

**UK AMBIENT HYDROCARBON AIR QUALITY NETWORK:
2000 AUDIT REPORT**

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National Physical Laboratory**

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Approved on behalf of Managing Director, NPL
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National Physical Laboratory

1. INTRODUCTION AND OBJECTIVES

This report summarises the results of the Hydrocarbon Network annual audit visits, carried out by NPL as Central Management and Control Unit (CMCU) for the Network on behalf of the Department of the Environment, Transport and the Regions under contract EPG 1/3/80.

Figures for measured concentrations, data capture, and other operational information for 2000 are given in the separate Summary of UK Ambient Hydrocarbon Network Operations during 2000 report.

The audits were carried out between September 2000 and November 2000. The schedule of audit visits is given in Table 1.

Table 1: Audit visit schedule

Site Name	Date of Audit	Auditor
Belfast	25/10/00	D Butterfield
Birmingham	14/11/00	A Andrews
Bristol	19/09/00	D Butterfield
Cardiff	20/09/00	D Butterfield
Edinburgh	16/10/00	A Andrews
Eltham	27/09/00	D Butterfield and J Brand
Harwell	15/11/00	A Andrews
Leeds	19/10/00	A Andrews
Liverpool	24/10/00	D Butterfield
London-UCL	28/09/00	D Butterfield
Middlesbrough	13/10/00	A Andrews
Southampton	23/11/00	A Andrews
Marylebone Road	28/09/00	D Butterfield and J Brand

1.1 OBJECTIVES:

The objectives of the audit visits were to:

- Assess the state of repair of the equipment and structure of the sites;
- ii Audit the performance of the Local Site Operators (particularly new deputies) in carrying out their routine duties;

- iii. Check the overall operation of the instrumentation;
- iv. Inject three inter-comparison gas mixtures to check instrument calibration and provide information on Network data quality;
- v. Request LSO feedback.

2. STATE OF REPAIR OF SITES

The state of repair of all sites was assessed. Table 2 lists all observations made about each site and details any actions arising from these.

Table 2: State of Repair of Sites

Site Name	State Of Equipment	Structural Repair	Other Observations	Actions
Belfast	H ₂ Generator failed during LSO calibration. Otherwise Good.	Good except Fuel stain on wall.	None	H ₂ Generator replaced with Hydrogen Cylinder.
Birmingham	Good	Good	None	None required
Bristol	Good	Floor in Dewar hut rotten.	Dryer and sample bypass filters changed.	Temporary repair to floor in dewar hut.
Cardiff	Good	Good	Insulation on LN ₂ transfer line renewed.	None required
Edinburgh	Good	Good	None	None required
Eltham	Good	Good	Repaired compressed air fitting.	None required
Harwell	Good	Good	None	None required
Leeds	Good	Good	None	None required
Liverpool	Good	Good	None	None required
London-UCL	Good	Good	None	None required
Middlesbrough	Good	Good	None	None required
Southampton	Good	Good	None	None required

2.1 ONGOING SITE EQUIPMENT ISSUES:

New, current-specification PCs were installed at all 12 DETR-owned sites in May 2000.

Electronic pressure gauges for the standard gas cylinders have also been installed at each site.

3. LSO AUDITS

The LSOs were observed performing their weekly checks and attaching the calibration standard (except as below).

Table 3: LSO audit

Site Name	Names of LSO's Audited	Weekly Checklist Completed OK	Site Standard applied correctly
Belfast	Grant Smith	✓	✓
Birmingham	Bob Appleby	✓	✓
Bristol	Cathy Derrick	✓	✓
Cardiff	Ian Warburton	✓	✓
Edinburgh	Archie Forrest	✓	✓
Eltham	Ellie Norris	✓	✓
Harwell	Tony Clarke	✓	✓
Leeds	Chris Hill	✓	✓
Liverpool	Alan Wilkins	✓	✓
London UCL	Andy Henderson	✓	✓ ¹
Middlesbrough	Anthony Luke	✓	N/A ²
Southampton	Sabi Grewal	✓	✓
Marylebone Road	N/A	N/A	N/A ³

1 This year the London-UCL site changed from an automatic calibration system to the manual method used at other sites.

2 The LSO at Middlesbrough was unable to perform a calibration due to other work commitments.

3 The site at Marylebone Road uses automated standard injection systems and the LSOs are not required to manually attach the calibration standards.

The performances of all LSOs were considered to be to a good standard, with no points of action arising.

4. ROUTINE OPERATION OF EQUIPMENT

The normal operation of the Chrompack VOC Air Gas Chromatographs, together with that of the associated ancillary equipment, was observed at the 12 DETR network sites. GC parameters were observed during the runs to ensure the GCs were maintaining the correct pressures and temperatures. All observed values were within acceptable operating parameters except those in bold or otherwise noted below.

Table 4: GC Temperature Control (all values in Celsius)

Site Name	Tube Cryogenic Temperature	Tube Desorption Temperature	Trap Cryogenic Temperature	Trap Injection Temperature
Belfast	-20	250	-93±1	128±3
Birmingham	-20	250	-93	125
Bristol	-20	252	-97	125
Cardiff	-20	252	-97	127
Edinburgh	-20	250	-120	120
Eltham	-20	252	-90	129
Harwell	-20	270	-100±6	125
Leeds	-20	250	-85	125
Liverpool	-20	251	-93±1	133±4
London-UCL	-20	246	-95	107
Middlesbrough	-20	250	-96	115
Southampton	-20	245	-98	116

Table 5: Flows and Pressures

Site Name	Pump Sample Flow (ml/min)	Pump Vacuum (bar)	Hydrogen Generator Pressure (bar)	Compressor Operating	LN ₂ Pressure (psi)
Belfast	9.9	-0.88	2.0	✓	14
Birmingham	9.9	-0.82	2.0	✓	12
Bristol	9.8	-0.86	3.0¹	✓	12
Cardiff	9.8	-0.86	2.11	✓	14
Edinburgh	9.9	-0.90	1.9	✓	25
Eltham	9.7	-0.90	2.07	✓	20
Harwell	14.9²	-0.89	1.8	✓	20
Leeds	9.8	-0.91	2.0	✓	18
Liverpool	9.8	-0.91	2.21	✓	10
London-UCL	10.1	-0.92	1.9	✓	14
Middlesbrough	9.8	-0.90	1.9	✓	18
Southampton	9.8	-0.90	1.9	✓	18

¹ The pressure gauge on this Hydrogen Generator is faulty.

² This system is operated with a nominal sample flow of 15ml/min.

The values above in bold have been noted and subsequent changes have been made.

5. INTERCOMPARISON GAS INJECTIONS

Three intercomparison gas mixtures were injected at each site, together with a set of calibration runs using the on-site calibration standard. The audit gas mixtures were as follows:

- i) Blank cylinder: a cylinder containing freeze dried nitrogen, containing negligible amounts of hydrocarbons, used to check for internal sources of hydrocarbons at each site;
- ii) Ambient standard: a cylinder of standard 30 component gas containing hydrocarbons at concentrations in the range 1 – 10 ppb (similar to kerbside levels), used for a more realistic accuracy check and to check the instruments' linearity. These standards have been recently developed at NPL as part of an EC-cofunded project;
- iii) Audit standard: a cylinder of standard 27 component gas, with concentrations in the range 5 – 50 ppb, of the same type used at the sites, used to check the values and application of the on site standard concentrations.

The three cylinders were attached to an automated valve box, which was connected to the input of the GC pump box in the same manner as the site standard. The valve box was used overnight to sequentially inject four hours of each gas into the GC, with one "rest" hour between each set. The order of the injections was blank, ambient and audit standard, to minimize carry-over or memory effects.

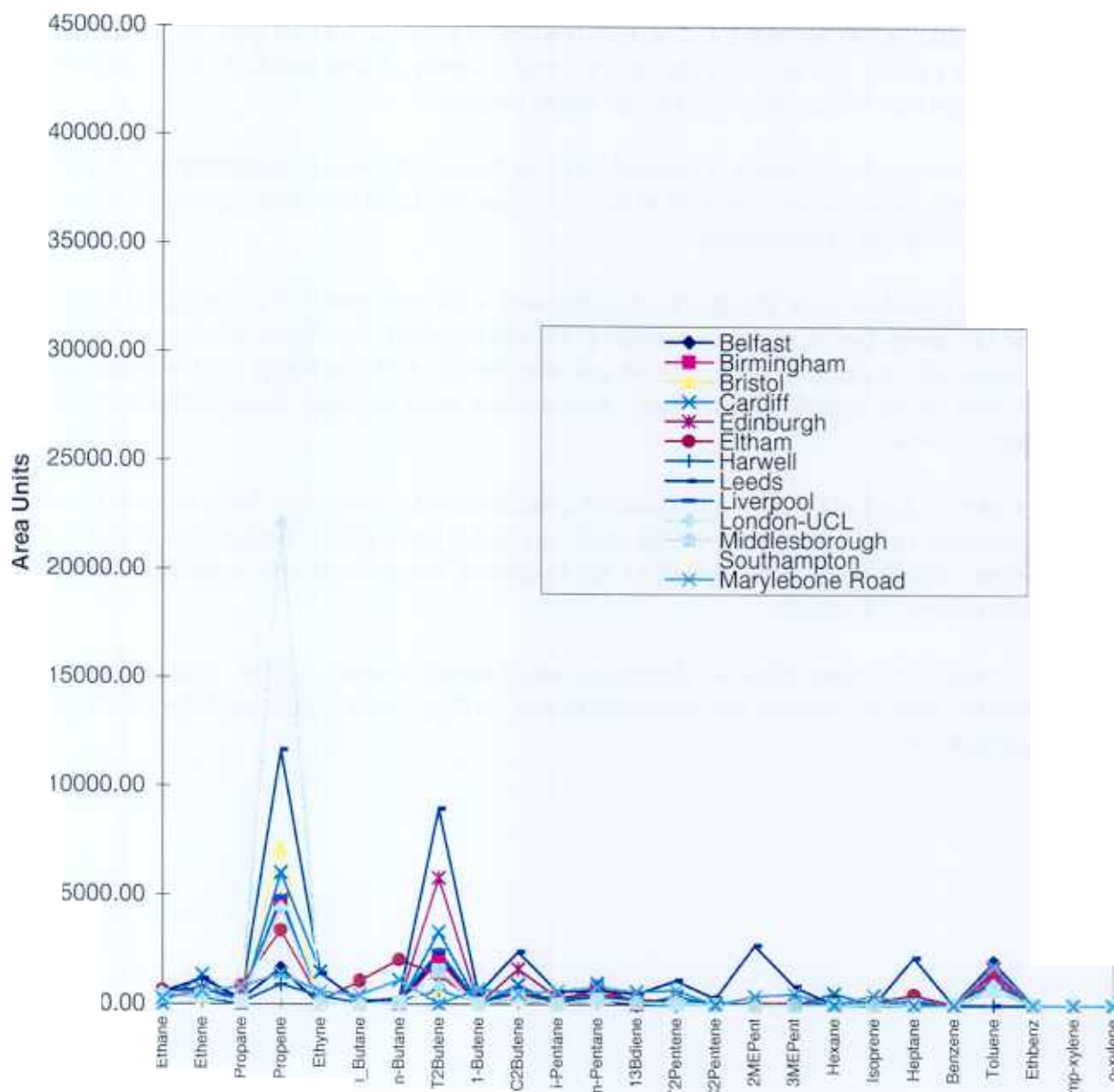
As a part of the LSO audit a site standard calibration was performed. This was used to derive the response factors for the site in the same way as for the regular fortnightly calibration. These response factors were then applied to the results of the ambient and audit standard and the concentrations calculated.

The blank runs were used to determine any internal sources. These internal levels were subtracted from all areas in the intercomparisons, giving 'blank corrected' response factors and concentrations.

5.1 BLANK INJECTION

Figure 1a and 1b show the measured areas from the blank runs performed in 1999 and 2000, with the same vertical scale, for comparison.

Figure 1a Measured areas from the blank cylinder runs in the 1999 audit

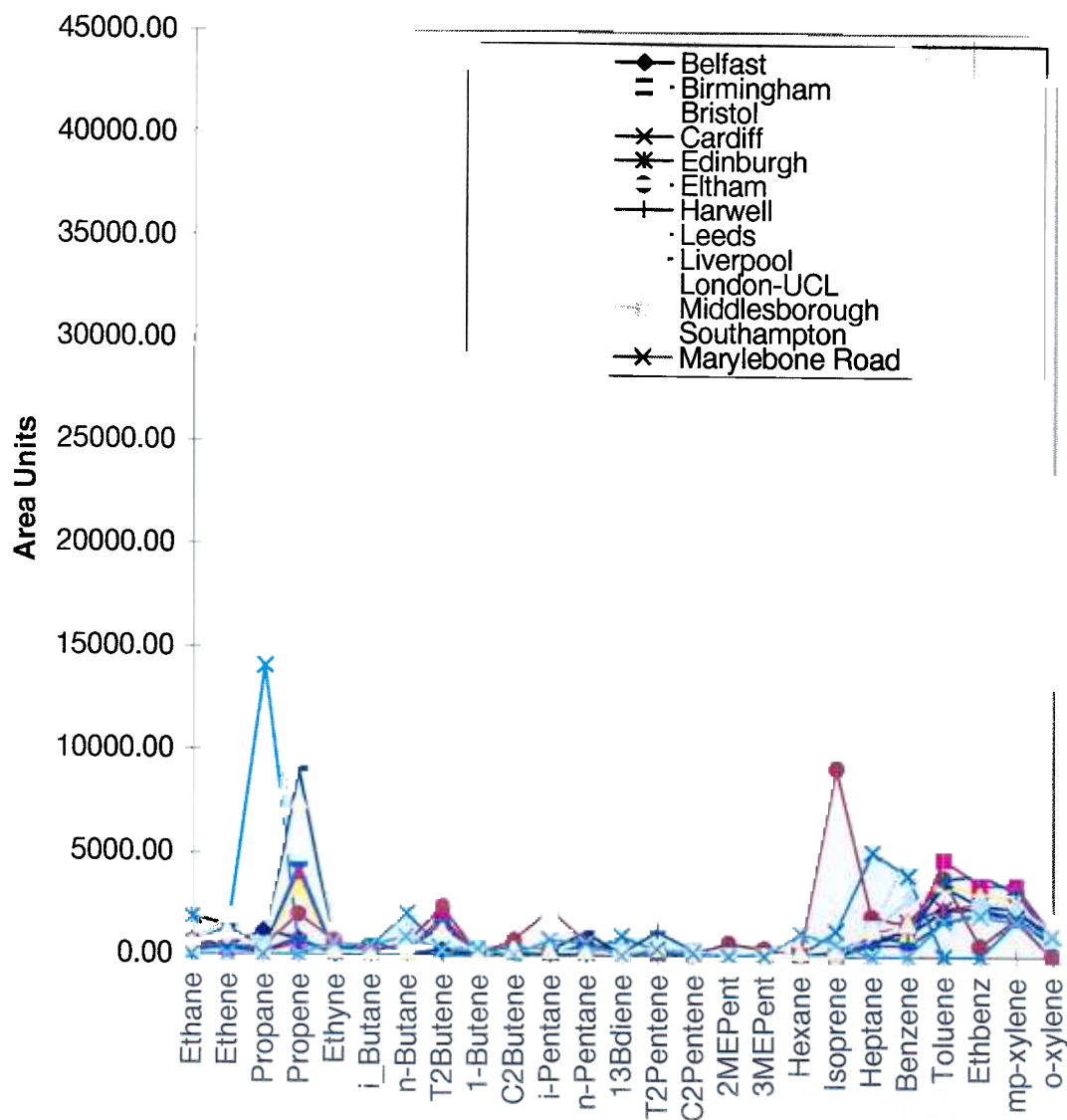


As previously reported, the 1999 exercise was compromised to some extent as the blank cylinder was subsequently found to contain benzene and C8s at the following concentrations:

Benzene	0.4	molar ppb
Ethyl-benzene	1.2	
mp-Xylene	4.4	
o-Xylene	0.9	

The blank values for these have therefore not been reported. However, there was no evidence of internal sources of these species from the results obtained.

Figure 1b Measured areas from the blank cylinder runs in the 2000 audit



In the 2000 set of blank runs the most notable difference is in the relatively high peak areas from the Middlesbrough site. This is likely to be a consequence of recent service work at the site. The size and pattern of 'blank' values at other sites is broadly similar to 1999.

Figure 1c Effect of blank corrections on concentration of ambient standard 2000

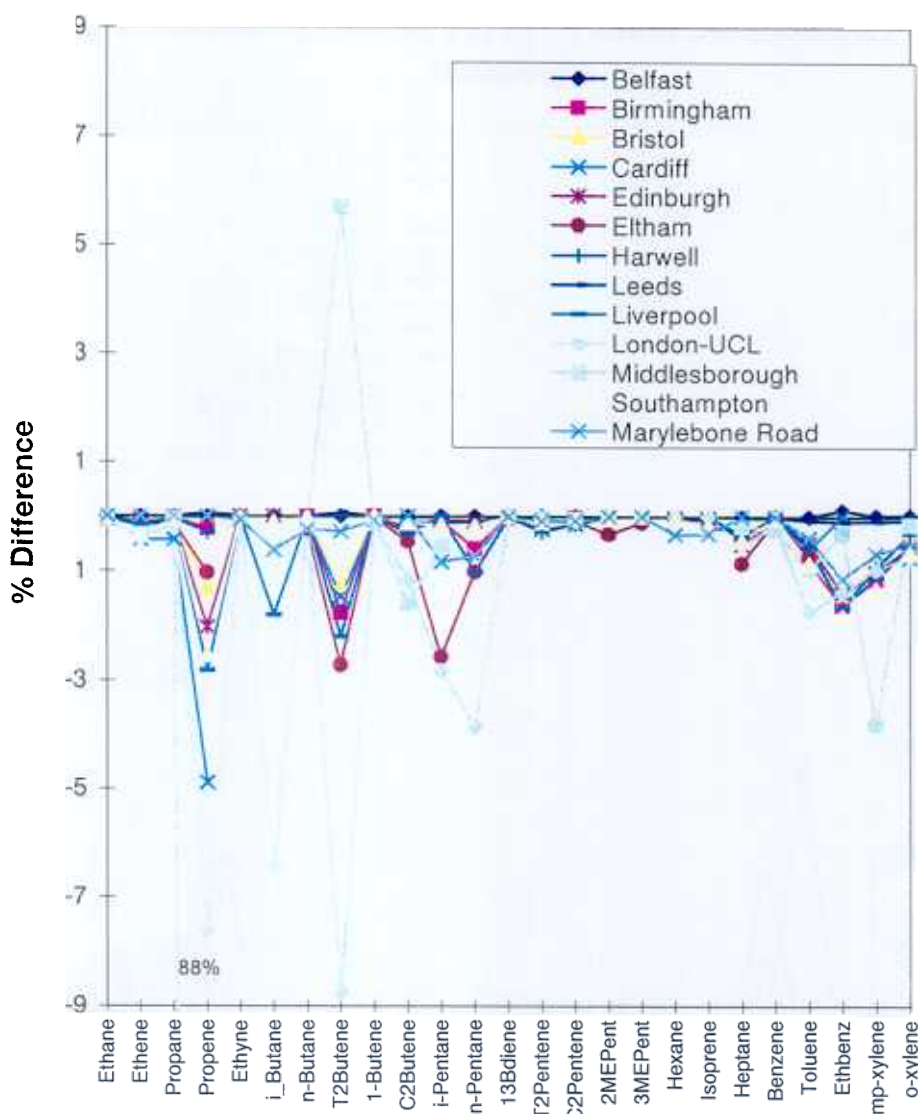


Figure 1c represents the percentage differences between the blank corrected measurement of the ambient standard cylinder and the non-blank corrected measurement. The values are a realistic snapshot of errors due to internal sources in the instruments.

The largest errors are for propene and t-2-butene, which are mostly smaller than in 1999. A graphical method for correcting propene by comparison to other alkenes data is routinely employed during ratification, and so these errors will not affect the ratified data. The large errors for propene, t-2-butene and m&p-xylene at Middlesbrough may be attributable to temporary problems, as this machine had just had major service work carried out on it. These problems have subsequently been resolved. However t-2-butene does appear as an internal source at most of the sites and in the future may need to be corrected during ratification.

Other errors are generally similar to 1999 at less than 5%, with 1,3-butadiene and benzene errors less than 1%

5.2 AUDIT STANDARD INJECTIONS

The concentrations in the audit standard were determined independently using response factors in normal use at each site, derived from the site standard calibrations and the normal ratification procedure. Figures 2a and 2b summarise the results from 1999 and 2000 respectively, showing the differences between the measured value at each site and the certificated value obtained at NPL.

Figure 2a 1999 Percentage Difference of measured audit standard from NPL Value (blank corrected)

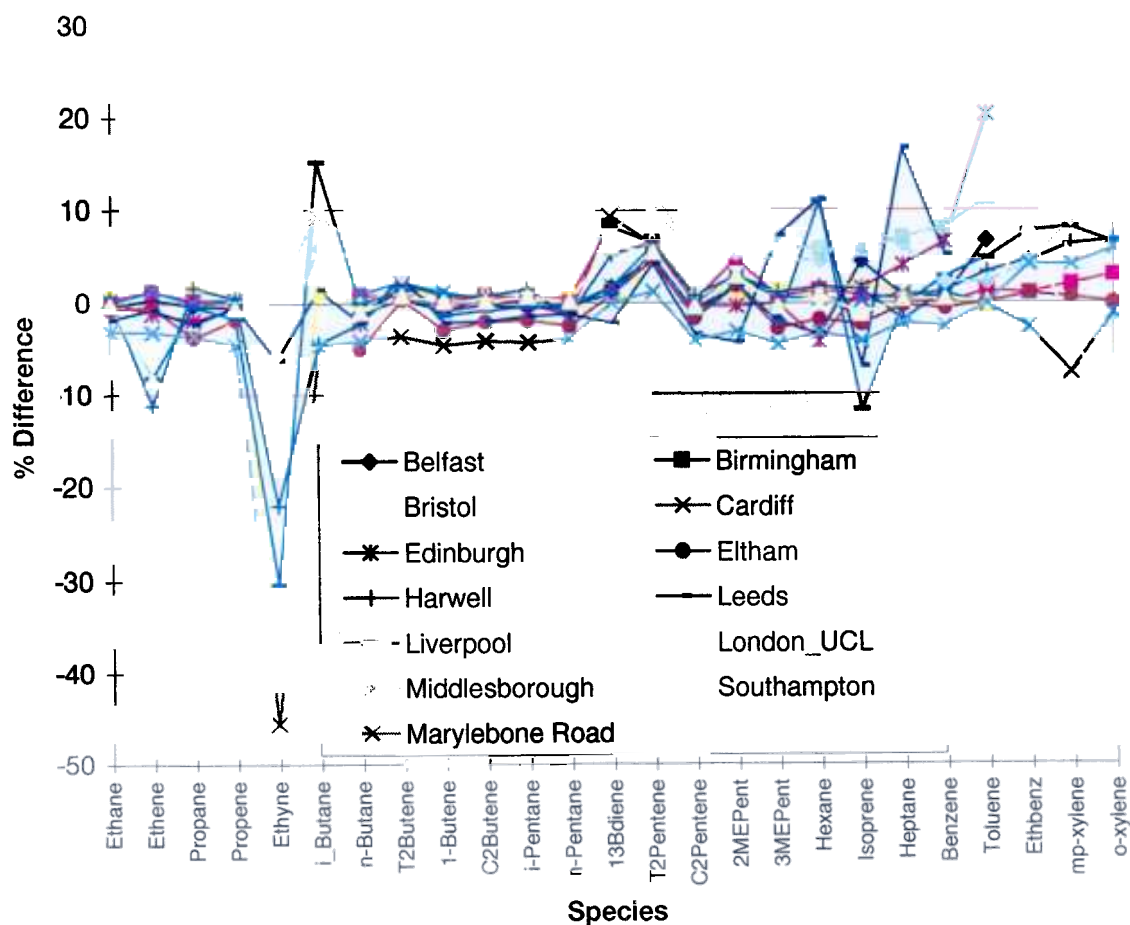
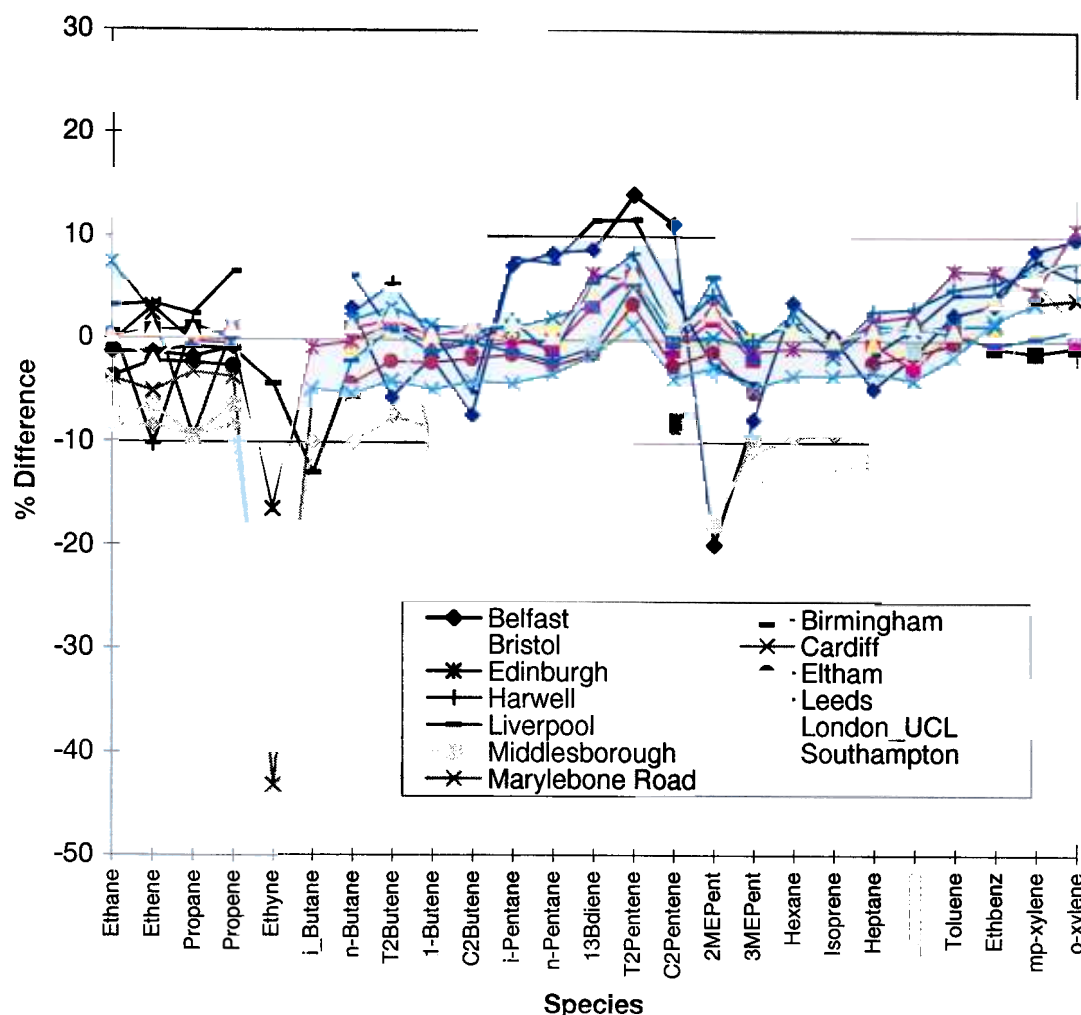


Figure 2b 2000 Percentage Difference of measured audit standard from NPL Value (blank corrected)



The results obtained in 2000 for measurements of benzene and 1,3-butadiene all agree to within ten percent, except for one site for each species, London-UCL for benzene and Leeds for 1,3-butadiene.

The results for other species show parity with those obtained in 1999, with most species agreeing to within ten percent. The deviations for ethyne can be attributed to varying amounts of coelution with i-butane, and also to changes at NPL in the method of calculation of the quantities of ethyne present in the calibration cylinders.

Varying amounts of coelution also explain the deviations at one or two sites for 2 & 3 methylpentane, and isoprene and n-hexane. The varying amounts of coelution are addressed in fully ratified data by using a subtraction method for ethyne and i-butane, a graphical method for n-hexane and isoprene, similar to that used to correct propene except using the corresponding alkanes, and an addition method for 2 & 3 methylpentane.

The calibration performed for the audit at London-UCL was found to be unrepresentative of the response factors for the site. An average of the response factors from the month's ratification

process was used. The machine at London-UCL may have been subject to instability during that period, as London-UCL shows higher than average errors on all species.

Middlesbrough also appears to have notably high errors for all species. This is probably due to recently concluded service work, as previously mentioned.

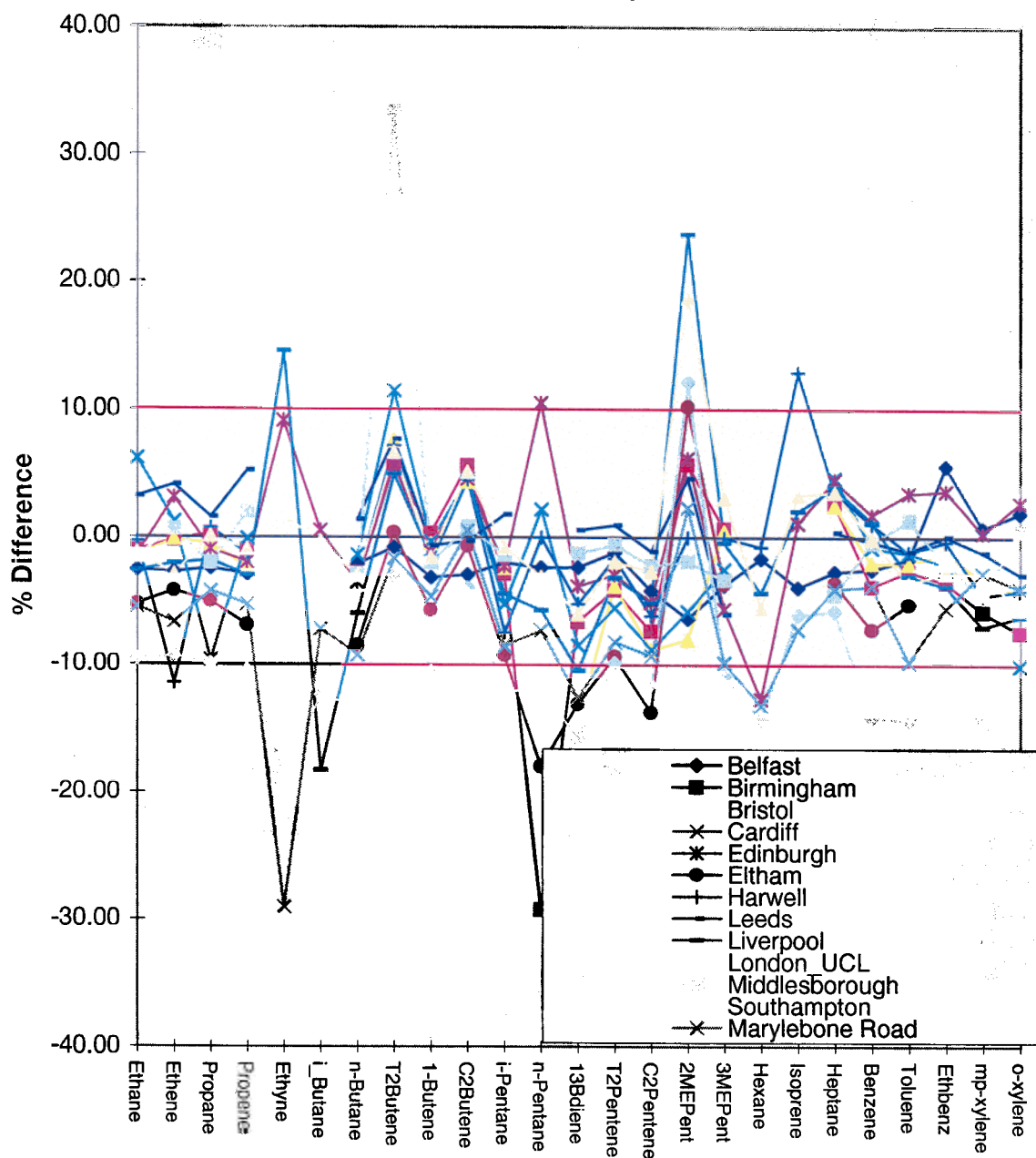
5.3 AMBIENT STANDARD INJECTIONS

As with the audit standard, the concentrations in the ambient standard were determined independently at each site, using response factors in normal use at the site, derived from the site standard calibrations, and standard ratification procedures. Figure 3a summarises the results from 2000, showing the difference between the measured value at each site and the certificated value obtained at NPL. This gives a realistic measure of accuracy across the Network at high-ambient concentrations, and would highlight problems due to non-linearity of instrument response as it compares ambient concentrations to those obtained from the audit cylinder.

It can be seen from the results that certain species show significantly larger errors than for the audit standard injection. However, results obtained for benzene (and most other species) all agree to within ten percent of the NPL measured value except again at London UCL. Most results obtained for 1,3-butadiene also agree to within ten percent, except those at Bristol, Eltham, Middlesbrough and Marylebone Road, which may be due to temporary instrument faults. There is a suggestion that non-linearities produce values for 1,3-butadiene which are about 5% too low when calibrated with the present method.

As with the audit cylinder deviations, the results for ethyne and i-butane can be explained by the differences in the method of calculating the concentration of ethyne and also in the varying amount of coelution. The same can also be said of n-hexane and isoprene. The problems seen with the results of 2- and 3-methylpentane can also be attributed to varying amounts of coelution, a problem which is overcome in disseminating the data by adding the two results together and reporting the total as 2&3-methylpentane. Temporary problems at Middlesbrough and London-UCL have been previously discussed.

**Figure 3a 2000 Percentage Difference of measured ambient
level standard from NPL Value
(blank corrected)**



6 CONCLUSIONS

6.1 OPERATIONAL MATTERS

During the series of 2000 audit visits all hydrocarbon monitoring sites were visited by a member of the Central Management Control Unit for the Hydrocarbon Network. A series of diagnostic checks were carried out on all major items of equipment to ensure optimum performance. All sites except Marylebone Road had an LSO audit, to maintain levels of training and to ensure the smooth running of the sites. All sites also had an inventory check on all equipment and spares to facilitate quick recovery of data in the event of minor operational problems.

All site PCs across the network were upgraded in May 2000

6.2 DATA QUALITY

All sites were intercompared using two calibration cylinders, one high concentration 27 component cylinder (as used on sites) and one lower concentration 30 component ambient cylinder (recently developed at NPL). A blank cylinder was also used to measure internal instrumental sources of hydrocarbons.

The results show consistency with previous results in 1999. In particular the results provide good evidence that benzene continues to be reported with a relative uncertainty of less than $\pm 10\%$ (95% confidence interval) at most sites, with similar results for 1,3-butadiene.

Specific issues highlighted were:

- Internal sources of propene and trans-2-butene at some sites

The particular problems of accurate ethyne measurement.

The audit results provide very valuable information on aspects of the data needing attention during data ratification, and both the audit and ratification procedures evolve to reflect this.