NPL REPORT AS 50

UK Non-Automatic Hydrocarbon Network:

Annual Report for 2009

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NOT RESTRICTED

APRIL 2010

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ISSN: 1754-2928

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by Alan Brewin, Business Leader, Analytical Science Division

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EXECUTIVE SUMMARY

This report summarises operational matters and the data obtained by the Non-Automatic Hydrocarbon Network in the year 2009.

The background, methods used and site locations are given in Sections 1 and 2.

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.

1. Introduction

1.1 General background, history and methods

The Automatic and Non-Automatic Hydrocarbon Networks exist within the framework of Defra's Atmosphere and Local Environment Programme, one of whose aims is 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

	Averaging period	*Limit value*	*Margin of tolerance*	*Date by which limit value is to be met*
Limit value for the protection of human health	Calendar year	5 µg/m^3	5 µg/m^3 reducing on 1st January 2006 and every 12 months thereafter by 1 µg/m^3 to reach 0 µg/m^3 by 1st January 2010	1st January 2010

Table 1: Benzene limit value and associated information

The concentration 5 µg/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 µg/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 (µg/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).

Ppb units are occasionally used to supplement μg/m^3 units in this report.

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

1 ppb = 3.25 μg/m^3
ie 1.54 ppb = 5 μg/m^3

1.4 Measurement uncertainty

The Data Quality Objective for the measurement uncertainty of fixed measurements of benzene in the EU Directive is ±25%, expressed at a 95% confidence level. This applies to annual average values, in the region of the limit value (5 μg/m^3).

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 2009

The sites in the Network in 2009 were located as in Figure 1.

Table 2 lists the sites with their Local Site Operators.

Figure 1: Map of Network sites in 2009.

Site	Classification	Zone / Agglomeration	Grid Reference Easting / Northing	Local Site Operator
Barnsley Gawber	Urban Background	Yorkshire & Humberside	432524, 407476	Barnsley Council
Bath Roadside	Roadside	South West	375460, 165843	Bath & North Somerset Council
Belfast Centre	Urban Centre	Belfast Urban Area	146230, 529911	Belfast City Council
Birmingham Roadside	Roadside	West Midlands Urban Area	409049,284267	Birmingham City Council
Birmingham Roadside 2	Roadside	West Midlands Urban Area	408824, 284570	Birmingham City Council
Birmingham Tyburn	Urban Background	West Midlands Urban Area	411598, 290432	Birmingham City Council
Bloomsbury	Urban Background	Greater London Urban Area	530117, 182039	Bureau Veritas
Bristol Old Market	Roadside	Bristol Urban Area	359552, 173167	Bristol City Council
Bury Roadside	Roadside	Greater Manchester Urban Area	380903, 404755	Bury Metropolitan Council
Cambridge Roadside	Roadside	Eastern	545277, 258140	Cambridge Council
Camden Kerbside	Kerbside	Greater London Urban Area	526629, 184391	King's College London
Carlisle Caldewgate	Roadside	North West & Merseyside	339433, 555963	Carlisle Council
Chesterfield	Roadside	East Midlands	436350, 370680	Chesterfield Council
Coventry Memorial Park	Urban Background	Coventry/Bedworth	432787, 277474	Coventry City Council
Eaglescliffe - Yarm	Roadside	North East	441637, 513672	Stockton on Tees BC
Grangemouth	Urban Industrial	Central Scotland	293844, 681047	Falkirk Council
Haringey Roadside	Roadside	Greater London Urban Area	533891, 190707	King's College London
Killingholme	Urban Industrial	Yorkshire & Humberside	514870,416098	North Lincolnshire Council
Leamington Spa	Urban Background	West Midlands	431941, 265731	Warwick District Council
Leeds Centre	Urban Centre	West Yorkshire Urban Area	429966, 434258	Leeds City Council
Leicester Centre	Urban Centre	Leicester Urban Area	458762, 304064	Leicester City Council
Liverpool Speke	Urban Centre	Liverpool Urban Area	343887, 383601	AECOM
Manchester Piccadilly	Urban Centre	Greater Manchester Urban Area	384310, 398335	Manchester City Council
Middlesbrough	Urban Industrial	Teesside Urban Area	450498, 519626	Middlesbrough BC
Newcastle	Urban Centre	Tyneside	425026, 564917	Newcastle City Council
Northampton	Urban Background	East Midlands	476111, 264509	Northampton BC
Norwich - Lakenfields	Urban Background	Eastern	623637, 306940	MDL Environmental
Nottingham Centre	Urban Centre	Nottingham Urban Area	457440, 340044	Nottingham City Council
Oxford Centre	Roadside	South East	451353, 206156	Oxford City Council
Oxford St Ebbes	Urban Background	South East	451167, 205381	Oxford City Council
Plymouth	Urban Centre	South West	247750, 54615	Plymouth City Council
Sheffield	Urban Centre	Sheffield Urban Area	435135, 386890	Sheffield City Council
Southampton	Urban Centre	Southampton Urban Area	442578, 112249	Southampton City Council
Stoke Centre	Urban Centre	The Potteries	388351, 347892	City of Stoke on Trent Council
Wigan Centre	Urban Background	North West & Merseyside	357815, 406021	Wigan Metropolitan BC
York Fishergate RS	Roadside	Yorkshire & Humberside	460745, 451036	York City Council

Table 2: Network sites in 2009

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://aurn.defra.gov.uk/stations/index.htm

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

2.1 Changes during 2009

The Birmingham Roadside sampler stopped sampling on 19/02/09 due to the closure of the site by the Local Council. A new site was installed around 200m down the road from the old site and measurements commenced here on 22/07/09. The new site name is Birmingham Roadside 2. Comparable concentrations of benzene are measured at both sites.

The Norwich Lakenfields AURN site was installed in November and monitoring started on 11/11/2009. This monitoring site replaced the Norwich Centre site that stopped monitoring in May 2008 when this AURN site was removed.

The South Killingholme site was closed on 17/03/10 as the measured concentrations were well below the European Limit Value and modelling no longer predicted an exceedence. The sampler was removed and installed into the new Chatham Roadside site in March 2010 and monitoring started on 25/03/10.

A roadside site in Leamington Spa has been identified by Bureau Veritas (BV) as a suitable site for the required West Midlands roadside site. A planning application was made for the site by BV in April 2010.

2.2 Site audits in 2009

All sites are visited by NPL staff on a 6 monthly basis to calibrate the sampling flows and carry out routine maintenance on the equipment. The schedule of these visits is given in Annex 1.

3. Data and Data Capture for 2009

3.1 Benzene: comparison with Limit Values and Objectives

Site	µg/m^3	ppb
Barnsley Gawber	0.55	0.17
Bath Roadside	0.78	0.24
Belfast Centre	0.72	0.22
Birmingham Tyburn	0.81	0.25
Bloomsbury	0.81	0.25
Bristol Old Market	1.24	0.38
Bury Roadside	0.85	0.26
Cambridge Roadside	0.85	0.26
Camden Kerbside	1.24	0.38
Carlisle Caldewgate	0.91	0.28
Chesterfield	0.88	0.27
Coventry Memorial Park	0.55	0.17
Eaglescliffe - Yarm	0.72	0.22
Grangemouth	1.33	0.41
Haringey Roadside	1.14	0.35
Killingholme	1.04	0.32
Leamington Spa	0.72	0.22
Leeds Centre	0.68	0.21
Leicester Centre	0.75	0.23
Liverpool Speke	0.85	0.26
Manchester Piccadilly	0.88	0.27
Middlesbrough	1.04	0.32
Newcastle	0.59	0.18
Northampton	0.59	0.18
Nottingham Centre	0.78	0.24
Oxford Centre	0.78	0.24
Oxford St Ebbes	0.52	0.16
Plymouth	0.65	0.20
Sheffield	0.75	0.23
Southampton	0.85	0.26
Stoke Centre	0.91	0.28
Wigan Centre	0.72	0.22
York Fishergate RS	0.91	0.28

Table 3: 2009 Benzene data for sites > 75% time coverage

The annual average concentration of benzene over the calendar year 2009 is given in Table 3, for each site that was operating for more than 75% of the year.

Annual average concentrations at all sites were below the Limit Value of 5 µg/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/m^3 to be achieved by 31 December 2010;
- for Scotland and Northern Ireland, a running annual mean of 3.25 µg/m^3 to be achieved by 31 December 2010.

These Objectives were met in 2009 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. All sites exceed a data capture rate of 95% except those shown in Table 4.

Site	Data capture, %
Sheffield	79
Middlesbrough	81
Bloomsbury	88
Newcastle	93
Birmingham Tyburn	93
Plymouth	93
Oxford St Ebbes	94
Liverpool Speke	94
Bury Roadside	94
Carlisle Caldewgate	94
Oxford Centre	94
Chesterfield	94

Table 4: 2009 Benzene data capture for sites < 95%

The main reasons for data loss at these sites were:

Sheffield Centre (79%)

19/03/09 - 08/06/09 – AURN Equipment Support Unit removed the sampling manifold from the site and did not connect the benzene pump box up to the new ambient air inlet. Concentrations were found to be too high, as the inlet pipe had been placed next to the fibreglass wall of the hut, which was a source of benzene.

Middlesbrough (81%)

28/07/09 – 24/09/09 – Major circuit board failure in the pump box led to unstable flows and improper switching of the main valve. Concentrations were uncharacteristically low and are considered to be unrepresentative of the true ambient concentration.

Bloomsbury (88%)

22/12/08 – 04/02/09 and 20/10/09 – 03/11/09 - Damaged O-ring in tube elbow causing a leak.

Sites between 93% and 94% data capture

The remaining sites listed above lost two sets of measurements over the year either for incorrectly installed tube elbows, blocked inlet pipe work or a missed LSO visit.

3.3 Episodes and anomalous results

No fortnightly values were recorded above the annual average Limit Value of 5 µg/m^3. There were no high benzene pollution episodes over the year.

The main notable feature was a widespread elevated concentration in January to February 2009, which coincided with the snow across the country. This has been observed in other Networks affecting many pollutants including NOx, 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 eight years of operation of the pumped samplers is shown in Figures 2 and 3. 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. The new monitoring site installed in 2008 delivered their first full calendar year's data in 2009. These sites have been included in Figure 3 to show the relative concentrations.

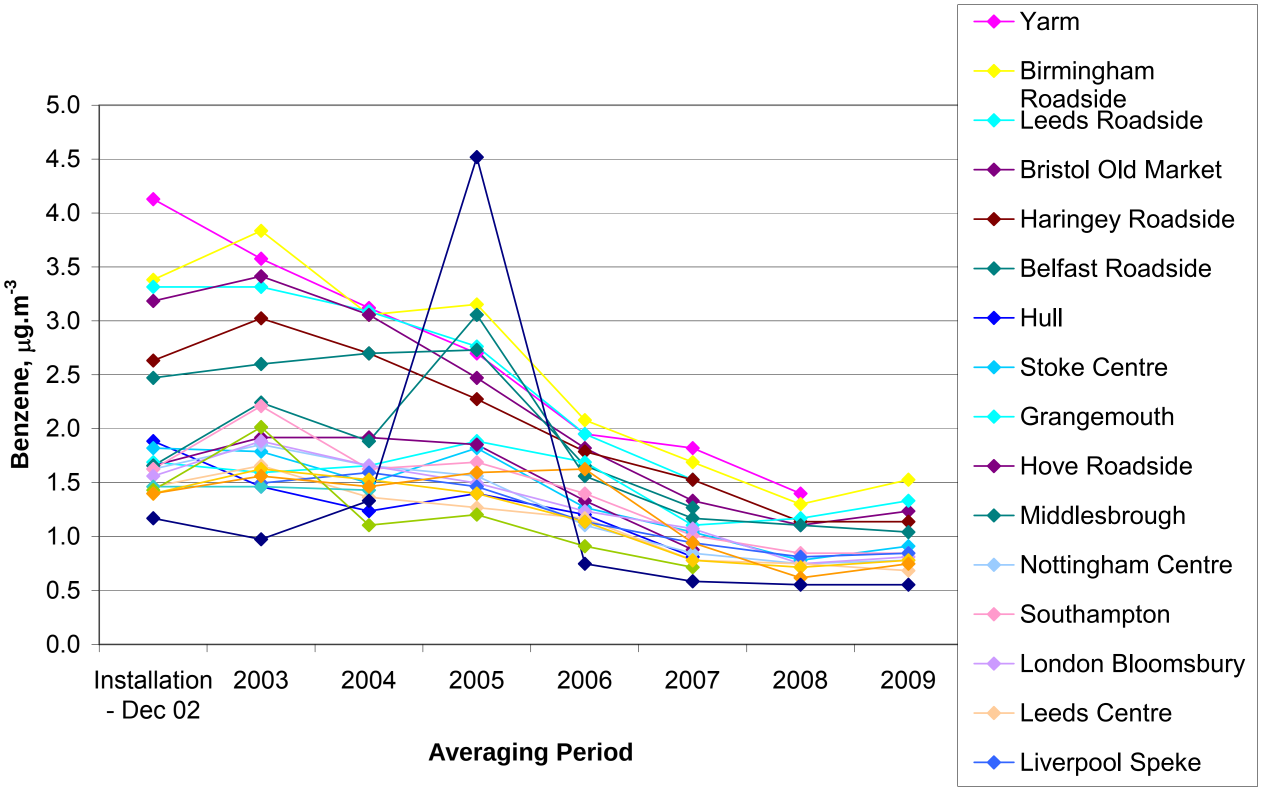


Figure 2 : Recent annual average benzene concentrations at "high concentration" sites

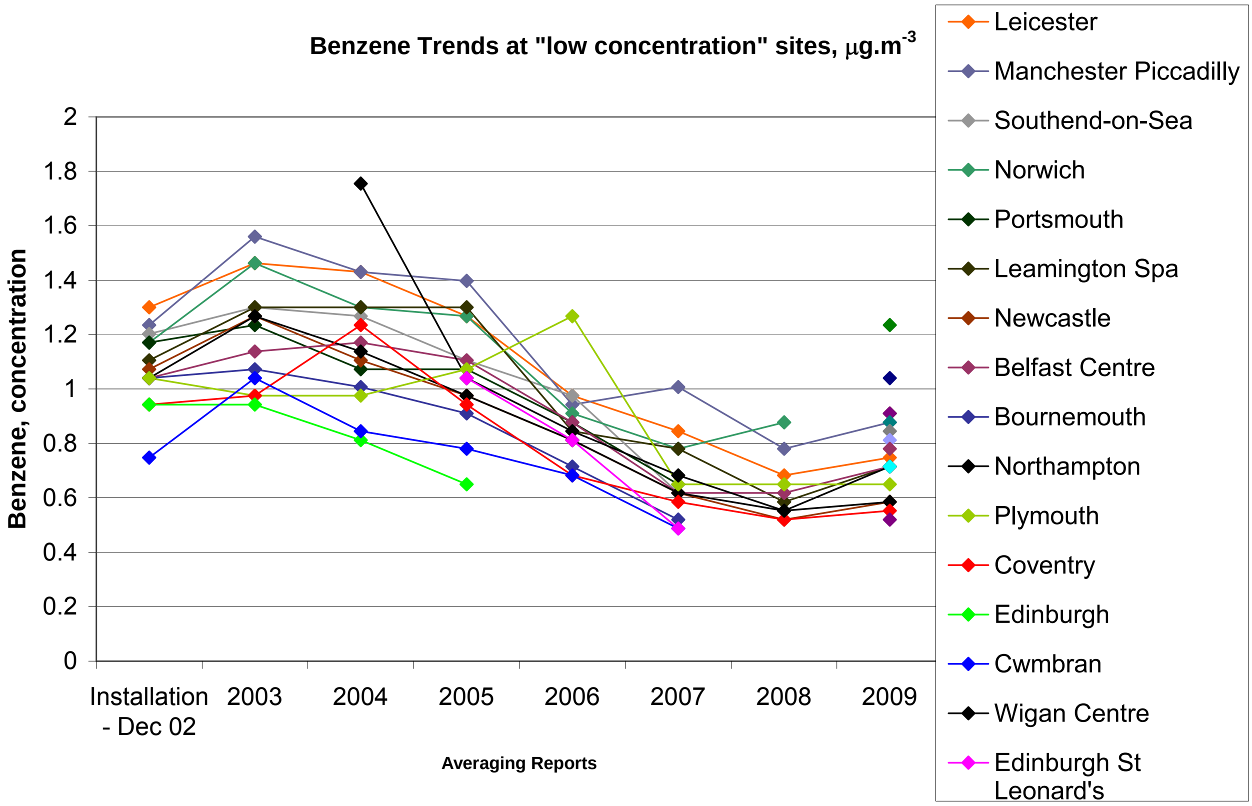


Figure 3: Recent annual average benzene concentrations at "low concentration" sites

The anomalous increases in concentration at Middlesbrough in 2005 and at Barnsley in 2004 and 2005 were due to local sources. It can be seen that concentrations for the last 3 years are fairly constant with the Network mean for 2007, 2008 and 2009 being 0.91, 0.81 and 0.85 µg/m^3 respectively.

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 4. 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 5. The most recent NAEI chart covers the period 1990 to 2007. It is notable that the NAEI trend since 2003 is for a small upward trend in benzene concentrations, while the measured concentrations from the Network show a downward trend over the same period. The fact that the road transport contribution shown in Figure 5 is decreasing would explain the continued drop at roadside locations, but the drop is also observed at urban centre and urban background sites.

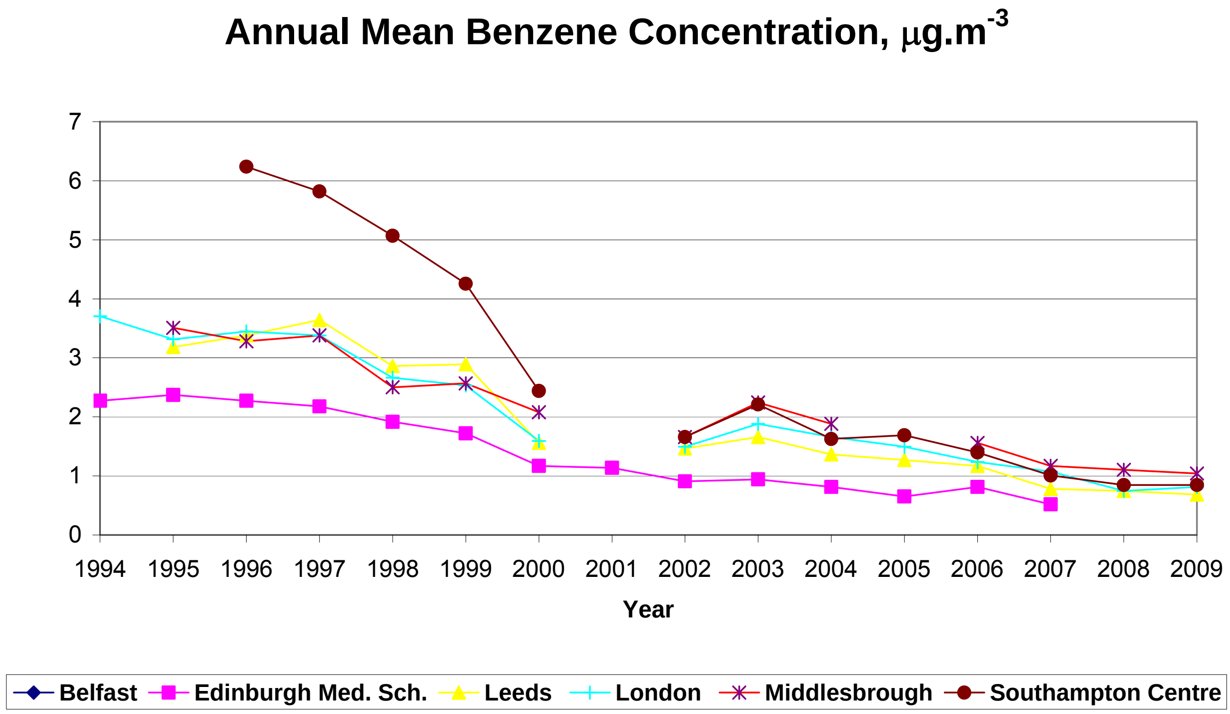


Figure 4: Long Term Trends in Benzene Concentration

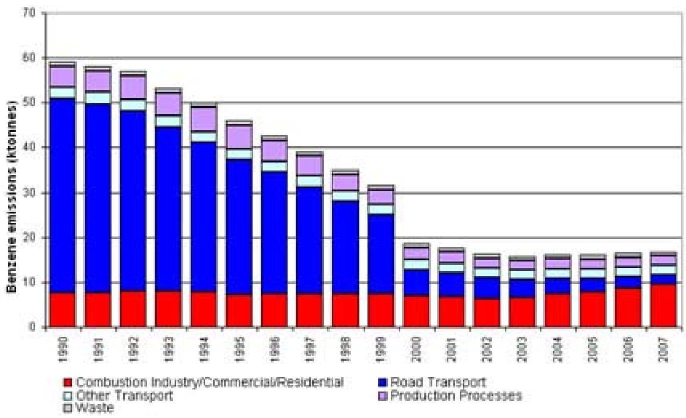


Figure 5: Emission Inventory Trend for Benzene

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 6.

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.

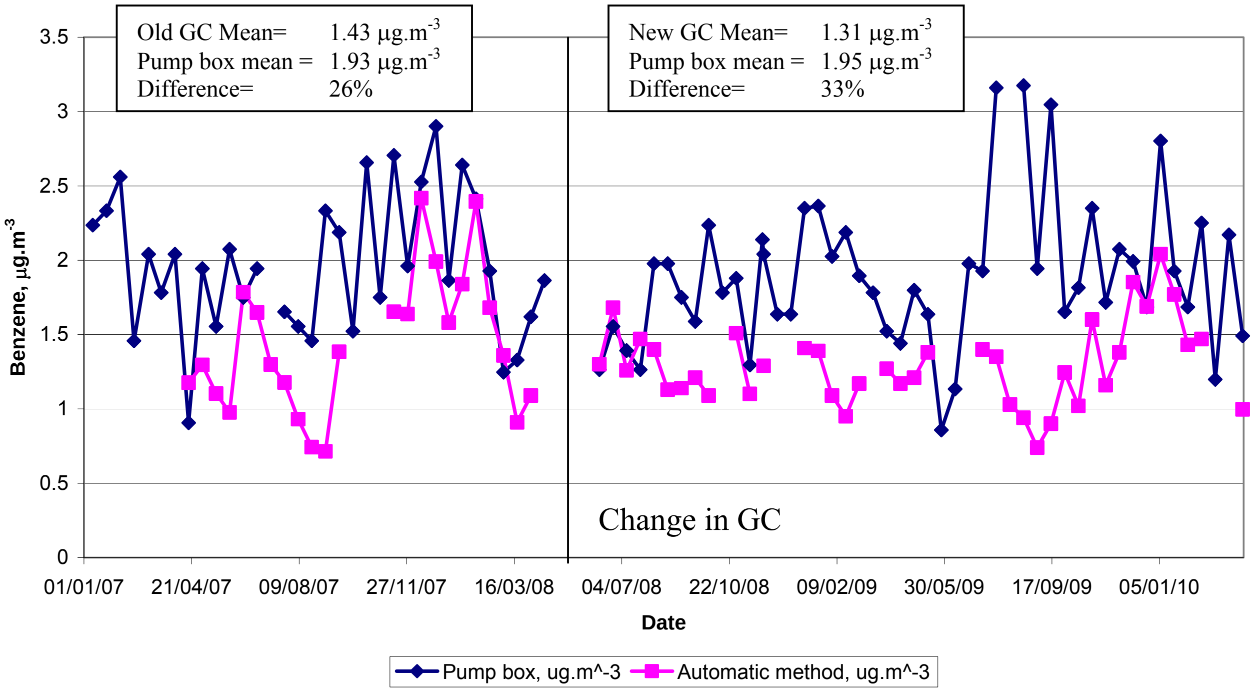


Figure 6: Comparison between pumped and automatic benzene data at Marylebone Road

4.2.2 Other Automatic Network sites

The available 2009 annual average concentrations for benzene on the Automatic Hydrocarbon Network are given in Table 5, with the 2007 and 2008 results for comparison.

Site	2007	2008	2009
Glasgow (Kerbside)	0.97 µg/m^3 (0.30 ppb)	1.04 µg/m^3 (0.32 ppb)	0.99 µg/m^3 (0.30 ppb)
London Eltham (urban background)	0.91 µg/m^3 (0.28 ppb)	0.73 µg/m^3 (0.22 ppb)	0.61 µg/m^3 (0.19 ppb)
Harwell (Rural)	0.33 µg/m^3 (0.10 ppb)	0.39 µg/m^3 (0.12 ppb)	0.35 µg/m^3 (0.11 ppb)

Table 5: Annual average benzene concentrations from the Automatic Hydrocarbon Network

Table 6 gives the Non-Automatic Network averages for different site classifications for comparison.

Site Classification	2007	2008	2009
Kerbside	1.95 µg/m^3 (0.60 ppb)	1.49 µg/m^3 (0.46 ppb)	1.24 µg/m^3 (0.38 ppb)
Roadside	1.35 µg/m^3 (0.42 ppb)	0.90 µg/m^3 (0.28 ppb)	0.98 µg/m^3 (0.30 ppb)
Urban Centre	0.84 µg/m^3 (0.26 ppb)	0.71 µg/m^3 (0.22 ppb)	0.75 µg/m^3 (0.23 ppb)
Urban Background	0.65 µg/m^3 (0.20 ppb)	0.64 µg/m^3 (0.20 ppb)	0.64 µg/m^3 (0.20 ppb)

The Non-Automatic Network has no sites in rural locations

Table 6: Annual average benzene 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. 2009 annual average benzene concentrations at sites not close to specific sources were all in the range 1.0 – 1.3 μg/m^3, while the two sites directly influenced by specific sources recorded 2.6 and 3.9 μg/m^3. These values are compatible with the Network concentration for the semi-industrial Grangemouth site of 1.33 μg/m^3.

4.4 Comparison with benzene modelling data

AEA Technology have supplied NPL with modelled (Pollution Climate Mapping, PCM) benzene data for the locations of Network sites in 2008, the most recent year available.

Table 8 gives the modelled data for 2007 and 2008 in the left hand columns. The next three columns give the Network data for the years 2007, 2008 and 2009 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 μg/m^3 are noted as implying the model predictions are "high" or "low". Differences greater than 1.0 μg/m^3 (seen in previous years) would be 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 2007 data, with all the main discrepancies being at roadside sites.

SITE (all concs in μg/m^3)	2007 modelled benzene	2008 modelled benzene	Measured benzene 2007	Measured benzene 2008	Measured benzene 2009	Mean measured 2007-09	Difference	Model implic-ation
Barnsley Gawber	0.66	0.68	0.58	0.55	0.55	0.56	0.12	
Belfast Centre	0.72	0.65	0.62	0.62	0.72	0.65	0.00	
Bloomsbury	1.39	1.00	1.07	0.75	0.81	0.88	0.12	
Bristol Old Market (rs)	1.00	0.80	1.33	1.11	1.24	1.23	-0.43	Low
Coventry Memorial Park	0.54	0.46	0.58	0.52	0.55	0.55	-0.09	
Haringey Roadside	1.20	0.96	1.52	1.14	1.14	1.27	-0.31	Low
Leamington Spa	0.57	0.54	0.78	0.59	0.72	0.70	-0.16	
Leeds Centre	0.81	0.62	0.78	0.75	0.68	0.74	-0.12	
Leicester Centre	0.81	0.71	0.84	0.68	0.75	0.76	-0.05	
Manchester Piccadilly	0.90	0.69	1.00	0.78	0.88	0.89	-0.20	
Newcastle Centre	0.77	0.61	0.62	0.52	0.59	0.58	0.03	
Northampton	0.46	0.47	0.62	0.55	0.59	0.59	-0.12	
Nottingham Centre	0.79	0.67	0.84	0.75	0.78	0.79	-0.12	
Oxford Centre	0.56	0.51	0.78	0.72	0.78	0.76	-0.25	
Plymouth Centre	0.43	0.47	0.65	0.65	0.65	0.65	-0.18	
Sheffield Centre	0.79	0.63	0.94	0.62	0.75	0.77	-0.14	
Wigan Centre	0.55	0.47	0.68	0.55	0.72	0.65	-0.18	
Yarm (roadside)	0.54	0.53	1.81	1.40	0.72	1.31	-0.78	Low

Table 8: comparison between recent benzene data and modelled data

5. South Killingholme

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 (AEA Technology[1]) that showed a possible exceedence of

[1] Kent, A.J., Grice, S.E., Stedman, J.R., Bush, T.J., Vincent, K.J., Abbott, J., Hobson, M. and Derwent, R.G. (2007). UK air quality modelling for annual reporting 2005 on ambient air quality assessment under Council Directives 96/62/EC, 1999/30/EC and 2000/69/EC. Report to the Department for Environment, Food and Rural Affairs, the Scottish Executive, Welsh Assembly Government and the Department of the Environment in Northern Ireland. AEA report. AEAT/ENV/R/2278 Issue 1. http://www.airquality.co.uk/archive/reports/reports.php?report_id=453

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 0.85 µg/m^3, while the average for 2009 was 1.04 µg/m^3. The highest fortnightly benzene concentration measured was between 13/12/09 to 04/01/10 and gave a concentration of 2.9 µg/m^3.

More recent modelling results (AEA Technology[2]) 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, the Acetate Products factory in Spondon. Annual average concentrations from the NPL pumped sampler are shown in Table 9:

Year	Benzene (µg/m^3)
2005	13.3
2006	7.64
2007	5.69
2008	5.79
2009	6.21

Table 9: 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.

Figure 9 shows the time series of the measurements over the year. The data capture is 82% due to power cuts at the monitoring site. This can have a significant effect as in 2009 the council switched to 4 weekly sampling, however the data capture is above the threshold of 75% required for an annual average to be calculated.

[2] Grice, S.E., Cooke, S.L., Stedman, J.R., Bush, T.J., Vincent, K.J., Hann, M., Abbott, J. and Kent, A.J. (2009). UK air quality modelling for annual reporting 2007 on ambient air quality assessment under Council Directives 96/62/EC, 1999/30/EC and 2000/69/EC. Report to the Department for Environment, Food and Rural Affairs, the Scottish Executive, Welsh Assembly Government and the Department of the Environment in Northern Ireland. AEA report. AEAT/ENV/R/2656 Issue 1. http://www.airquality.co.uk/reports/cat09/0905061048_dd12007mapsrep_v8.pdf

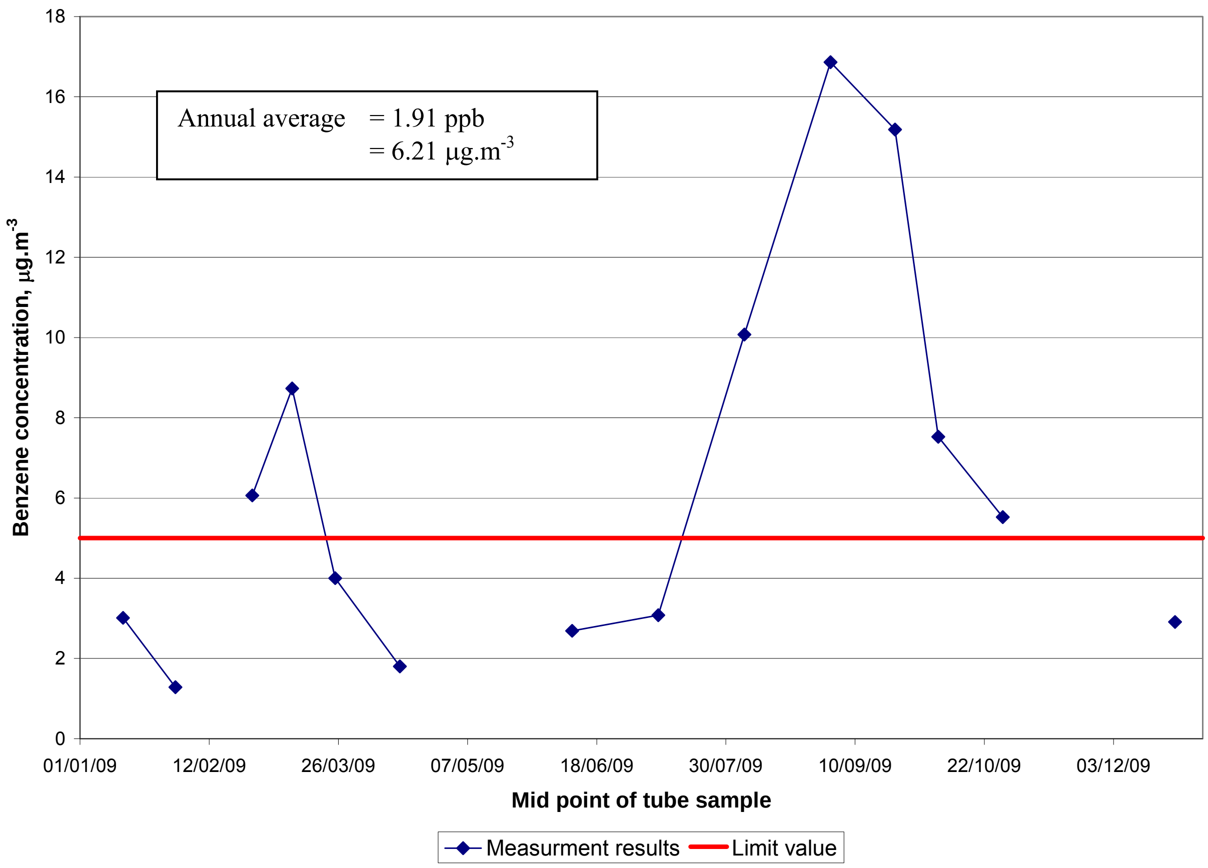


Figure 9 **Time series of benzene concentrations measured by the Derby Spondon pump box**

Table 10 shows the capital investment work that the Acetate Products plant has carried out over the last 10 years. 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 steal pipes with stainless teal to reduce likelihood of leaks. Replacement of benzene pumps with self-priming pumps to reduce emissions on start up.
2008 - 2009	Installation of standby units on an existing abatement system, plus installation of conservation venting on solvent sumps.

Table 10 **Abatement Measures**

The plant considers that the ability of the active LDAR and the OPSIS system to identify abnormal levels are the main reasons for the reduced emissions of benzene from the site.

The Local Authority expects that the 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. It is not clear 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 Carbopack 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 Carbopack 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 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).

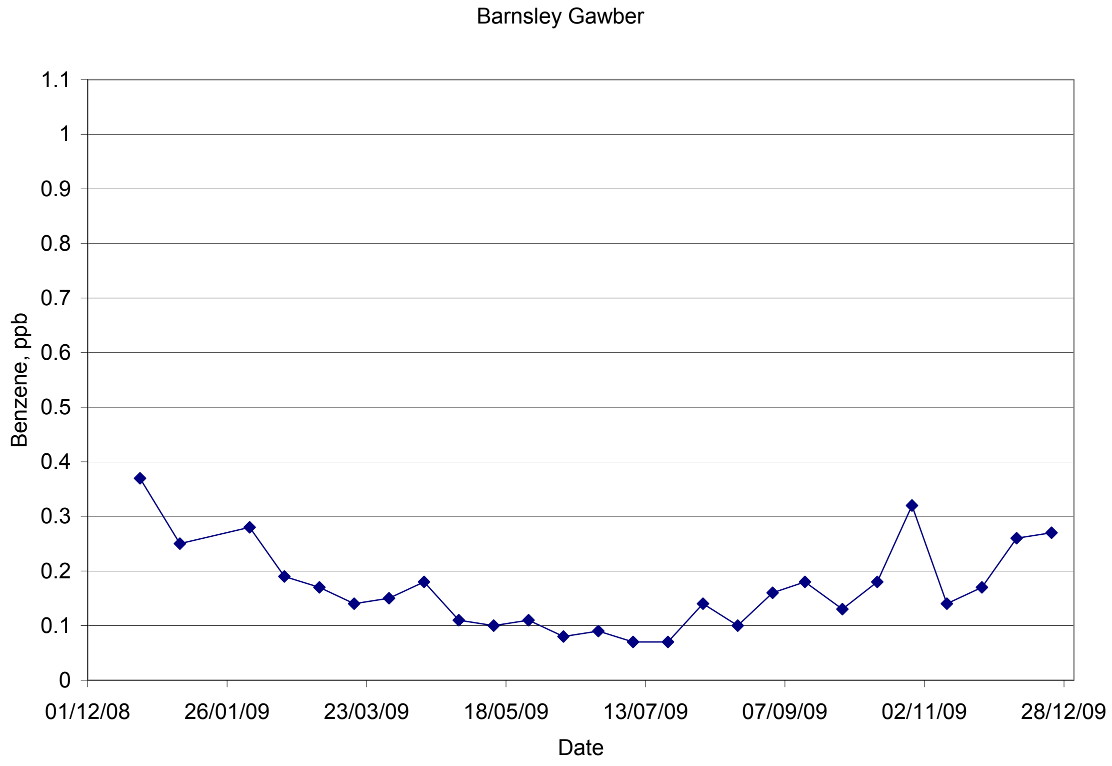
A related paper has been submitted to J Geophysical Research.

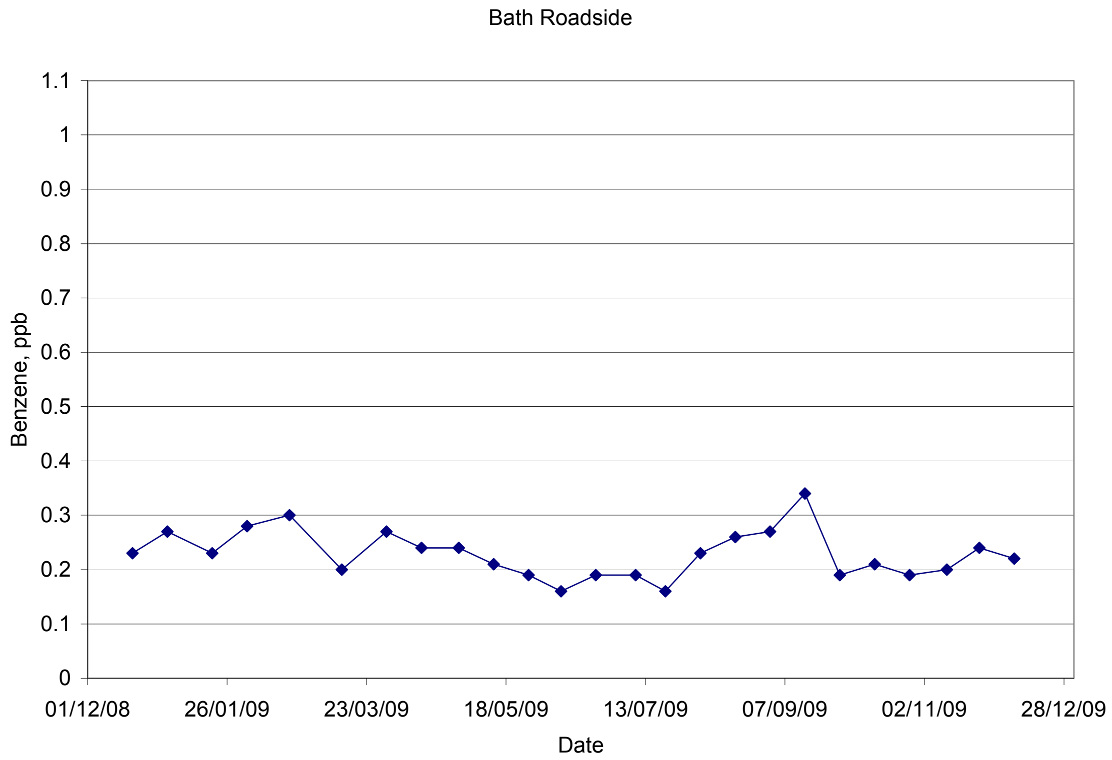
EC intercomparison of VOC measurements between national reference laboratories, P Pérez Ballesta et al, EUR 23529 EN.

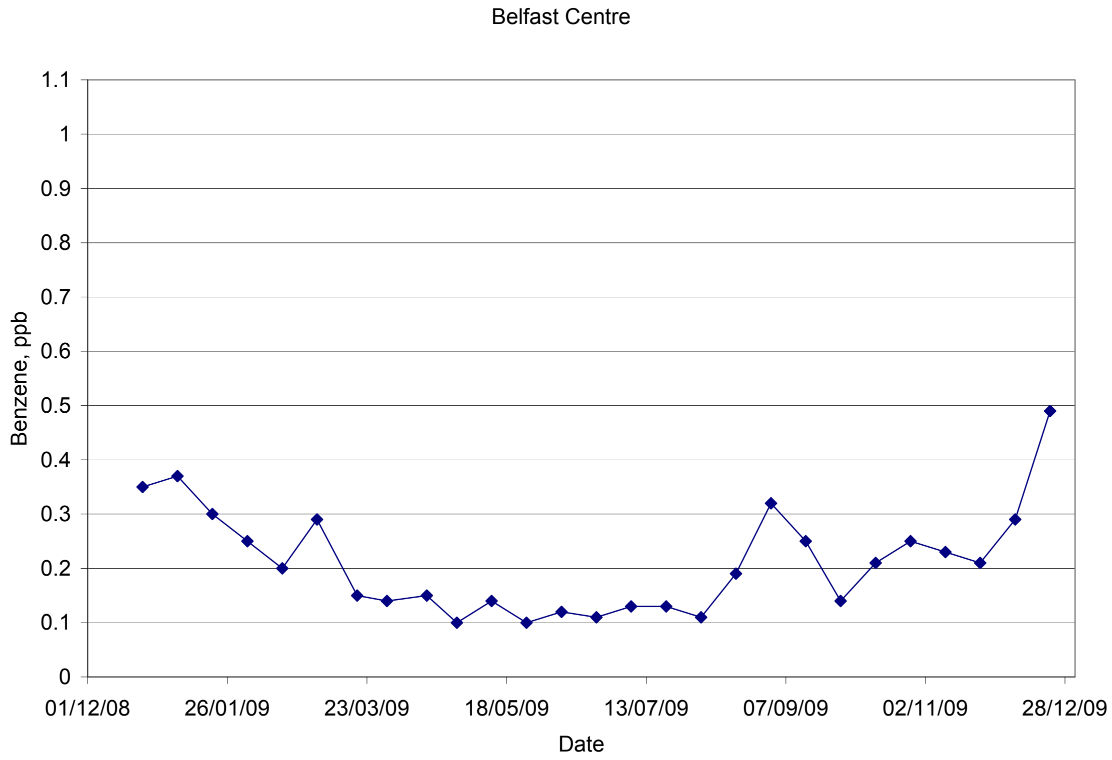
Annex 1 – 2009 Audit Schedule

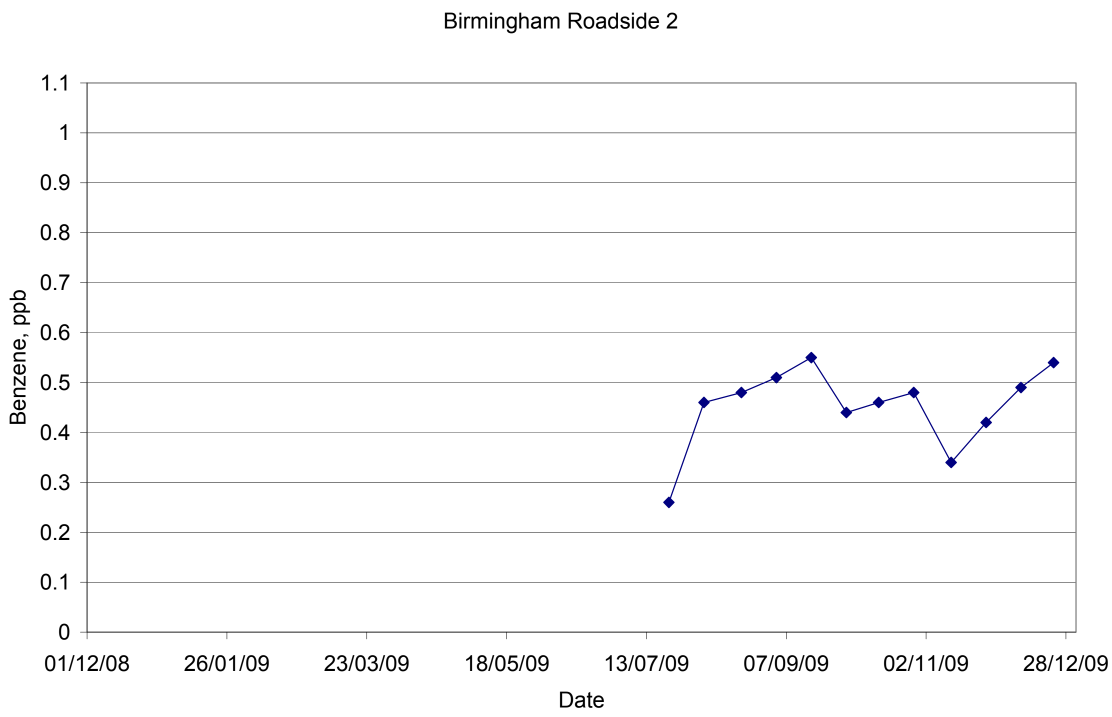
Site	Date	Date	Date	Date
Barnsley Gawber	24/02/2009	15/09/2009		
Bath Roadside	17/03/2009	06/10/2009		
Belfast Centre	27/01/2009	16/06/2009		
Birmingham Roadside 1	19/02/2009			
Birmingham Roadside 2	22/07/2009			
Birmingham Tyburn	08/04/2009	21/10/2009		
Bloomsbury	27/04/2009	02/10/2009		
Bristol Old Market	17/03/2009	07/10/2009		
Bury Roadside	21/01/2009	08/07/2009	03/09/2009	
Cambridge Roadside	04/02/2009	14/07/2009		
Camden Kerbside	14/04/2009	15/10/2009		
Carlisle Caldewgate	28/04/2009	27/10/2009		
Chesterfield	11/02/2009	02/09/2009		
Coventry Memorial Park	10/03/2009	14/10/2009		
Eaglescliffe - Yarm	26/03/2009	25/09/2009		
Grangemouth	28/04/2009	28/10/2009		
Haringey Roadside	05/02/2009	20/08/2009		
Killingholme	11/02/2009			
Leamington Spa	10/03/2009	14/10/2009		
Leeds Centre	24/02/2009	02/09/2009		
Leicester Centre	27/02/2009	11/08/2009		
Liverpool Speke	26/01/2009	21/07/2009		
Manchester Piccadilly	20/01/2009	07/07/2009		
Middlesbrough	26/03/2009	24/09/2009	16/12/2009	
Newcastle	26/03/2009	24/09/2009		
Northampton	12/02/2009	23/04/2009	19/08/2009	
Norwich - Lakenham	11/11/2009			
Nottingham Centre	26/02/2009	11/08/2009		
Oxford Centre	03/04/2009	26/06/2009		
Oxford St Ebbes	03/04/2009	26/06/2009		
Plymouth	17/03/2009	06/10/2009		
Sheffield	11/02/2009	26/05/2009	08/06/2009	02/09/2009
Southampton	15/01/2009	18/08/2009		
Stoke Centre	26/01/2009	21/07/2009		
Wigan Centre	20/01/2009	07/07/2009		
York Fishergate RS	25/02/2009	15/09/2009		

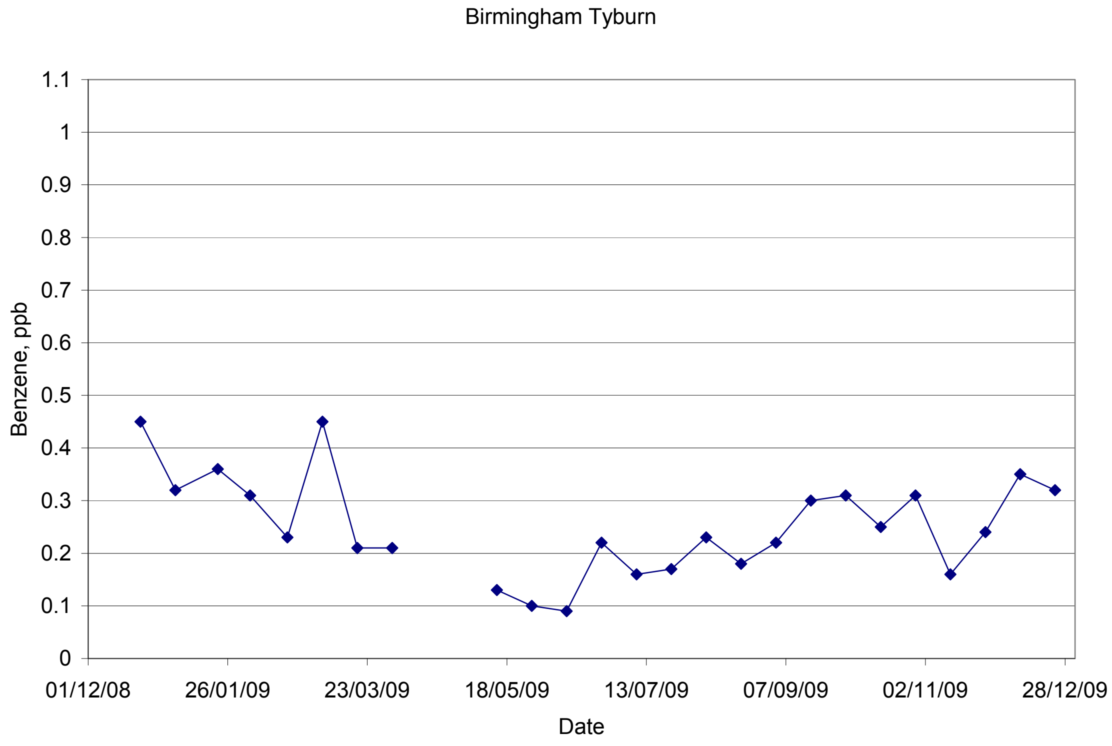
Annex 2 – 2009 Benzene Concentration Data






Belfast Centre
Benzene, ppb
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
01/12/08
26/01/09
23/03/09
18/05/09
13/07/09
07/09/09
02/11/09
28/12/09
Date


Birmingham Roadside 2
Benzene, ppb
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
01/12/08
26/01/09
23/03/09
18/05/09
13/07/09
07/09/09
02/11/09
28/12/09
Date


Birmingham Tyburn
Benzene, ppb
Date
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
1.1
01/12/08
26/01/09
23/03/09
18/05/09
13/07/09
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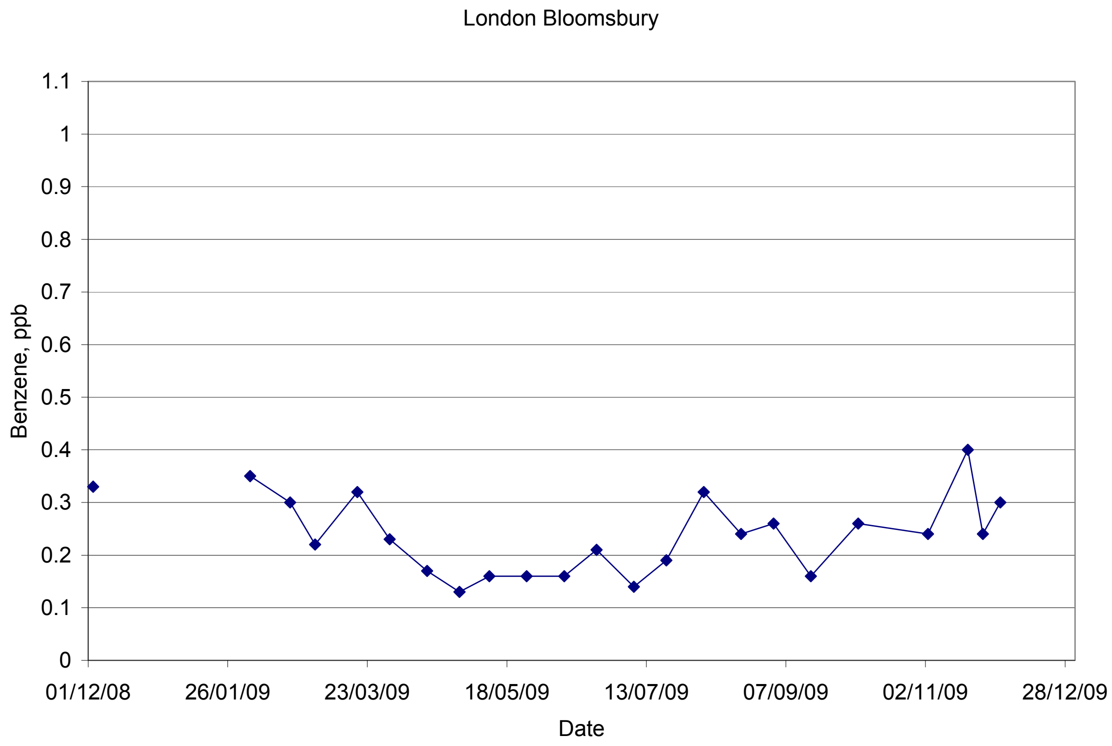
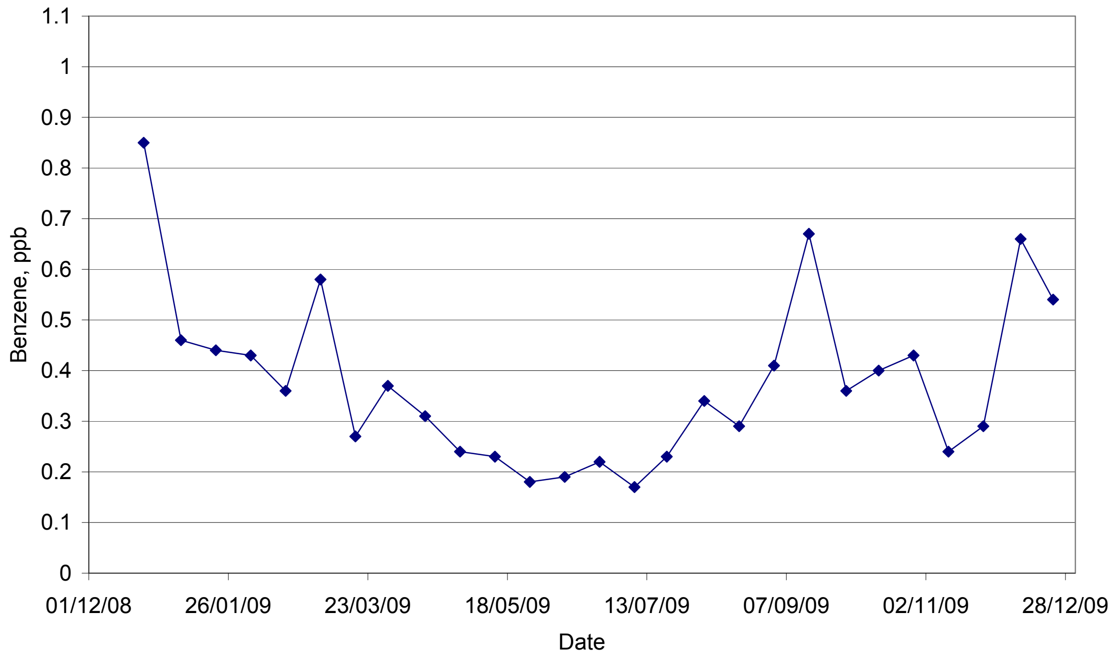
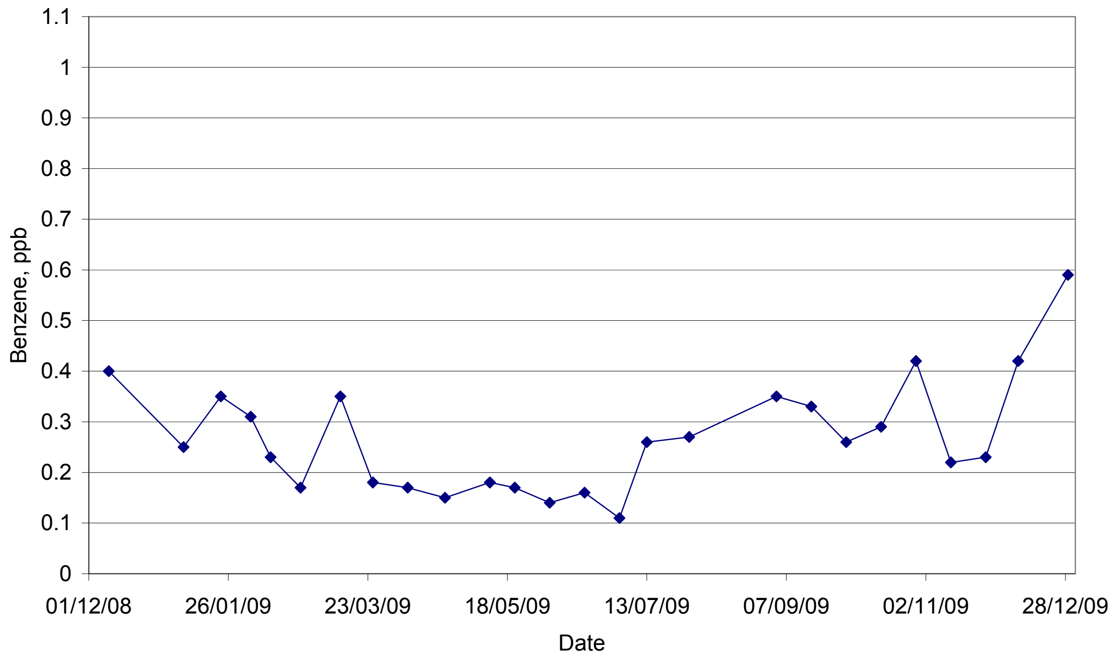
02/11/09
28/12/09

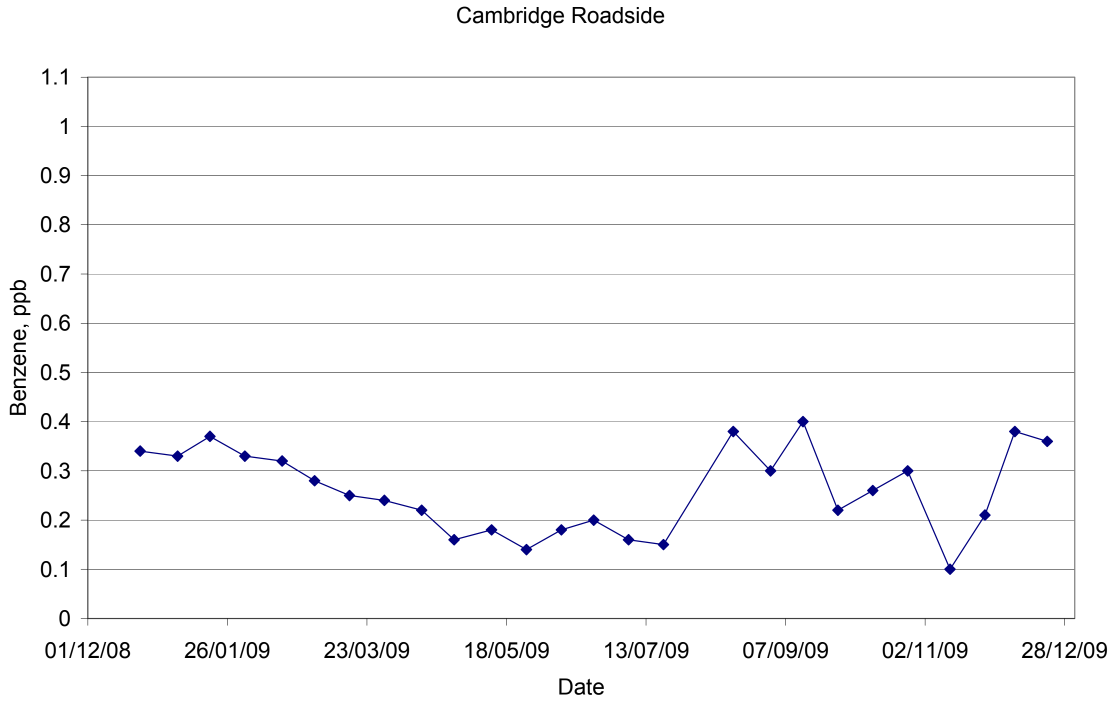

London Bloomsbury
Benzene, ppb
Date
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
1.1
01/12/08
26/01/09
23/03/09
18/05/09
13/07/09
07/09/09
02/11/09
28/12/09

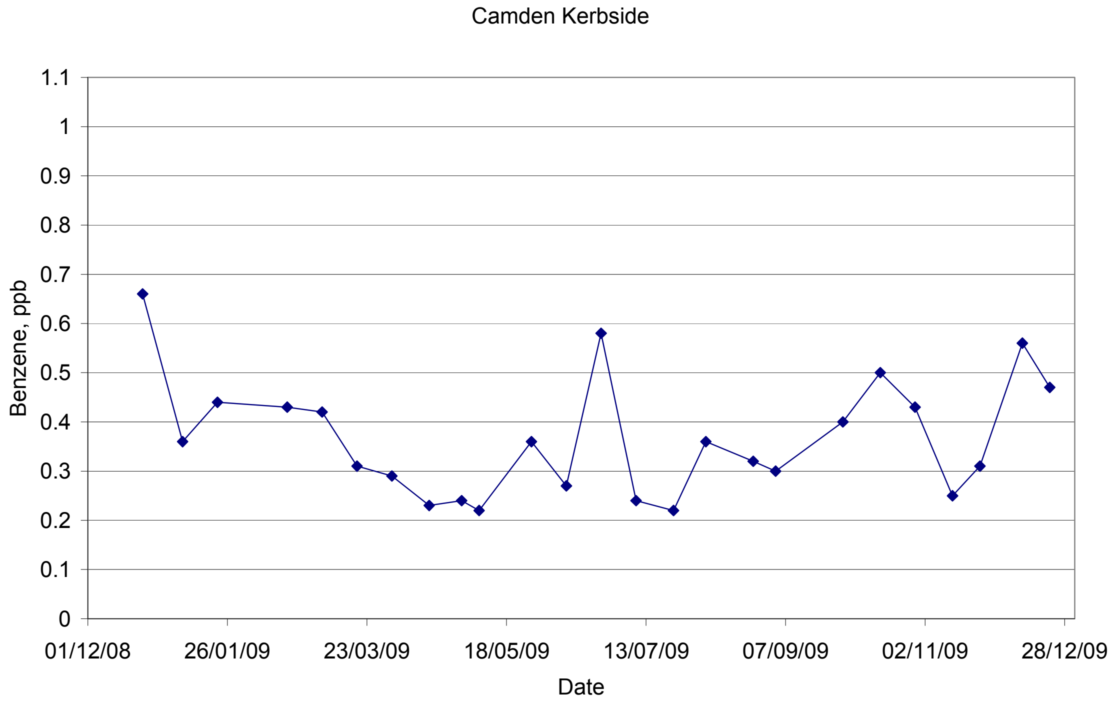
Bristol Old Market

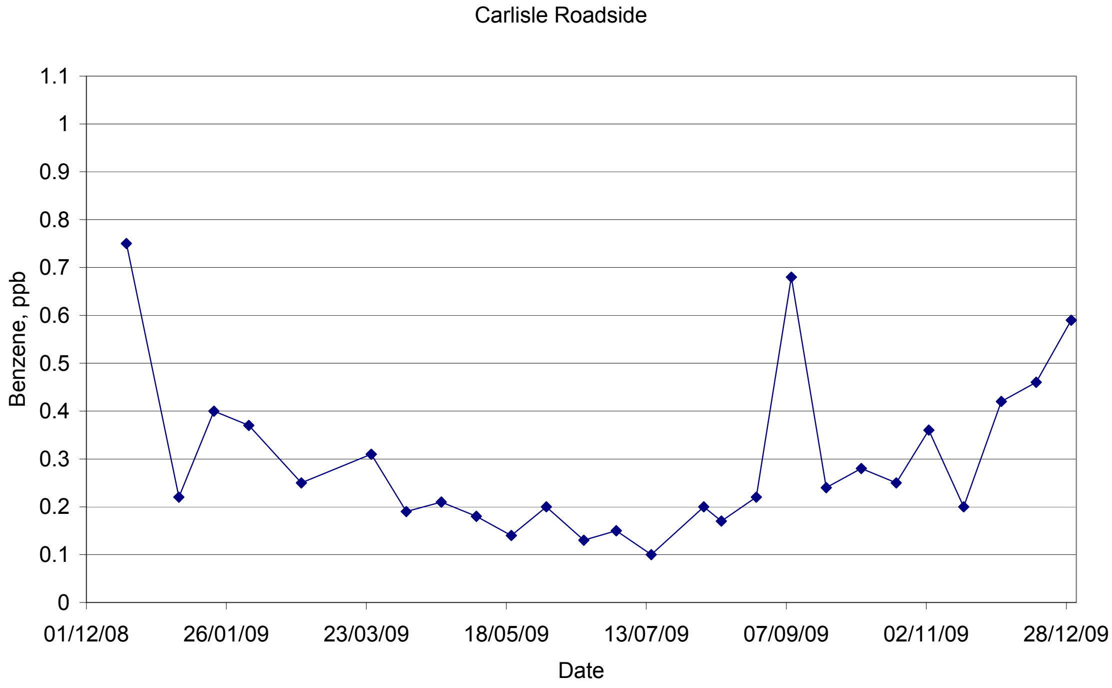


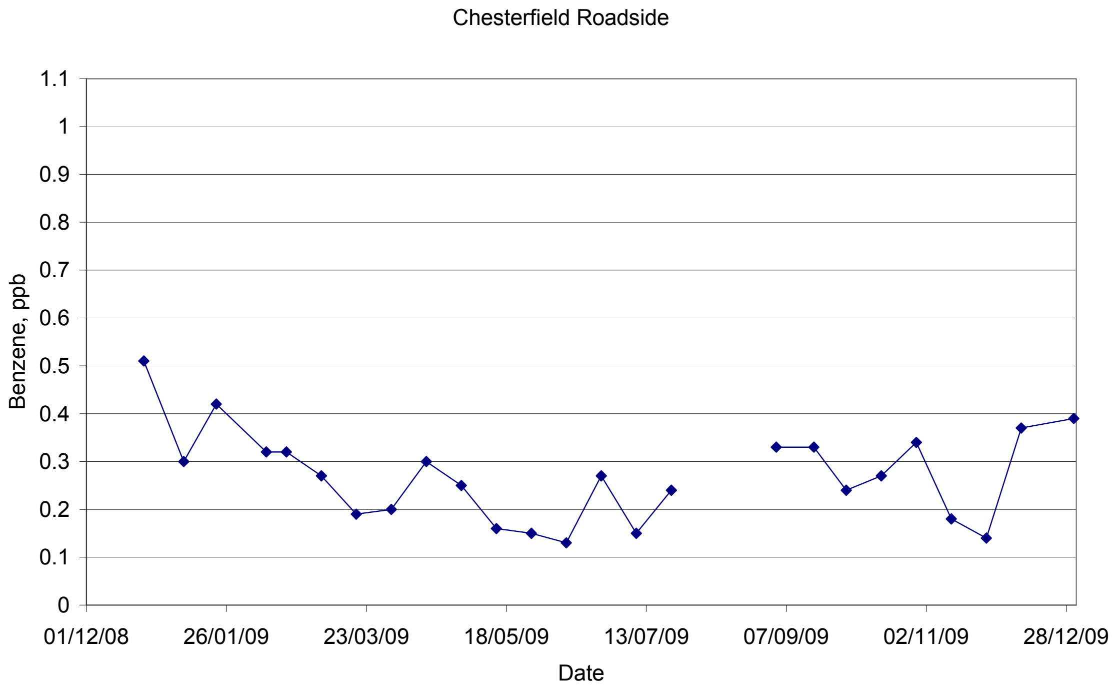
Bury Roadside




Cambridge Roadside
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Benzene, ppb
01/12/08
26/01/09
23/03/09
18/05/09
13/07/09
07/09/09
02/11/09
28/12/09
Date


Camden Kerbside
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Benzene, ppb
01/12/08
26/01/09
23/03/09
18/05/09
13/07/09
07/09/09
02/11/09
28/12/09
Date


Carlisle Roadside
Benzene, ppb
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
01/12/08
26/01/09
23/03/09
18/05/09
13/07/09
07/09/09
02/11/09
28/12/09
Date


Chesterfield Roadside
Benzene, ppb
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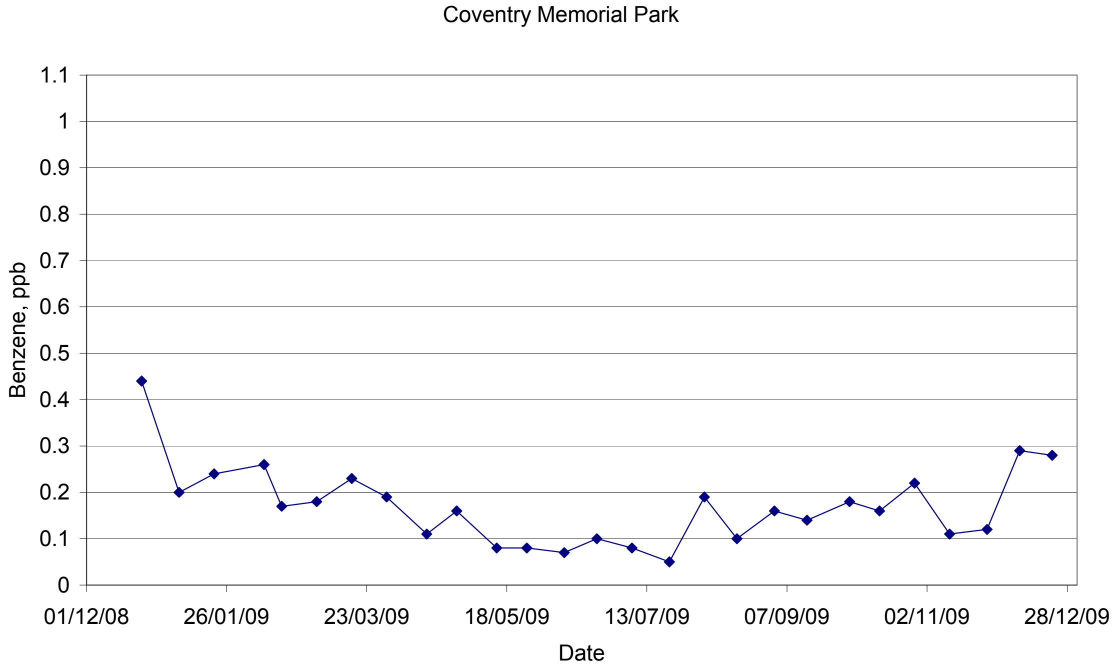
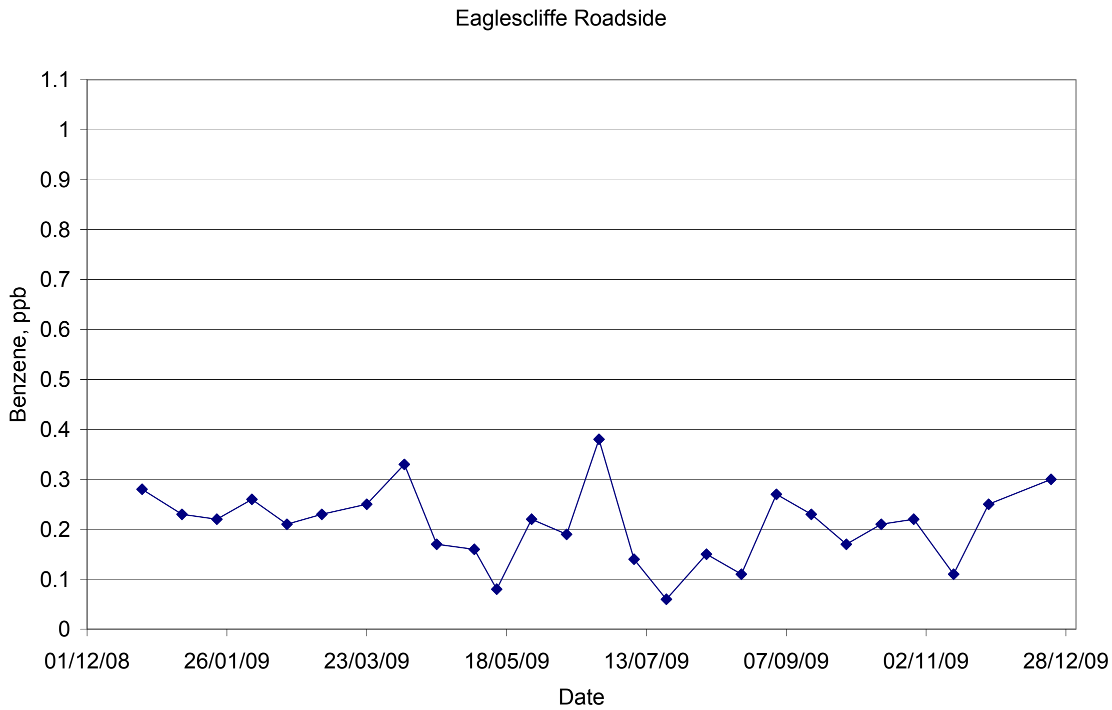
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
01/12/08
26/01/09
23/03/09
18/05/09
13/07/09
07/09/09
02/11/09
28/12/09
Date


Coventry Memorial Park
Benzene, ppb
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
01/12/08
26/01/09
23/03/09
18/05/09
13/07/09
07/09/09
02/11/09
28/12/09
Date


Eaglescliffe Roadside
Benzene, ppb
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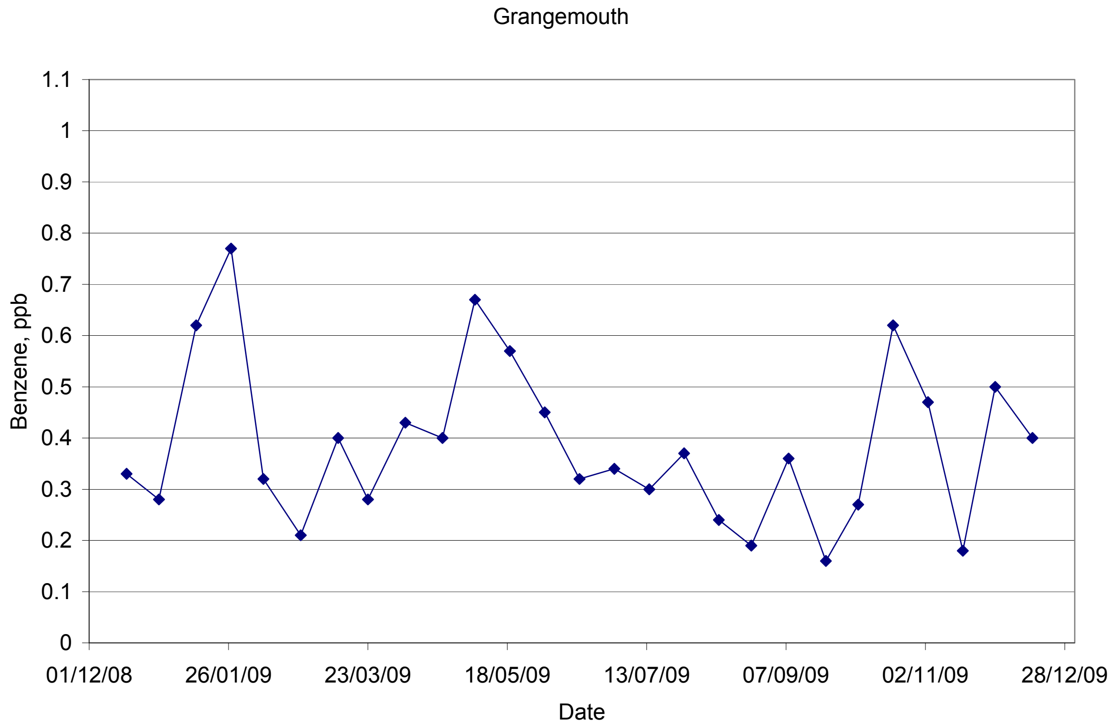
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
01/12/08
26/01/09
23/03/09
18/05/09
13/07/09
07/09/09
02/11/09
28/12/09
Date


Grangemouth
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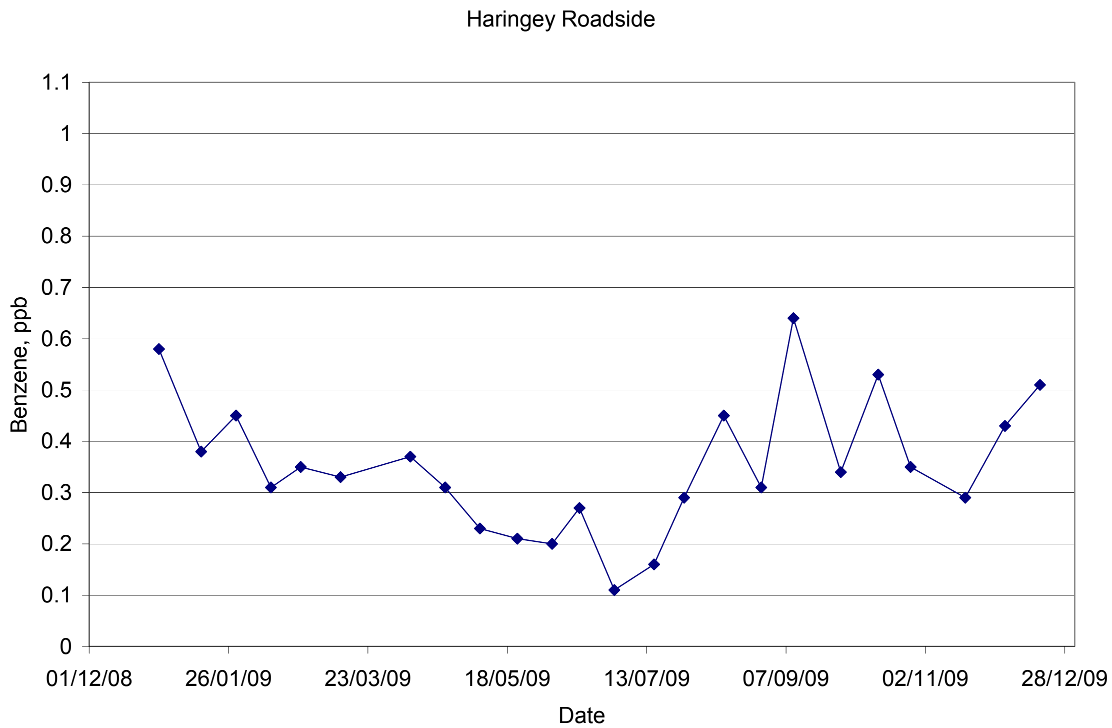
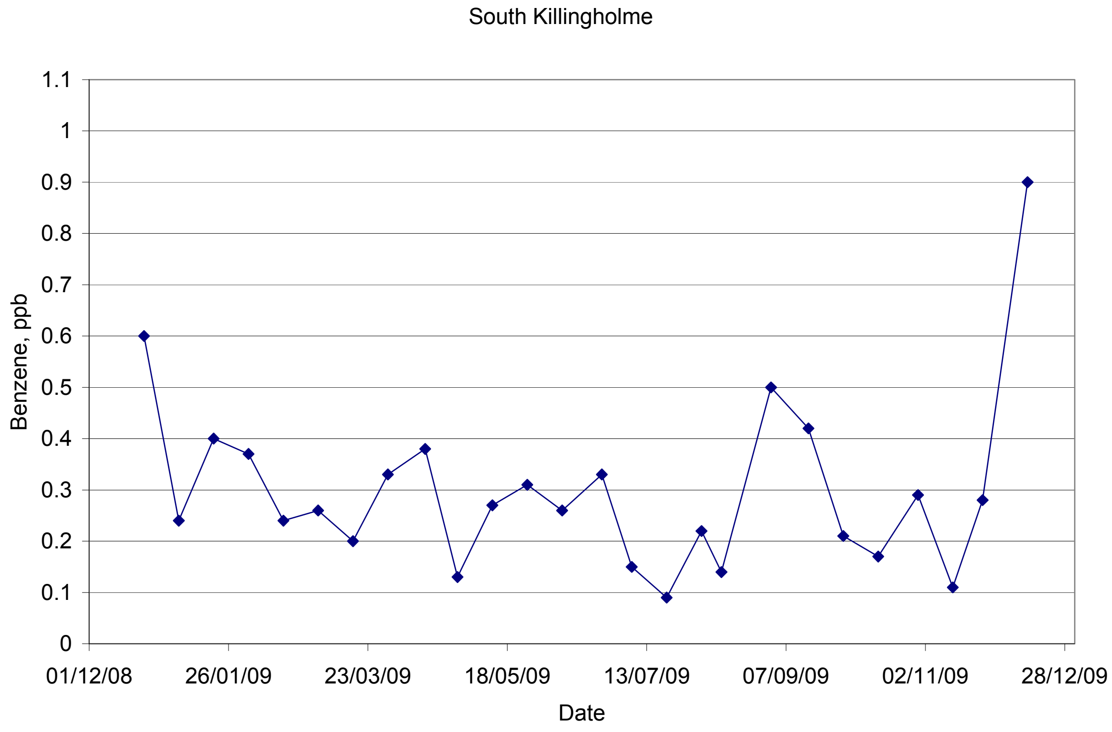
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Benzene, ppb
01/12/08
26/01/09
23/03/09
18/05/09
13/07/09
07/09/09
02/11/09
28/12/09
Date


Haringey Roadside
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Benzene, ppb
01/12/08
26/01/09
23/03/09
18/05/09
13/07/09
07/09/09
02/11/09
28/12/09
Date


South Killingholme
Benzene, ppb
1.1
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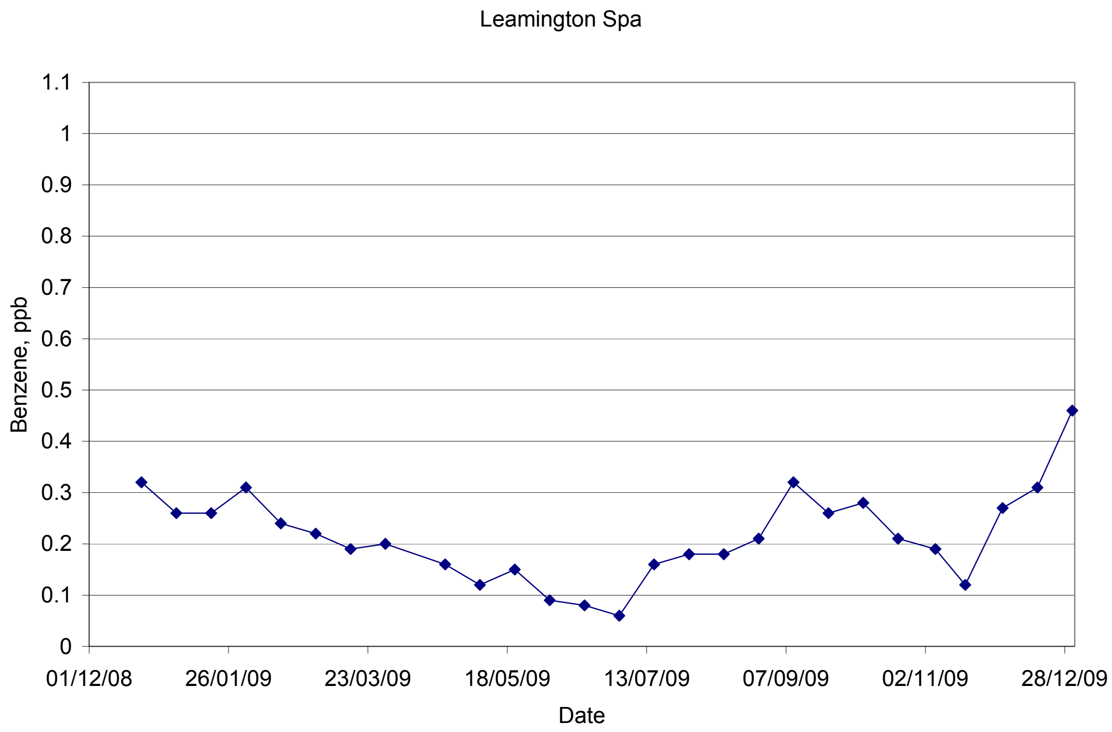
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
01/12/08
26/01/09
23/03/09
18/05/09
13/07/09
07/09/09
02/11/09
28/12/09
Date


Leamington Spa
Benzene, ppb
1.1
1
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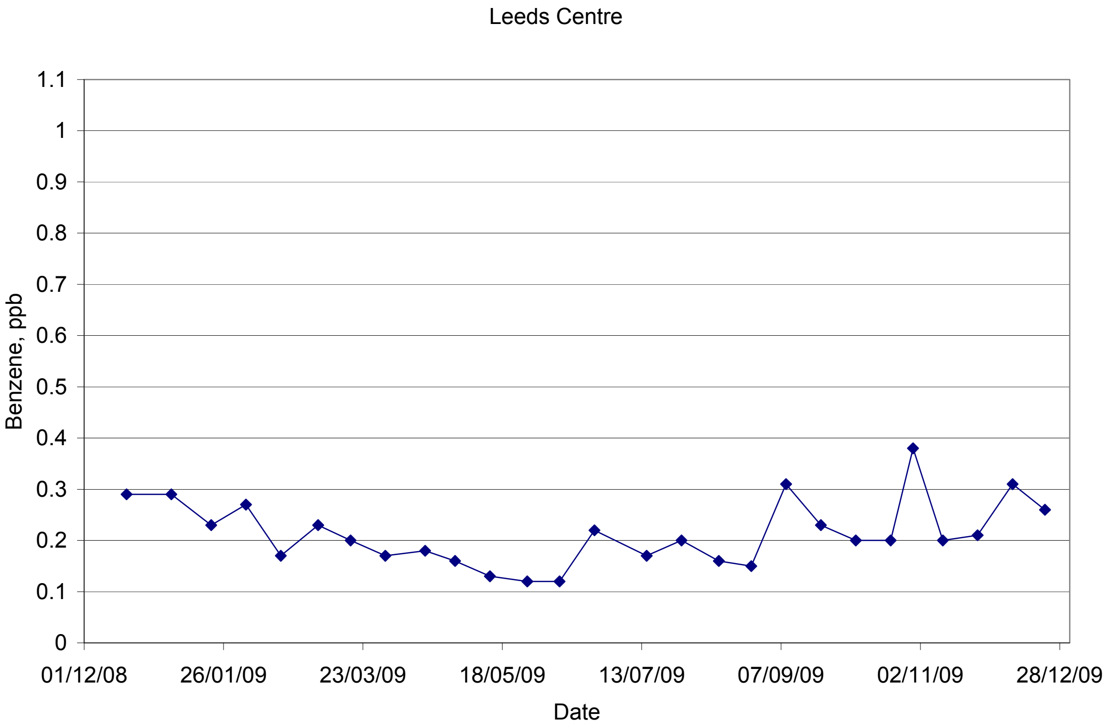
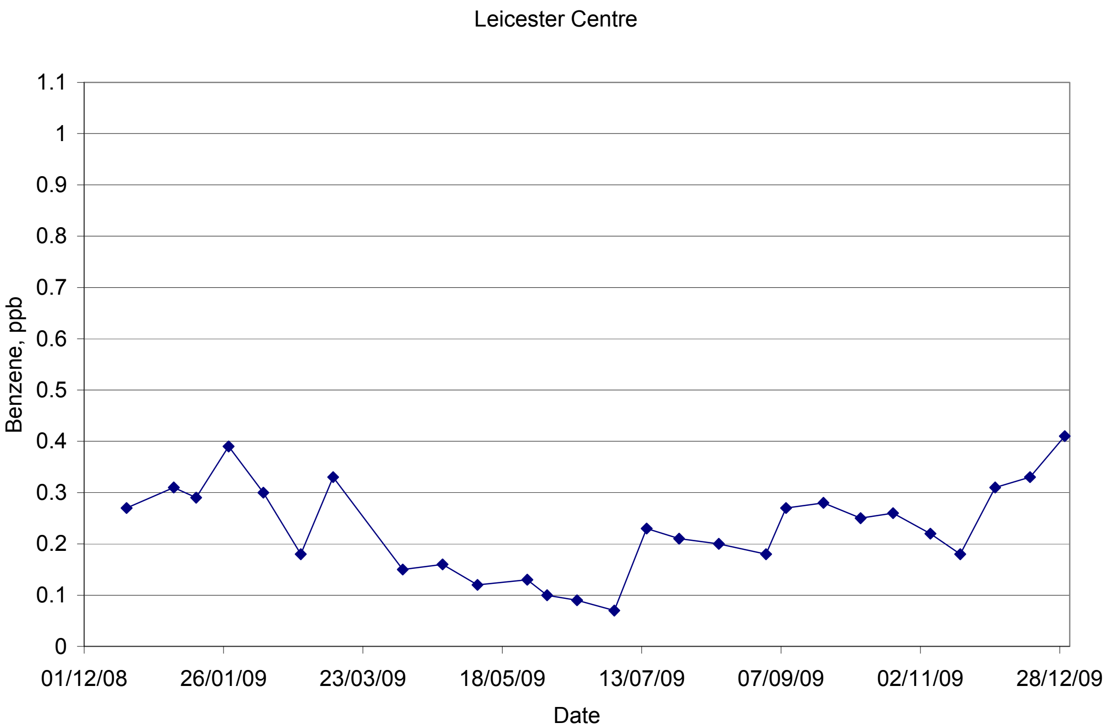
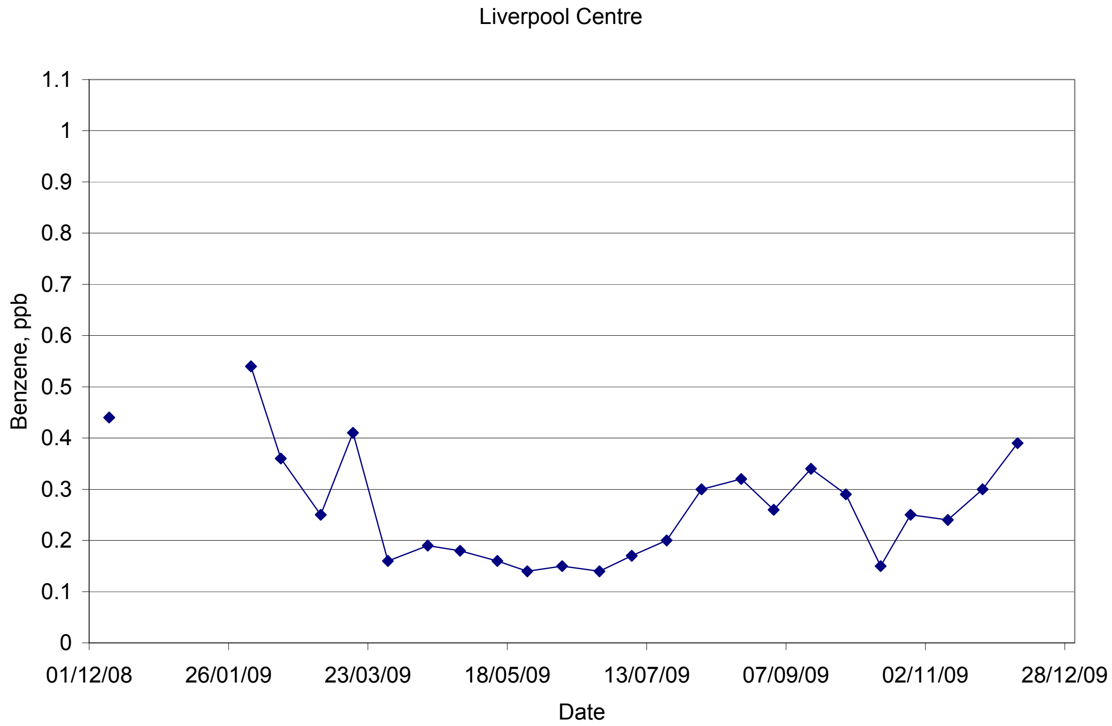
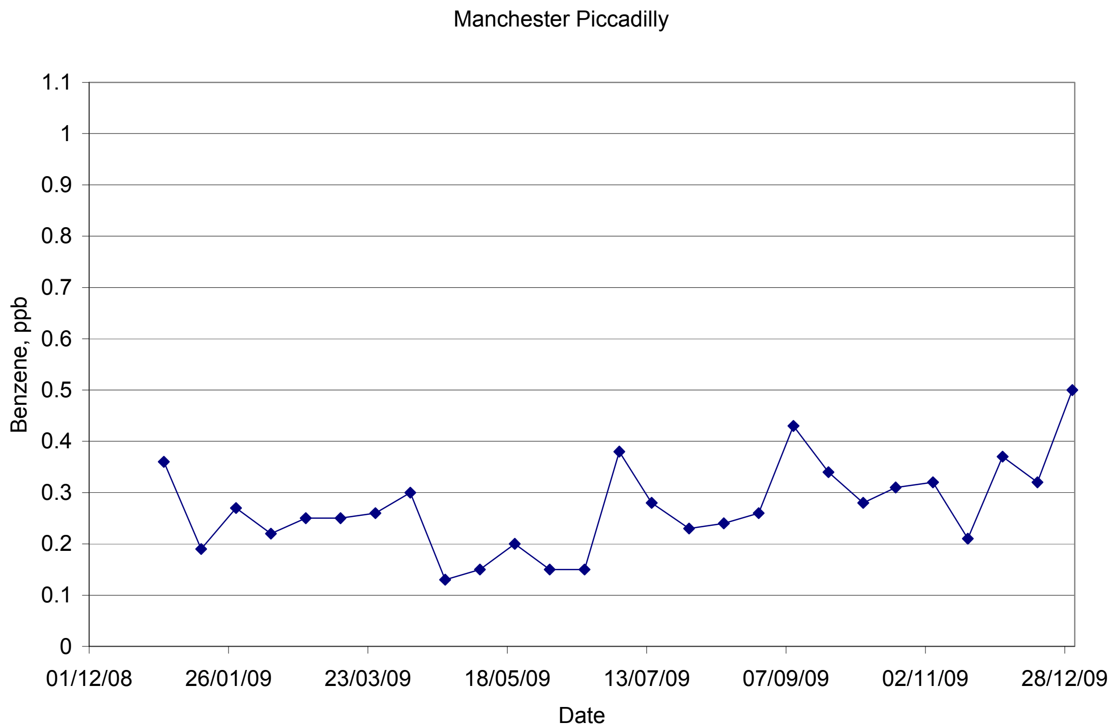
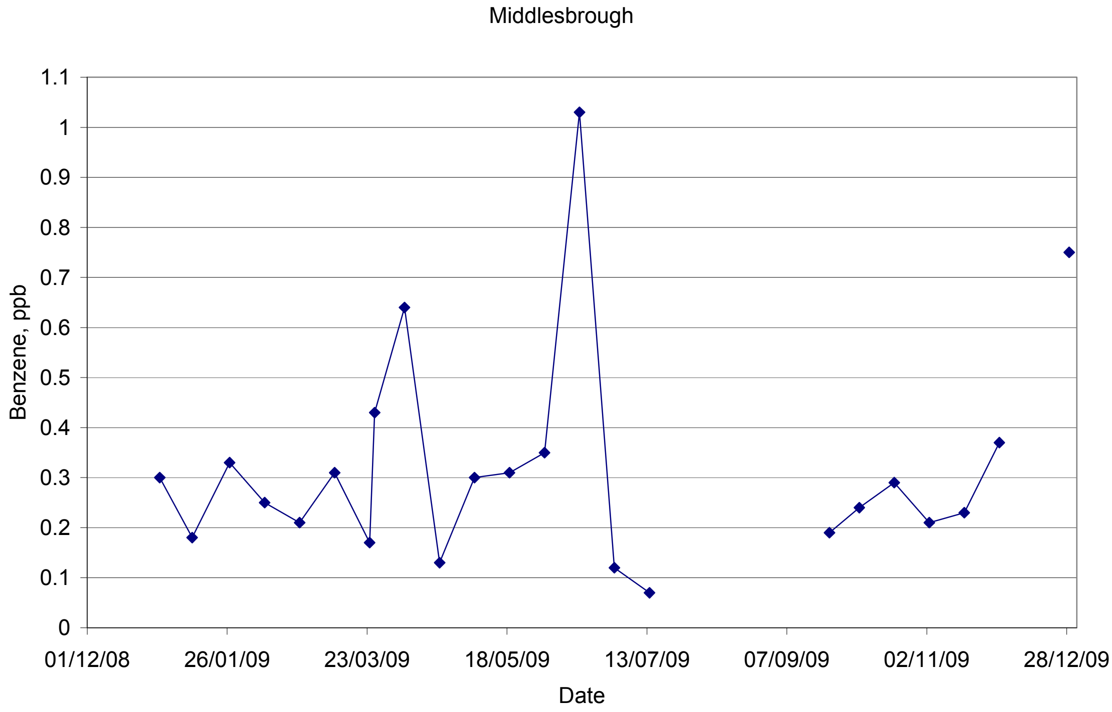
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
01/12/08
26/01/09
23/03/09
18/05/09
13/07/09
07/09/09
02/11/09
28/12/09
Date

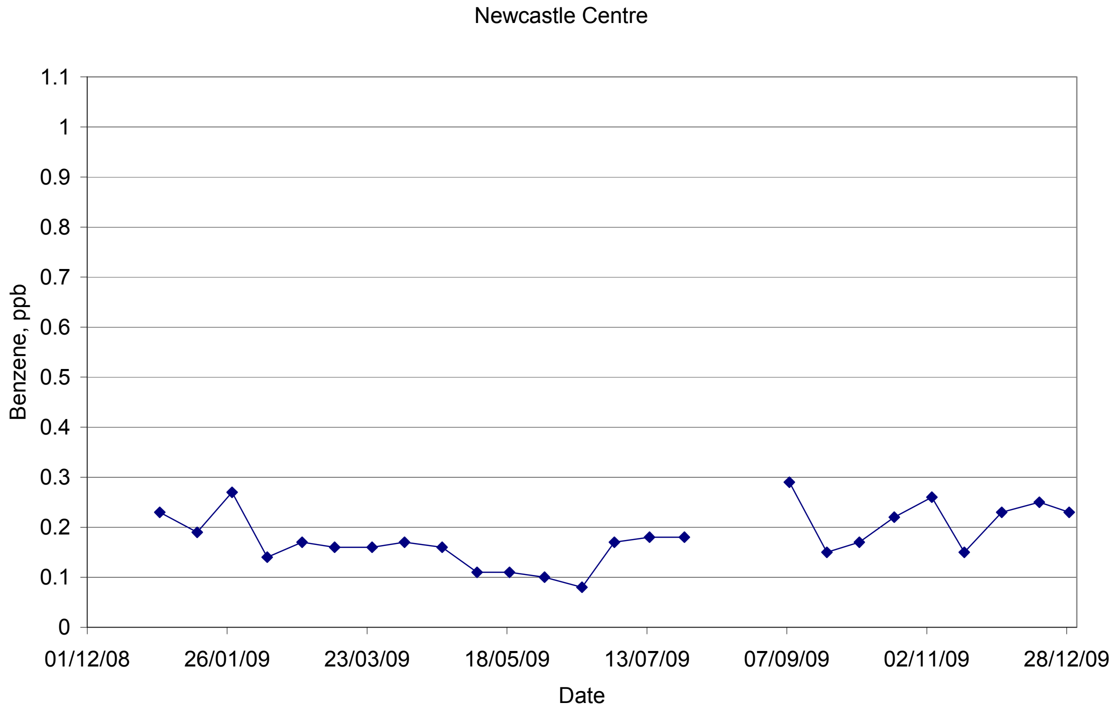

Leeds Centre
Benzene, ppb
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
01/12/08
26/01/09
23/03/09
18/05/09
13/07/09
07/09/09
02/11/09
28/12/09
Date

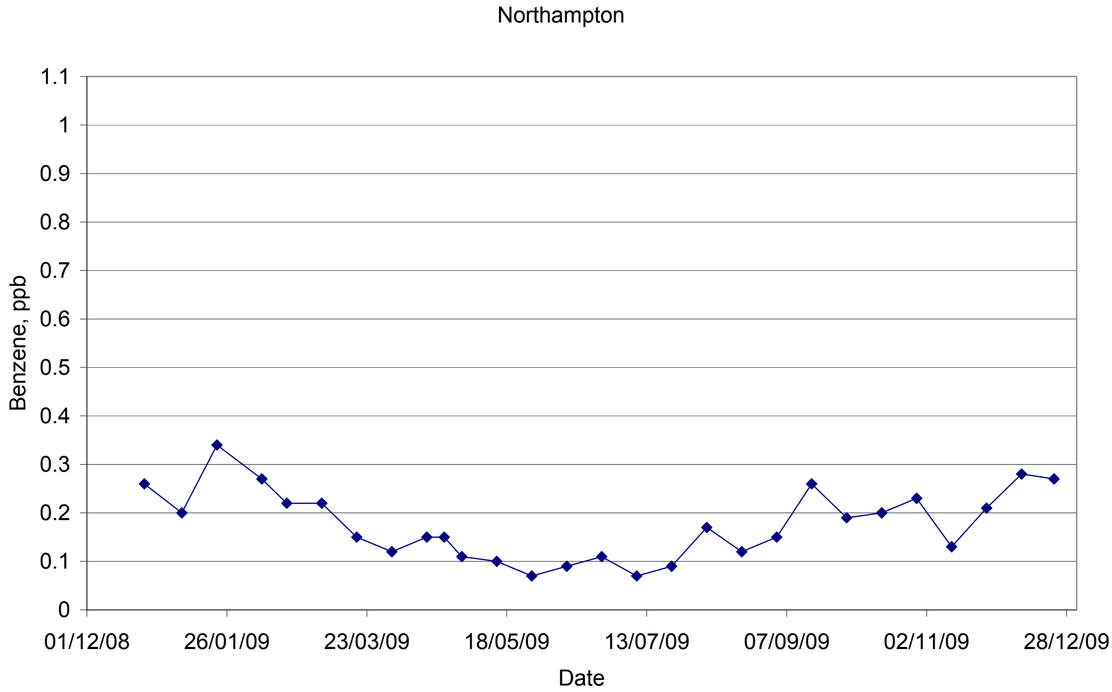

Leicester Centre
Benzene, ppb
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
01/12/08
26/01/09
23/03/09
18/05/09
13/07/09
07/09/09
02/11/09
28/12/09
Date

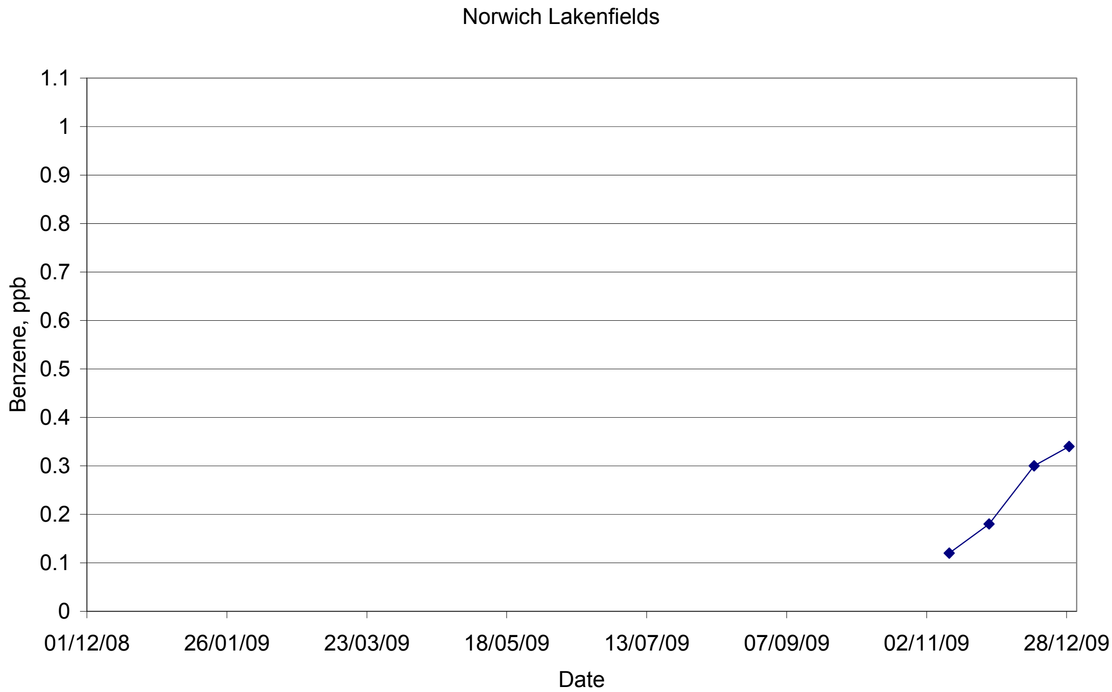

Liverpool Centre
Benzene, ppb
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
01/12/08
26/01/09
23/03/09
18/05/09
13/07/09
07/09/09
02/11/09
28/12/09
Date

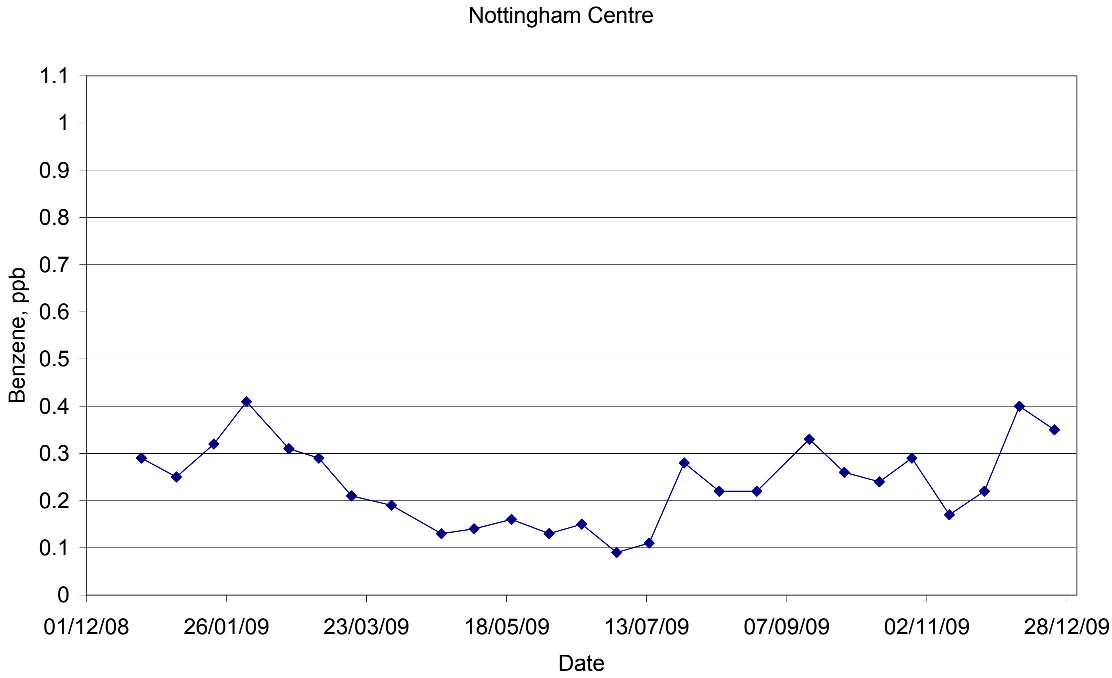

Manchester Piccadilly
Benzene, ppb
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
01/12/08
26/01/09
23/03/09
18/05/09
13/07/09
07/09/09
02/11/09
28/12/09
Date

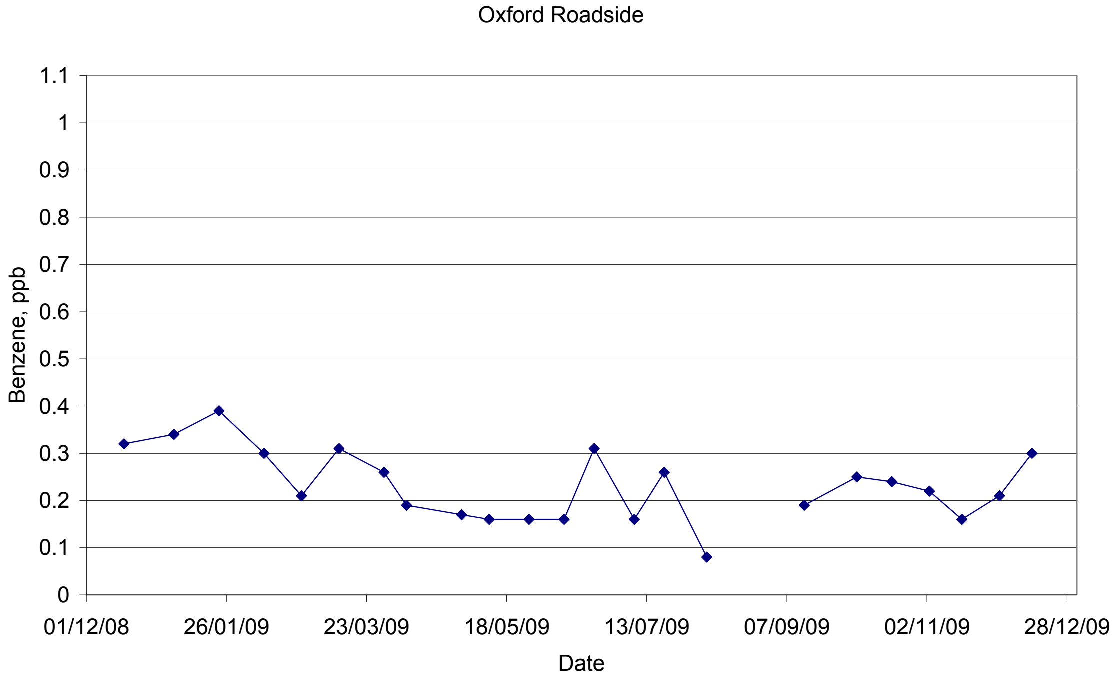

Middlesbrough
Benzene, ppb
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
01/12/08
26/01/09
23/03/09
18/05/09
13/07/09
07/09/09
02/11/09
28/12/09
Date

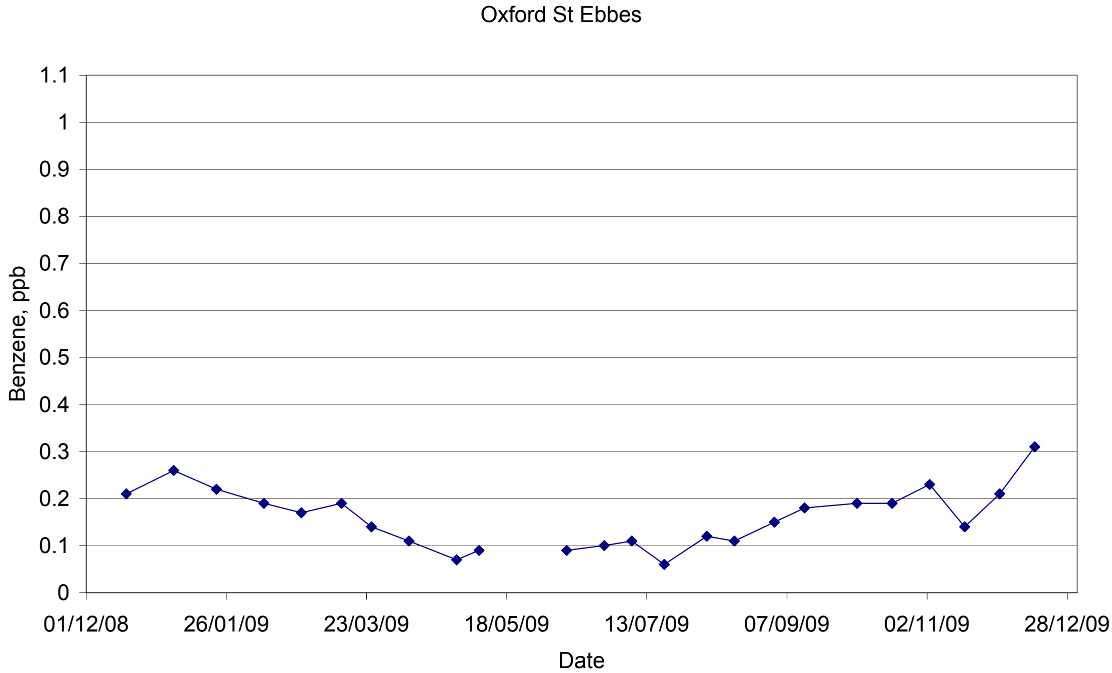

Newcastle Centre
Benzene, ppb
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
01/12/08
26/01/09
23/03/09
18/05/09
13/07/09
07/09/09
02/11/09
28/12/09
Date


Northampton
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Benzene, ppb
01/12/08
26/01/09
23/03/09
18/05/09
13/07/09
07/09/09
02/11/09
28/12/09
Date

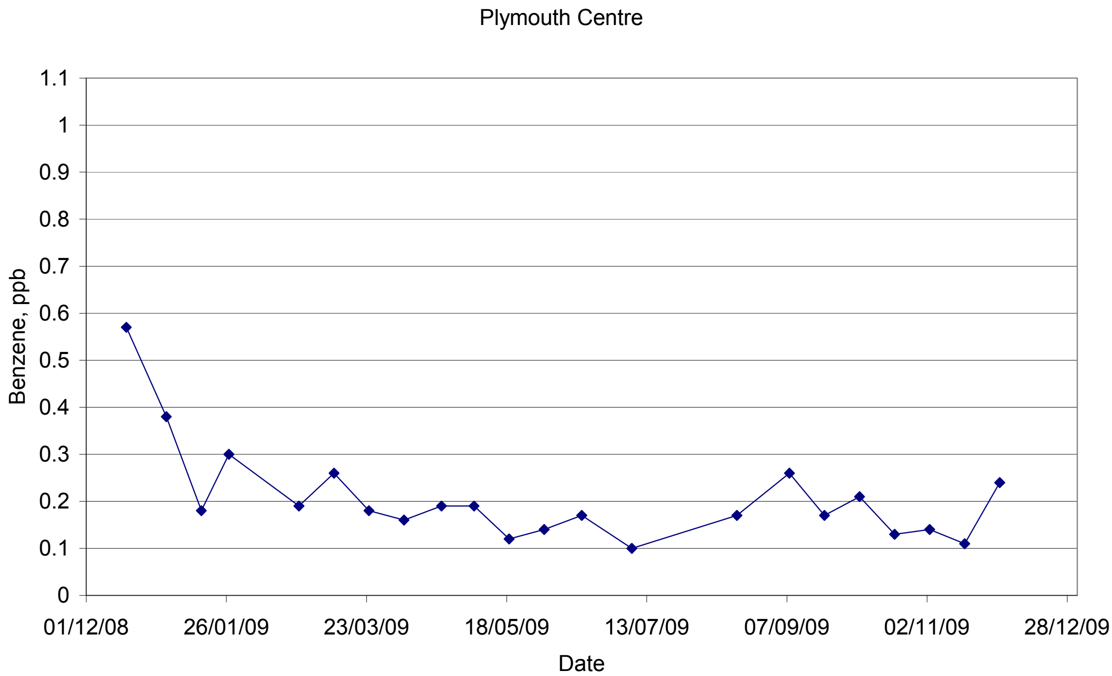

Norwich Lakenfields
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Benzene, ppb
01/12/08
26/01/09
23/03/09
18/05/09
13/07/09
07/09/09
02/11/09
28/12/09
Date


Nottingham Centre
Benzene, ppb
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
01/12/08
26/01/09
23/03/09
18/05/09
13/07/09
07/09/09
02/11/09
28/12/09
Date

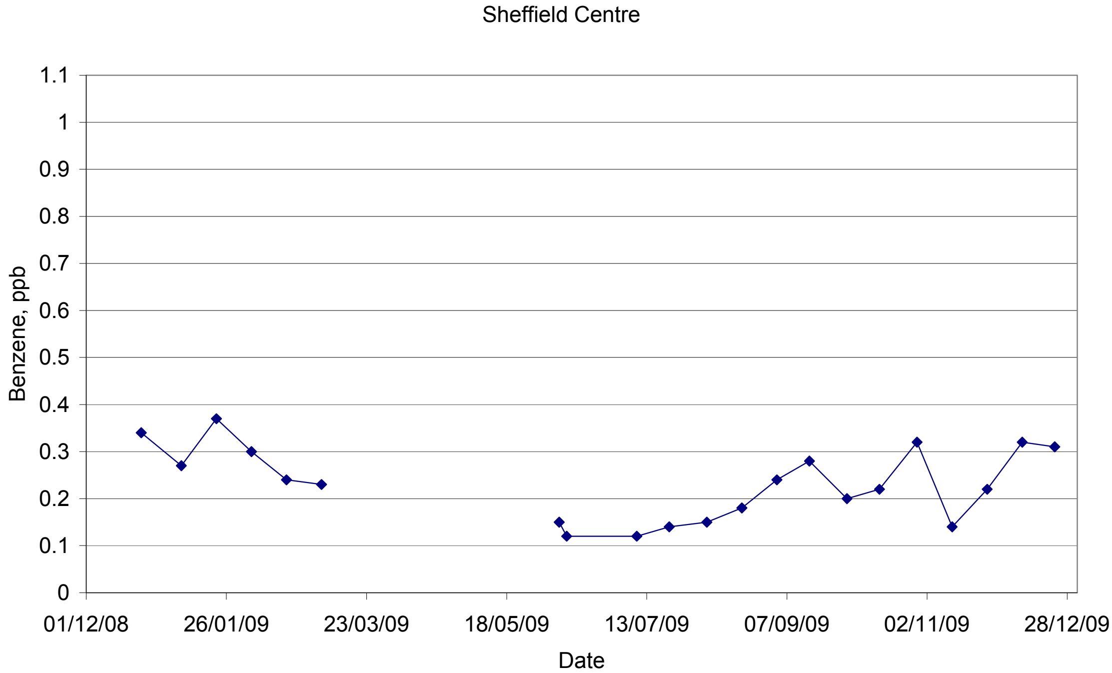

Oxford Roadside
Benzene, ppb
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
01/12/08
26/01/09
23/03/09
18/05/09
13/07/09
07/09/09
02/11/09
28/12/09
Date

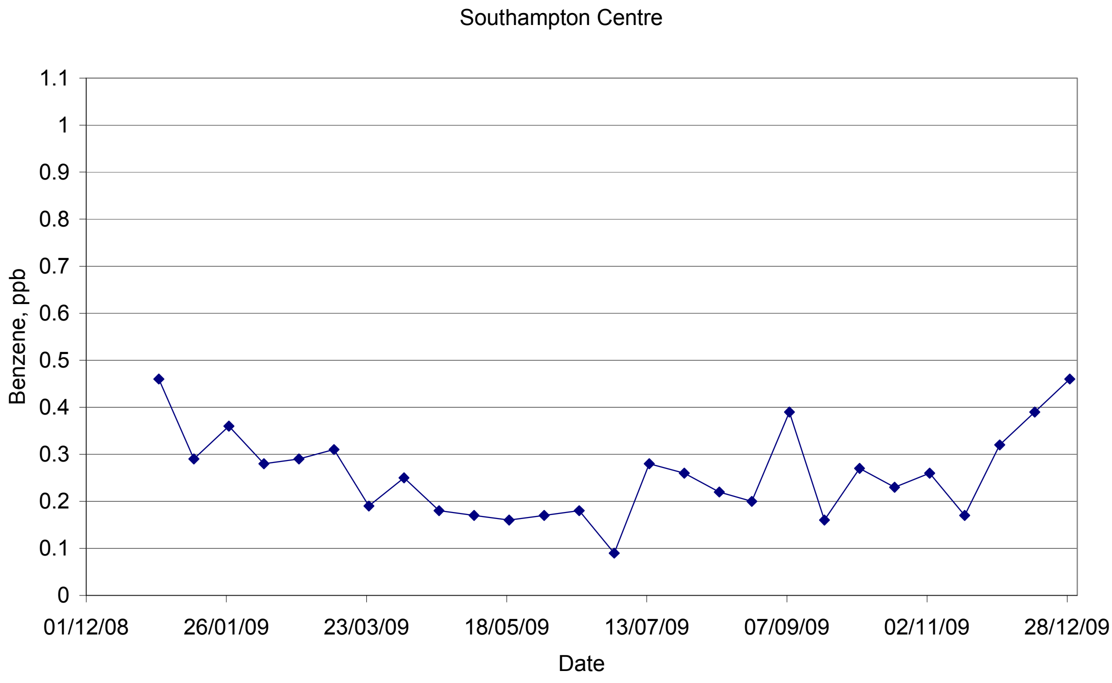


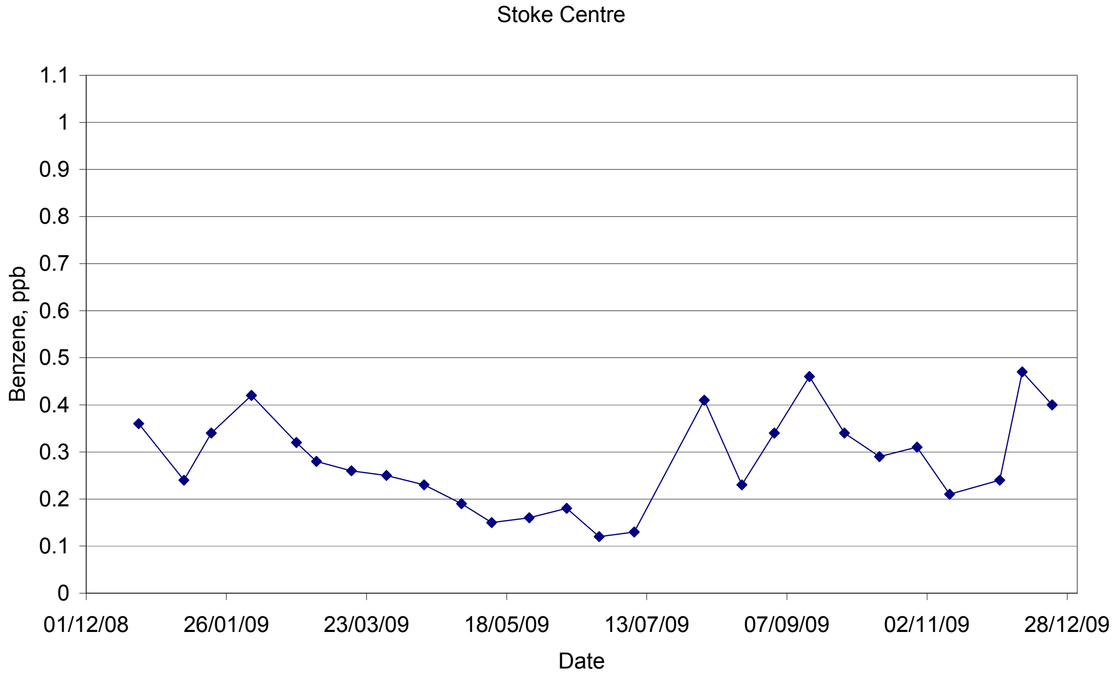
Oxford St Ebbes
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Benzene, ppb
01/12/08
26/01/09
23/03/09
18/05/09
13/07/09
07/09/09
02/11/09
28/12/09
Date

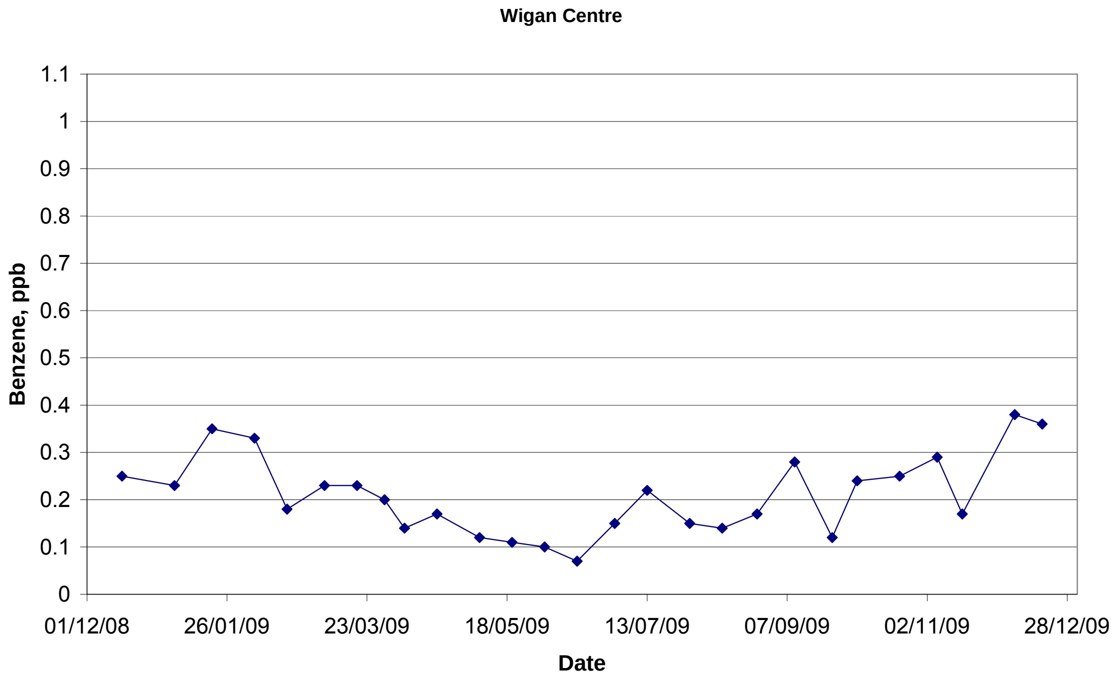


Plymouth Centre
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Benzene, ppb
01/12/08
26/01/09
23/03/09
18/05/09
13/07/09
07/09/09
02/11/09
28/12/09
Date


Sheffield Centre
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Benzene, ppb
01/12/08
26/01/09
23/03/09
18/05/09
13/07/09
07/09/09
02/11/09
28/12/09
Date


Southampton Centre
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Benzene, ppb
01/12/08
26/01/09
23/03/09
18/05/09
13/07/09
07/09/09
02/11/09
28/12/09
Date


Stoke Centre
Benzene, ppb
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
01/12/08
26/01/09
23/03/09
18/05/09
13/07/09
07/09/09
02/11/09
28/12/09
Date


Wigan Centre
Benzene, ppb
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
01/12/08
26/01/09
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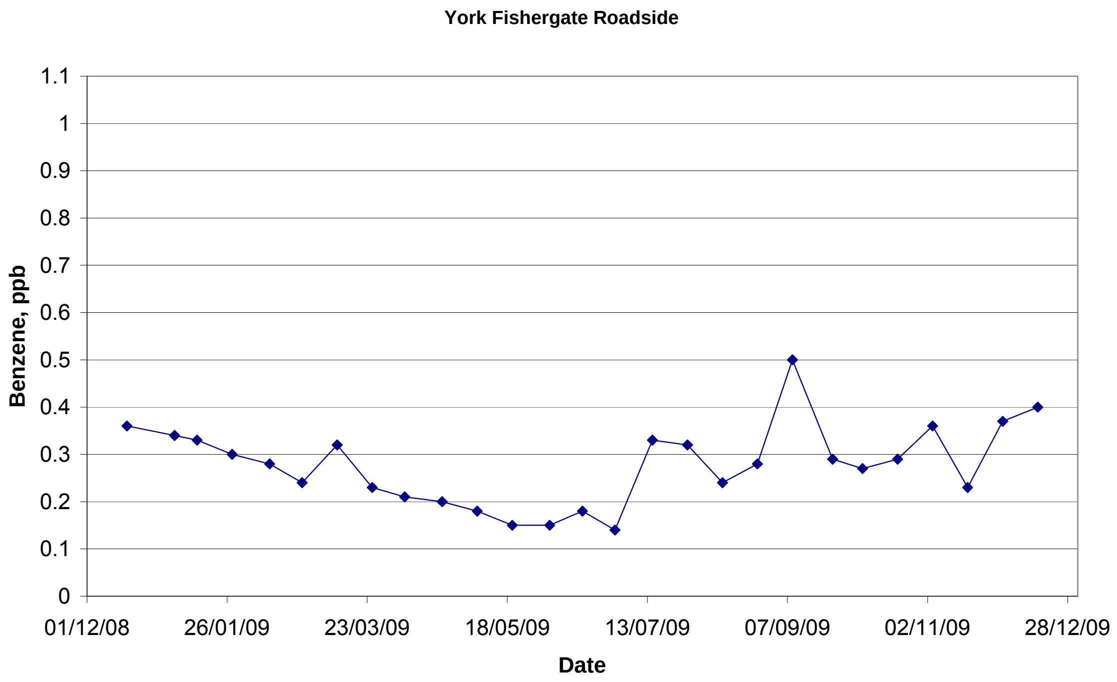
18/05/09
13/07/09
07/09/09
02/11/09
28/12/09
Date


York Fishergate Roadside
Benzene, ppb
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
01/12/08
26/01/09
23/03/09
18/05/09
13/07/09
07/09/09
02/11/09
28/12/09
Date