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DQL-AS 017

UK Non-Automatic Hydrocarbon Network:

Measurement of Selected Ozone Precursors from Existing Chromatograms

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NOT RESTRICTED

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Approved on behalf of the Managing Director, NPL
by Dr Stuart Windsor, Business Leader, Analytical Science Group

Executive Summary

Existing chromatograms from the Network sites Grangemouth, Birmingham Roadside, Haringey Roadside, Leeds Roadside, and Leeds Centre for the year 2004 were examined for information on the 29 hydrocarbons included in the EU Ambient Air Ozone Directive 2002/3/EC. These are:

ethane	1,3-butadiene	i-octane (2,2,4-trimethyl
ethene (ethylene)	n-pentane	pentane)
ethyne (acetylene)	i-pentane (2 methyl butane)	benzene
propane	1-pentene	toluene
propene	(trans) 2-pentene	o-xylene
n-butane	isoprene (2 methyl 1,3-butadiene)	m-xylene
i-butane (2 methyl propane)	n-hexane	ethyl benzene
1-butene	i-hexane (2 methyl pentane)	1,2,3-trimethyl benzene
trans-2-butene	n-heptane	1,2,4-trimethyl benzene
cis-2-butene	n-octane	1,3,5-trimethyl benzene

For each species, an evaluation was made of the quality of data available at the different sites.

For those species and sites where reasonable data could be obtained, an estimate was made of the annual average concentrations.

These concentrations were then compared for absolute and relative values with data from the automatic hydrocarbon network and the National Atmospheric Emissions Inventory.

With no further development or changes to analytical methods, there is good evidence that valid data can be obtained for the species:

n-pentane	n-octane
i-pentane (2 methyl butane)	i-octane (2,2,4-trimethyl pentane)
isoprene (2 methyl 1,3-butadiene)	benzene
n-hexane	toluene
i-hexane (2 methyl pentane)	o-xylene
n-heptane	m-xylene
	ethyl benzene

from those sites taking pumped samples, and for the species:

n-butane	1,3-butadiene
i-butane (2 methyl propane)	n-pentane
1-butene	i-pentane (2 methyl butane)
trans-2-butene	1-pentene
cis-2-butene	(trans) 2-pentene

from those sites taking diffusive samples.

Of these species, the ten most important in terms of ozone forming potential are expected to be (in decreasing order of importance, according to the NAEI) n-butane, toluene, m-xylene, n-pentane, n-hexane, i-pentane, o-xylene, n-heptane and ethyl benzene. Thus there is much relevant information available from all the pumped sites, while the diffusive method provides information about the single most important ozone precursor species, n-butane.

The results show good qualitative agreement with existing data on speciated hydrocarbons from the Automatic Hydrocarbon Network, and generally good correspondence with the data in the National Atmospheric Emissions Inventory.

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UK Non-Automatic Hydrocarbon Network

Measurement of Selected Ozone Precursors from Existing Chromatograms

1 Introduction

As currently operated, all 35 sites in the Network pump approximately 100 litres of air through each of a pair of sorbent-filled samplers every fortnight, while another 10 sites produce tubes that have been sampling diffusively onto the same sorbent (Carbopack X), with an effective sampled volume of around 10 litres. The samples are analysed for hydrocarbons at NPL using gas chromatography. Further information about the Network is give in Annual Reports, for example NPL Report DQL-AS 016.

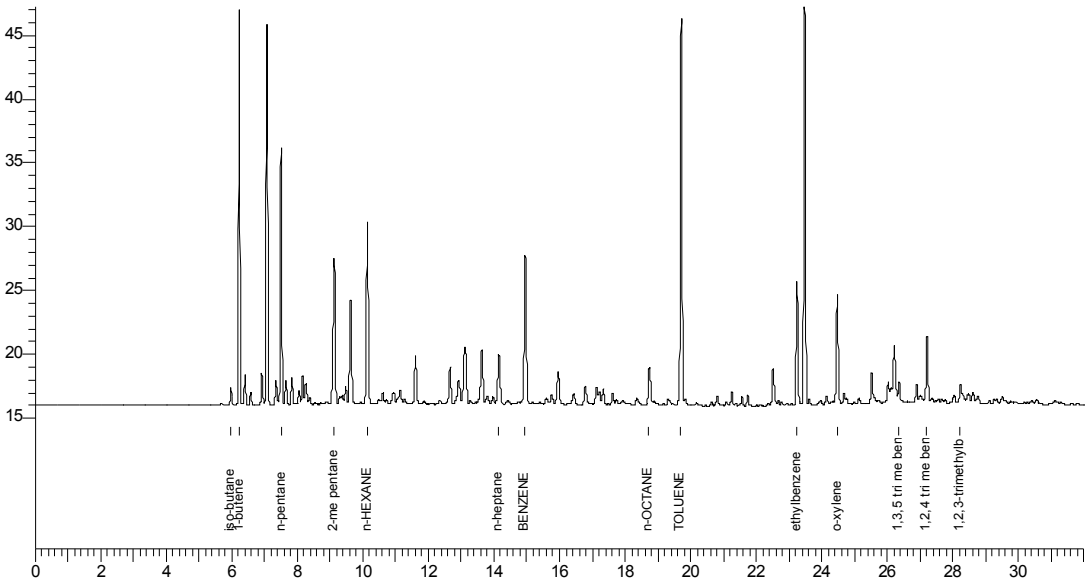
The large pumped volume allows easy determination of the benzene concentration, as the flow rate (10 ml/min) is large enough to control accurately, and the mass of benzene is relatively large. The volume is very comfortably within the safe sampling volume for benzene on Carbopack X, beyond which some of the hydrocarbon would pass right through the tube and not be measured.

The gas chromatographic analysis of the tubes produces peaks for all the absorbed hydrocarbons, though at present only benzene (on the pumped tubes) and 1,3-butadiene (on the diffusive tubes) are reported.

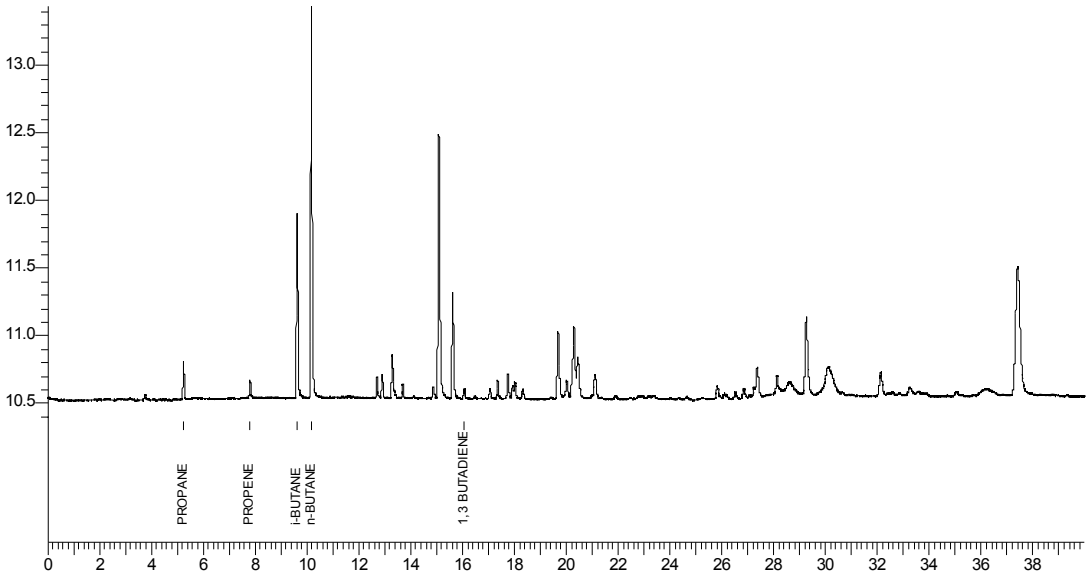
Reliable data on many other species is available from the same chromatograms, depending on the following factors:

- Correct identification of the peak and absence of coelution;
- Validated calibration of the peak response factor for the specific analytical run, by comparison with a known standard;
- In the case of pumped samples, verification that the sampled volume is not larger than the safe sampling volume for the combination of species and sorbent. The safe sampling volume drops dramatically for lighter species, which is why 1,3-butadiene measurements cannot be obtained from the pumped samples;
- In the case of diffusive samples, verification that back diffusion or other factors is properly taken into account in the diffusive uptake rate;
- Concentrations being above the detection limit for the method, set in part by the cleaning protocol used for the tubes.

Typical chromatograms from pumped and diffusive tubes are shown below:



Pumped



Diffusive

Different GC columns are used for the two measurements – ZB1701 for the pumped and Al_2O_3/KCl for the diffusive - to optimise the chromatography for benzene and 1,3-butadiene, so different information is available.

2 Evaluation of Data Available

2.1 Pumped Samples

2.1.1 Identified Peaks

Pure samples of the remaining ozone precursor compounds were obtained and aliquots analysed on the same column under the same conditions to obtain accurate retention time data.

The peaks identified in the pumped samples were:

n-butane	i-octane (2,2,4- trimethyl pentane)
i-butane (2 methyl propane)	benzene
n-pentane	toluene
i-pentane (2 methyl butane)	o-xylene
1-pentene	m-xylene
isoprene (2 methyl 1,3-butadiene)	ethyl benzene
n-hexane	1,2,3-trimethyl benzene
i-hexane (2 methyl pentane)	1,2,4-trimethyl benzene
n-heptane	1,3,5-trimethyl benzene
n-octane	

2.1.2 Exceedence of Safe Sampling Volume

Inspection of the data shows that the values for n-butane, i-butane and 1-pentene from the pumped method are anomalously low. This is almost certainly due to a significant fraction of the molecules of these species being pumped right through the sorbent material, and thus not being available for analysis.

2.1.3 Efficient Desorption

It is expected that the heaviest hydrocarbons will be difficult to desorb from the Carbopack X sorbent. While this can to some extent be compensated for during the calibration process, it leaves such data with significant additional uncertainties. Experience and inspection of the data suggests that the trimethyl benzenes will all suffer from this effect.

2.1.4 Calibration

To enable quantification of the extra ozone precursor compounds in each data set the response factor of the closest known calibrant was applied to each unknown. In order to simplify the quantification process a specimen calibration was chosen for both the C3-C5 Ozone Precursor analyses and C6-C10 Ozone Precursor analyses. One of the greatest influences on the response factor for an analyte is the split ratio. These ratios for all the analytical runs under examination were examined and a median point analytical run for each of the two analysis types chosen. The response factors from these runs were applied to all of the analytical runs examined. If necessary the retention times of the analytes were adjusted but the response factors were not altered. The quantitative results obtained by this

method will not be strictly accurate but, given the complexity of the data involved, will provide a useful estimate of what results can be achieved for the ozone precursor compounds from the existing Hydrocarbon Network samples.

The one exception to the use of approximate calibration factors is benzene, where the fully ratified data from the samples is readily available and has been used.

Concentrations of ozone precursors from the pumped samples are therefore reported for the following species:

n-pentane	n-octane
i-pentane (2 methyl butane)	i-octane (2,2,4-trimethyl pentane)
isoprene (2 methyl 1,3-butadiene)	benzene
n-hexane	toluene
i-hexane (2 methyl pentane)	o-xylene
n-heptane	m-xylene
	ethyl benzene

2.2 Diffusive Samples

2.2.1 Identified Peaks

Pure samples of the remaining ozone precursor compounds were obtained and aliquots analysed on the same column under the same conditions to obtain accurate retention time data.

The peaks identified in the diffusive samples were:

ethane	1,3-butadiene
ethene (ethylene)	n-pentane
propane	i-pentane (2 methyl butane)
propene	1-pentene
n-butane	(trans) 2-pentene
i-butane (2 methyl propane)	
1-butene	
trans-2-butene	
cis-2-butene	

2.2.2 Back Diffusion

Very light molecules are difficult to trap reliably by diffusive methods. Inspection of the data shows that the values for ethane, ethane, propane and propene from the diffusive method are anomalously low, and this is almost certainly due to very inefficient trapping of the material.

2.2.3 Calibration

A similar procedure for analytical calibration was adopted for the diffusive samples as for the pumped ones. The fully ratified data for 1,3-butadiene has been used.

For diffusive samplers the diffusive uptake rate is needed to determine the sampled volume. For this study, estimates based on established values for similar compounds with the same sampler tube were used. It should be emphasised that this procedure makes the diffusive method intrinsically less accurate than the pumped method.

Concentrations of ozone precursors from the diffusive samples are therefore reported for the following species:

n-butane	1,3-butadiene
i-butane (2 methyl propane)	n-pentane
1-butene	i-pentane (2 methyl butane)
trans-2-butene	1-pentene
cis-2-butene	(trans) 2-pentene

2.3 Available Results

The Table below summarises the results available for all 29 nominated ozone precursors from both the pumped (P) and diffusive (D) samples. A total of 21 species can be obtained, with results from two of them (n-pentane and i-pentane) available from both samples.

ethane	-	1,3-butadiene	D	i-octane (2,2,4-trimethyl	
ethene (ethylene)	-	n-pentane	D/P	pentane)	P
ethyne (acetylene)	-	i-pentane (2 methyl butane)	D/P	benzene	P
propane	-	1-pentene	D	toluene	P
propene	-	(trans) 2-pentene	D	o-xylene	P
n-butane	D	isoprene (2 methyl 1,3-		m-xylene	P
i-butane (2 methyl		butadiene)	P	ethyl benzene	P
propane)	D	n-hexane	P	1,2,3-trimethyl benzene	-
1-butene	D	i-hexane (2 methyl pentane)	P	1,2,4-trimethyl benzene	-
trans-2-butene	D	n-heptane	P	1,3,5-trimethyl benzene	-
cis-2-butene	D	n-octane	P		

3 Annual Average Concentrations

3.1 Pumped Data

The annual average data (in µg/m^3) for each species available from the pumped tubes is given in Table 1 below.

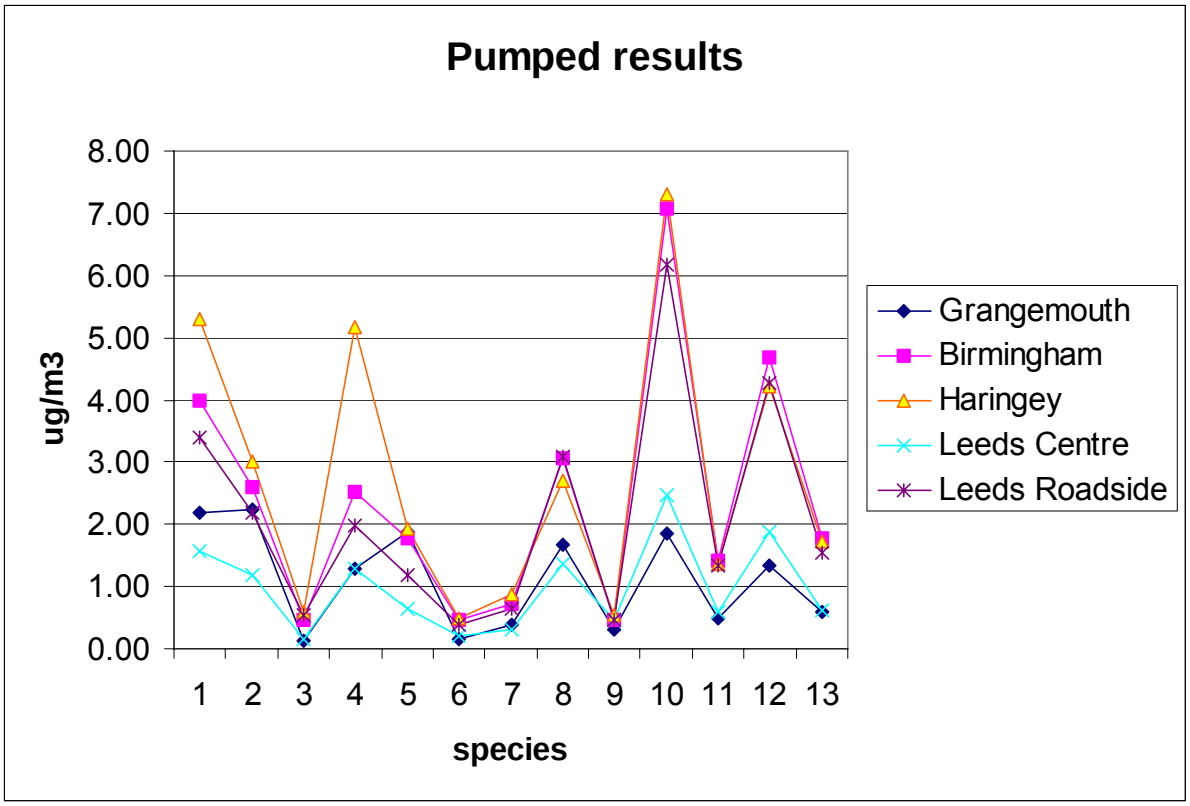
Table 1: Pumped Data

Species no.	1	2	3	4	5	6	7	8	9
	i pentane	**n pentane**	**isoprene**	**i hexane**	**n hexane**	**i octane**	**n heptane**	**benzene**	**n-octane**
Grangemouth	2.20	2.23	0.13	1.29	1.88	0.15	0.38	1.66	0.31
Birmingham	4.00	2.61	0.47	2.53	1.78	0.46	0.71	3.06	0.47
Haringey	5.29	3.02	0.59	5.18	1.94	0.49	0.87	2.70	0.55
Leeds Centre	1.56	1.18	0.15	1.28	0.63	0.20	0.30	1.37	0.46
Leeds Roadside	3.39	2.18	0.54	1.98	1.19	0.40	0.64	3.09	0.46

10	11	12	13
toluene	**ethylbenzene**	**m-xylene**	**o-xylene**
1.86	0.49	1.33	0.60
7.07	1.41	4.67	1.77
7.31	1.36	4.21	1.73
2.47	0.59	1.88	0.62
6.18	1.33	4.28	1.55

These are shown graphically in Figure 1:

Figure 1: Pumped Results; the Species Key is Given in Table 1



The results show a broadly similar pattern of concentrations for the hydrocarbon species, with the lowest concentrations at the urban background (Leeds Centre) and industrial (Grangemouth) sites. Benzene (8), toluene (10) and the xylenes (12,13) are notably higher in the other sites, which are much more affected by road transport. Haringey appears to have a local source of i-hexane (2 methyl pentane) (4).

3.2 Diffusive Data

The annual average data (in µg/m^3) for each species available from the diffusive tubes is given in Table 2.

Table 2: Diffusive Data

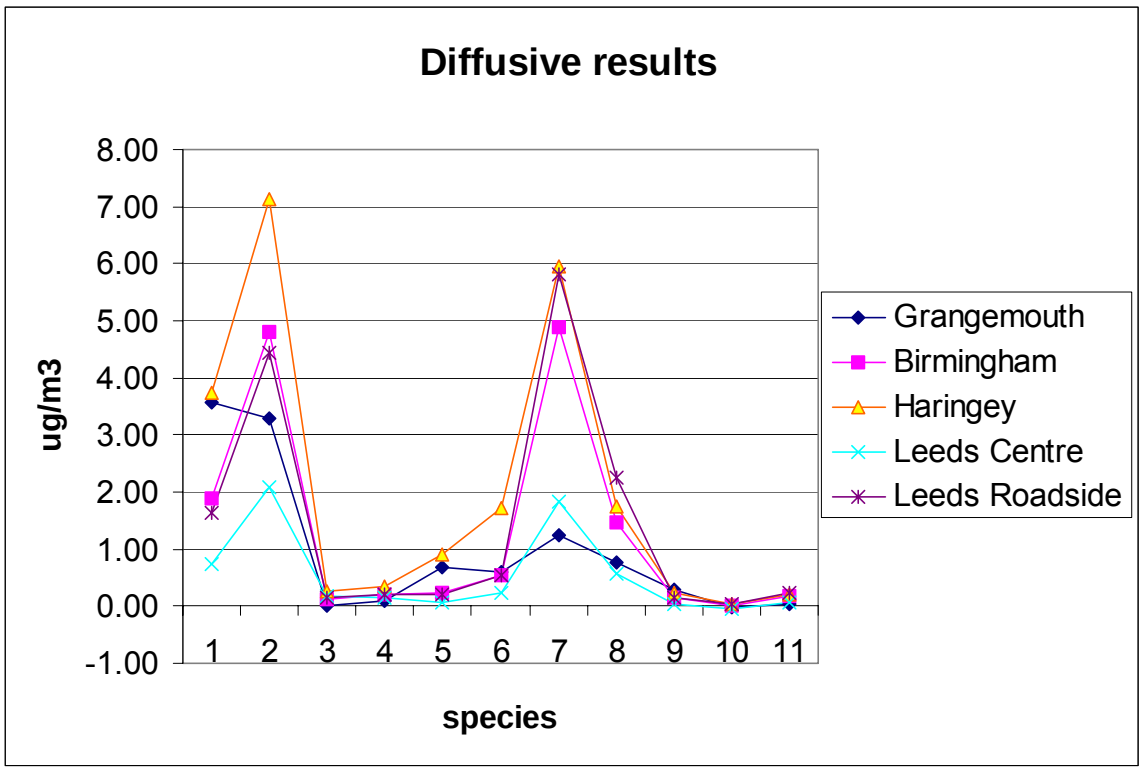
Species no.	1	2	3	4	5	6
	i-butane	n-butane	trans-2-butene	1-butene	cis-2-butene	1 pentene
Grangemouth*	3.57	3.30	0.01	0.08	0.68	0.59
Birmingham	1.88	4.80	0.12	0.20	0.23	0.54
Haringey	3.73	7.12	0.25	0.34	0.91	1.72
Leeds Centre	0.75	2.10	0.17	0.15	0.07	0.25
Leeds Roadside	1.64	4.45	0.14	0.19	0.21	0.54

7	8	9	10	11
i-pentane	n-pentane	1,3-butadiene	trans 2 pentene	cis 2 pentene
1.26	0.75	0.29	-0.03	0.02
4.89	1.46	0.16	0.01	0.18
5.94	1.75	0.22	0.05	0.20
1.84	0.58	0.04	-0.04	0.06
5.80	2.24	0.16	0.04	0.24

*Grangemouth had very low data capture (26%) for its diffusive tubes during 2004 due to the persistent theft of the tubes and subsequent changes to the security of the site. The data is included in this study nevertheless.

These are shown graphically in Figure 2.

Figure 2: Diffusive results; the species key in given in Table 2



Again the results show a broadly similar pattern of concentrations for the available hydrocarbon species, with the lowest concentrations at the urban background (Leeds Centre) and industrial (Grangemouth) sites. One notable feature is the anomalously high concentration of i-butane (1) at Grangemouth, which can be attributed to the presence of the oil refinery. The butanes (1,2) and pentanes (7,8) are again notably affected by road transport.

3.3 Comparison of Pumped and Diffusive Data

Two species are common to both analyses, n-pentane and i-pentane. There are many possible reasons why the independent methods may give differing results, for example that the diffusive technique has not had the benefit of validated uptake rates for these species, and that different data capture issues mean that slightly different periods were sampled.

Averaged over all sites except Grangemouth, which had very low diffusive data capture, the pumped method gave 3.6 and 2.2 µg/m^3 respectively for i-pentane and n-pentane, while the diffusive method gave 4.6 and 1.5 µg/m^3. While not close by normal measurement standards, given the limitations of the study and the low concentrations, these can be seen as providing another element of validation to the fitness-for-purpose of the results.

4 Comparison With Other Data

While there are no results available that can be compared with these results directly, useful comparisons can be made with speciated hydrocarbon data from other sites, and with expected speciated emissions from the National Atmospheric Emissions Inventory. This should highlight anomalies in the relative concentrations of the hydrocarbon species.

4.1 Automatic Hydrocarbon Network Data

Speciated hydrocarbon concentration data is currently generated at the Marylebone Road and Eltham sites. However, the Eltham site data is not yet available, and the Marylebone Road site is unrepresentative of the wider UK picture, being a very busy roadside site. For the sake of a comparison in this study, data has been taken from the old Hydrocarbon Network in 1999, at the Leeds Centre site.

The comparison with the pumped data and diffusive data is given in Figures 3 and 4. The octanes and 1-pentene were not measured in the old Hydrocarbon Network.

Given the limitations of comparing data from different years and sites, there is an acceptable correspondence between the measurement data from three entirely different sources, with no significant anomalies.

Figure 3: Comparison with Automatic Network Results; the Species Key is Given in Table 1

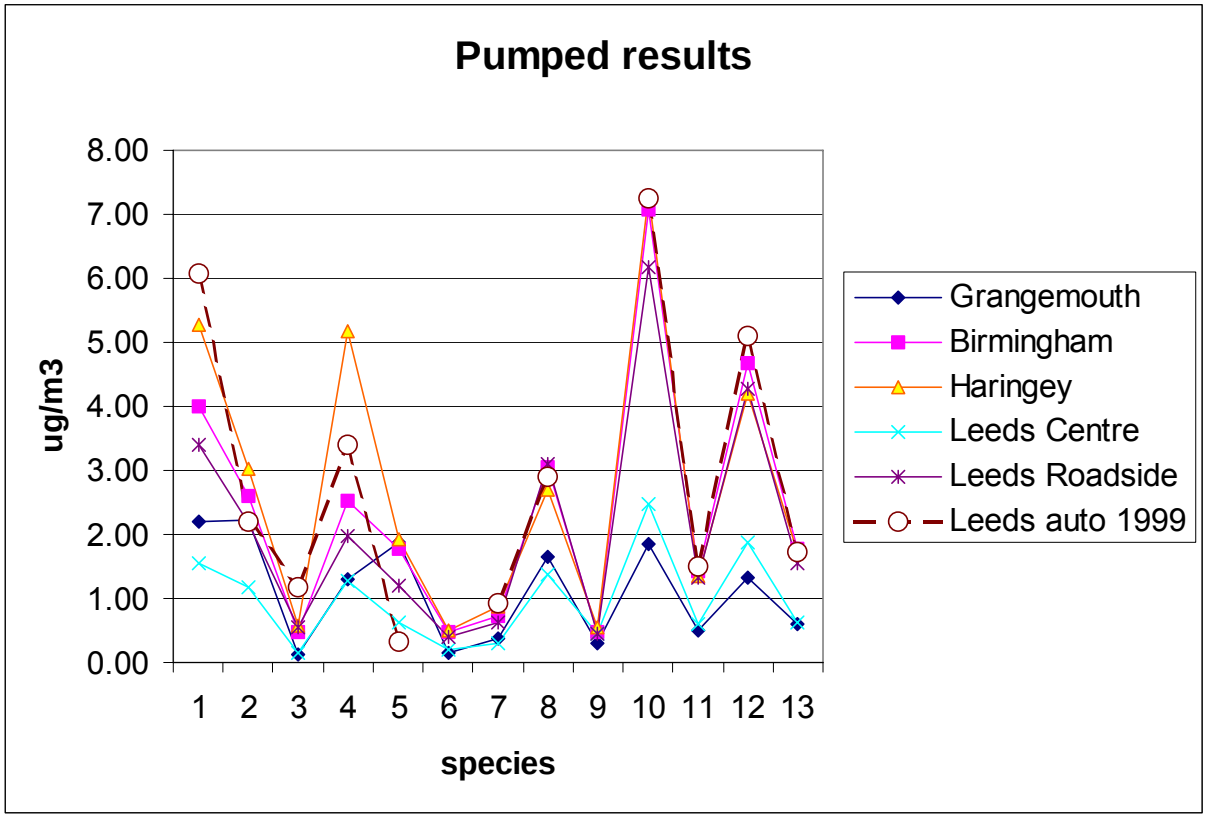
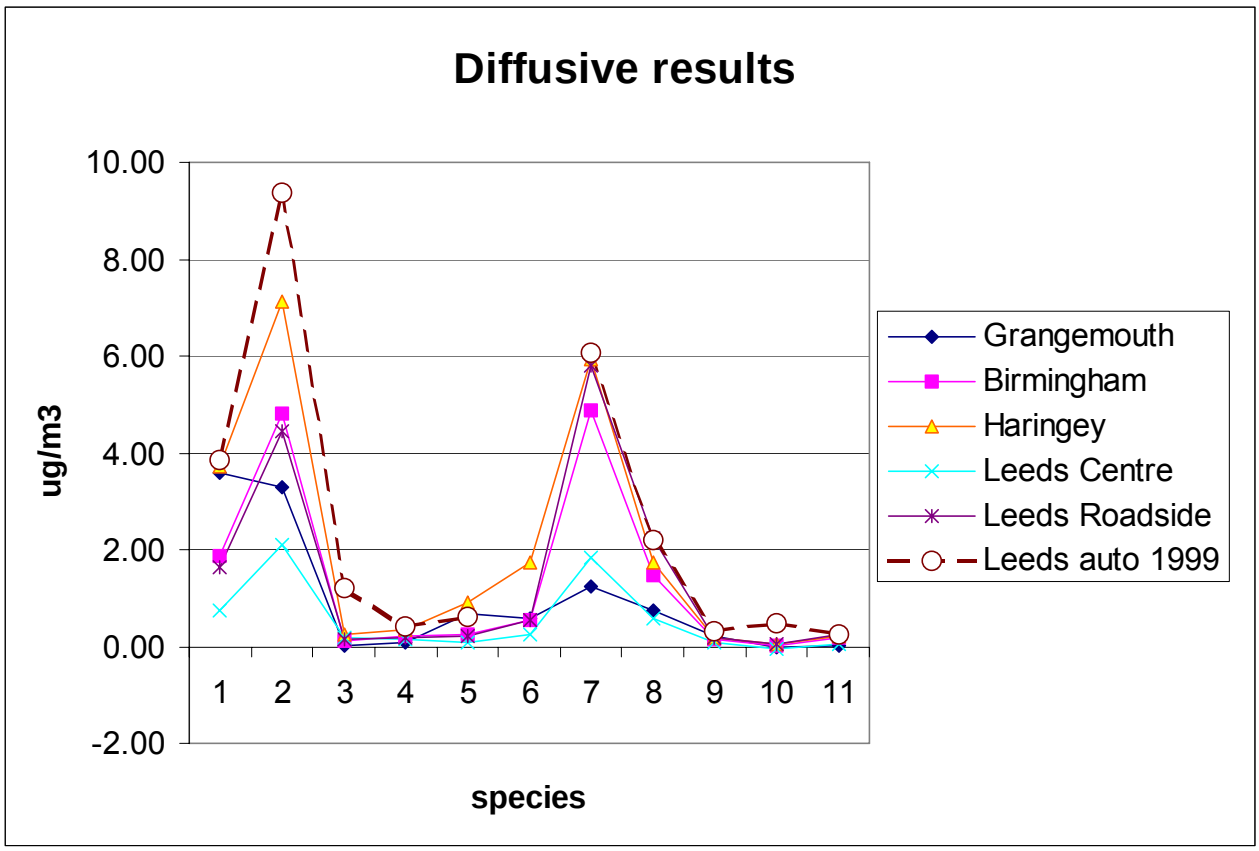


Figure 4: Comparison with Automatic Network Results; the Species Key is Given in Table 2



4.2 National Atmospheric Emissions Inventory

The most recent data available from the NAEI is for 2002. The Table lists those species in the Ozone Directive for which estimated mass emissions are given (assumed to be in tonnes), as one of the top 50 emitted Volatile Organic Compounds by mass.

ethane	66.0	1,3-butadiene	3.7	i-octane (2,2,4-trimethyl pentane)	-
ethene (ethylene)	27.8	n-pentane	43.0	benzene	13.5
ethyne (acetylene)	-	i-pentane (2 methyl butane)	34.2	toluene	38.0
propane	52.9	1-pentene	1.5	o-xylene	9.7
propene	15.9	(trans) 2-pentene	3.4	m-xylene	19.7
n-butane	112.5	isoprene (2 methyl 1,3-butadiene)	-	ethyl benzene	12.0
i-butane (2 methyl propane)	21.6	n-hexane	30.4	1,2,3-trimethyl benzene	3.2
1-butene	2.5	i-hexane (2 methyl pentane)	4.3	1,2,4-trimethyl benzene	11.2
trans-2-butene	7.4	n-heptane	19.1	1,3,5-trimethyl benzene	4.1
cis-2-butene	4.4	n-octane	15.5		

With many caveats about dispersion from localised sources, the relative mass emissions should correspond to the relative concentrations measured. The NAEI data is presented graphically using an arbitrary scaling factor which is the same for both the pumped and diffusive examples.

Figure 5: Comparison with NAEI; the Species Key is Given in Table 1

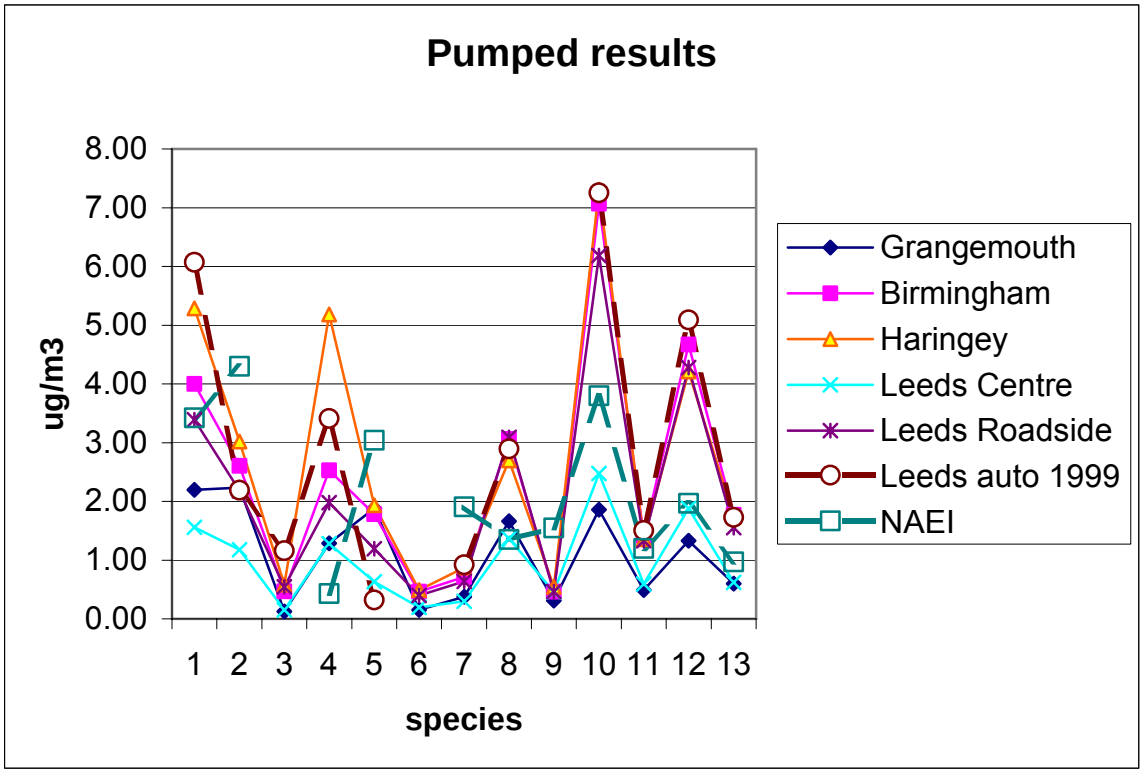
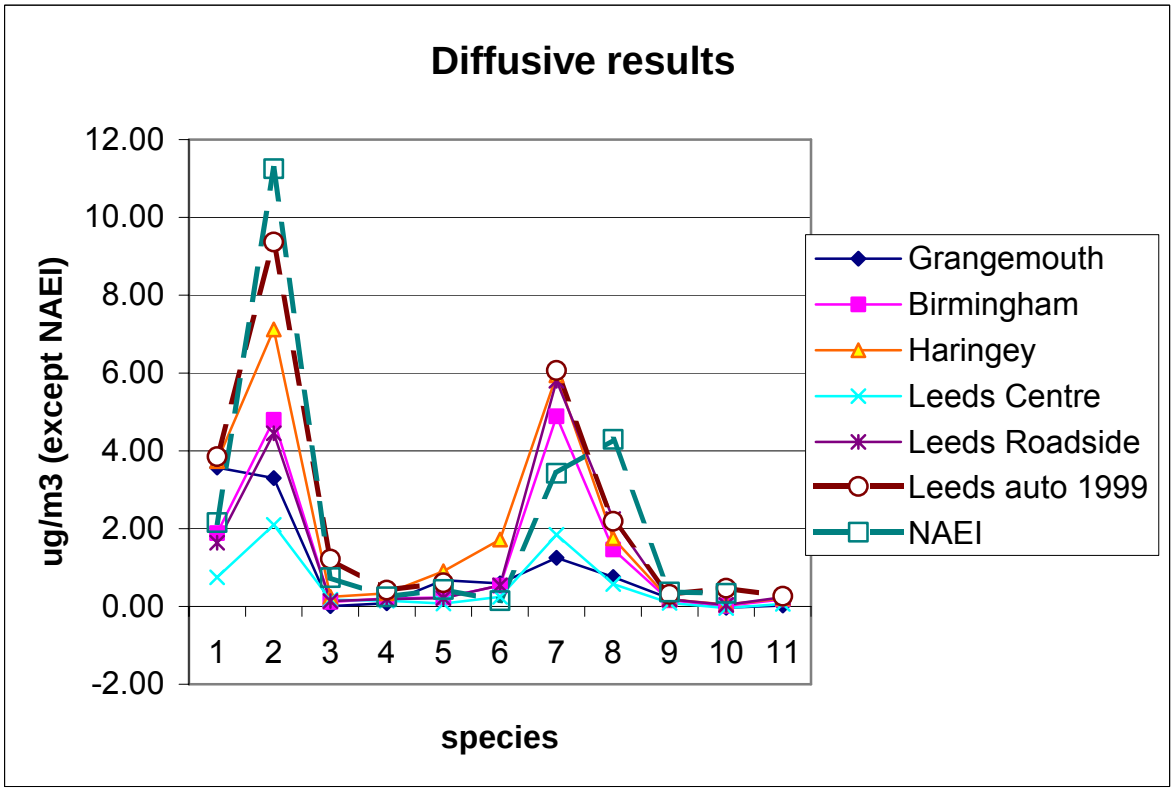


Figure 6: Comparison with Automatic Network Results; the Species Key is Given in Table 2



While the overall agreement is good, there are some notable anomalies such as the relative amounts of i- and n-pentane (1 and 2 in the Pumped data and 7 and 8 in the Diffusive data) and of i- and n-hexane (4 and 5 in the Pumped data). Possible reasons for these go beyond the scope of this study.

There is also an indication that benzene emissions may be underestimated.

5 Conclusions

The primary purpose of the study was to determine what information about concentrations of the ozone precursor hydrocarbons specified within the EU Ambient Air Ozone Directive 2002/3/EC could be extracted from chromatograms already obtained by the Non-Automatic Hydrocarbon Network.

With no further development or changes to analytical methods, there is good evidence that valid data can be obtained for the species:

n-pentane	n-octane
i-pentane (2 methyl butane)	i-octane (2,2,4-trimethyl pentane)
isoprene (2 methyl 1,3-butadiene)	benzene
n-hexane	toluene
i-hexane (2 methyl pentane)	o-xylene
n-heptane	m-xylene
	ethyl benzene

from those sites taking pumped samples, and for the species:

n-butane	1,3-butadiene
i-butane (2 methyl propane)	n-pentane
1-butene	i-pentane (2 methyl butane)
trans-2-butene	1-pentene
cis-2-butene	(trans) 2-pentene

from those sites taking diffusive samples.

Of these species, the ten most important in terms of ozone forming potential are expected to be (in decreasing order of importance, according to the NAEI) n-butane, toluene, m-xylene, n-pentane, n-hexane, i-pentane, o-xylene, n-heptane and ethyl benzene. Thus there is much relevant information available from all the pumped sites, while the diffusive method provides information about the single most important ozone precursor species, n-butane.

The results show good qualitative agreement with existing data on speciated hydrocarbons from the Automatic Hydrocarbon Network, and generally good correspondence with the data in the National Atmospheric Emissions Inventory.