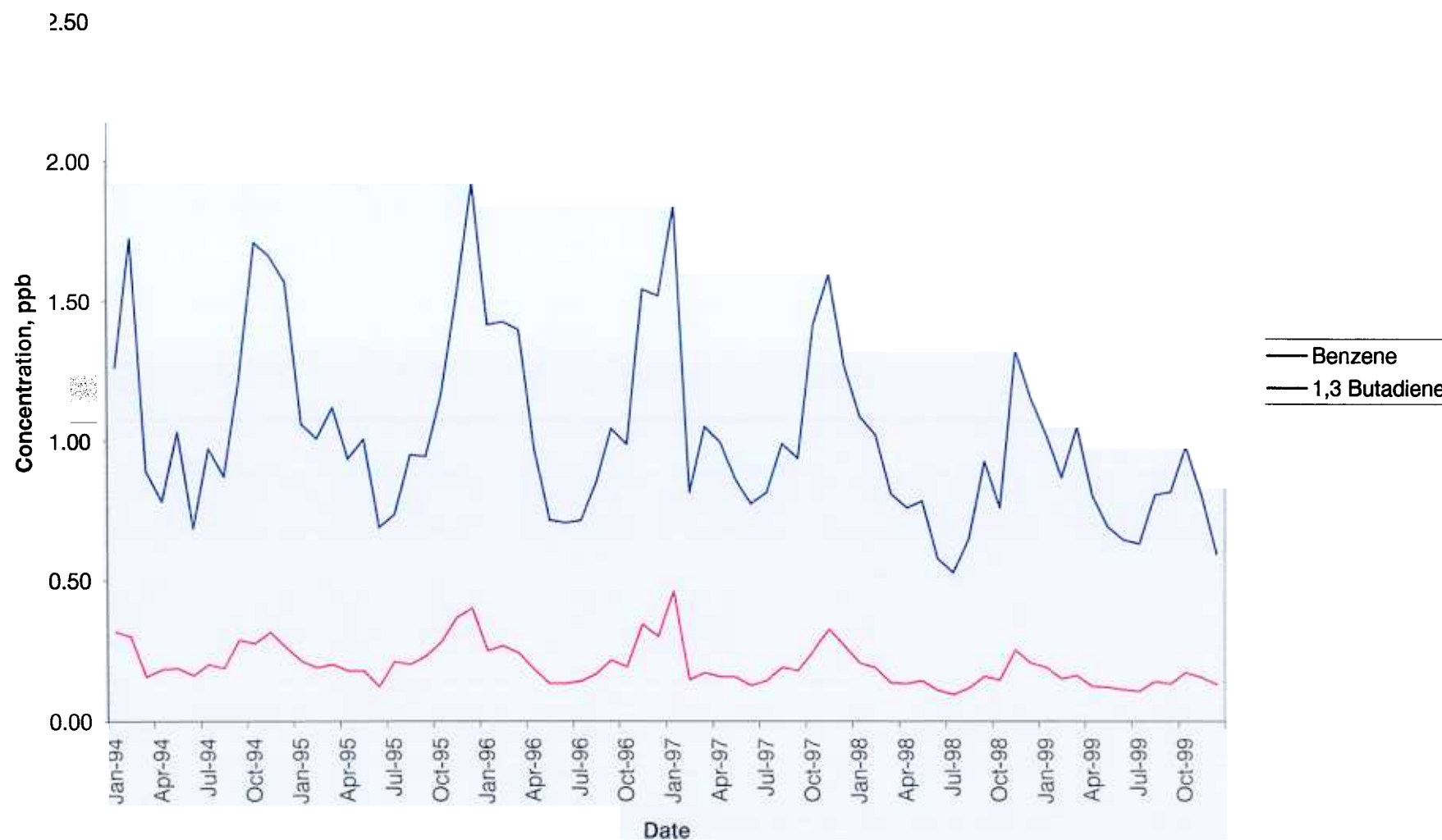


Figure 4a. Benzene mean diurnal variation for 1999 (all sites)

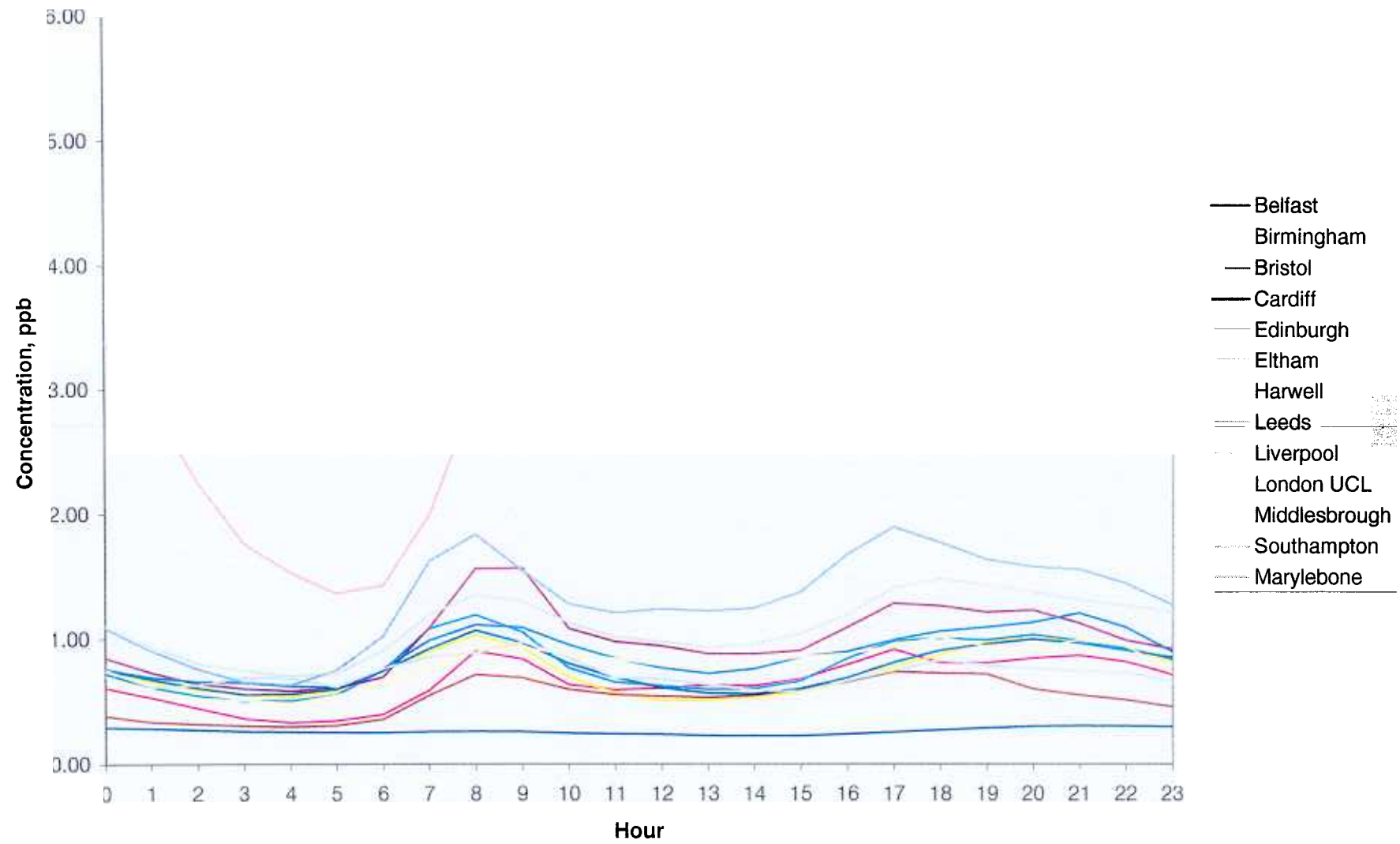


Figure 4b. Benzene mean diurnal variation for 1999 (all sites except Marylebone Road)

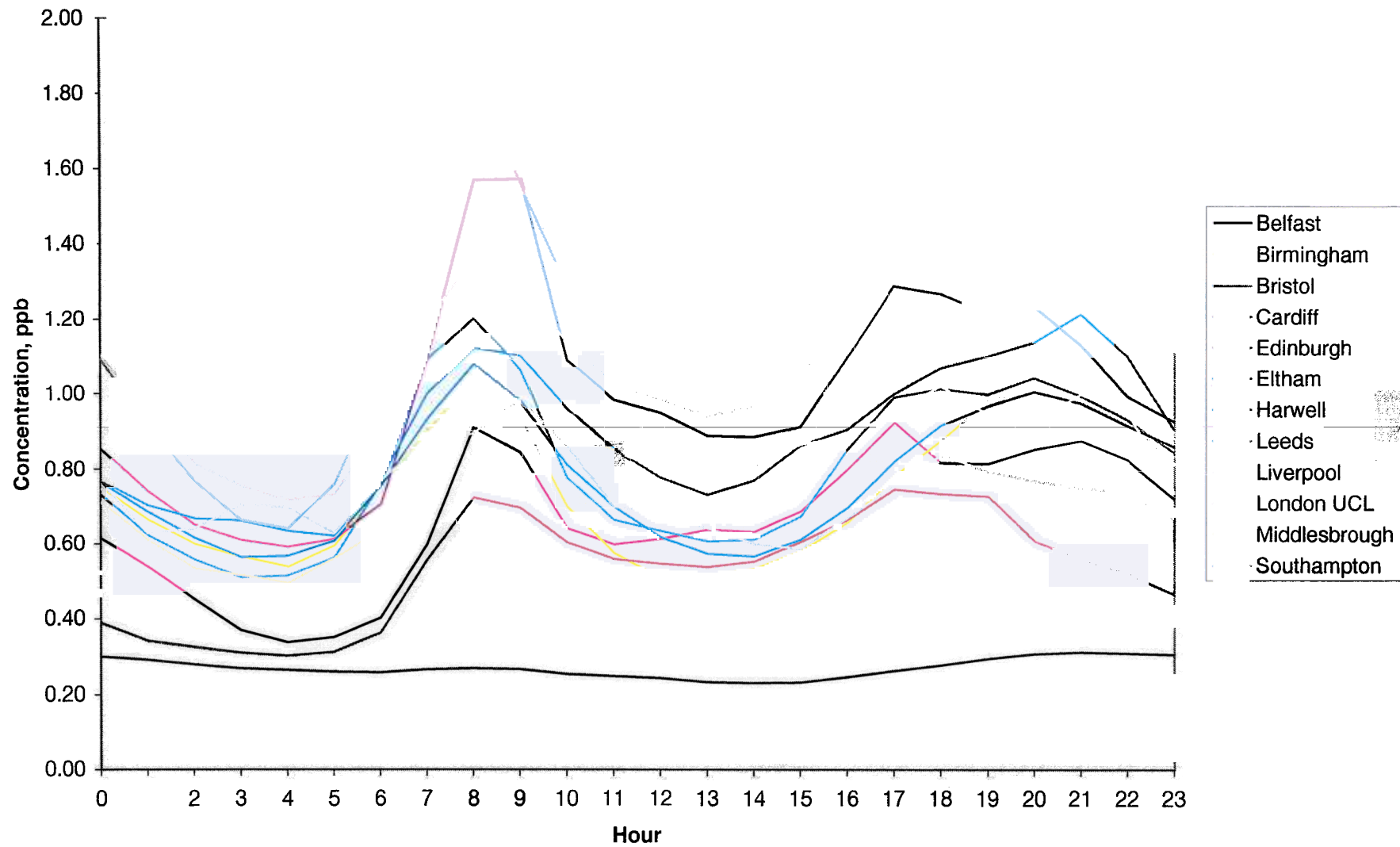


Figure 4c. 1,3-Butadiene mean diurnal variation for 1999 (all sites)

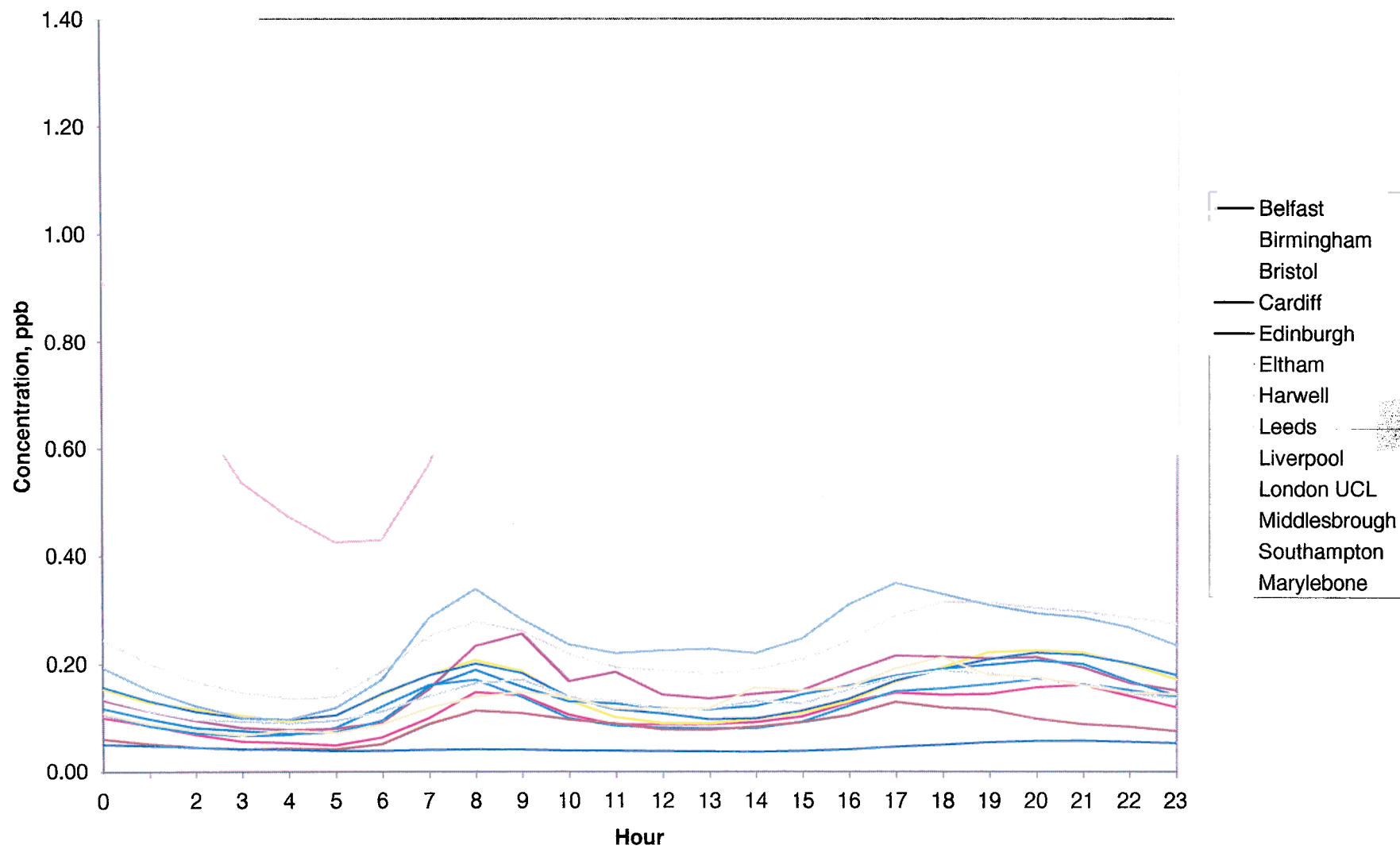


Figure 4d. 1,3-Butadiene mean diurnal variation for 1999 (all sites except Marylebone Road)

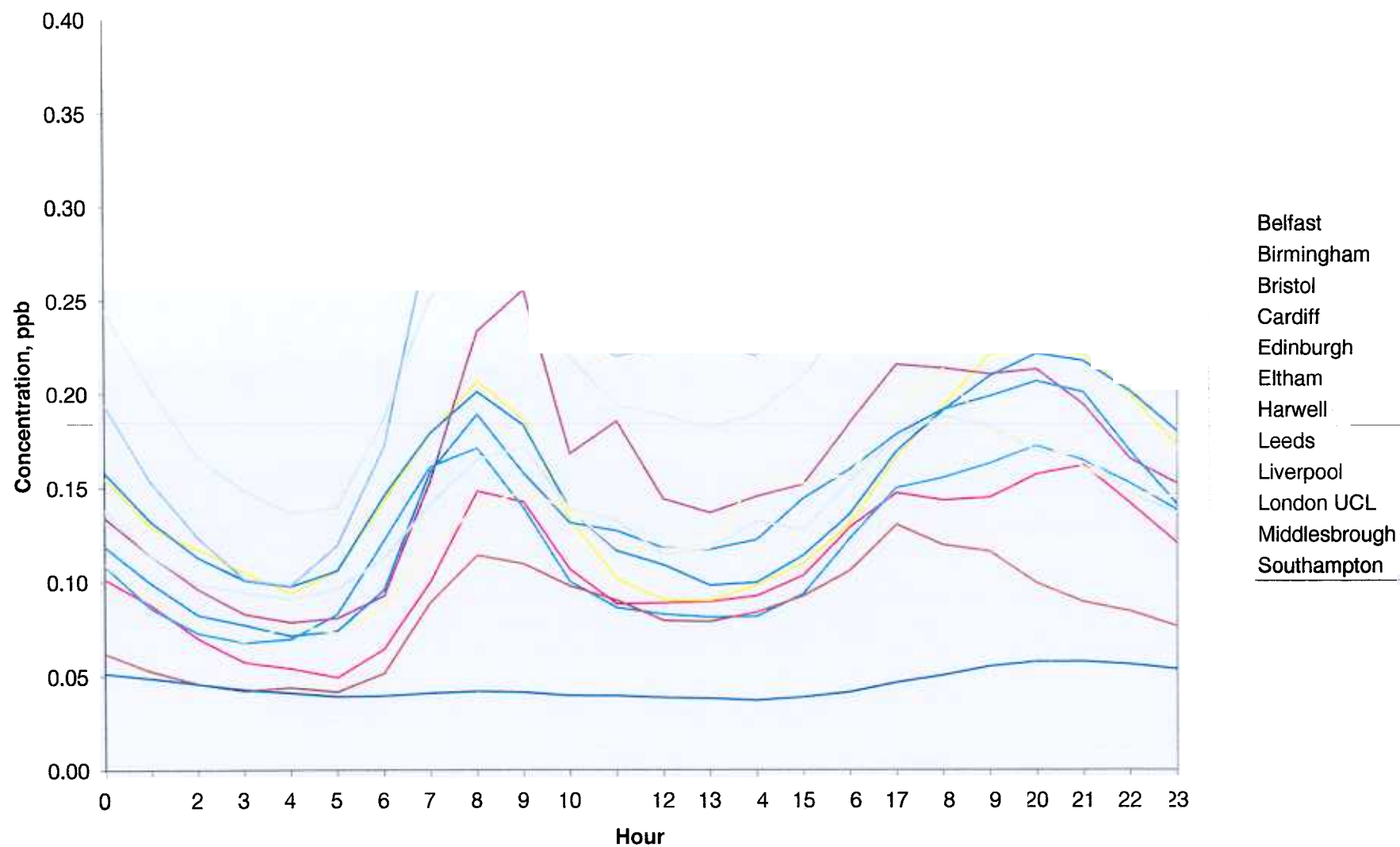


Figure 5a. Benzene/1,3 Butadiene concentration ratios: average monthly values for all sites in 1998

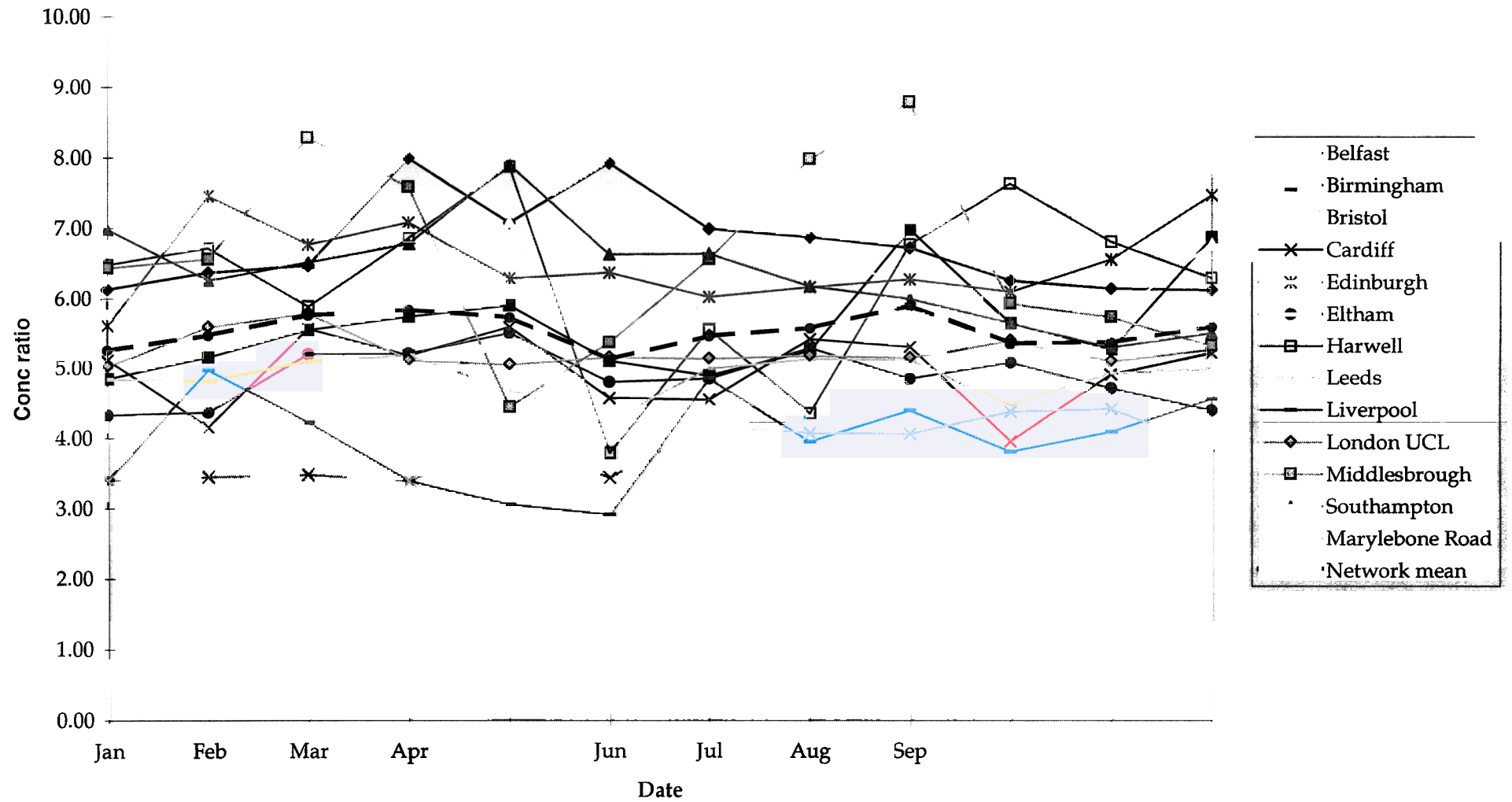


Figure 5b. Benzene/ 1,3-Butadiene concentration ratios: average monthly values for all sites in 1999

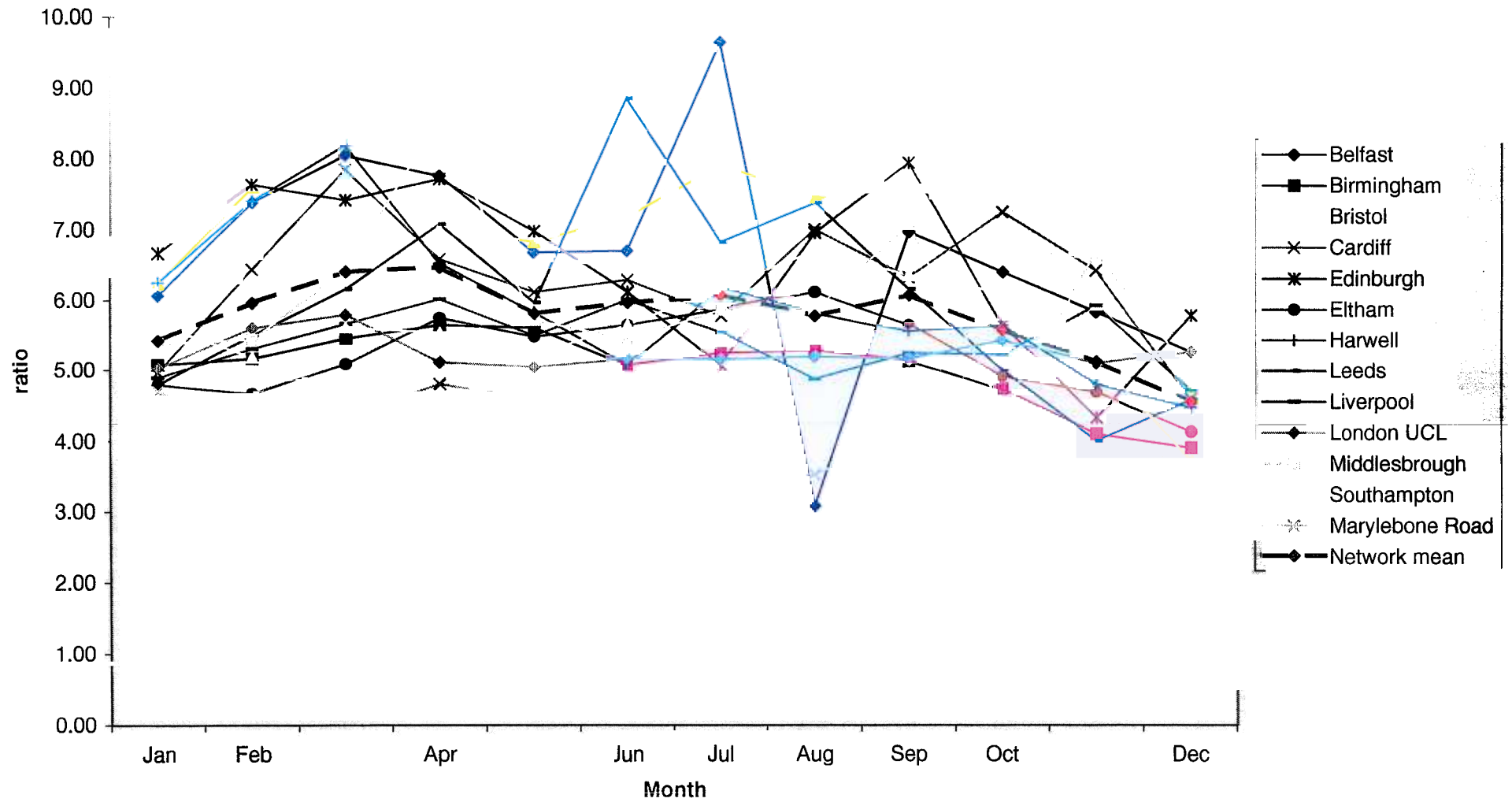


Figure 5c- Benzene/1,3 Butadiene concentration ratios: monthly network averages in 1998 and 1999

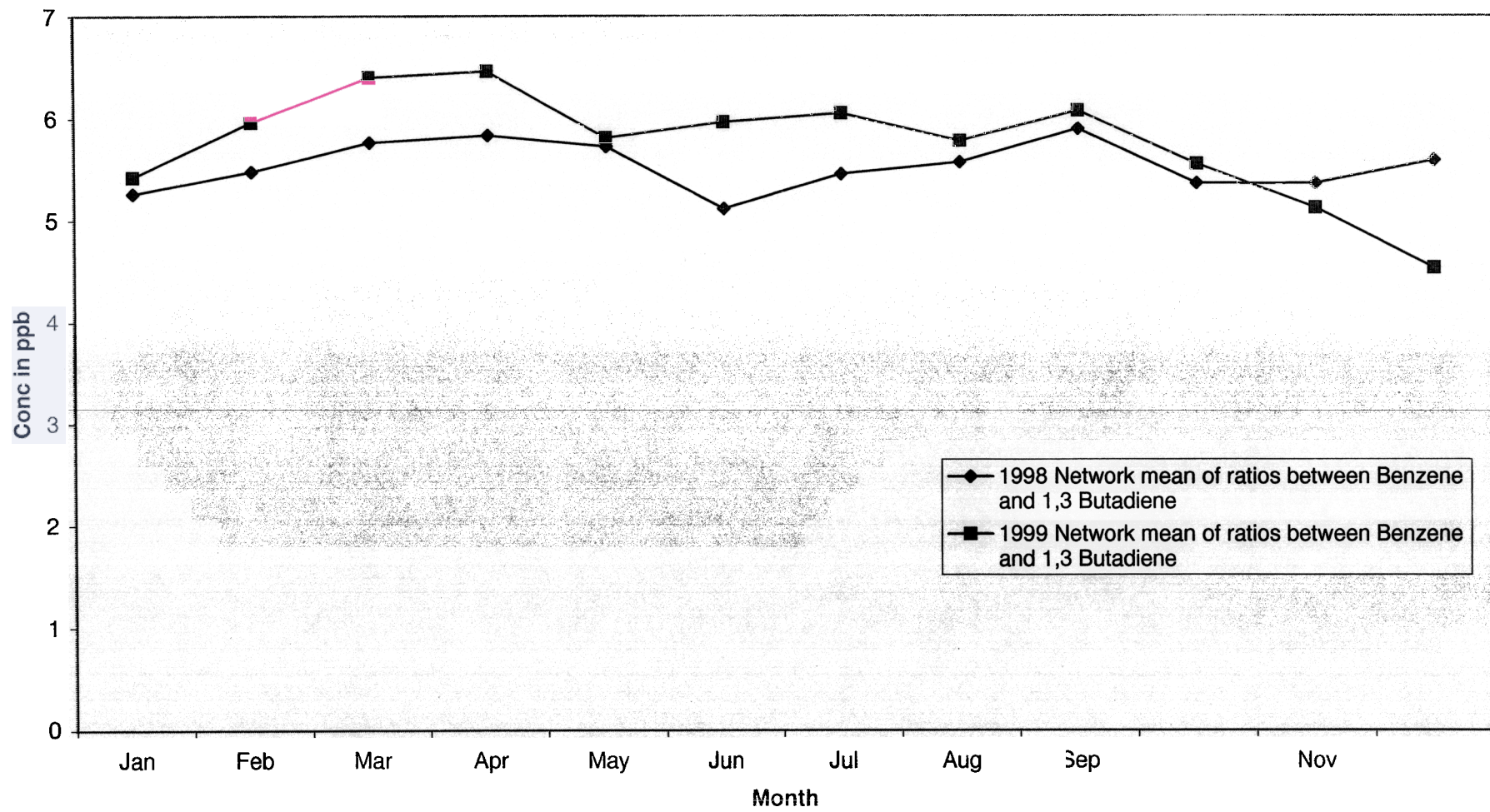


Figure 6a. Concentrations of hydrocarbons at Birmingham on the 21st and 22nd January 1999

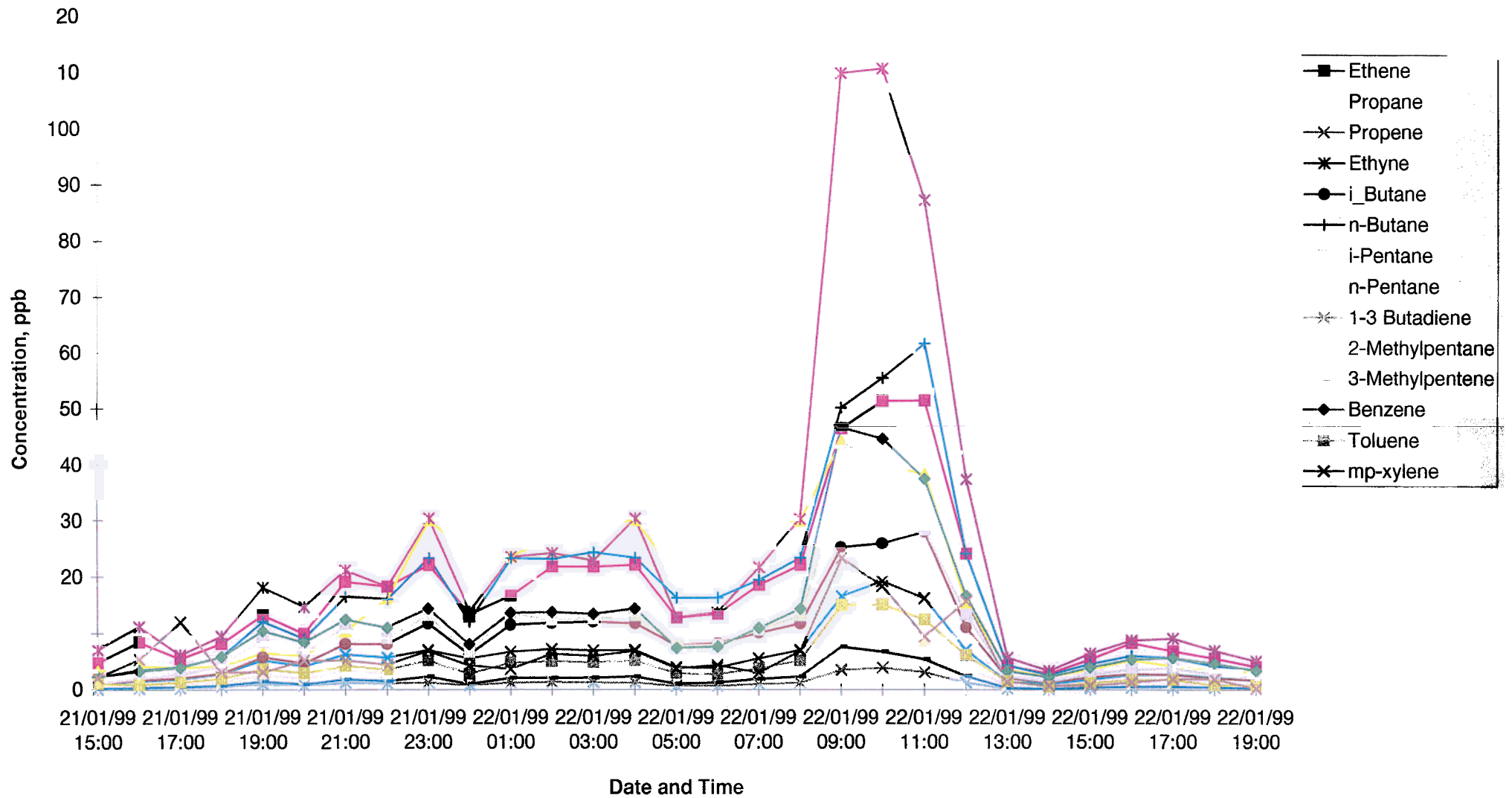


Figure 6c. Concentrations of hydrocarbons at Middlesbrough on the 2nd and 3rd of July 1999

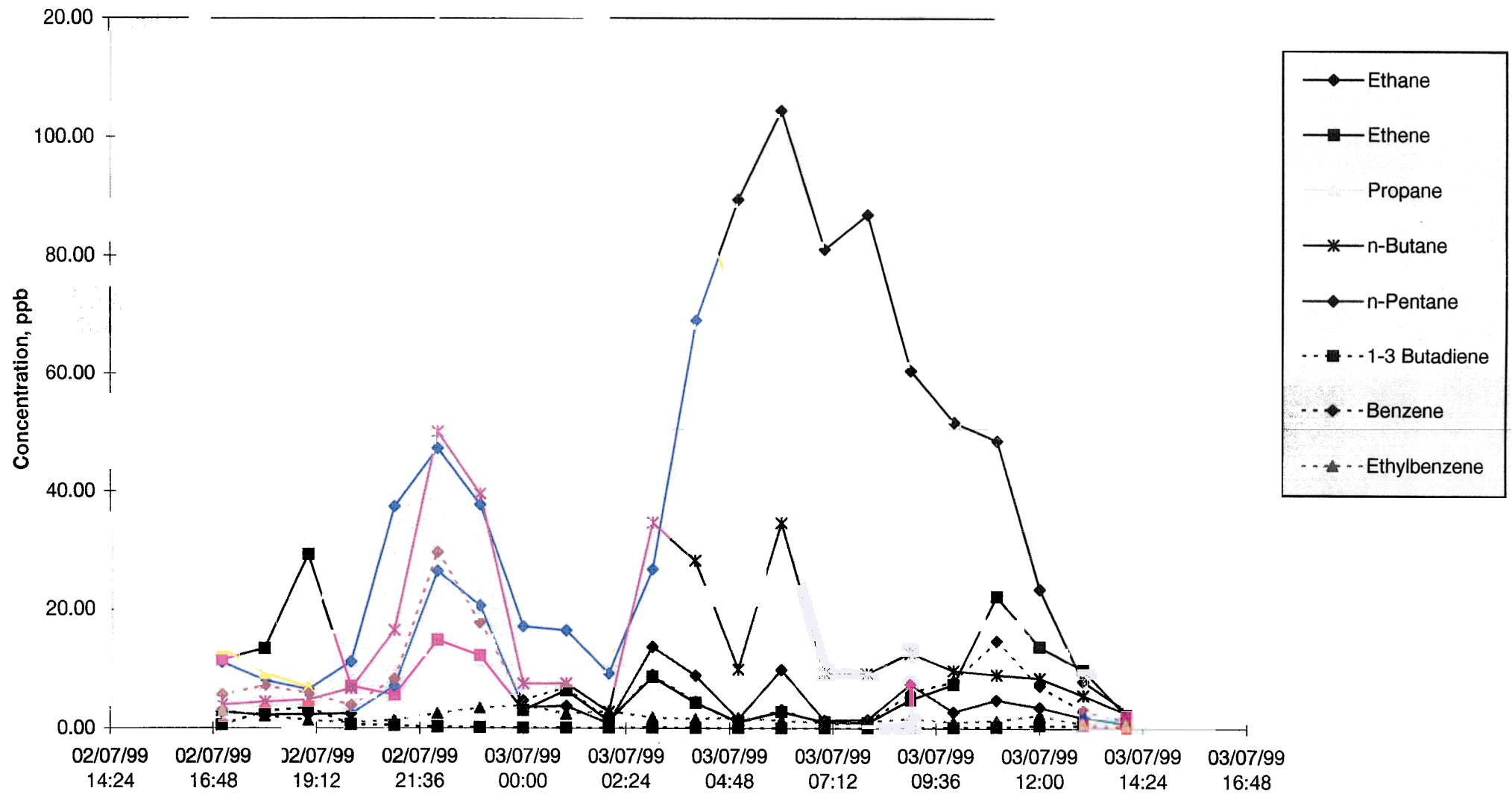


Figure 6b. Concentrations of selected hydrocarbons at Birmingham on the 17th and 18th March 1999

