UK Ambient Hydrocarbon Air Quality Network: 1999 Audit Report

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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 1999 are given in the separate 1999 Summary of Network Operations report.

The audits were carried out between October 1999 and January 2000. The schedule of audit visits is given in Table 1.

Table 1: Audit visit schedule

Site Name	Date of Audit	Auditor
Belfast	19/10/99	D Butterfield
Birmingham [1]	02/11/99	A Andrews
Bristol	26/10/99	A Andrews
Cardiff	25/10/99	A Andrews
Edinburgh	11/10/99	A Andrews
Eltham	30/11/99	D Butterfield and A Andrews
Harwell	09/11/99	D Butterfield
Leeds	14/10/99	A Andrews
Liverpool	17/10/99	D Butterfield
London-UCL	05/10/99	R Robinson
Middlesbrough	13/10/99	A Andrews
Southampton [2]	08/11/99	R Robinson
Marylebone Road	26/01/00	D Butterfield

[1] Due to a problem with sample collection the site required re-auditing, and this was carried out on 23rd and 24th March 2000.

[2] Due to a problem with the valve switches in the Audit Box the site required re-auditing, and this was carried out on 3rd and 4th April 2000.

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;

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. The table 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	Good	Good	Manifold possibly contaminated - inlet and tube to the pump unit replaced	None required.
Birmingham	Good	Good	Audit highlighted a sample collection problem - later traced to a broken pipe connecting the TCT to the pump unit	Pipe work replaced and the site re-audited
Bristol	High volume centrifugal pump showing signs of wear	Good	None	Pump replaced
Cardiff	Dewars are not maintaining pressure. Will require refurbishing	Good	None	Manifold and insulation on LN_2 line may need minor maintenance
Edinburgh	Good	Good	None	None required
Eltham	Good	Good	Sample inlet pipe renewed	None required
Harwell	Good	Good	Cleaned sample inlet pipe	Glass manifold requires cleaning
Leeds	Good	Good	None	None required
Liverpool	Good	Good	None	LSO requested safety catches for taps on the LN_2 vessel to stop accidental opening
London-UCL	Good	Good	None	None required
Middlesbrough	Good	Good	Pump connection replaced	LSO requested replacement of manifold pipe work and fixing of pipe work for standard
Southampton	Good	Good	Replaced sample pump tube	None required

2.1 ONGOING SITE EQUIPMENT ISSUES:

New, current-specification PCs have been purchased and installed at all 12 DETR-owned sites.

Electronic pressure gauges for the standard gas cylinders have also been purchased, and special T-piece connectors made. These are due to be fitted at the next round of site visits.

Manifold pipe work which has not already been replaced will be changed at the next round of audit trips.

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 LSOs Audited	Weekly Checklist Completed OK	Site Standard applied correctly
Belfast	Grant Smith	✓	✓
Birmingham	Peter Porter	✓	✓
Bristol	Graham Mills	✓	✓
Cardiff	Ian Warburton	✓	✓
Edinburgh	Archie Forrest	✓	✓
Eltham	N/A	N/A	N/A
Harwell	Brian Jones and Tony Clarke	✓	✓
Leeds	Chris Hills and Shona McNamara	✓	✓
Liverpool	Peter Robinson and Keith Sharp	✓	✓
.London UCL	Neil Rose and Tom Davidson	✓	N/A
Middlesbrough	Anthony Luke	✓	✓
Southampton	Chris Bannister	✓	✓

Hands-on training was provided for new deputy LSOs.

The auditor and Eltham LSO (part of the NPL-SEIPH CMCU partnership) were not able to arrange a mutually convenient time within the audit schedule, so the site was audited without the LSO present.

The site at London-UCL uses automated standard injection systems and the LSOs were not required to manually attach the calibration standards. These LSOs were however required to show they were able to run an automated calibration on request.

The performances of the LSOs were all 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	252	-94	125
Birmingham	-20	250	-93	125
Bristol	-20	250	-95	125
Cardiff	-20	250	-90	125
Edinburgh	-20	250	**-130**	115 - 135
Eltham	-20	251	-90	125
Harwell	-20	249	-98	125
Leeds	-20	250	-90	125
Liverpool	-21	251	-94	127
London-UCL	-21	248	-99	**107**
Middlesbrough	-20	**275**	-93	**115**
Southampton	-21	255	-103	**117**

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

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	-0.93	2.0	✓	13
Birmingham	9.9	-0.88	2.0	✓	12
Bristol	9.8	-0.9	2.0	✓	18
Cardiff	9.8	-0.88	2.1	✓	10 [1]
Edinburgh	9.9	-0.9	2.5	✓	48 [2]
Eltham	10.0	-0.85	2.0	✓	16
Harwell	14.7 [3]	-0.85	1.8	✓	20
Leeds	9.8	-0.94	1.9	✓	N/A
Liverpool	9.8	-0.89	2.3	✓	9
London-UCL	10.0	-1.0	1.7	✓	12
Middlesbrough	9.8	-0.92	1.9	✓	18
Southampton	10.4	-0.94	1.8	✓	22

This dewar was not maintaining pressure and was exchanged and refurbished at a later date

[2] This dewar is shared with the university and maintains a higher operating pressure.

[3] This system is operated with a nominal sample flow of 15ml/min.

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 (but see below);

ii) 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;

iii) 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.

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.

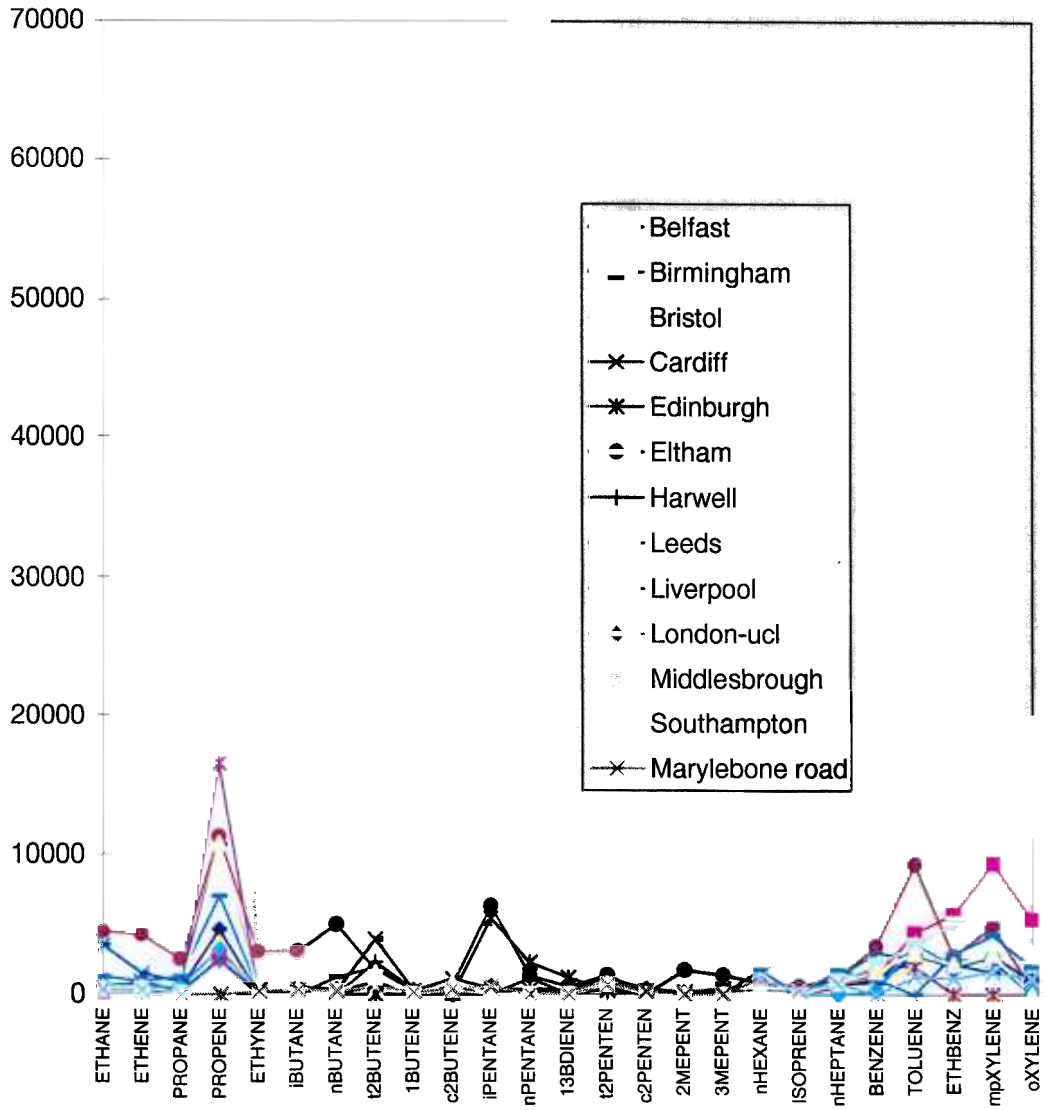
As a part of the LSO audit a site standard calibration was performed. This was used to derive the response factors for the site in the same way as for the regular fortnightly calibration. These response factors were then applied to the results of the ambient and audit standard and the concentrations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

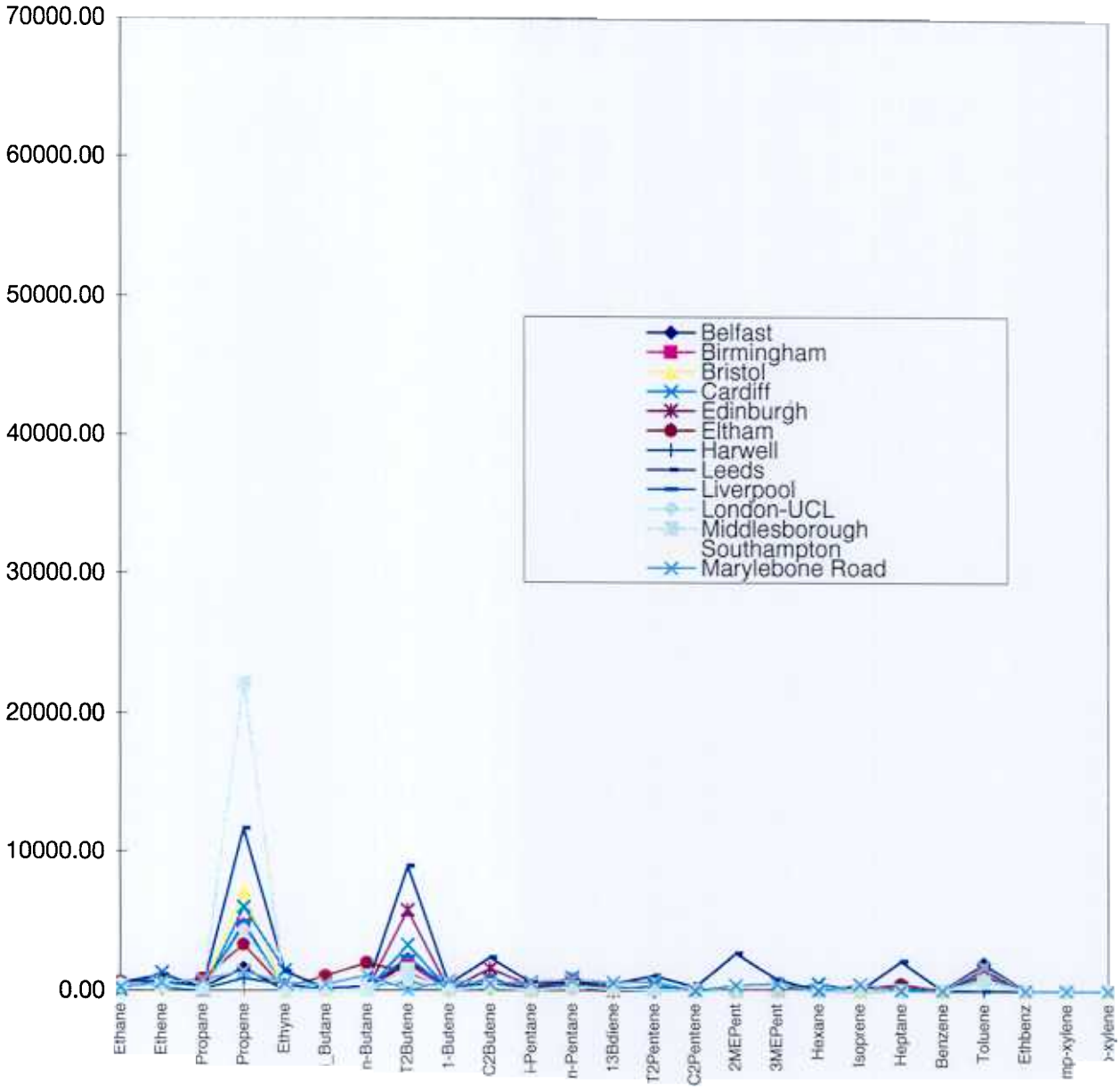
Figure 1a and 1b show the measured areas from the blank runs performed in 1998 and 1999, with the same vertical scale, for comparison.

Figure 1a Measured areas from the blank cylinder runs in the 1998 audit



The most significant internal sources measured during the blank cylinder runs were propene and t-2-butene. Most sites also showed a small degree of toluene contamination, probably as a result of carry over from ambient sampling. As with the data from 1998, Middlesborough showed the highest propene area, though this area is reduced by more than half in the 1999 audit. At most of the sites an overall decrease in internal sources was observed.

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



The exercise was compromised to some extent as the blank cylinder used during the 1999 audits 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 1c Effect of blank corrections on concentration of ambient standard

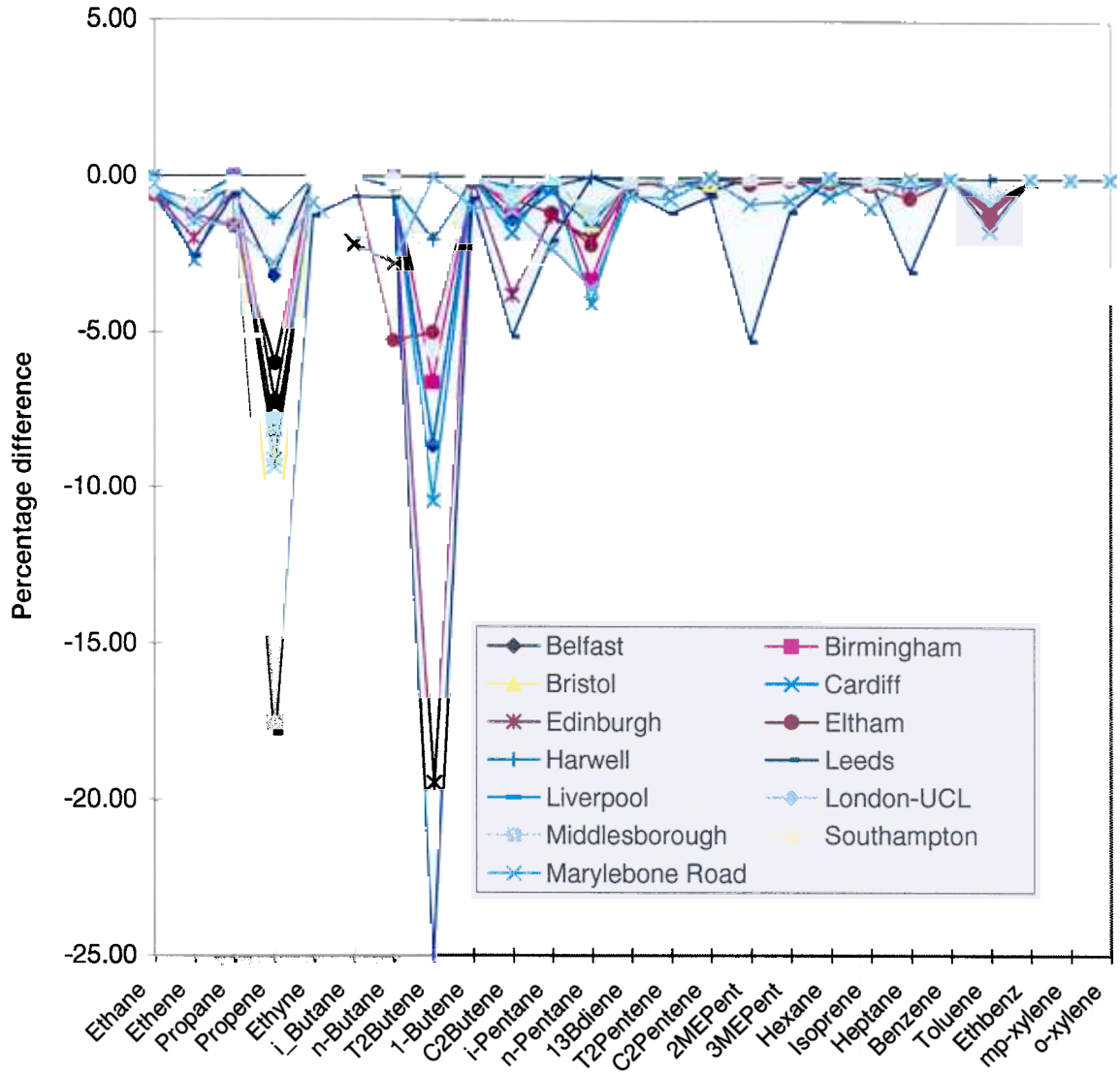


Figure 1c represents the percentage differences between the blank corrected measurement of the ambient standard cylinder and the non-blank corrected measurement. The values are a realistic snapshot of errors due to internal sources in the instruments.

The largest errors are for propene and t-2-butene, which are larger than in 1998. 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 in t-2-butene at Leeds and Edinburgh may be attributable to temporary problems, as these machines were subject to ongoing servicing due to poor chromatography and carry-over after calibration at the time of the audit. 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 in the same manner as propene.

Other errors are generally similar to 1998 at less than 5%, with 1,3-butadiene errors less than 1%. Benzene internal source errors could not be assessed because of the blank cylinder problem, but previous audits have shown them to be around 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 1998 and 1999 respectively, showing the differences between the measured value at each site and the certificated value obtained at NPL.

Figure 2a Percentage difference of measured audit standard from the NPL Value (blank corrected) in 1998 audit

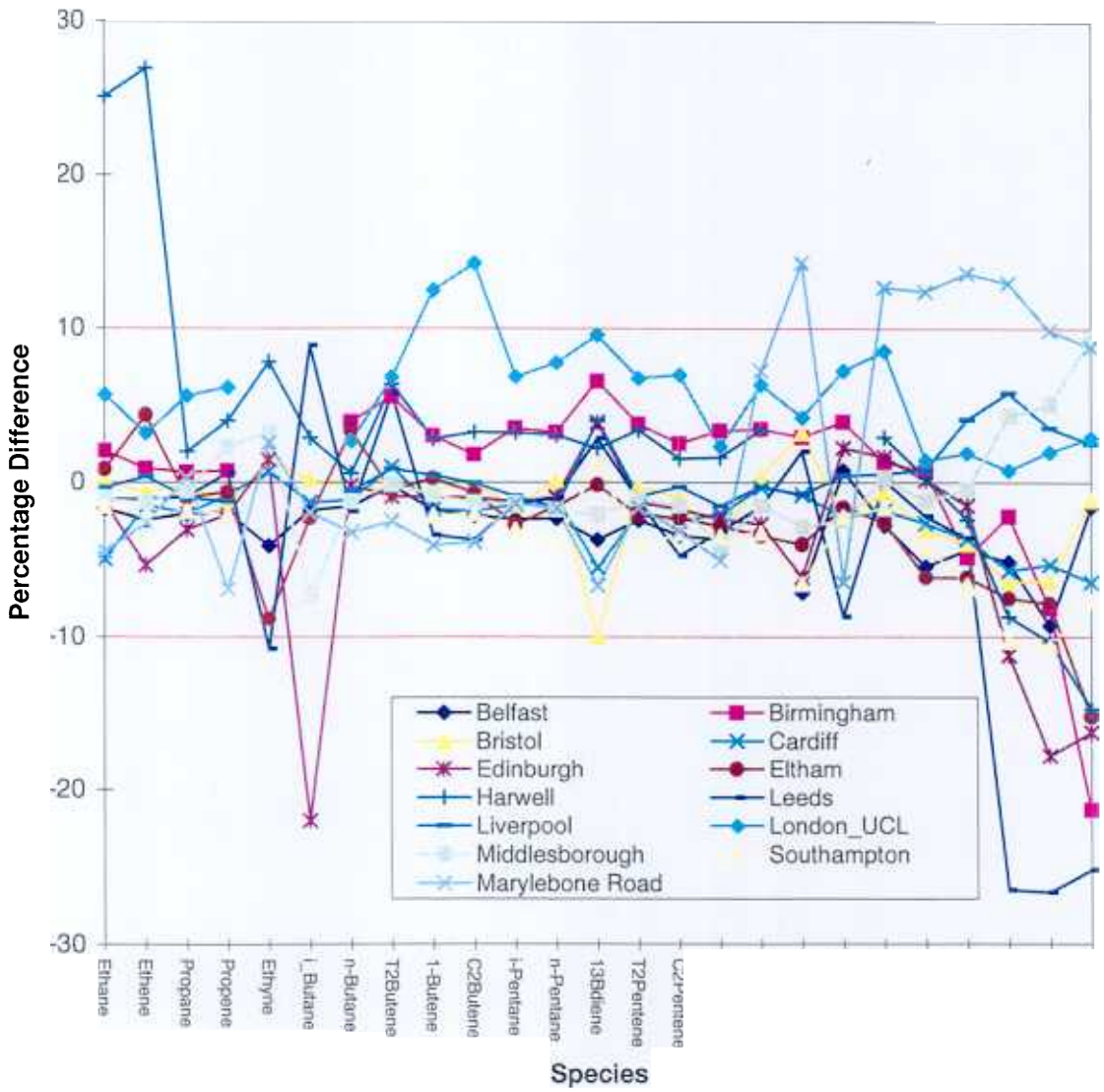
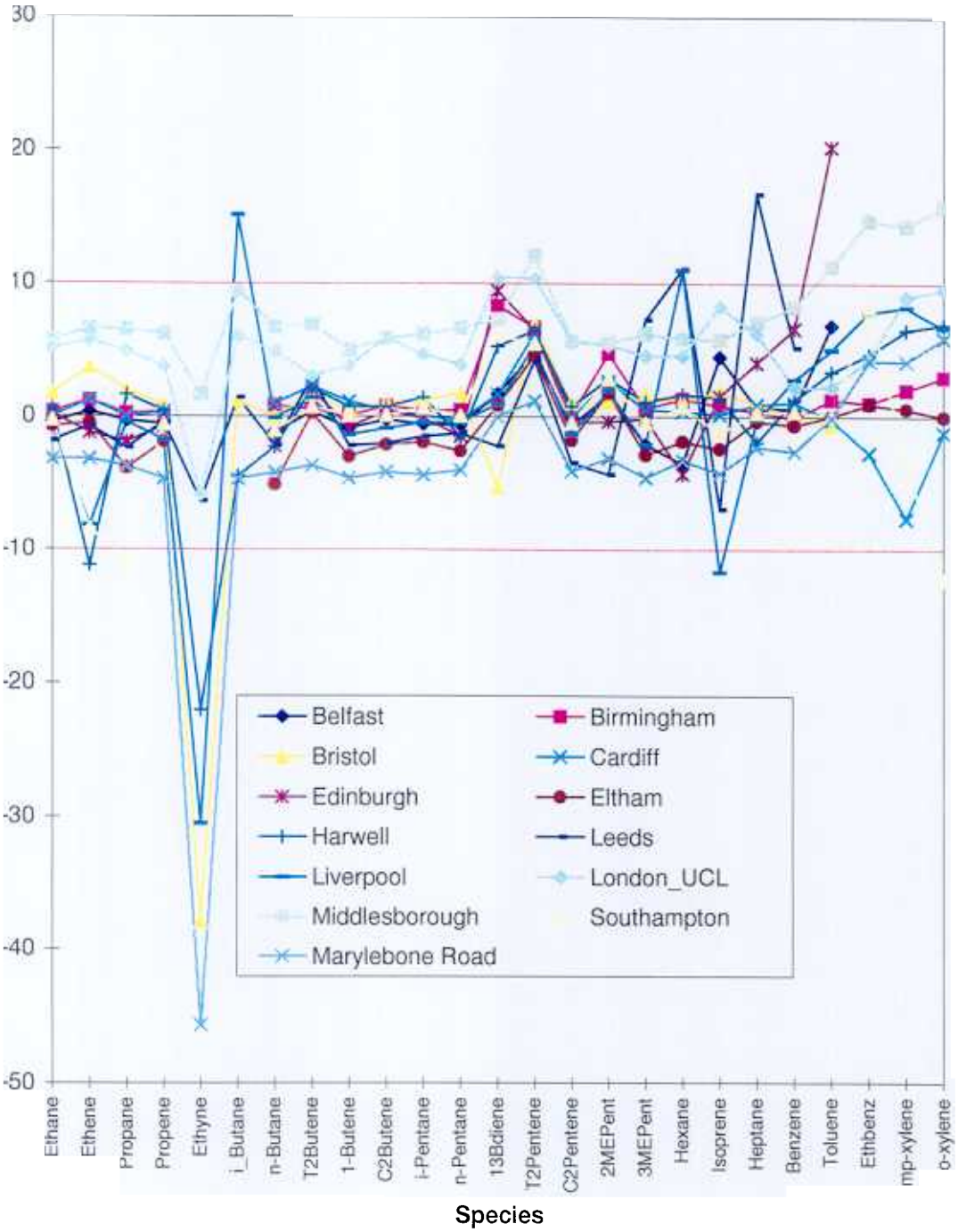


Figure 2b 1999 Percentage Difference of measured audit standard from NPL Value (blank corrected)



As in 1998 the results obtained in 1999 for measurements of benzene and 1,3-butadiene all agree to within ten percent, which is a good indication of satisfactory cylinder stability and ratification procedures.

With the exception of ethyne, the 1999 results are in general slightly better than those obtained in 1998, 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. The

particular difficulties of measuring ethyne, and the consequent higher uncertainties for measurements of it, have been described previously.

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

There is one rogue toluene point at Edinburgh, which can be attributed to the temporary poor chromatography and carry over mentioned previously.

Middlesborough appears to be notably high for all species. This may be due to a problem with an offset and this is currently under review.

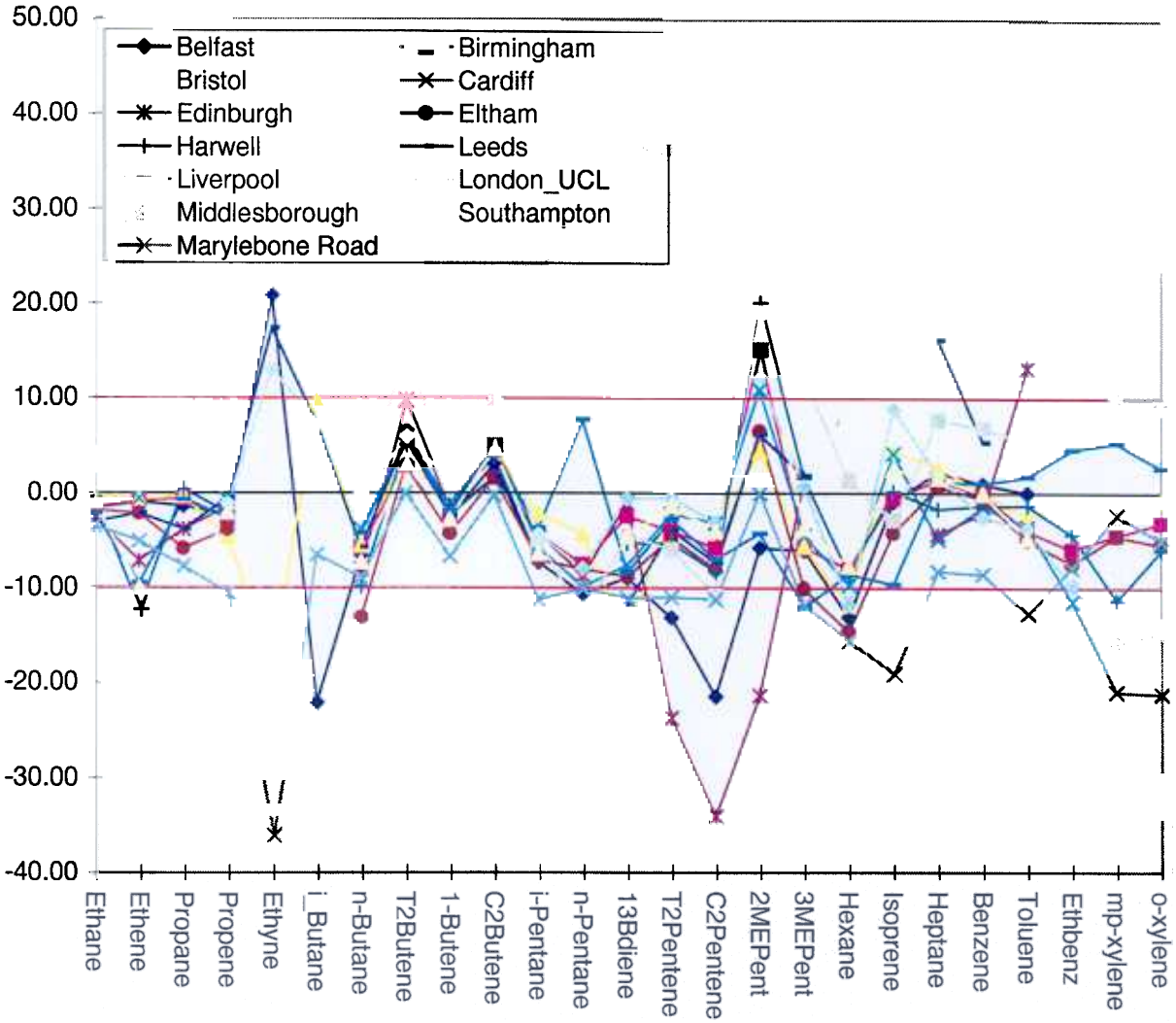
5.3 AMBIENT STANDARD INJECTIONS

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 1999, 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. Most results obtained for 1,3-butadiene also agree to within ten percent, except those at Bristol, Leeds 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 Leeds and Edinburgh have been previously discussed.

Figure 3a 1999 Percentage Difference of measured ambient level standard from NPL Value (blank corrected)



6 CONCLUSIONS

6.1 OPERATIONAL MATTERS

During the series of 1999 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 Eltham and 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 had been upgraded in the first half of 2000. During the audit visits several of the sites had their manifold pipe work cleaned or replaced, with the rest of the sites to be done at a later date.

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 showed a general improvement over the previous results in 1998. In particular the results provide good evidence that benzene continues to be consistently reported with a relative uncertainty of less than ±10% (95% confidence interval) at all 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.