

REPORT

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**UK Non-Automatic
Hydrocarbon Network:**

Annual Report for 2008

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Kevin Whiteside and
Paul Quincey**

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Approved on behalf of the Managing Director, NPL
by Alan Brewin, Business Leader, Analytical Science Division

EXECUTIVE SUMMARY

This report summarises operational matters and the data obtained by the Non-Automatic Hydrocarbon Network in the year 2008.

The background, methods used and site locations are given in Sections 1 and 2. The restructuring of the Network for benzene that started in 2007 was completed in 2008, with several further site changes. 1,3-butadiene measurements within the Network stopped during 2007.

Annual average data for benzene, and data capture, are given in Section 3. No sites exceeded the European Union Limit Value or the UK Air Quality Objectives for benzene.

No notable episodes or anomalous measurements were observed during the year.

Section 4 examines long term trends for benzene and compares them with the trends expected from the UK National Atmospheric Emissions Inventory. Trends in concentration over the period 1994 to 2002 are significantly downward and agree well between the two data sets. Trends in benzene since 2002 are generally downward, especially at sites measuring higher concentrations.

Comparability with data from the Automatic Hydrocarbon Network and other sources are discussed.

Sections 5 and 6 provide some information relating to measurements and modelling near South Killingholme in Humberside, and measurements made outside of the Network near an industrial source in Derby.

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1. Introduction

1.1 General background, history and methods

The Automatic and Non-Automatic Hydrocarbon Networks exist within the framework of Defra's Air Quality and Industrial Pollution, the aims of which are to determine the magnitude of sources, exposure and effects of air pollutants on human health and the natural environment, to develop a better understanding of underlying processes, and to underpin the development and implementation of national and international strategies in order to reduce the impacts of air pollution, including compliance with national and EU legislation. The Programme includes a combination of monitoring Networks, emission inventories, atmospheric modelling, strategic evaluation, scientific research and dissemination, to assist in these aims.

The Automatic and Non-Automatic Hydrocarbon Networks were established in 2002, following on from the previous Hydrocarbon Network, which measured 25 species of hydrocarbon on an hourly basis at 13 sites. As more benzene monitoring sites were needed to comply with regulations, the Non-Automatic Network was set up using a less expensive method to produce benzene measurements as fortnightly averages at 35 sites. During the reorganisation of the network in 2008 the number of sites increased to 36. Some of the sites are at the same location as the previous Hydrocarbon Network sites, so that long term trends can be evaluated.

The sites provide direct evaluations of compliance with benzene limit values and objectives, and also essential calibration data for national benzene concentration models.

The benzene monitoring method involves pumping ambient air at a rate of about 10 ml/min through nominally duplicate tubes containing the sorbent Carbopack X, with subsequent laboratory analysis of the benzene content of the tubes. This method was validated over a year-long pilot study, whose results are available through the Defra website:

http://www.airquality.co.uk/archive/reports/cat05/0407061411_btex_npl_pilot_final.pdf

The method is described in the paper:

Studies using the sorbent Carbopack X for measuring environmental benzene with Perkin-Elmer-type pumped and diffusive samplers, Nicholas A Martin, David J Marlow, Malcolm H Henderson, Brian A Goody and Paul G Quincey: *Atmospheric Environment* **37** (2003) 871-879.

1.2 REGULATORY BACKGROUND

The current ambient benzene legislation is set out in The Air Quality Strategy for England, Scotland, Wales and Northern Ireland, Cm 7169 (July 2007). The requirements are based on those of the EU Directive 2008/50/EC (which for benzene

effectively duplicates the earlier Directive 2000/69/EC). The relevant information for benzene is given in Table 1 below:

Benzene

	<i>Averaging period</i>	<i>Limit value</i>	<i>Margin of tolerance</i>	<i>Date by which limit value is to be met</i>
Limit value for the protection of human health	Calendar year	5 $\mu\text{g}/\text{m}^3$	5 $\mu\text{g}/\text{m}^3$ reducing on 1st January 2006 and every 12 months thereafter by 1 $\mu\text{g}/\text{m}^3$ to reach 0 $\mu\text{g}/\text{m}^3$ by 1st January 2010	1st January 2010

Table 1: Benzene limit value and associated information

The concentration 5 $\mu\text{g}/\text{m}^3$ is to be expressed at 293 K and 101.3 kPa, and is equivalent to an amount (molar) fraction of 1.54 ppb.

The Margin of Tolerance means that Member States can exceed the Limit Value for a limited period if necessary.

As part of the National Air Quality Strategy there are also Air Quality Objectives, which can be stricter than the EU Limit Value.

The benzene Objective for England and Wales is the same as that given above.

The benzene Objective for Scotland and Northern Ireland is an annual average of 3.25 $\mu\text{g}/\text{m}^3$ (1 ppb), by 1st January 2010.

Standard methods for measuring benzene concentration, which include the method used in the Network, have been published by CEN as EN 14662 Parts 1 to 5.

1.3 Units of measurement

Regulations in the United Kingdom have in the past expressed concentrations of gases in units of parts per billion (1,000,000,000) – ppb (moles per mole). This is the number of benzene molecules, for example, within a billion molecules of air. These units have the advantage that if the temperature or pressure of the air changes, the value remains the same.

Current UK and European legislation sets limit value concentrations as micrograms of pollutant per cubic metre of air ($\mu\text{g}/\text{m}^3$). When these units are used without correcting to a standard temperature and pressure, the same “packet” of air will have a different concentration as these properties of the air change. The legislation specifies that the air volume must be corrected to be at a standard temperature of 293 K (about 20°C), and a pressure of 101.3 kPa (about average atmospheric pressure at sea level).

Both sets of units are used in this report.

The relationship between the two sets of units for benzene is:

$$\begin{aligned} 1 \text{ ppb} &= 3.25 \text{ } \mu\text{g.m}^{-3} \\ \text{ie } 1.54 \text{ ppb} &= 5 \text{ } \mu\text{g.m}^{-3} \end{aligned}$$

1.4 Measurement uncertainty

The Data Quality Objective for the measurement uncertainty of fixed measurements of benzene in the EU Directive is $\pm 25\%$, expressed at a 95% confidence level. This applies to annual average values, in the region of the limit value (1.54 ppb).

In the Pilot Study referenced in Section 1.1, the uncertainty for a single tube measurement using the pumped tube method was evaluated as 11.5% (95% confidence). This will reduce when more than one measurement is averaged to form the annual average. Therefore, 11.5% is a conservative estimate of the total combined expanded uncertainty of the annual mean, expressed with a level of confidence of 95%, and this comfortably meets the EU Data Quality Objective.

2. Network sites during 2008

2.1 Start of the year



Figure 1: Map of network sites at the start of 2008

At the beginning of 2008, the sites in the Network were located as in Figure 1.

Table 2 lists the sites with their Local Site Operators.

Site Name	Type	Local Site Operator
Barnsley Gawber		Barnsley Council
Belfast centre		Belfast City Council
Birmingham roadside	Roadside	Birmingham City Council
Birmingham Tyburn		Birmingham City Council
Bloomsbury		Casella Stanger
Bristol Old Market	Roadside	Bristol City Council
Camden kerbside	Kerbside	King's College London
Coventry Memorial Park		Coventry City Council
Grangemouth	Industrial	Falkirk Council
Haringey roadside	Roadside	King's College London
Leamington Spa		Warwick District Council
Leeds centre		Leeds City Council
Leicester centre		Leicester City Council
Liverpool Speke		Faber Maunsell
Manchester Piccadilly		Manchester City Council
Middlesbrough	Industrial	Middlesbrough BC
Newcastle		Newcastle City Council
Northampton		Northampton BC
Norwich centre		Faber Maunsell
Nottingham centre		Nottingham City Council
Oxford centre	Roadside	Oxford City Council
Plymouth		Plymouth City Council
Sheffield		Sheffield City Council
Southampton		Southampton City Council
Stoke centre		City of Stoke on Trent
Wigan centre		Wigan Metropolitan BC
Yarm	Roadside	Stockton on Tees BC

Table 2: Network sites at the start of 2008

All sites in Table 2 are Urban Background except where stated in the Type column. Further details on these sites can be found on the UK Automatic Urban and Rural Network Site Information Archive at:

<http://www.airquality.co.uk/autoinfo.php>

2.2 Changes during 2008

In anticipation of the siting requirements in the new Air Quality Directive, some of the site locations in the Network were changed in a process that started in 2007. These changes involved the closure of 10 existing sites and the opening of 11 new sites for benzene monitoring in the UK. The closures all took place in 2007. The 11 new sites listed in Table 3 opened in 2008 or December 2007.

Suitable locations for sites in West Midlands (roadside) and South East (roadside) are still to be identified and samplers will be installed as soon as the site details have been finalised. The South Killingholme site will then be closed (see Section 5) to make a total of 36 sites.

There is also a pumped sampler operating at London Marylebone Road, as described in Section 4.

Sites opened in 2007-2008

Site	Start Date	Classification	Map Reference
Birmingham Tyburn	18/12/07	Urban Background	411650, 290550
Camden Roadside	19/12/07	Kerbside	526650, 184460
Bury Roadside	17/01/08	Roadside	380950, 404850
Bath Roadside	28/01/08	Roadside	375550, 165850
Oxford St Ebbes	30/01/08	Urban Background	451250, 205450
Cambridge Roadside	04/02/08	Roadside	545250, 258250
York Fishergate	13/02/08	Roadside	460882, 450760
Carlisle Caldewgate	09/04/08	Roadside	339467, 555974
Chesterfield	06/06/08	Roadside	436350, 370650
South Killingholme	02/09/08	Urban Industrial	514927, 416067
Eaglescliffe - Yarm	30/09/08	Urban Background	440463, 514534

Table 3: New benzene monitoring sites in 2007/2008

Site	Local Site Operator
Bury Roadside	Bury Metropolitan BC
Bath Roadside	Bath and NE Somerset Council
Oxford St Ebbes	Oxford City Council
Cambridge Roadside	Cambridge City Council
York Fishergate	City of York Council
Carlisle Caldewgate	Carlisle City Council
Chesterfield	Chesterfield BC
South Killingholme	North Lincolnshire Council
Eaglescliffe - Yarm	Stockton on Tees BC

Table 4 LSOs for sites new in 2008

Yarm Roadside ceased monitoring on 24/09/08 and was relocated to Eaglescliffe – Yarm.

Norwich Centre stopped monitoring on 13/05/08 and the pump box is awaiting installation in the new Norwich AURN site being commissioned by Bureau Veritas. It is hoped that the site will be monitoring again by May 2009. The sites operating at the end of 2008 are shown in Figure 2.



Figure 2: Map of Network sites at the end of 2008. (The Norwich site is temporarily out of action.)

3. Data and Data Capture for 2008

3.1 Benzene: comparison with Limit Values and Objectives

Site	ppb	$\mu\text{g}/\text{m}^3$
Barnsley Gawber	0.17	0.55
Bath roadside	0.20	0.65
Belfast centre	0.19	0.62
Birmingham roadside	0.40	1.30
Birmingham Tyburn	0.23	0.75
Bloomsbury	0.24	0.78
Bristol Old Market	0.35	1.13
Bury roadside	0.26	0.84
Cambridge roadside	0.23	0.75
Camden kerbside	0.37	1.20
Coventry Memorial Park	0.16	0.52
Grangemouth	0.36	1.17
Haringey roadside	0.35	1.13
Leamington Spa	0.19	0.62
Leeds centre	0.23	0.75
Leicester centre	0.21	0.68
Liverpool Speke	0.25	0.81
Manchester Piccadilly	0.24	0.78
Middlesbrough	0.34	1.10
Newcastle	0.16	0.52
Northampton	0.17	0.55
Nottingham centre	0.23	0.75
Oxford centre	0.23	0.75
Oxford St Ebbes	0.15	0.49
Plymouth	0.21	0.68
Sheffield	0.19	0.62
Southampton	0.26	0.84
Stoke centre	0.24	0.78
Wigan centre	0.18	0.58
York Fishergate	0.25	0.81

Table 5: 2008 Benzene data for sites > 75% time coverage

The annual average concentration of benzene over the calendar year 2008 is given in Table 5, for each site that was operating for more than 75% of the year. For those sites that closed during the year, the average for the period of operation is given.

Data for the sites open for less than 75% of the year (Carlisle Caldewdate, Chesterfield, Norwich centre, South Killingholme, Yarm and Eaglescliffe-Yarm) can be seen in Annex 1.

Annual average concentrations at all sites were below the Limit Value of $5 \mu\text{g}\cdot\text{m}^{-3}$ set by the European Ambient Air Quality Directive.

As mentioned above, within the UK Air Quality Strategy the Objectives for benzene are:

- for England and Wales, an annual average of 5 µg/m³ to be achieved by 31 December 2010;
- for Scotland and Northern Ireland, a running annual mean of 3.25 µg/m³ to be achieved by 31 December 2010.

These Objectives were met in 2008 for all sites.

3.2 Data Capture

The measurement method has proved very reliable and robust, with high levels of data capture across the Network. Only two sites had a data capture below 95%.

Data capture figures for these sites are given in Table 6.

Site	Data Capture, %
Bloomsbury	93
Plymouth	92

Table 6: 2008 Benzene data capture for sites < 95%

The main reasons for data loss at these sites were:

Plymouth (92%)

14/08/08 – 16/09/08 - Damaged O-ring in tube elbow causing a leak.

Bloomsbury (93%)

22/12/08 – 04/02/09 – Damaged O-ring in tube elbow causing a leak.

3.3 Episodes and anomalous results

Time series data for all sites are presented graphically in Annex 1. No fortnightly values were recorded above the annual average Limit Value of 1.54 ppb (5 µg/m³). There were no high benzene pollution episodes over the year.

The main notable feature was a widespread elevated concentration in early February 2008. This has been observed in other Networks affecting many pollutants including NO_x, Black Smoke and metals, and can be attributed to meteorological conditions.

As in previous years, measured benzene concentrations were generally higher in winter than summer.

4. Long term trends and comparisons with the UK emission inventory and other data

4.1 Long term trends and Emissions Inventory

Benzene data from the seven years of operation of the pumped samplers is shown in Figures 3 and 4. For clarity the sites have been divided into two graphs according to concentration in the first year. Benzene concentrations have generally dropped substantially over the history of the Network. The reductions in concentration are more notable at the higher concentration (typically traffic influenced) sites.

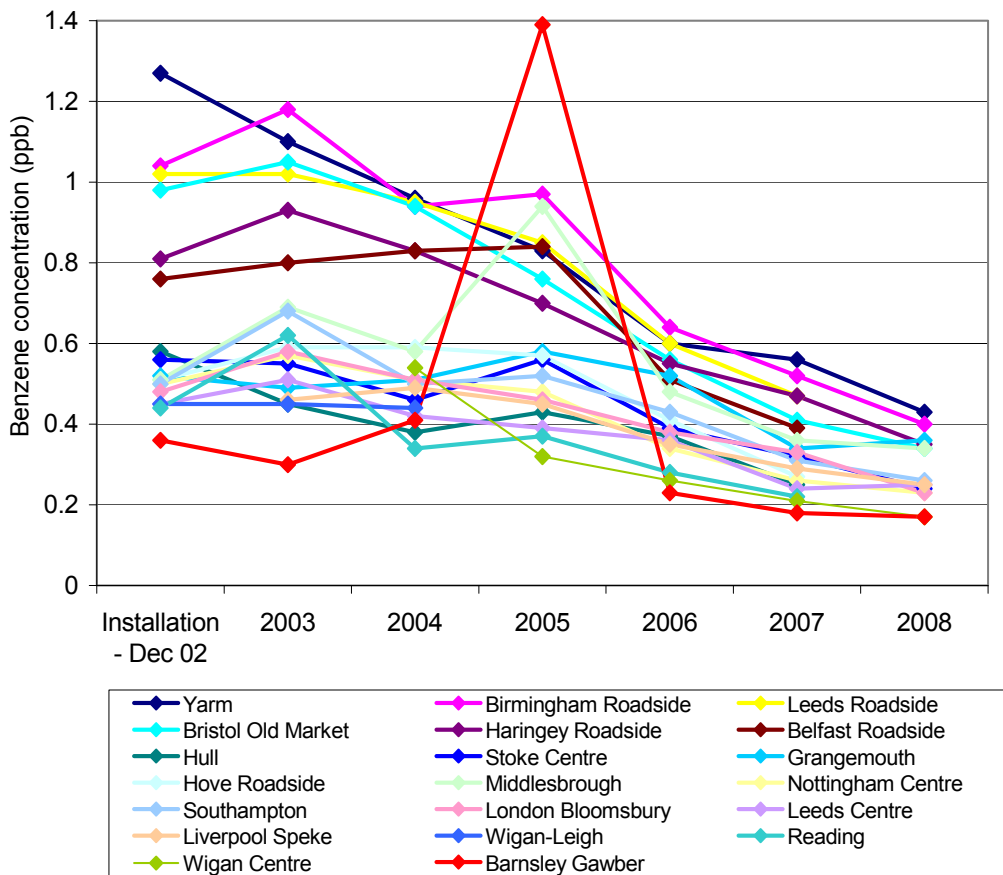


Figure 3 : Recent annual average benzene concentrations at “high concentration” sites

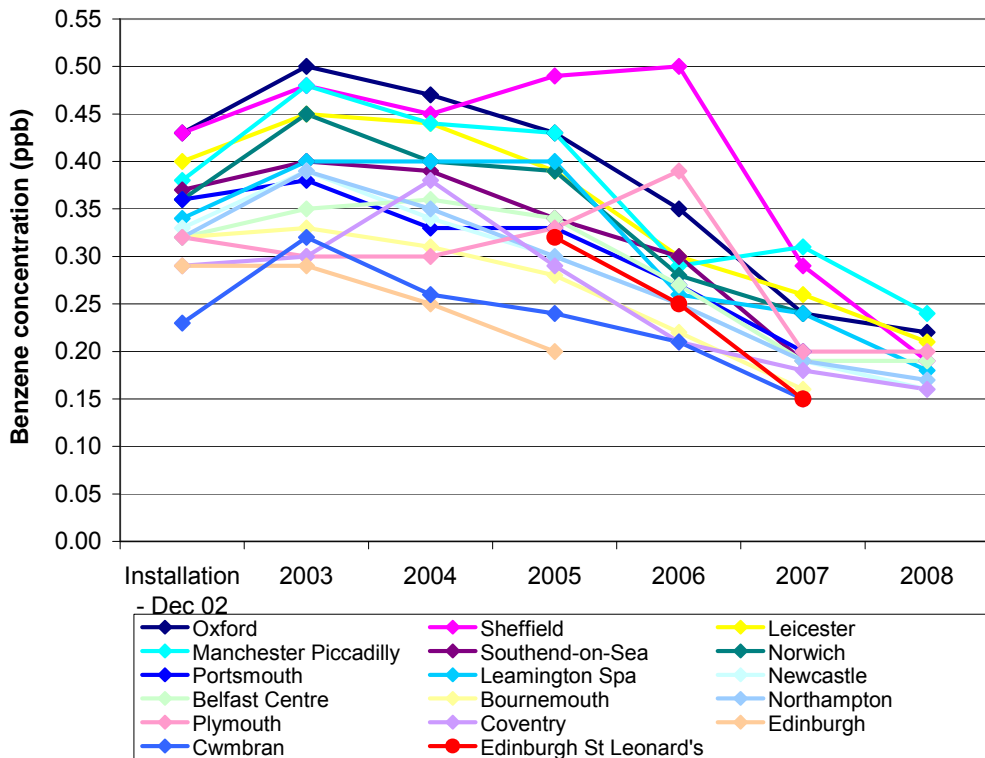


Figure 4: Recent annual average benzene concentrations at “low concentration” sites

The anomalous increases in concentration at Middlesbrough in 2005 and at Barnsley in 2004 and 2005 were due to local sources.

The only site to show an increase in concentration between 2007 and 2008 was Grangemouth (from 0.34 to 0.36 ppb). This site is heavily influenced by local industrial emissions, which would explain why it did not follow the wider trend.

Longer term trends can be gauged from data at sites that were also monitoring benzene in the previous Hydrocarbon Network. These are shown in Figure 5. The Middlesbrough peak in 2005 has been removed. Data capture in 2001 was affected by the changeover of Networks.

This long term benzene trend is well matched by the trend predicted by the National Atmospheric Emissions Inventory, shown in Figure 6. The most recent NAEI chart covers the period 1990 to 2006.

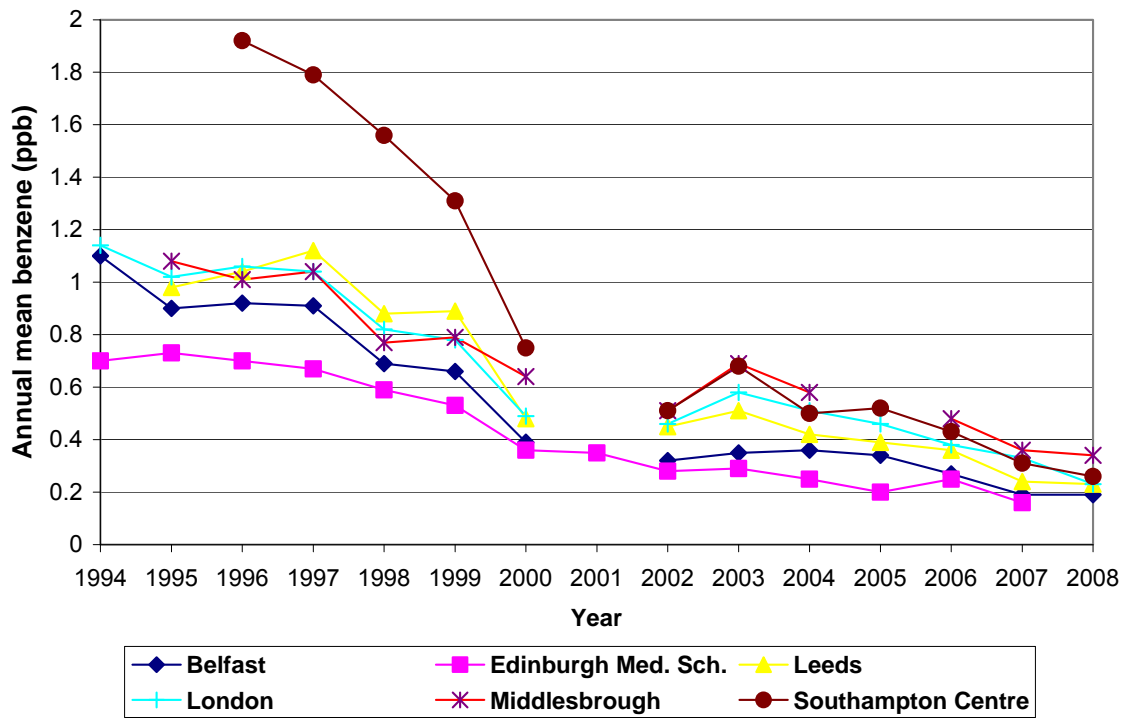


Figure 5: Long Term Trends in Benzene Concentration

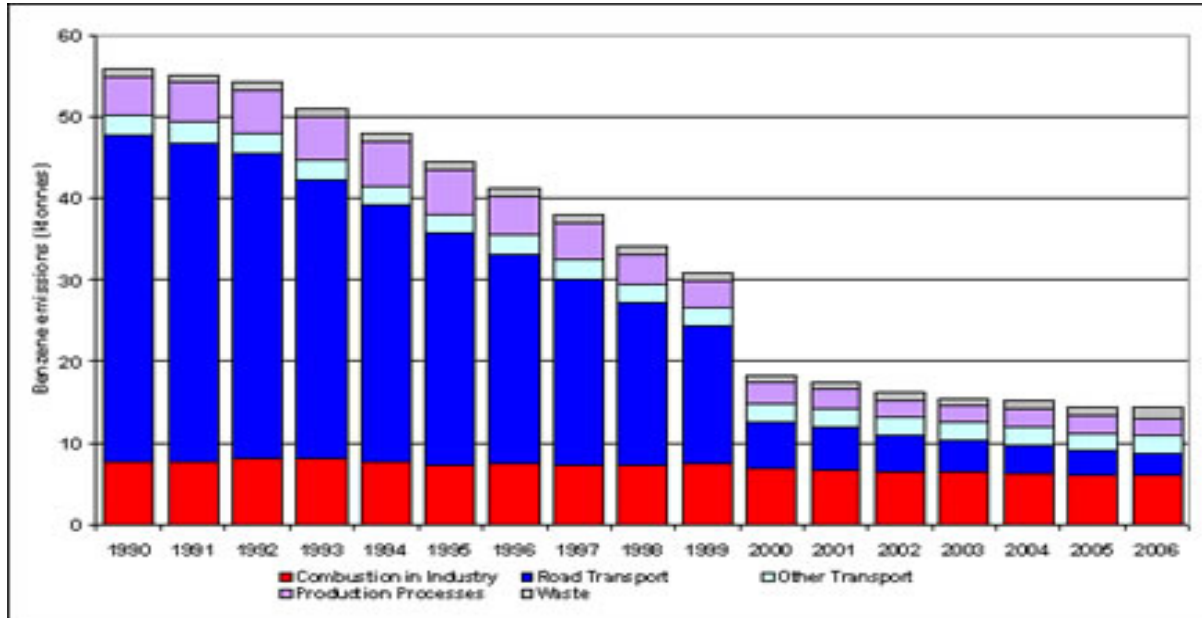


Figure 6: Emission Inventory Trend for Benzene

4.2 Automatic Hydrocarbon Network

4.2.1 Marylebone Road

As part of an ongoing investigation, parallel measurements with an NPL pumped system and the Automatic Hydrocarbon Network instrument have been made at Marylebone Road since 2007, sharing the same inlet so that there should be no differences arising from different sampling points. The pumped sampler is not formally part of the Non-Automatic Network. The results are shown in Figure 7.

In 2007 a discrepancy between the two methods was noted. In May 2008 (indicated by the gap in both sets of data), the automatic instrument was changed from a Perkin Elmer Ozone Precursor model gas chromatograph (GC) to the current version of the same analyser. Missing data from the automatic method corresponds to measurement periods where the data capture for the automatic method was below 75%. There is no simple relationship between the sets of data with either GC, but the results indicate that in general both automatic GCs record, on average, significantly lower concentrations than the pump box system.

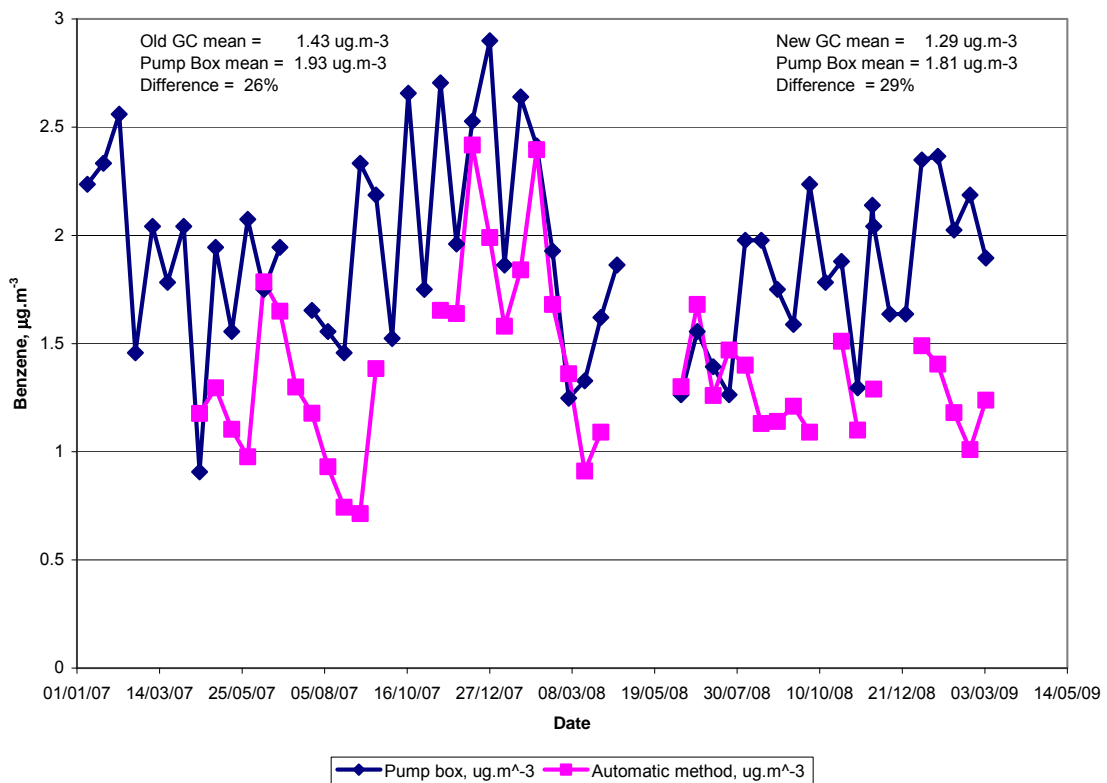


Figure 7: Comparison between pumped and automatic benzene data at Marylebone Road

4.2.2 Other Automatic Network sites

The available 2008 annual average concentrations for benzene on the Automatic Hydrocarbon Network are given in Table 7a, with the 2007 results for comparison.

Site	2007	2008
Glasgow (Kerbside)	0.97 $\mu\text{g}/\text{m}^3$ (0.30 ppb)	1.04 $\mu\text{g}/\text{m}^3$ (0.32 ppb)
London Eltham (urban background)	0.91 $\mu\text{g}/\text{m}^3$ (0.28 ppb)	0.73 $\mu\text{g}/\text{m}^3$ (0.22 ppb)
Harwell (Rural)	0.33 $\mu\text{g}/\text{m}^3$ (0.10 ppb)	0.39 $\mu\text{g}/\text{m}^3$ (0.12 ppb)

Table 7a: Annual benzene average concentrations from the Automatic Hydrocarbon Network

Table 7b gives the Non-Automatic Network averages for different site classifications for comparison.

Site Classification	2007	2008
Kerbside	1.95 $\mu\text{g}/\text{m}^3$ (0.60 ppb)	1.49 $\mu\text{g}/\text{m}^3$ (0.46 ppb)
Roadside	1.35 $\mu\text{g}/\text{m}^3$ (0.42 ppb)	0.90 $\mu\text{g}/\text{m}^3$ (0.28 ppb)
Urban Centre	0.84 $\mu\text{g}/\text{m}^3$ (0.26 ppb)	0.71 $\mu\text{g}/\text{m}^3$ (0.22 ppb)
Urban Background	0.65 $\mu\text{g}/\text{m}^3$ (0.20 ppb)	0.64 $\mu\text{g}/\text{m}^3$ (0.20 ppb)

The Non-Automatic Network has no sites in rural locations

Table 7b: Annual benzene average concentrations from the Non-Automatic Hydrocarbon Network

4.3 Grangemouth survey

NPL carries out a regular survey of hydrocarbon concentrations around Grangemouth on behalf of Ineos Manufacturing (Scotland) Ltd, using diffusive samplers. 2008 annual average benzene concentrations at sites not close to specific sources were all in the range 0.3 – 0.5 ppb, while the two sites directly influenced by specific sources recorded 0.9 and 1.3 ppb. These values are compatible with the Network concentration for the semi-industrial Grangemouth site of 0.36 ppb.

4.4 Comparison with benzene modelling data

AEA Technology have supplied NPL with modelled benzene data for the locations of Network sites in 2007. Unlike the similar comparison in the 2007 Annual Report, modelled data were not supplied for some roadside or industrial sites, as the model is geared to representing background concentrations. Also, modelled data for Liverpool Speke were unavailable due to “underestimation of results”.

Table 8 gives the modelled data in the left hand column. The next three columns give the Network data for the years 2006, 2007 and 2008, with the mean of these in the next column. The difference between the modelled data and the measured average is in the penultimate column, with negative values in red.

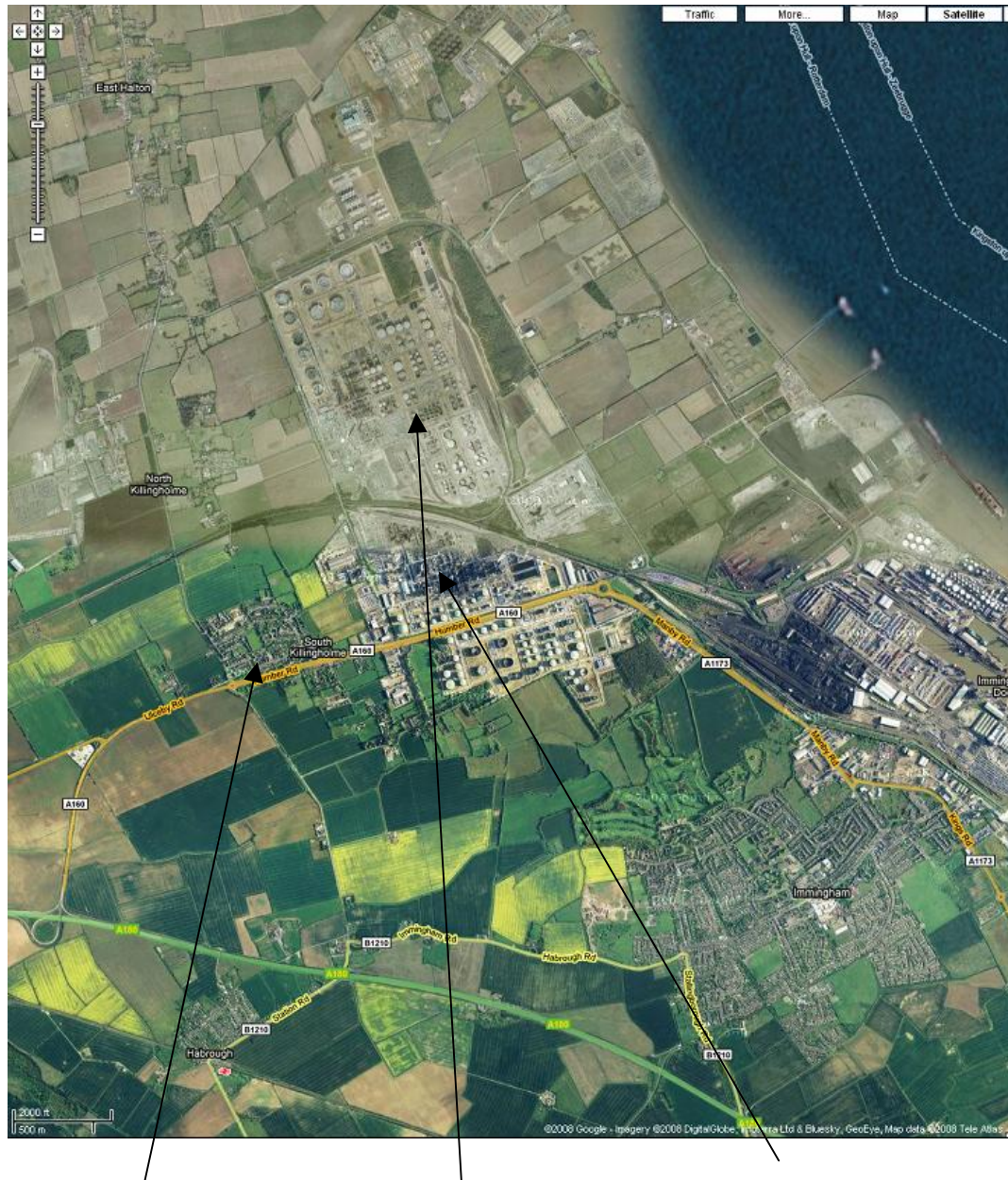
The final column gives a grading to the difference between the modelled and measured data, where differences greater than 0.3 $\mu\text{g}/\text{m}^3$ are noted as implying the model predictions are “high” or “low”, while differences greater than 1.0 $\mu\text{g}/\text{m}^3$ are graded “very high” or “very low”.

In general the modelled data appears somewhat lower than the measured average, though the agreement is closer than for the 2006 data, with the main discrepancies at roadside sites.

SITE (all concs in $\mu\text{g}/\text{m}^3$)	2007 modelled benzene	Measured benzene 2006	Measured benzene 2007	Measured benzene 2008	Mean measured 2006-08	Difference	Model implic- ation
Barnsley Gawber	0.66	0.75	0.58	0.55	0.63	0.03	
Belfast Centre	0.72	0.88	0.62	0.62	0.71	0.01	
Birmingham Roadside	0.91	2.08	1.68	1.30	1.69	-0.78	Low
Bloomsbury	1.39	1.24	1.07	0.75	1.02	0.37	High
Bristol Old Market (rs)	1.00	1.82	1.33	1.11	1.42	-0.42	Low
Coventry Memorial Park	0.54	0.68	0.58	0.52	0.59	-0.05	
Haringey Roadside	1.20	1.79	1.52	1.14	1.48	-0.28	
Leamington Spa	0.57	0.85	0.78	0.59	0.74	-0.17	
Leeds Centre	0.81	1.17	0.78	0.75	0.90	-0.09	
Leicester Centre	0.81	0.98	0.84	0.68	0.83	-0.02	
Manchester Piccadilly	0.90	0.94	1.00	0.78	0.91	-0.01	
Newcastle Centre	0.77	0.81	0.62	0.52	0.65	0.12	
Northampton	0.46	0.81	0.62	0.55	0.66	-0.20	
Nottingham Centre	0.79	1.11	0.84	0.75	0.90	-0.11	
Oxford Centre	0.56	1.14	0.78	0.72	0.88	-0.32	Low
Plymouth Centre	0.43	1.27	0.65	0.65	0.86	-0.43	Low
Sheffield Centre	0.79	1.63	0.94	0.62	1.06	-0.27	
Wigan Centre	0.55	0.85	0.68	0.55	0.69	-0.14	
Yarm (roadside)	0.54	1.95	1.81	1.40	1.72	-1.18	V low

Table 8: comparison between recent benzene data and modelled data

5. South Killingholme



Monitoring site

Lindsey Oil

Conoco Phillips

Figure 8: Aerial view of South Killingholme (from Google Earth)

The South Killingholme site, shown in Figure 8, was installed in September 2008 as a consequence of modelling results (PCM 2005, from AEA Technology) that showed a possible exceedence of the benzene limit value in the vicinity of two industrial sources. For practical reasons the site was installed close to the industrial sources, but in a generally south-west, ie upwind direction.

Measured concentrations have not been elevated in comparison with other monitoring sites in the Network. The average concentration for September to December 2008 was 0.26 ppb.

Start Date	End Date	Benzene, ppb	Average Wind	
			Direction, Deg	Speed, m.sec ⁻¹
02/09/2008	16/09/2008	0.26	171 (S)	0.5
16/09/2008	30/09/2008	0.33	54 (NE)	0.4
30/09/2008	14/10/2008	0.14	267 (W)	0.8
14/10/2008	29/10/2008	0.12	266 (W)	1.0
29/10/2008	12/11/2008	0.33	34 (NE)	0.3

Table 9: South Killingholme data with wind information

Table 9 shows some of the fortnightly benzene data with the associated average wind speeds and directions measured on site. Concentrations appear to be higher when the site was generally downwind of the sources (shown in red), but the levels do not indicate that an exceedence is likely.

More recent modelling results (PCM 2007, from AEA Technology) no longer predict an exceedence, though they still predict higher concentrations than have been measured.

6 Derby Spondon

Benzene monitoring was requested by Derby City Council directly from NPL in 2005, as their diffusion tube measurements showed that a local residential area was going to exceed the EU Limit Value, and they wanted supporting measurements made using the same methods as the National Network.

The site is roughly due west of the industrial source. Annual average concentrations from the NPL pumped sampler are shown in Table 10:

Year	Benzene (ppb)
2005	4.10
2006	2.35
2007	1.75
2008	1.78

Table 10: Benzene concentrations at Derby Spondon.

These concentrations are considerably higher than are seen elsewhere on the Network, and although they have dropped markedly since 2005, they still exceed the Limit Value.

Table 11 shows the capital investment work that Celanese Acetates have done on their plant over the last 10 years along with planned future investment. It can be seen that the large drop in concentrations between 2005 and 2007 highlighted in Table 10 corresponds to the additional abatement installed between 2005 and 2008.

Year	Abatement measures
1999 - 2002	Poor seals replaced on Anhydride Plant + additional capital investment on atmospheric storage
2004 - 2005	OPSIS UV system installed on boundary line allowing quick identification of abnormal levels
2005 - 2008	Regular plant cleaning process implemented to reduce emissions. Implementation of Leak Detection And Repair (LDAR) to reduce fugitive emissions throughout the plant. Replacement of mild steel pipes with stainless steel to reduce likelihood of leaks. Replacement of benzene pumps with self-priming pumps to reduce emissions on start up.
2008 - 2009	Planned installation of standby units on an existing abatement system, plus planned installation of conservation venting on solvent sumps.

Table 11 Abatement Measures On The Celanese Acetate Plant

Celanese consider the implementation of active LDAR and the installation of the OPSIS system to identify abnormal levels to be the main drivers for the reduced emissions of benzene from the site.

The Local Authority expects that the planned abatement measures will bring the benzene concentrations down to below the Limit Value by 2010.

The benzene point source at Derby Spondon is included in the National Atmospheric Emissions Inventory with a relatively low emission rate (about 60 times less than South Killingholme, for example). Modelled concentrations are consequently much smaller than those measured. Further investigation is required into whether the industrial emissions have been underestimated, in which case other similar industrial sites may have similarly high benzene concentrations that are not apparent from modelling, or whether special factors apply to the Derby Spondon site.

7 Other recent relevant work

The usefulness of chromatographic data from this method, and the earlier 1,3-butadiene diffusive method, for monitoring other ozone precursors, was investigated and published as:

Monitoring of ozone precursors in ambient air using pumped and diffusive sampling on the sorbent Carbo-pack X, Paul Quincey, David Butterfield, Hansa D'Souza, Malcolm Henderson, Atmospheric Environment **41** (2007) 7865 – 7873.

The 1,3-butadiene method was published as:

Studies using the sorbent Carbo-pack X for measuring environmental 1,3-butadiene with pumped and diffusive samplers, Nicholas A Martin, Philippa Duckworth, Malcolm H Henderson, Nigel R W Swann, Simon T Granshaw, Robert P Lipscombe, Brian A Goody: Atmospheric Environment **39** (2005) 1069-1077.

An investigation into potential errors caused by using liquid-loaded sorbent tubes to calibrate gas chromatographs for this type of measurement was published as:

A comparison of gas- and liquid-loaded sorbent standards for the calibration of measurements of volatile organic compounds, Nicholas A Martin, Natalie L A S Barber, John K Black, Robert P Lipscombe, Christopher A Taig, *Atmospheric Environment* **41** (2007) 7666 – 7671.

NPL's multi-component ambient VOC standards were used as the basis for a combined EURAMET and AQUILA comparison, directly relevant to automated hydrocarbon measurements, which was reported in 2008. The AQUILA comparison included mixtures with a real air matrix in addition to the pure nitrogen matrix generally used for these standards. The results demonstrate both the high reliability of the NPL gas standards and the strength of NPL's analytical capabilities for these components.

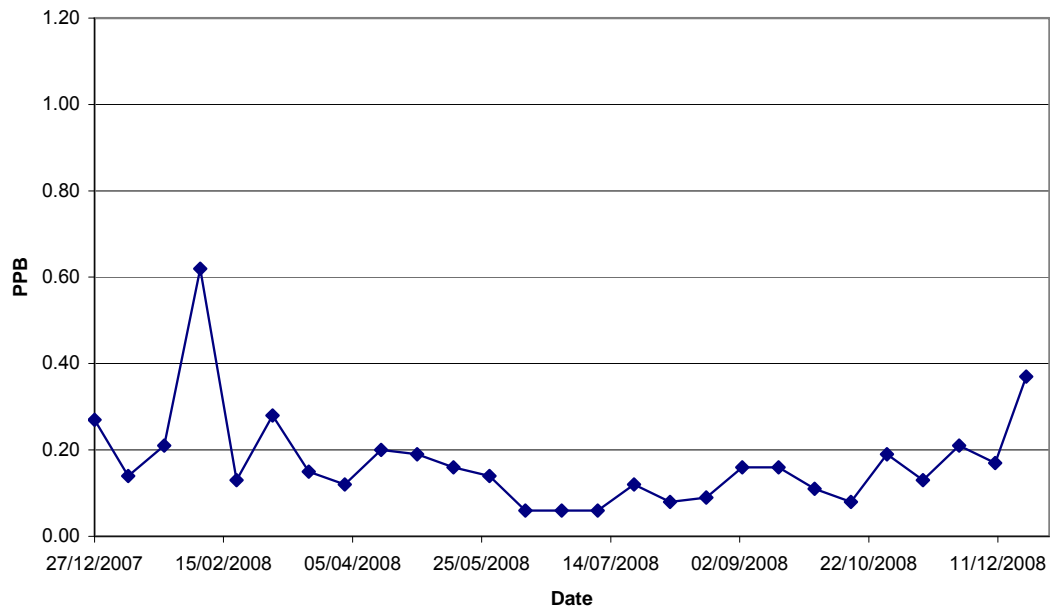
The reports are:

EURAMET 886 comparison of multicomponent ambient VOC measurements - Final report. Grenfell, R, Brookes, C, Vargha, G, Quincey, P, Milton, M, Woods, P, Harris, P, NPL Report AS 29, December 2008 (available through the NPL website).

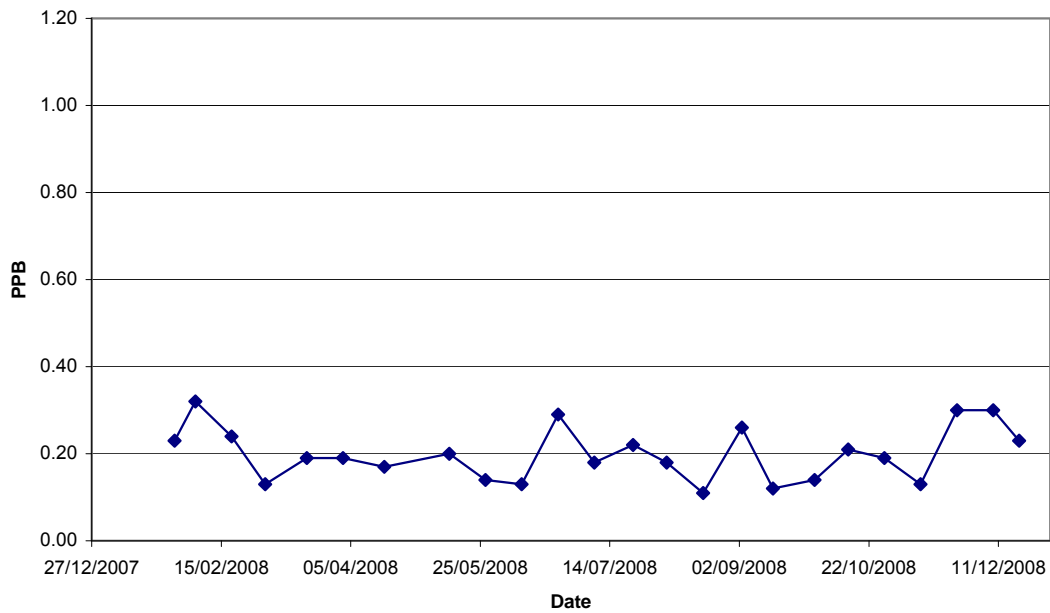
EC intercomparison of VOC measurements between national reference laboratories, P Pérez Ballesta et al, EUR 23529 EN (in press).

Annex 1 – 2008 benzene concentration data

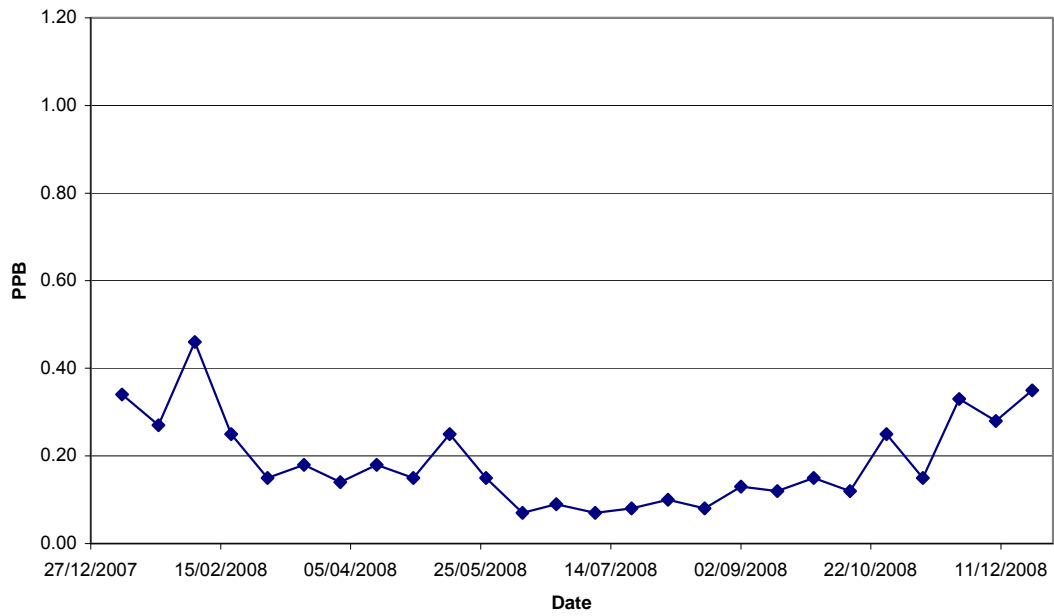
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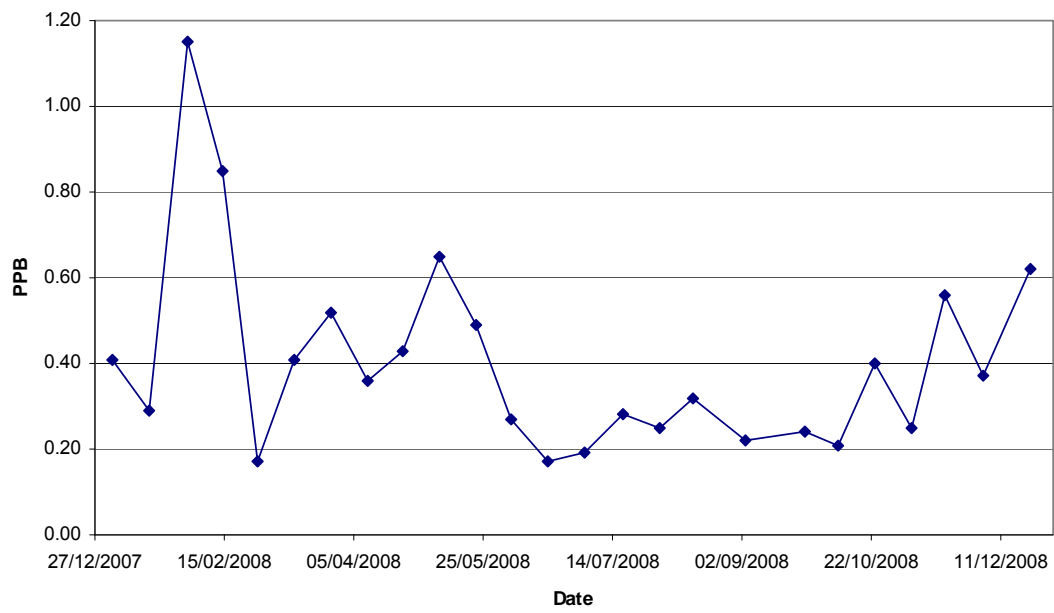
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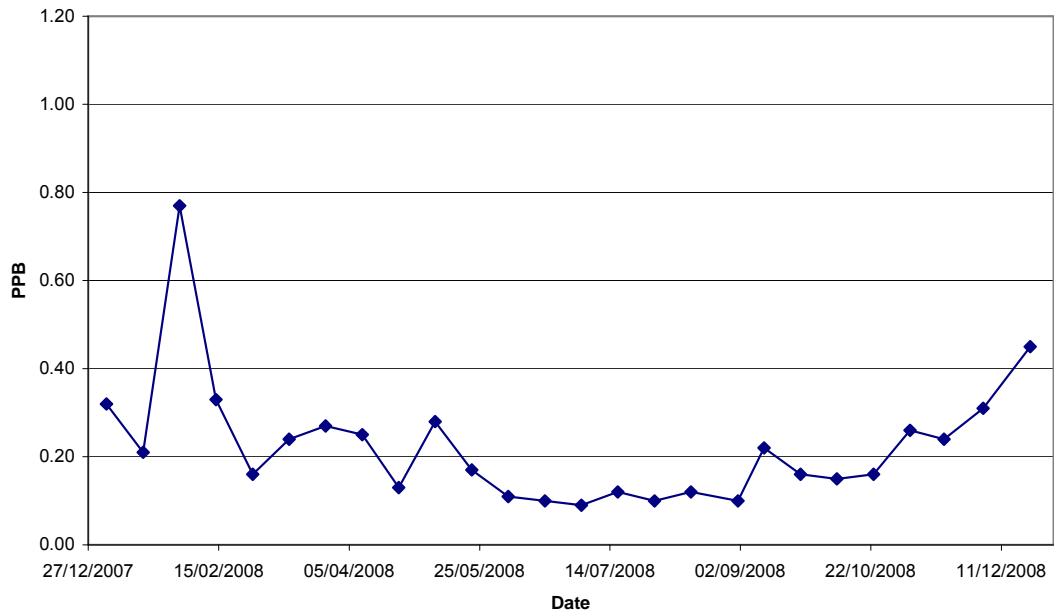
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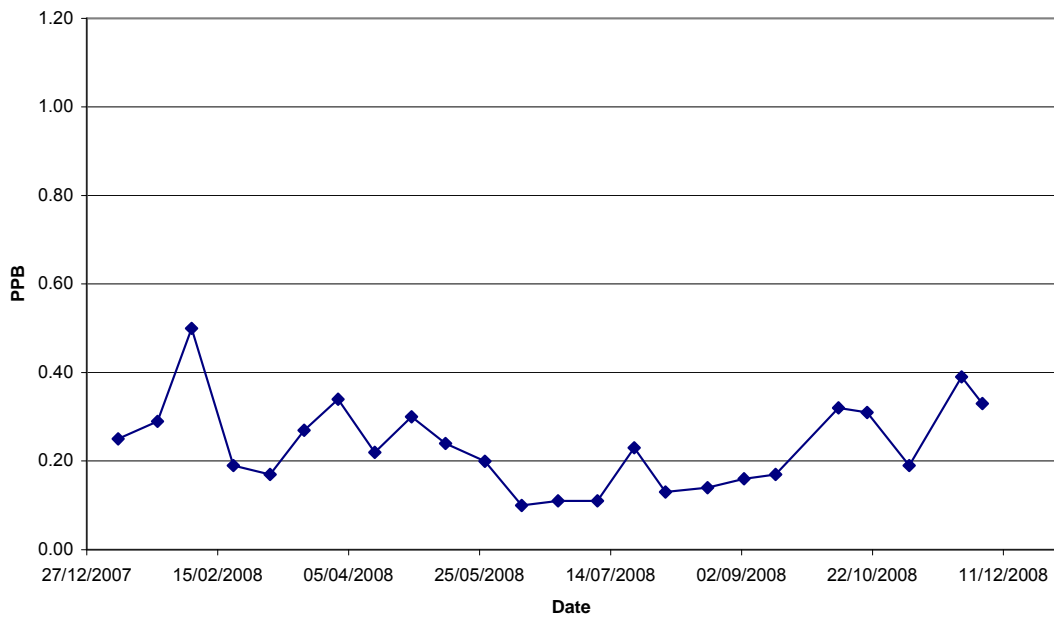
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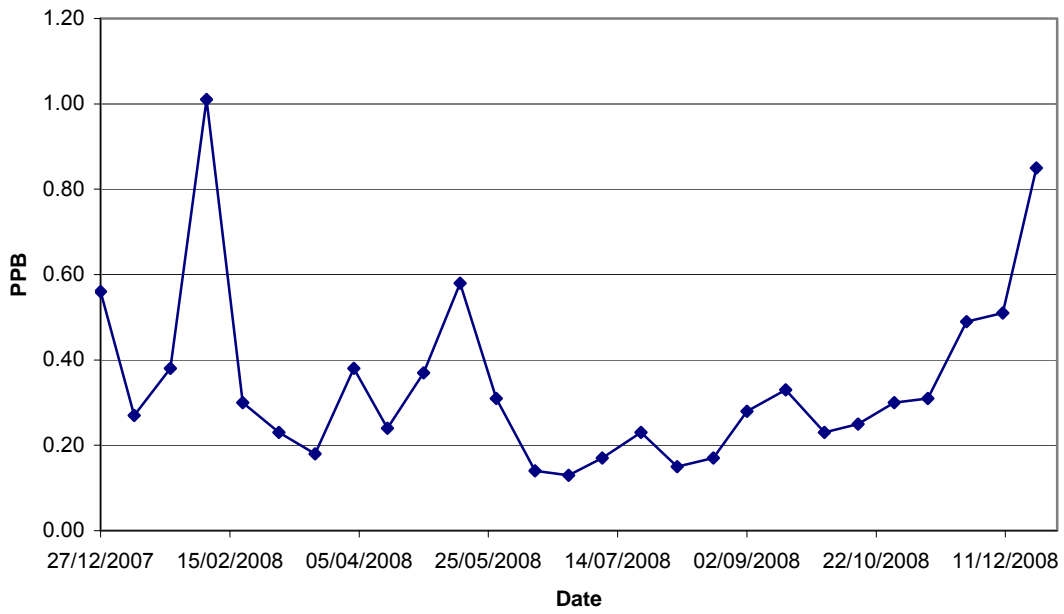
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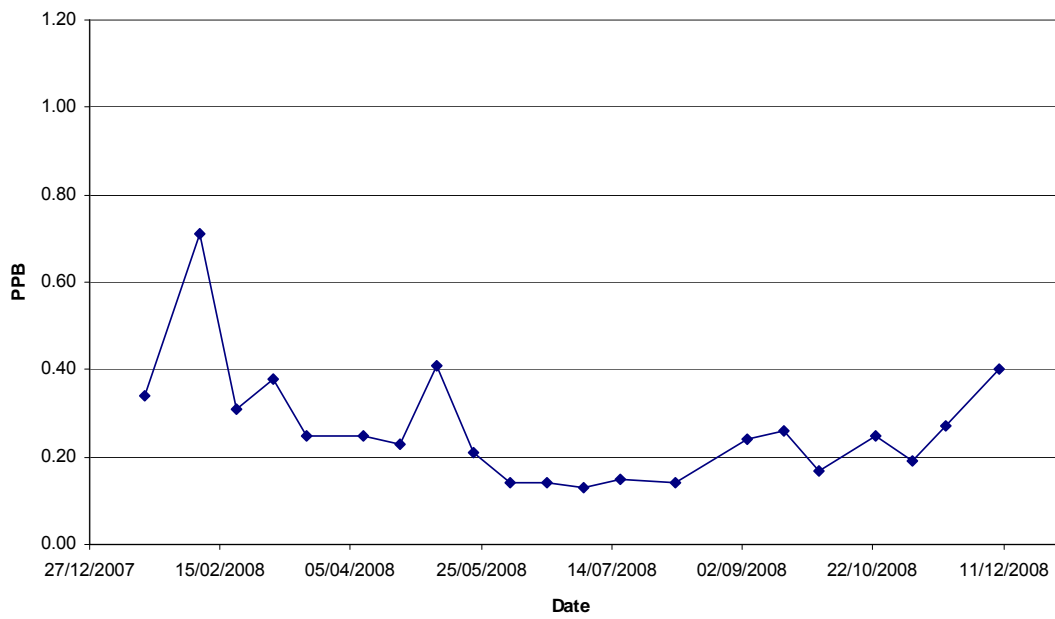
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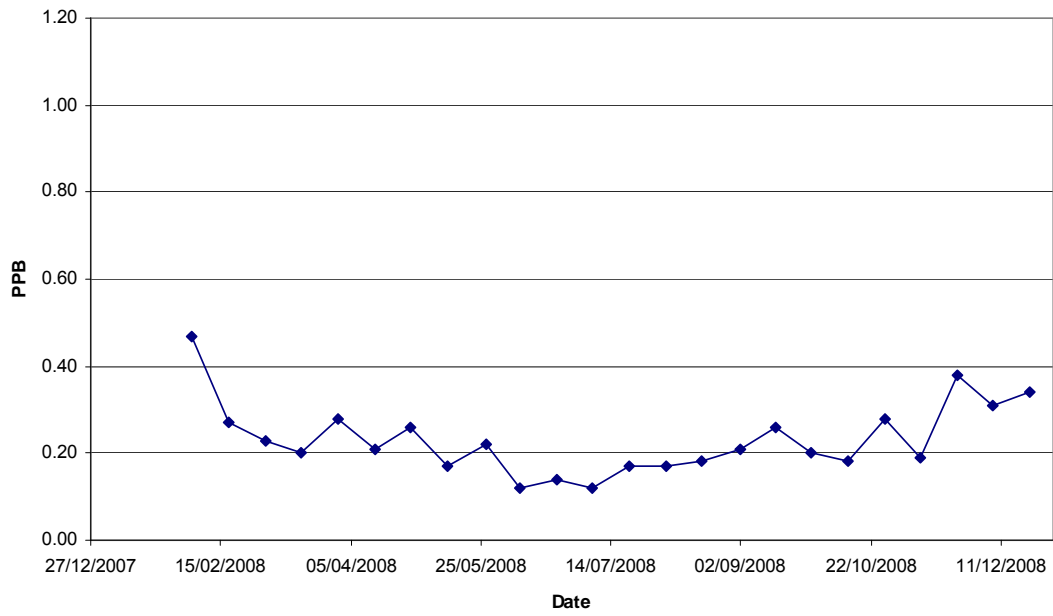
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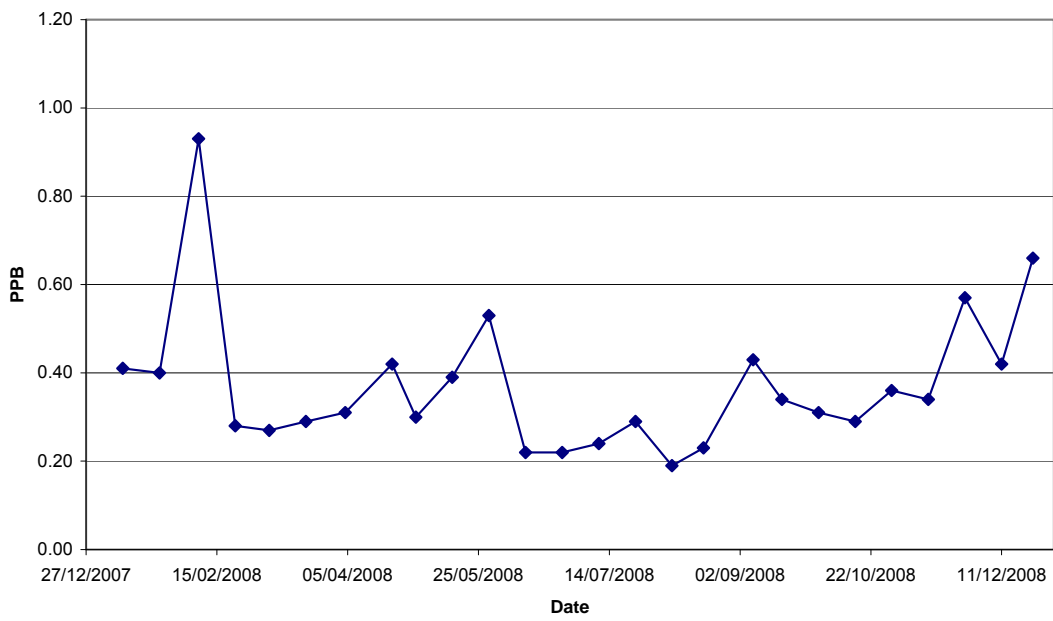
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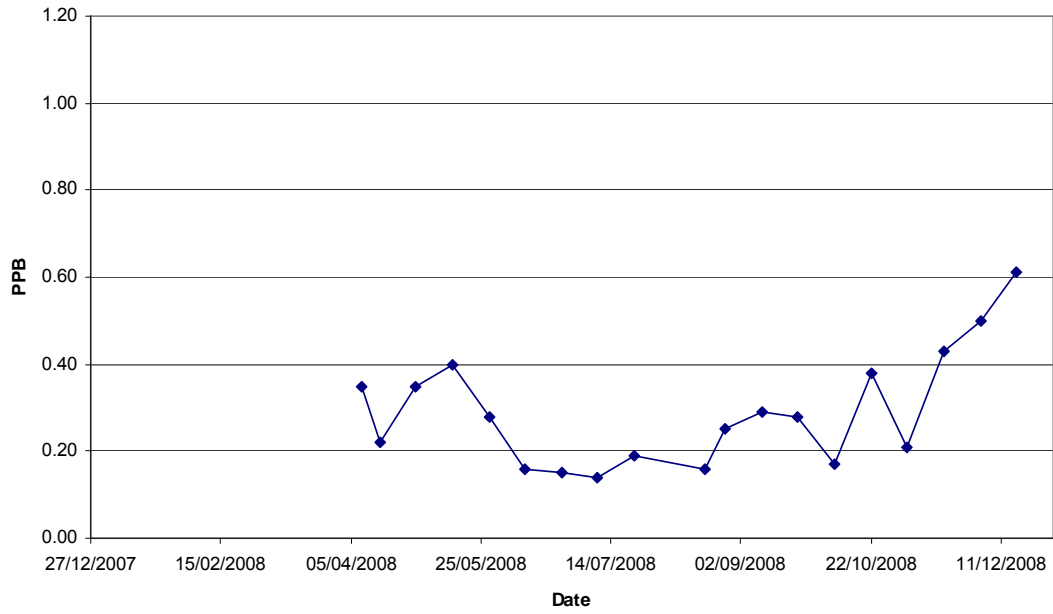
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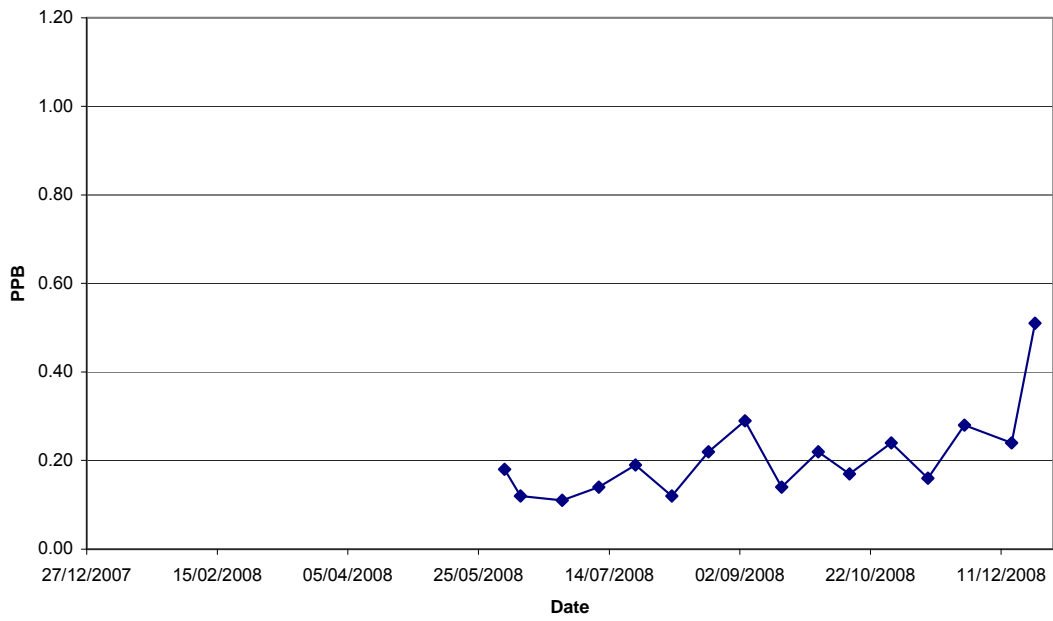
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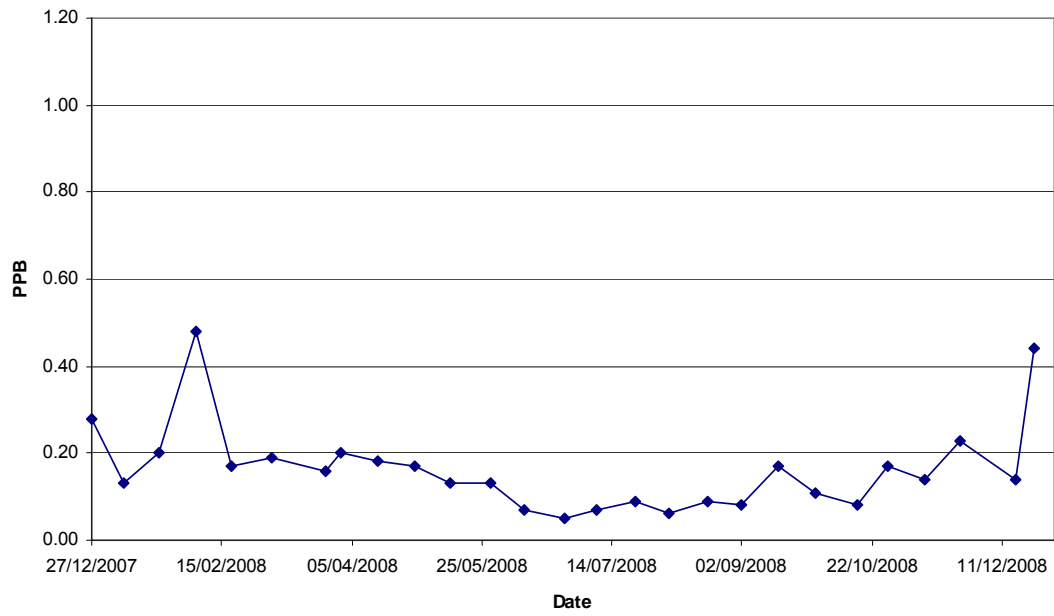
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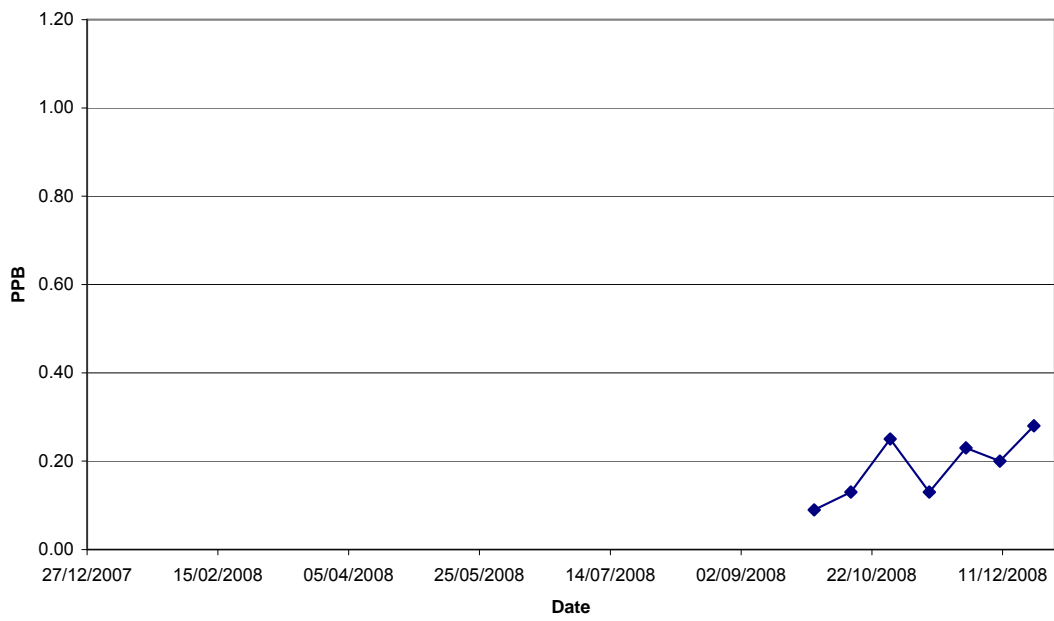
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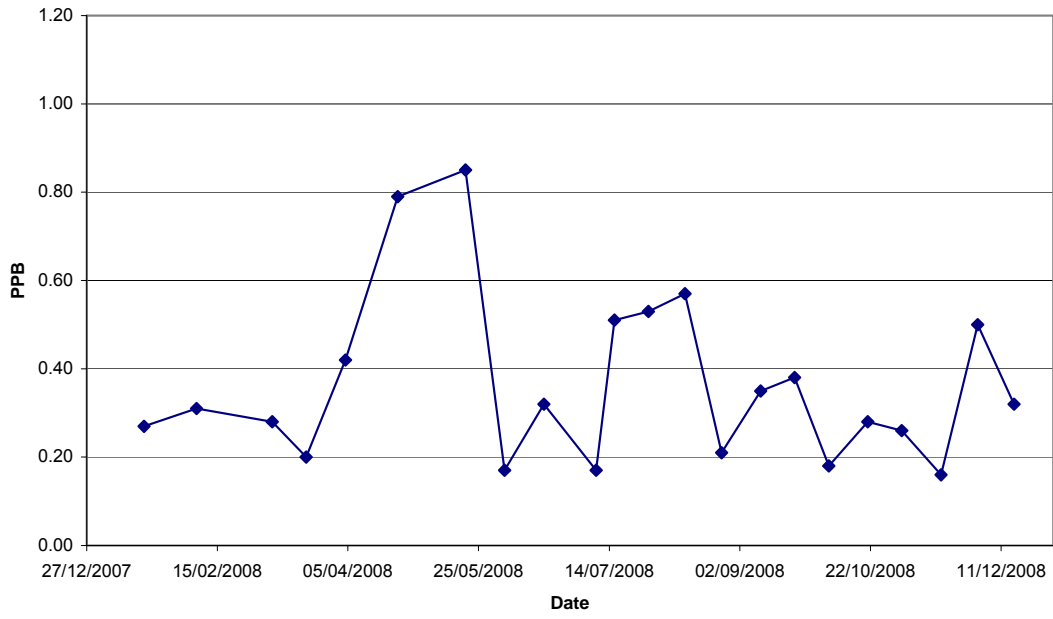
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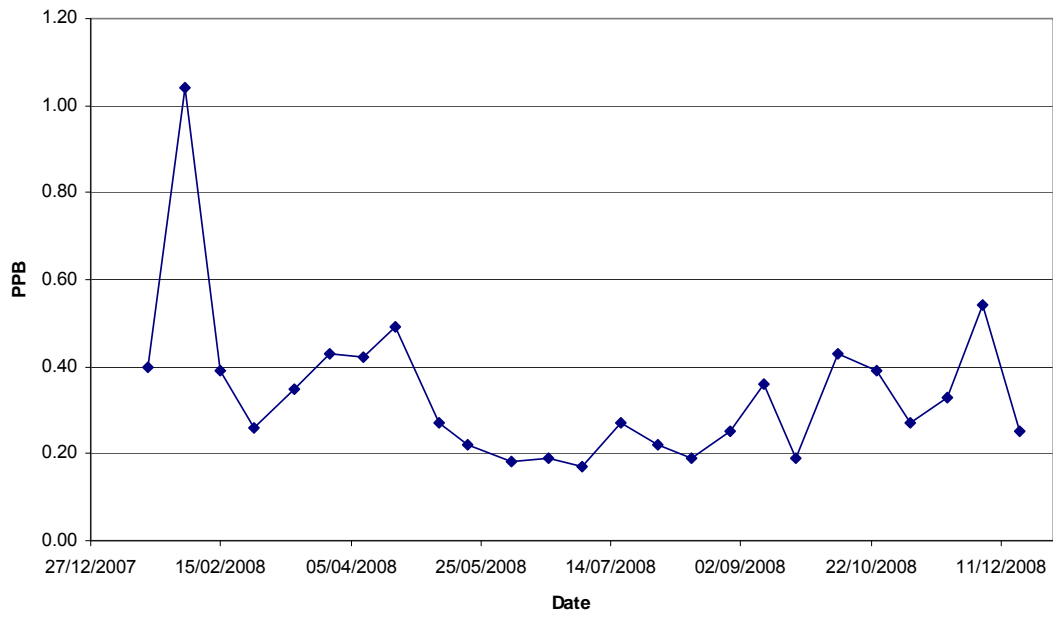
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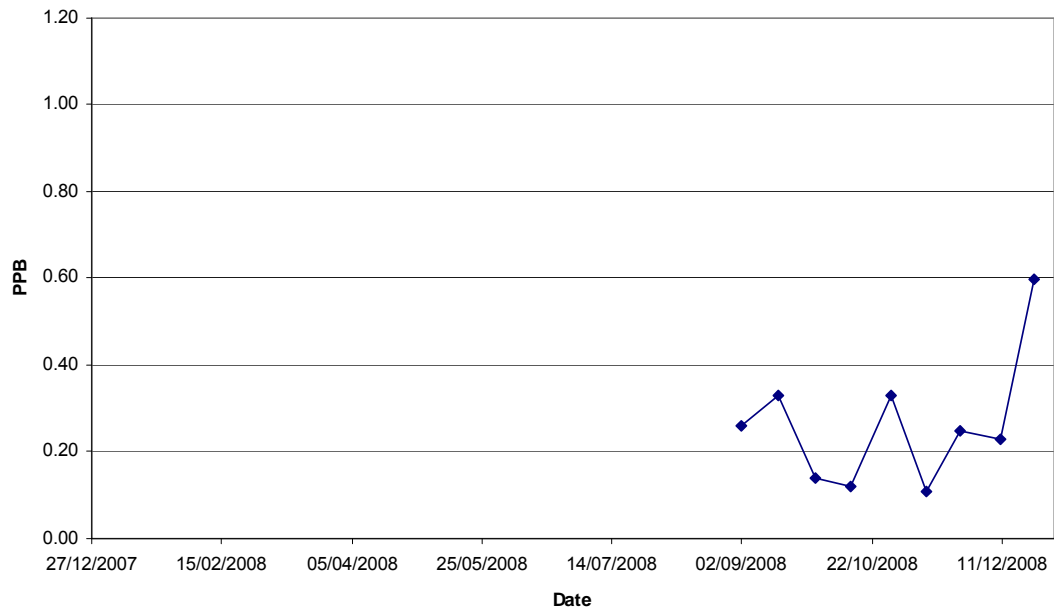
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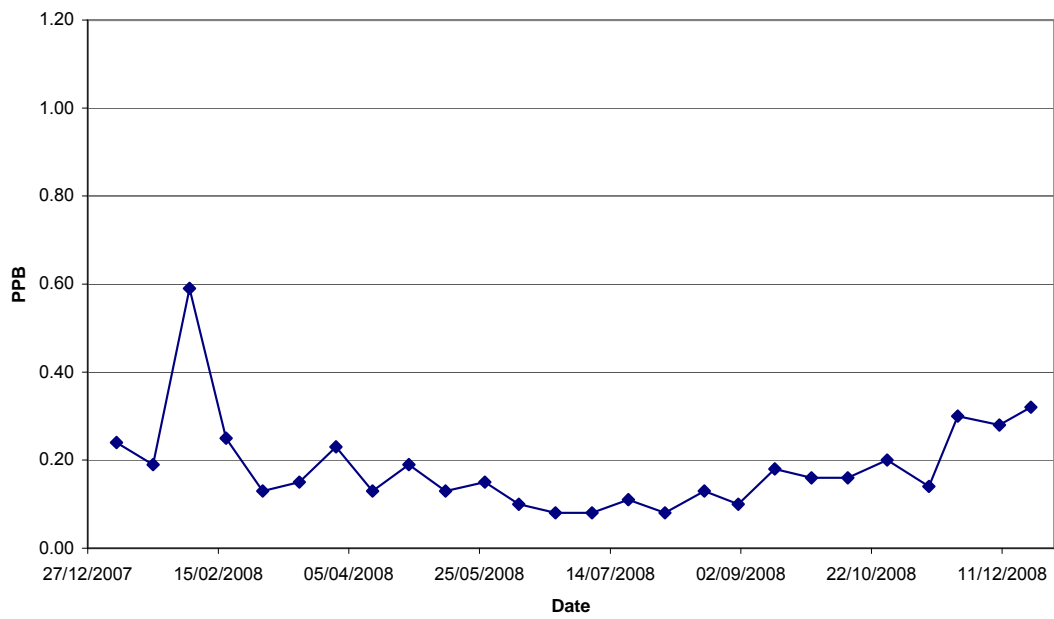
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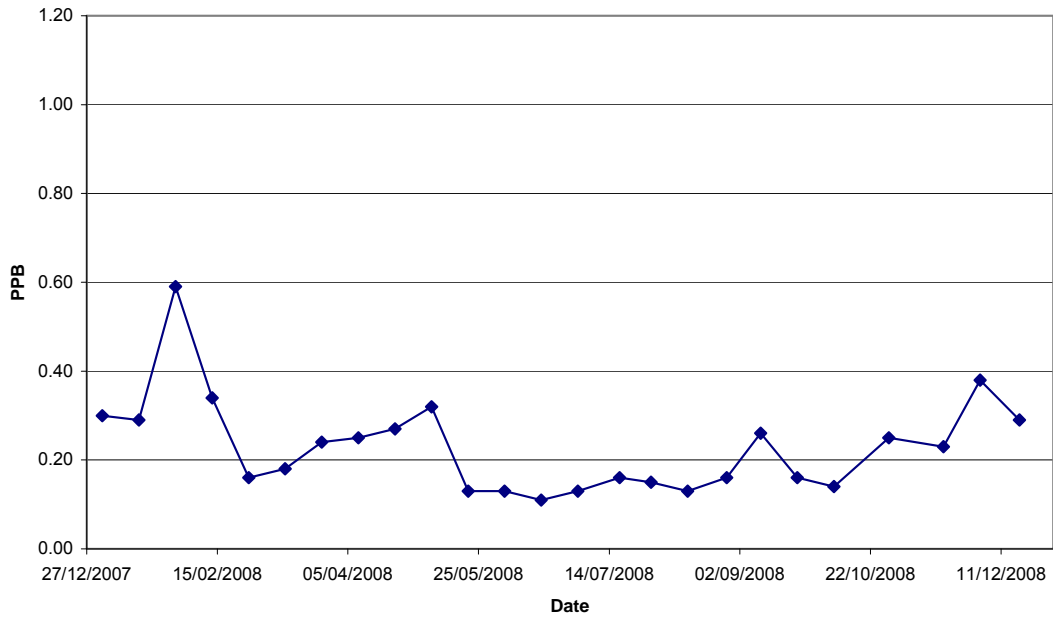
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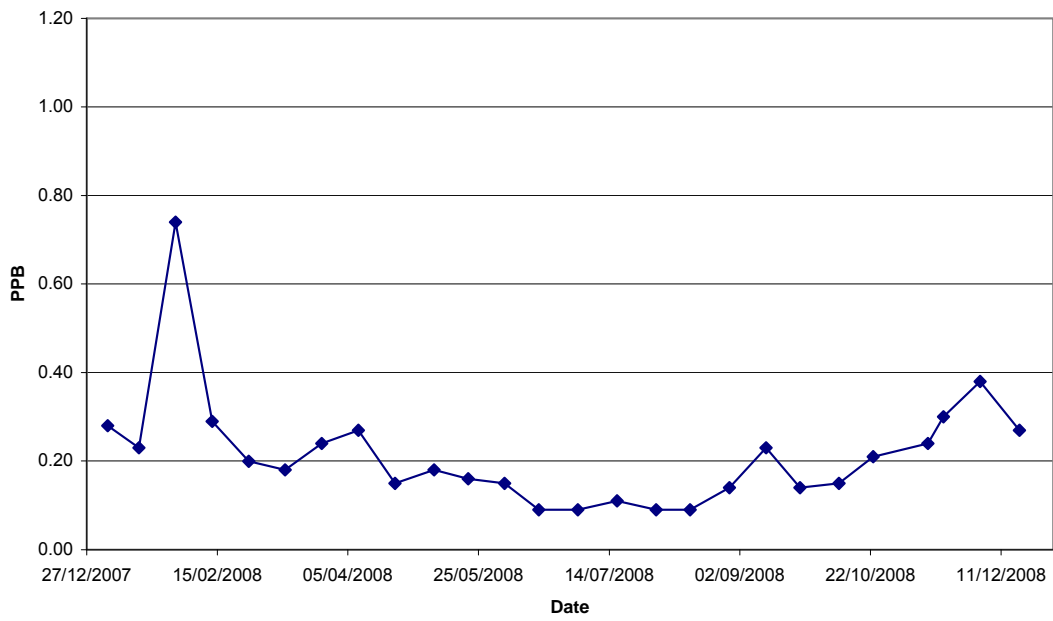
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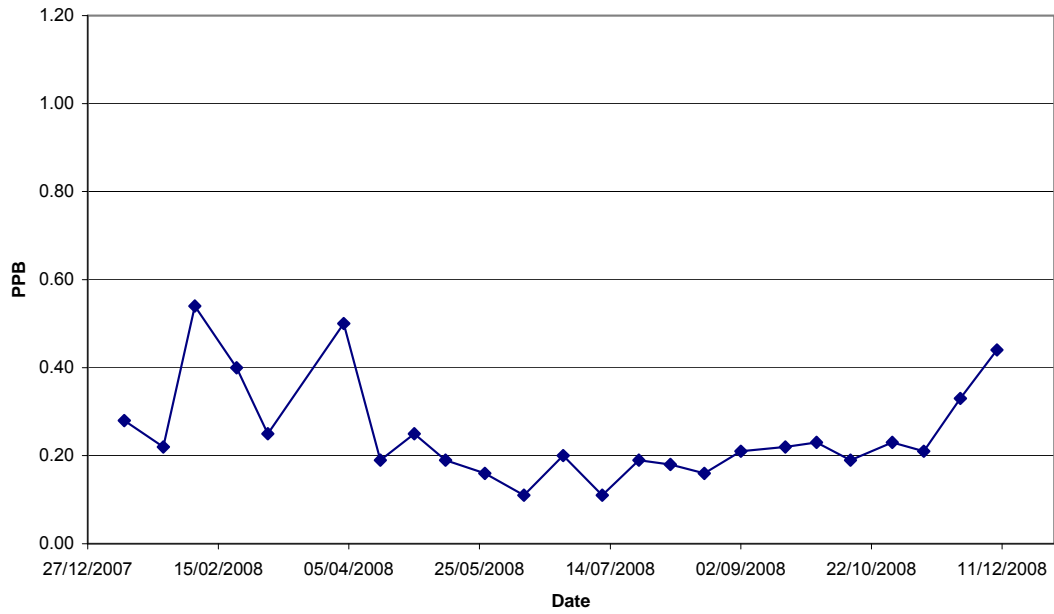
Leeds Centre



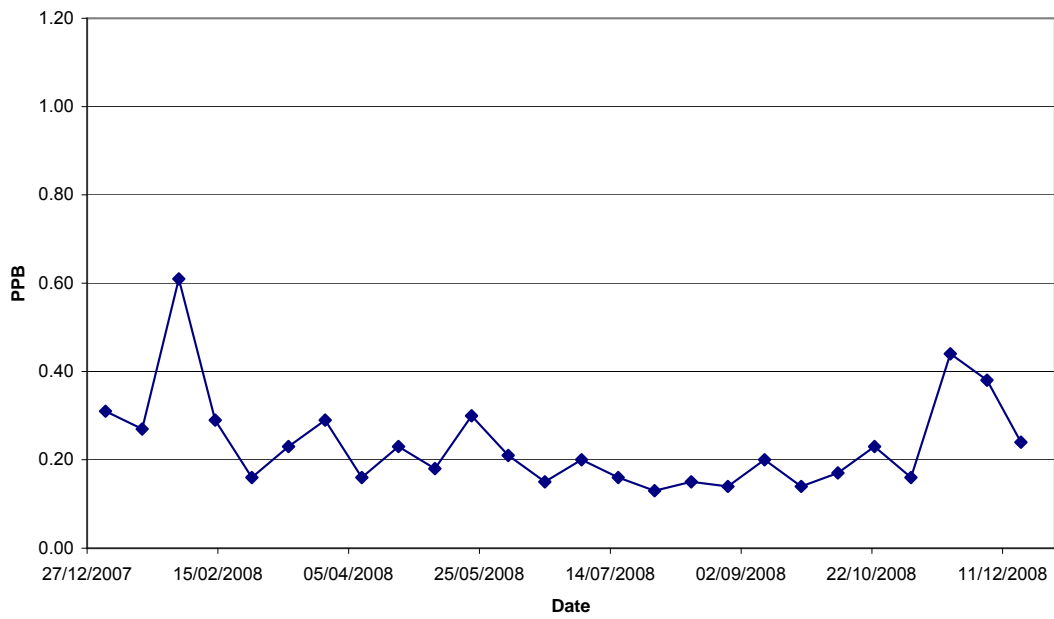
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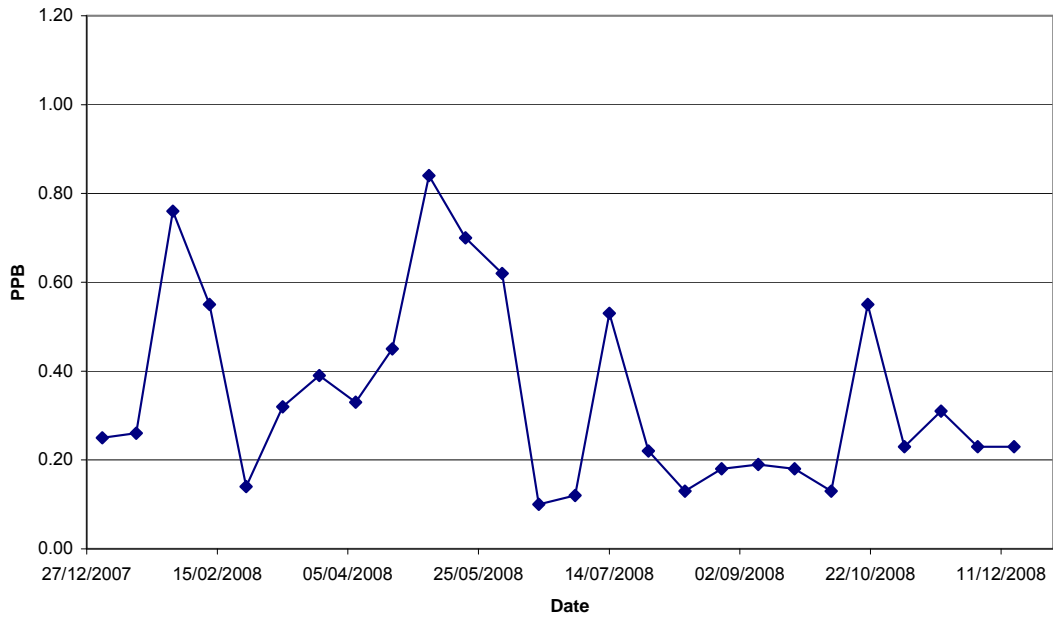
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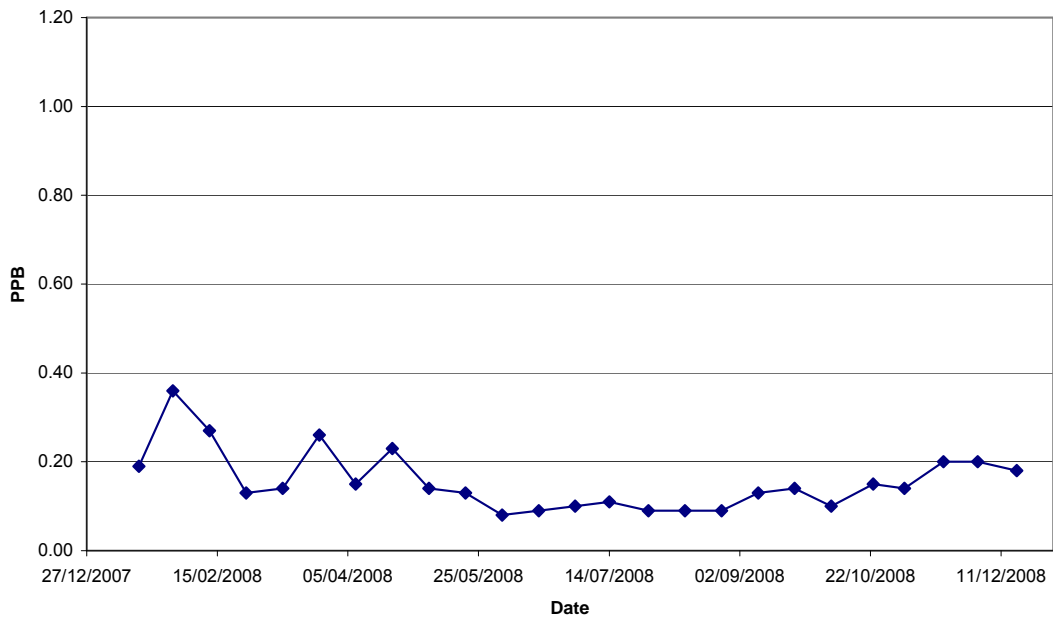
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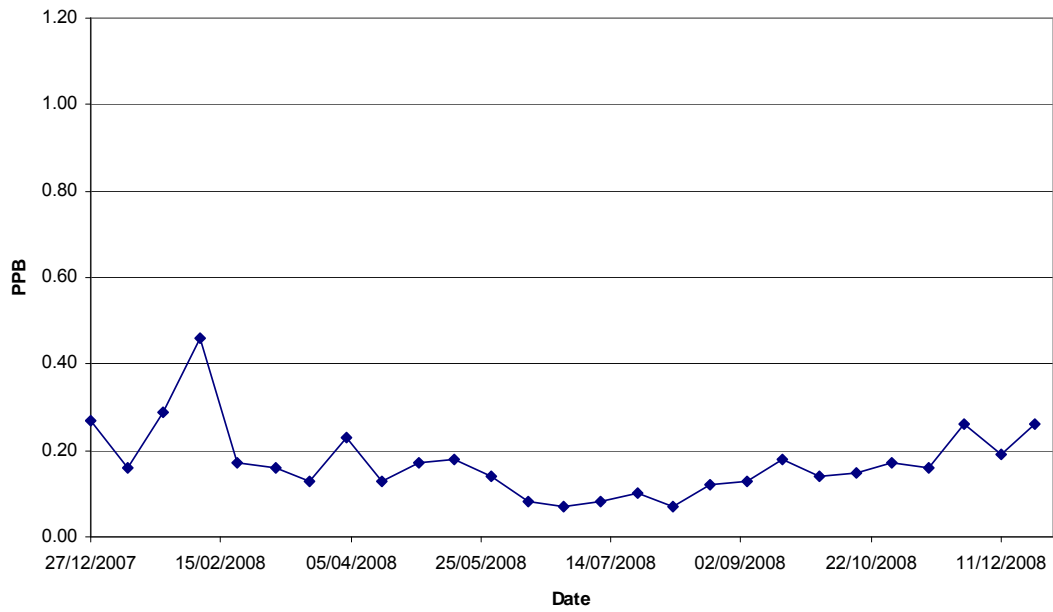
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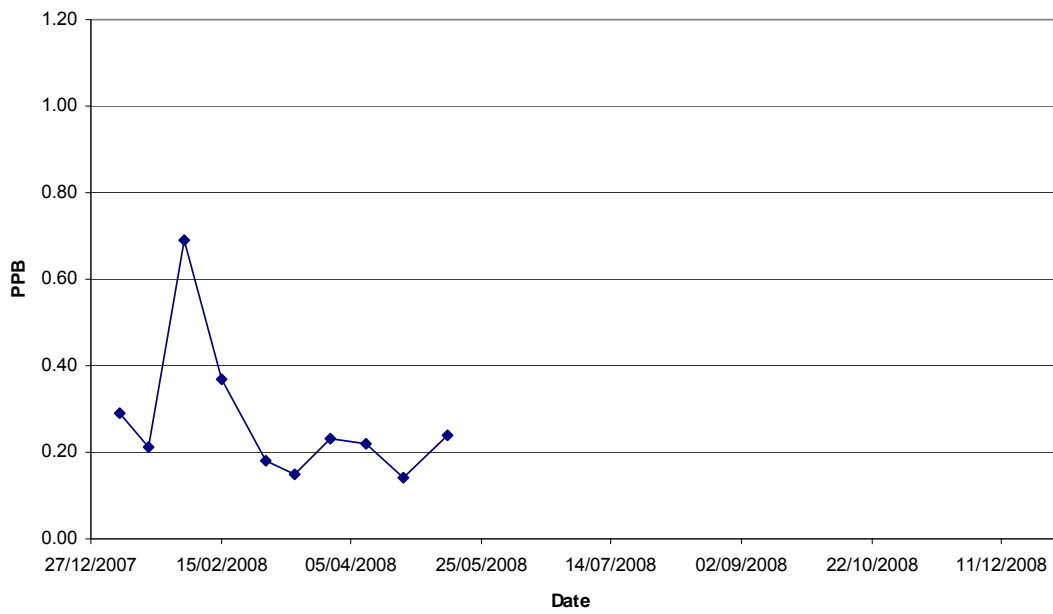
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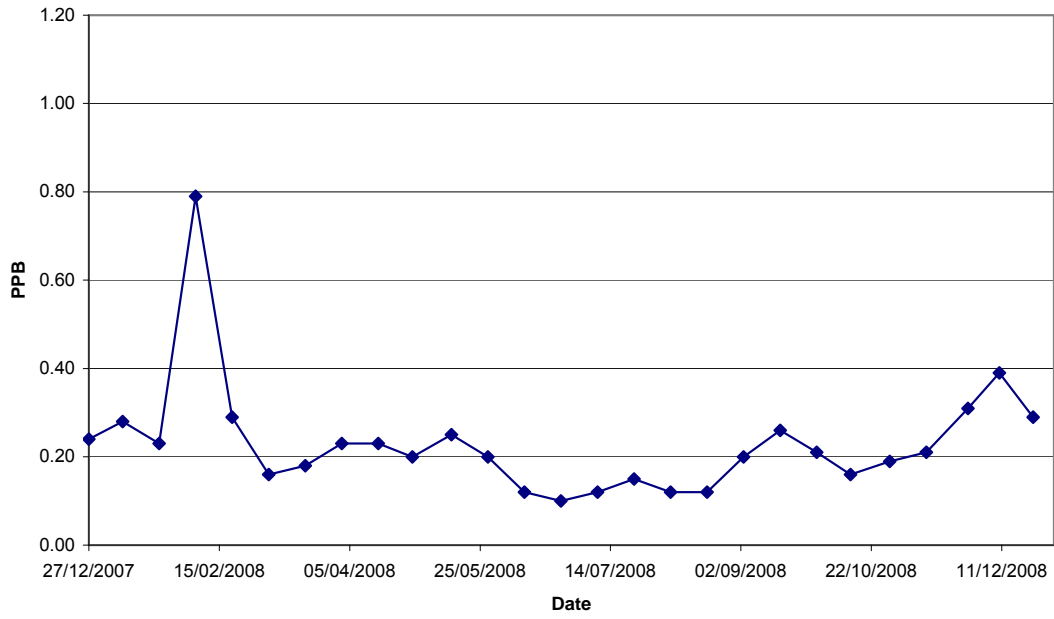
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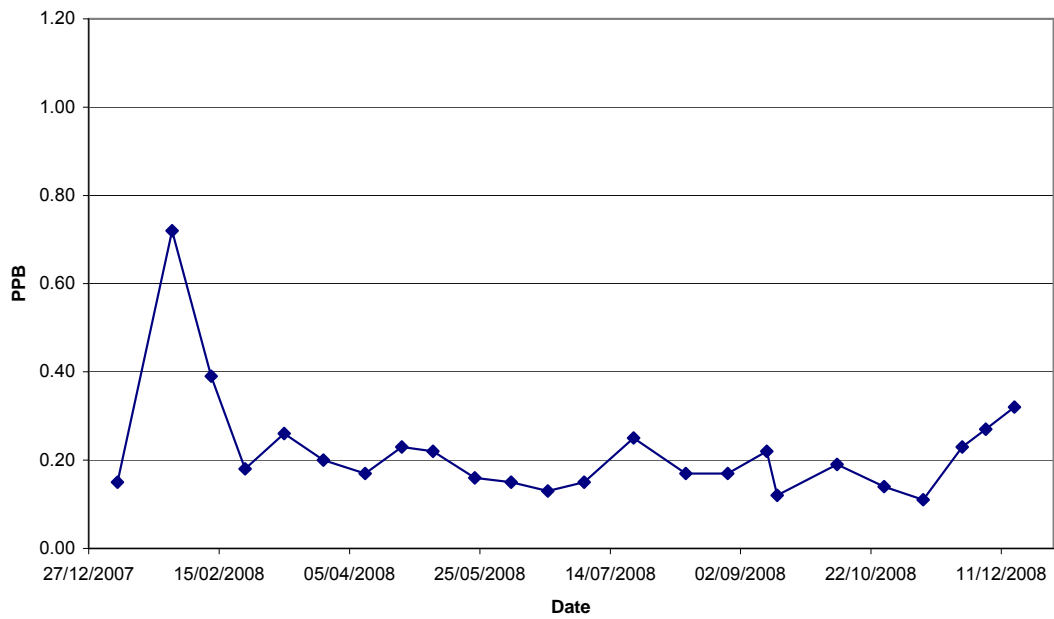
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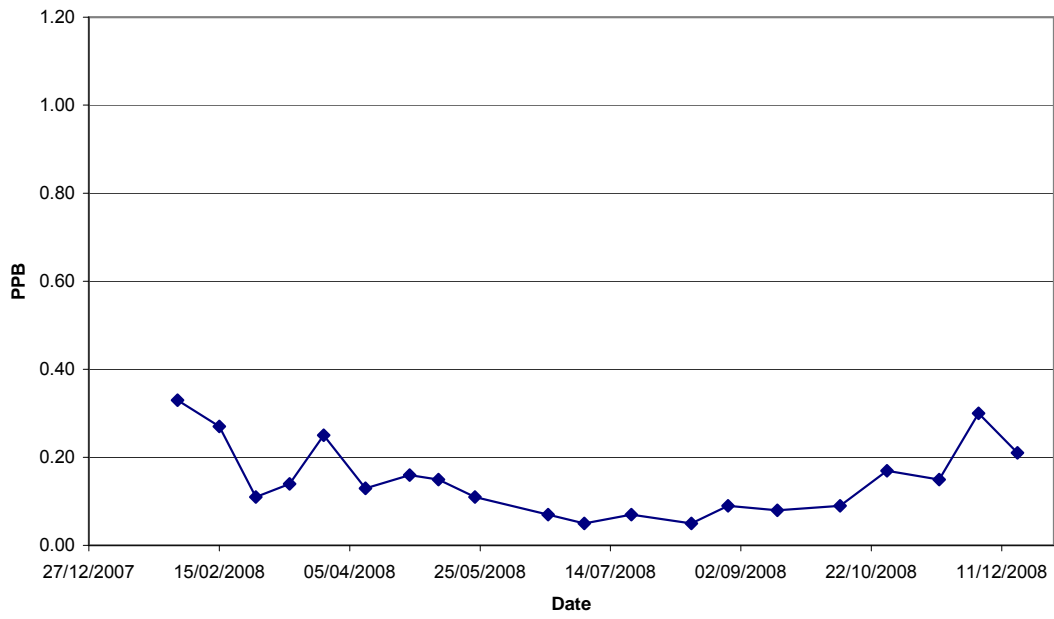
Nottingham Centre



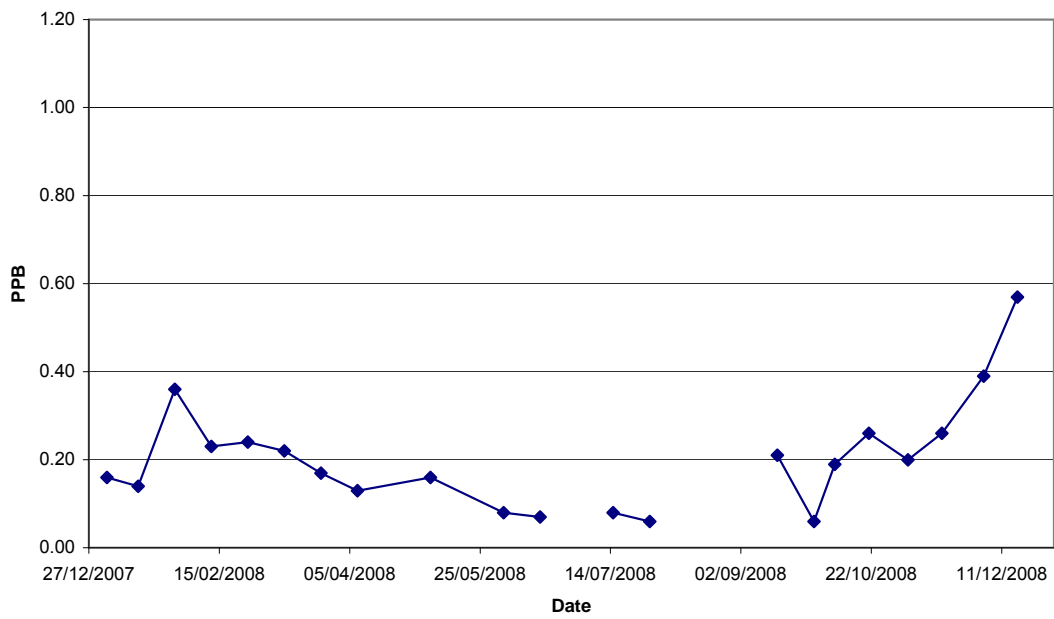
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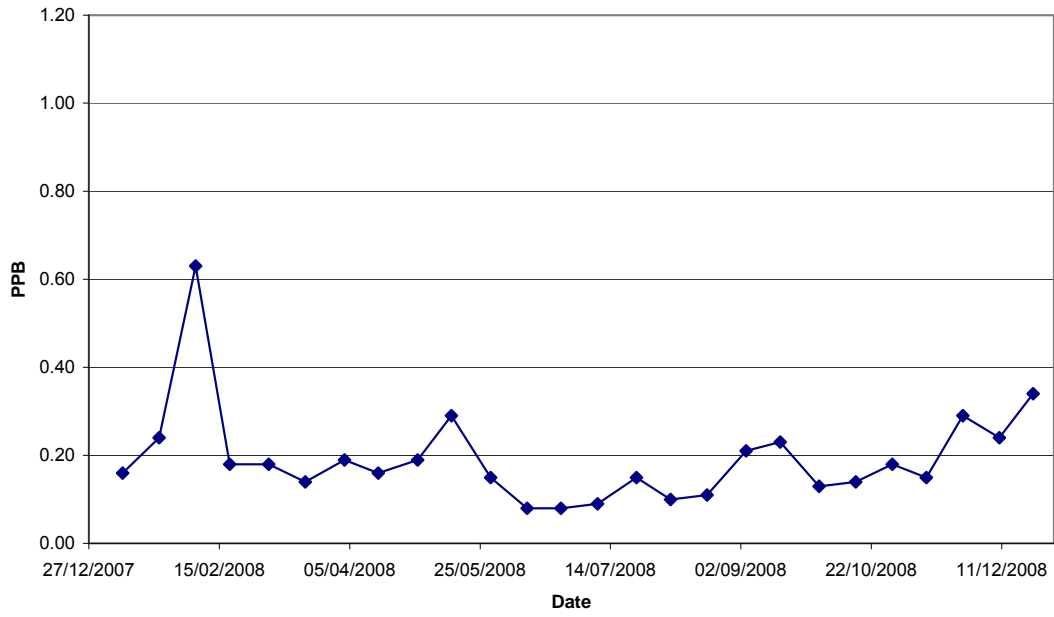
Oxford St Ebbes



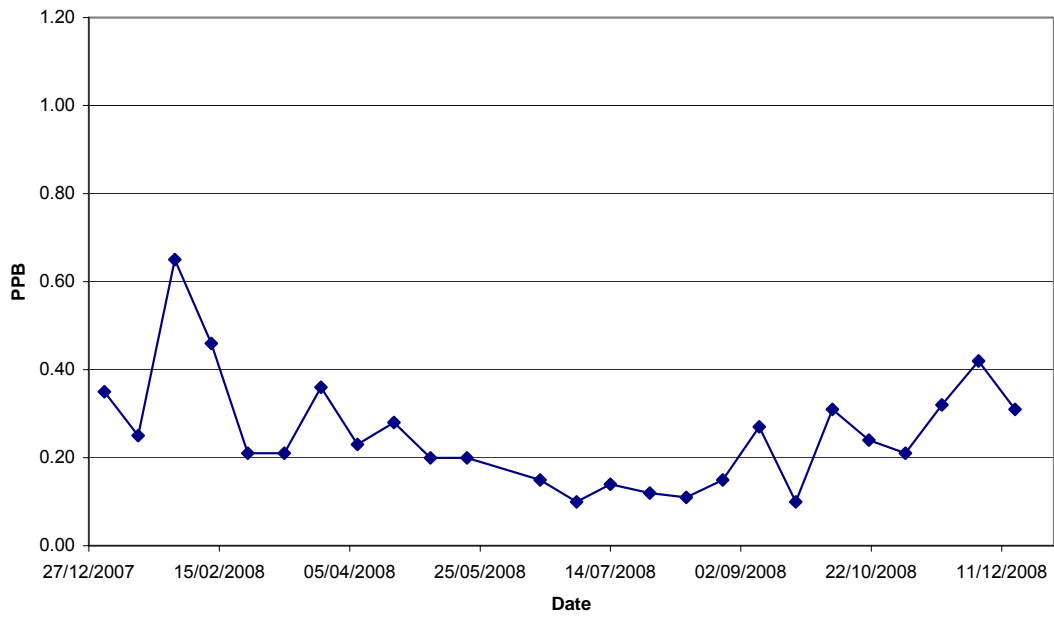
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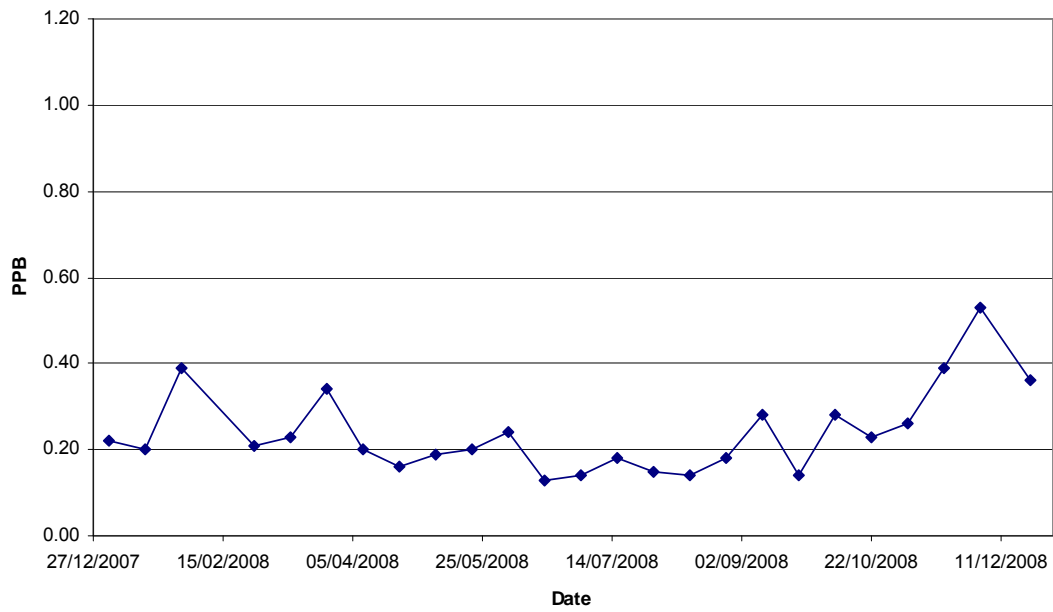
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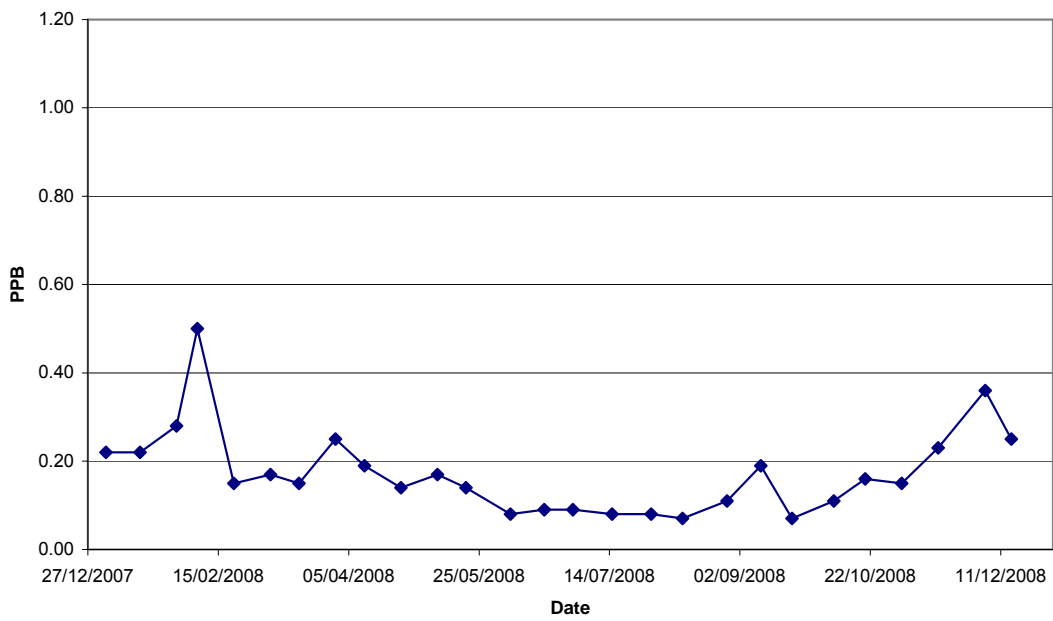
Southampton

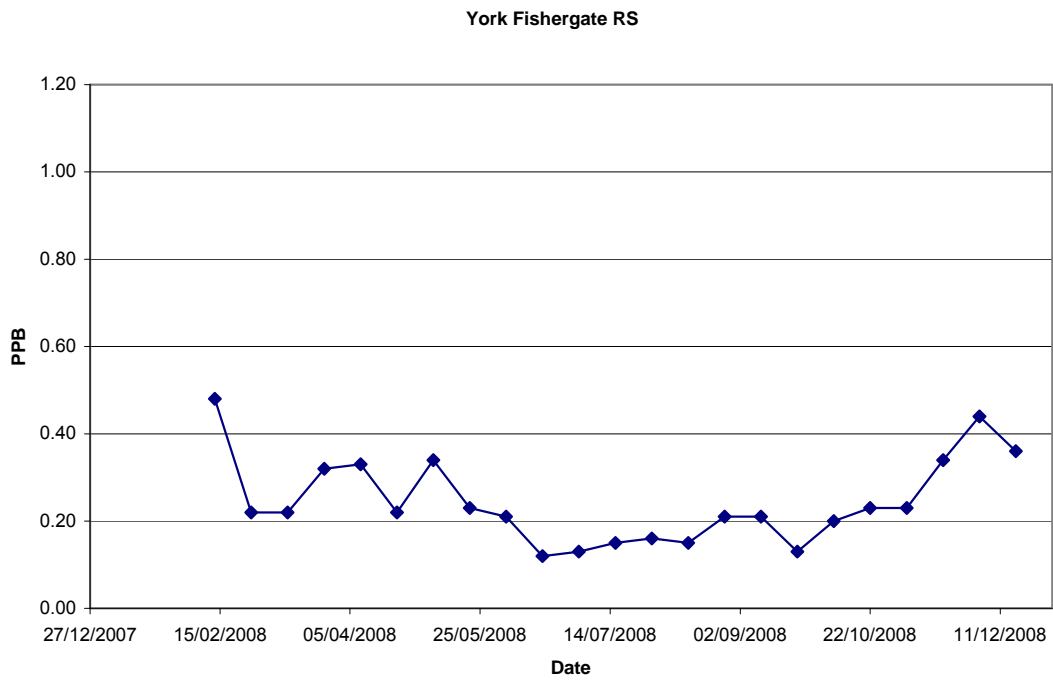
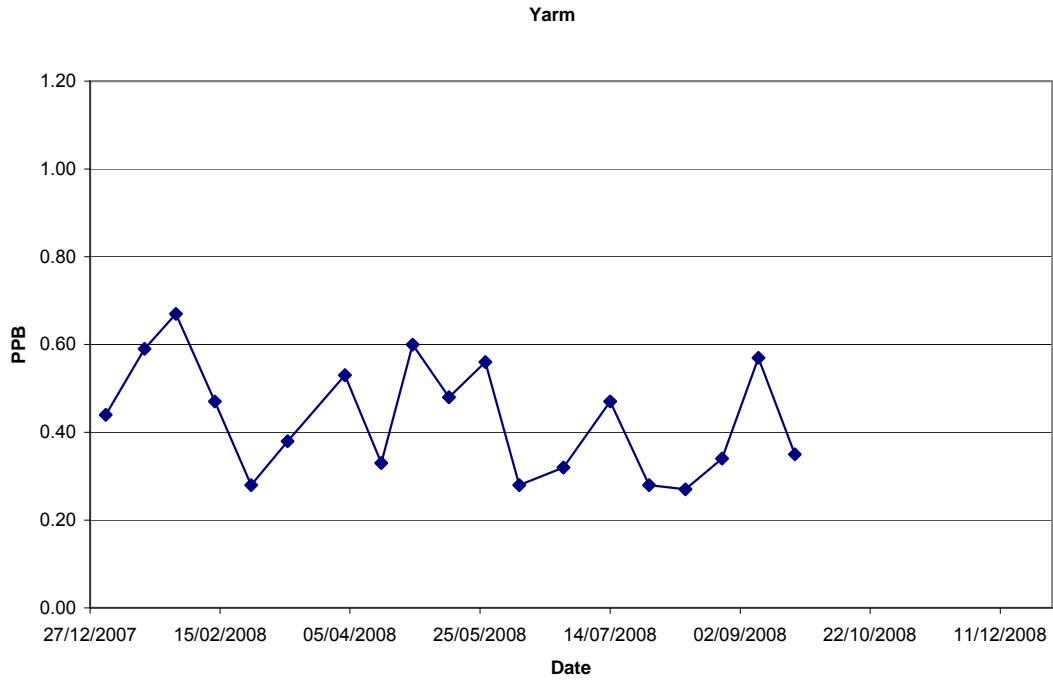


Stoke Centre



Wigan Centre





Annex 2 – Audit schedule

Site	Date	Date	Date
Barnsley Gawber	27/02/2008	05/08/2008	
Bath Roadside	28/01/2008	24/09/2008	
Belfast Centre	22/01/2008	08/07/2008	
Birmingham Roadside	21/01/2008	30/10/2008	
Birmingham Tyburn	16/04/2008	11/11/2008	
Bloomsbury	19/03/2008	05/09/2008	
Bristol Old Market	12/03/2008	24/09/2008	
Bury Roadside	17/01/2008	25/07/2008	
Cambridge Roadside	04/02/2008	04/07/2008	
Camden Kerbside	23/04/2008	21/10/2008	
Carlisle Caldewgate	09/04/2008	09/10/2008	
Chesterfield	04/06/2008		
Coventry Memorial Park	21/02/2008	28/08/2008	
Eaglescliffe - Yarm	30/09/2008		
Grangemouth	08/04/2008	08/10/2008	
Haringey Roadside	20/02/2008	21/08/2008	
Killingholme	02/09/2008		
Leamington Spa	21/02/2008	28/08/2008	
Leeds Centre	12/02/2008	05/08/2008	
Leicester Centre	02/04/2008	20/08/2008	
Liverpool Speke	16/01/2008	07/07/2008	
Manchester Piccadilly	16/01/2008	24/07/2008	
Marylebone Rd	23/04/2008	24/10/2008	25/11/2008
Middlesbrough	12/02/2008	30/09/2008	
Newcastle	01/04/2008	01/10/2008	
Northampton	26/02/2008	20/08/2008	
Norwich Centre	18/03/2008	13/05/2008	
Nottingham Centre	26/02/2008	19/08/2008	
Oxford Centre	16/04/2008	16/09/2008	26/11/2008
Oxford St Ebbes	30/01/2008	16/09/2008	
Plymouth	11/03/2008	01/07/2008	
Sheffield	12/02/2008	25/07/2008	
Southampton	25/01/2008	22/07/2008	
Stoke Centre	17/01/2008	08/08/2008	
Wigan Centre	16/01/2008	24/07/2008	
Yarm	01/04/2008		
York Fishergate RS	13/02/2008	06/08/2008	