Environmental Protection Agency
An Ghníomhaireacht um Chaomhnú Comhshaoil

Ambient Air Monitoring

In

Marino, Dublin

5th December 2000 - 9th April 2001

Contents

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Summary

An assessment of air quality was carried out at a site in the Dublin city suburb of Marino from 5th December 2000 until 9th April 2001. No limit values were exceeded during the measurement period.

Concentrations of carbon monoxide, sulphur dioxide, benzene and lead were below their respective lower assessment thresholds. Levels of nitrogen dioxide exceeded the lower assessment threshold but not the upper assessment threshold while levels of PM_{10} exceeded the upper assessment threshold.

	Below Lower Assessment Threshold	**Below Upper Assessment Threshold**	**Above Upper Assessment Threshold**	**Above Limit**
PM_{10}				
NO_2				
CO				
SO_2				
Benzene				
Pb				

The results of this assessment are that within this area of Dublin

- Levels of PM_{10} will need to be measured continuously
- Levels of NO_2 will need to be assessed using a combination of measurement and modelling
- Levels of CO, SO_2, benzene and lead can be assessed using modelling or objective estimation techniques.

The directive states that modelling or objective estimation techniques may be used to assess ambient air quality if levels of the pollutant in question in that zone are below the lower assessment threshold. A combination of modelling and measurements may be used to assess ambient air quality if levels are below the upper assessment threshold, while continuous monitoring is required if levels exceed the upper assessment threshold. Marino is located in Zone A (Dublin), an agglomeration with a population in excess of 250,000, measurement is mandatory within agglomerations.

Introduction

The European Union introduced a new approach to the monitoring, assessment and management of air quality in 1996 when it introduced a framework directive on air quality (96/62/EC, 2nd September 1996). The basic principle of the framework directive is that each country should be divided into zones and that the monitoring, assessment, management and reporting of air quality will be undertaken in relation to these zones. For the purposes of the directive, Ireland has been divided into four zones; Dublin (Zone A), Cork Urban Area (Zone B), specified population centres > 15,000 inhabitants (Zone C) and non-urban areas (Zone D).

Limit values are set for each individual pollutant which need to be met by a specific attainment date. Upper and lower assessment thresholds are also set for each pollutant, assessment thresholds are levels below the limit value, used solely in the determination of the level of monitoring needed for that pollutant in a particular zone. The extent of monitoring in any zone is determined by population size and air quality status. Measurement is mandatory in agglomerations (population >250,000) and where concentrations are above the lower assessment threshold. The greatest monitoring effort applies if concentrations are above the upper assessment threshold. Less intensive monitoring is required when concentrations are between the two assessment thresholds.

Limit values, assessment thresholds, measurement techniques and other specifics for each pollutant are defined in a series of daughter directives. The first daughter directive was adopted in April 1999 (1999/30/EC) and covered SO_2, NO_X, particulate matter and lead. The second daughter directive was adopted in November 2000 (2000/69/EC) and covers CO and Benzene. The directives were transposed into Irish law as the Air Quality Standard Regulations 2002 (S.I No. 271 of 2002).
To comply with the directive the Environmental Protection Agency uses mobile laboratories to carry out assessments in areas with no history of air pollution measurements. These trailers contained the following instruments:

- Monitoring instruments which continuously measure and record concentrations of the pollutants sulphur dioxide, nitrogen oxides and carbon monoxide.
- Instrument which continuously measures and records the levels of particulate matter.
- Gas chromatograph which measures levels of benzene and toluene.
- Sampler for particulate matter (the official method specified for this parameter by the EU commission involves collection of the particulate matter on a filter on site followed by laboratory determination of the filter's increase in weight).
- Sampler for lead and other metals in air (collection on filter for determination in the laboratory).
- Mini meteorological station for measuring and recording temperature, relative humidity, wind speed and direction.

The sample inlets are at a height of ~3m.
For further information please contact
John Finnan, Barbara O' Leary or Ciaran O' Donnell

Time Period

The mobile laboratory was in place from 5th December 2000 until 9th April 2001.

Siting

The mobile laboratory was located in premises owned by Dublin Corporation in the Dublin city suburb of Marino. The site was accessed from the Malahide road. In this location the trailer was approximately 75 metres distant from Griffith Avenue and approximately 400 metres distant from the Malahide road, both busy thoroughfares. The area is a residential district of Dublin city.

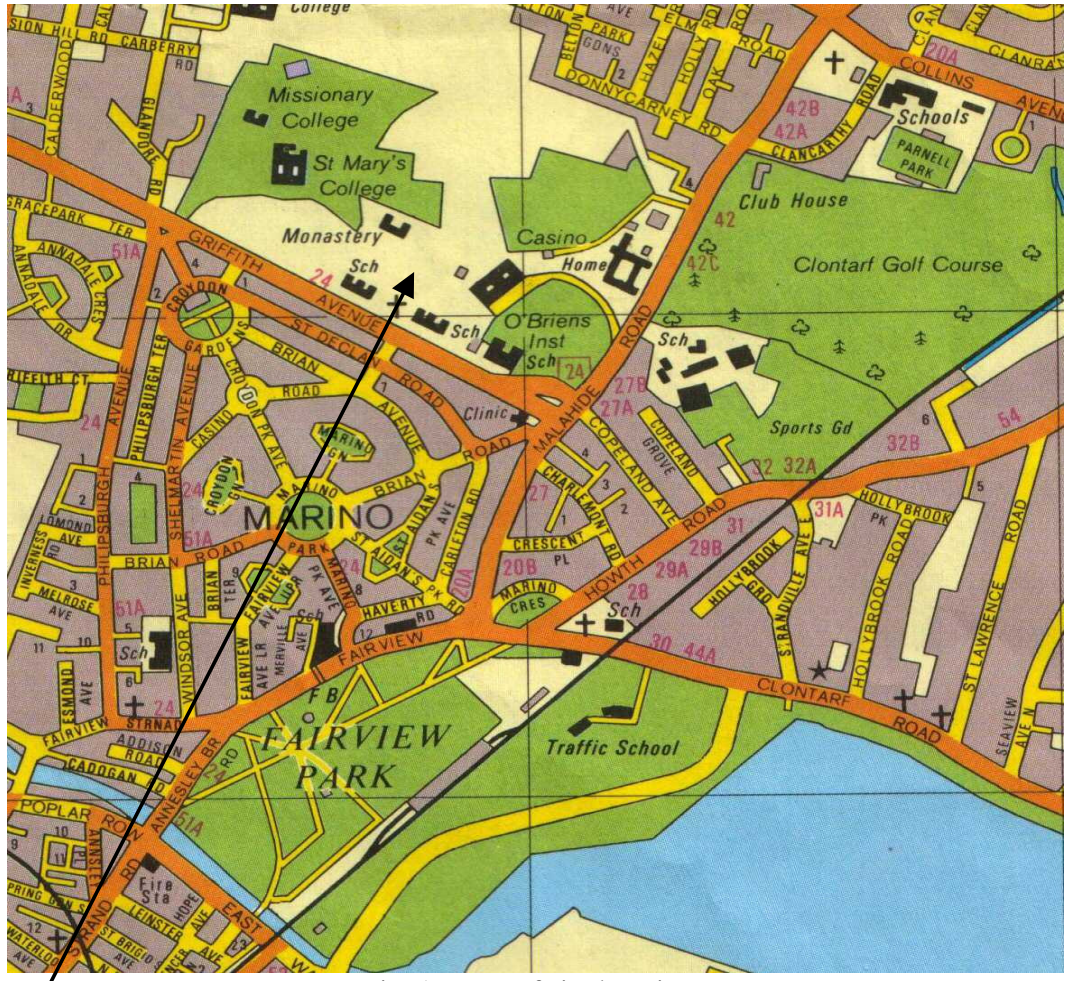

Fig. 1 Map of site location

Location of Monitoring Unit

Monitoring Methods

Carbon Monoxide

Carbon monoxide was monitored using a Gas Filter Correlation CO Analyser (Model 300, Advanced Pollution Instrumentation, 6565 Nancy Ridge Drive, San Diego, California). This is a continuous analyser based on the absorption of infrared radiation by CO molecules at wavelengths near 4.7μm. This is the reference method for CO as specified in Council Directive 2000/69/EC (Annex viii).

Sulphur Dioxide

Sulphur dioxide was monitored using an Advanced Pollution Instrumentation SO_2 Fluorescent Analyser - Model 100A. This is a continuous analyser which measures the fluorescence of SO_2 molecules after excitation by ultraviolet radiation. This is the reference method for SO_2 as specified in Council Directive 1999/30/EC (Annex ix).

Nitrogen Dioxide and Oxides of Nitrogen

NO_x species were monitored using an Advanced Pollution Instrumentation Chemiluminescent $NO/NO_2/NO_x$ Analyser - Model 200A. This is a continuous analyser which utilises the chemiluminescent reaction between nitric oxide in the sample and ozone to measure concentrations of NO. Any NO_2 present is then reduced to NO by a molybdenum converter giving a second value for total NO_x concentration. The amount of NO_2 present is found by subtraction. This is the reference method for oxides of nitrogen as specified in Council Directive 1999/30/EC (Annex ix).

Particulate Matter

A gravimetric method was used to monitor PM_{10} particles (as defined in European Standard, prEN12341, July 1998, Central Secretariat, rue de Stassart, 36, B-1050 Brussels). An inertial impactor sampling head restricted the sampled particles to those with a diameter less than 10μm. The particles were collected on preweighed glassfibre filters (Whatman GF/A, 47mm). The filters were equilibrated at constant temperature and humidity (T = 293±1°K, R.H. = 50±3%) for at least 48 hours in a WTB Binder APT.Line KBF115 Climatic Chamber prior to weighing. An Ambient Dust Automatic Monitor (Model SM200CD with β source removed, OPSIS, S-24402, Furulund, Sweden) was used to change the filters daily at midnight. This is the reference method for PM_{10} as specified in Council Directive 1999/30/EC (Annex ix).

Particulate matter was also measured using an OSIRIS Environmental Dust Monitor (Turnkey Instruments, 1&2 Dalby Court, Gadbrook Business Centre, Northwitch, Cheshire CW9 7TN). This instrument uses a light scattering technique to determine the concentration of airborne particles and dust; it is not an approved method. Results are given for total suspended particulates, PM_{10}, $PM_{2.5}$ and PM_1.

Benzene

Benzene was measured using a gas chromatograph (BTX Analyser GC855 supplied by Syntech Spectras, G. Meirstraat 11, 9728 TB Groningen, Nederland). This gas chromatograph samples automatically over a 15 minute cycle and is equipped with a photoionisation detector. This is a reference method for the determination of benzene which conforms with the method for the sampling/analysis of benzene set out in Council Directive 2000/69/EC (Annex viii).

Lead and Other Metals

Ambient air was pumped through a Metricel membrane filter (Gelman, 37mm, 0.8μm) situated in a calming chamber. The filters were changed every 1-2 weeks. They were digested in conc. HNO_3 and analysed for lead and other metals using ICP-MS (Inductively Coupled Plasma-Mass Spectrometry). This is the prescribed method for the determination of lead. Methods for other metals have yet to be prescribed.

All results for CO, SO2, NO_X and the continuous particulate monitor were integrated to give 1-hour average values as required for comparison with the Directive limit values. 24 hour and rolling 8 hr averages were calculated as required. Metal levels were averaged over the whole monitoring period.

Results

Carbon Monoxide

No. of hours	2946	
Missing values	3	
(including routine maintenance)	1	
No. of measured values	2943	
Percentage covered	99.9%	
Maximum hourly value	5.0	$mg.m^{-3}$
98 percentile for hourly values	2.4	$mg.m^{-3}$
Mean hourly value	0.6	$mg.m^{-3}$
Maximum 8-hour mean	3.1	$mg.m^{-3}$
98 percentile for 8-hour mean	1.9	$mg.m^{-3}$

Proposed Directive Limits

	Averaging Period	Limit Value	Date by which limit value is to be met
Limit Value for the protection of human health	8-hour running average	10 mg m^{-3}	1 January 2005
Upper assessment threshold	8-hour running average	7 mg m^{-3}	
Lower assessment threshold	8-hour running average	5 mg m^{-3}	

The lower assessment threshold was not exceeded during the measurement period (Figure 2).

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Fig. 2 Carbon Monoxide 8-hour Running Average
Trailer 2 in Marino 5/12/00-9/4/01

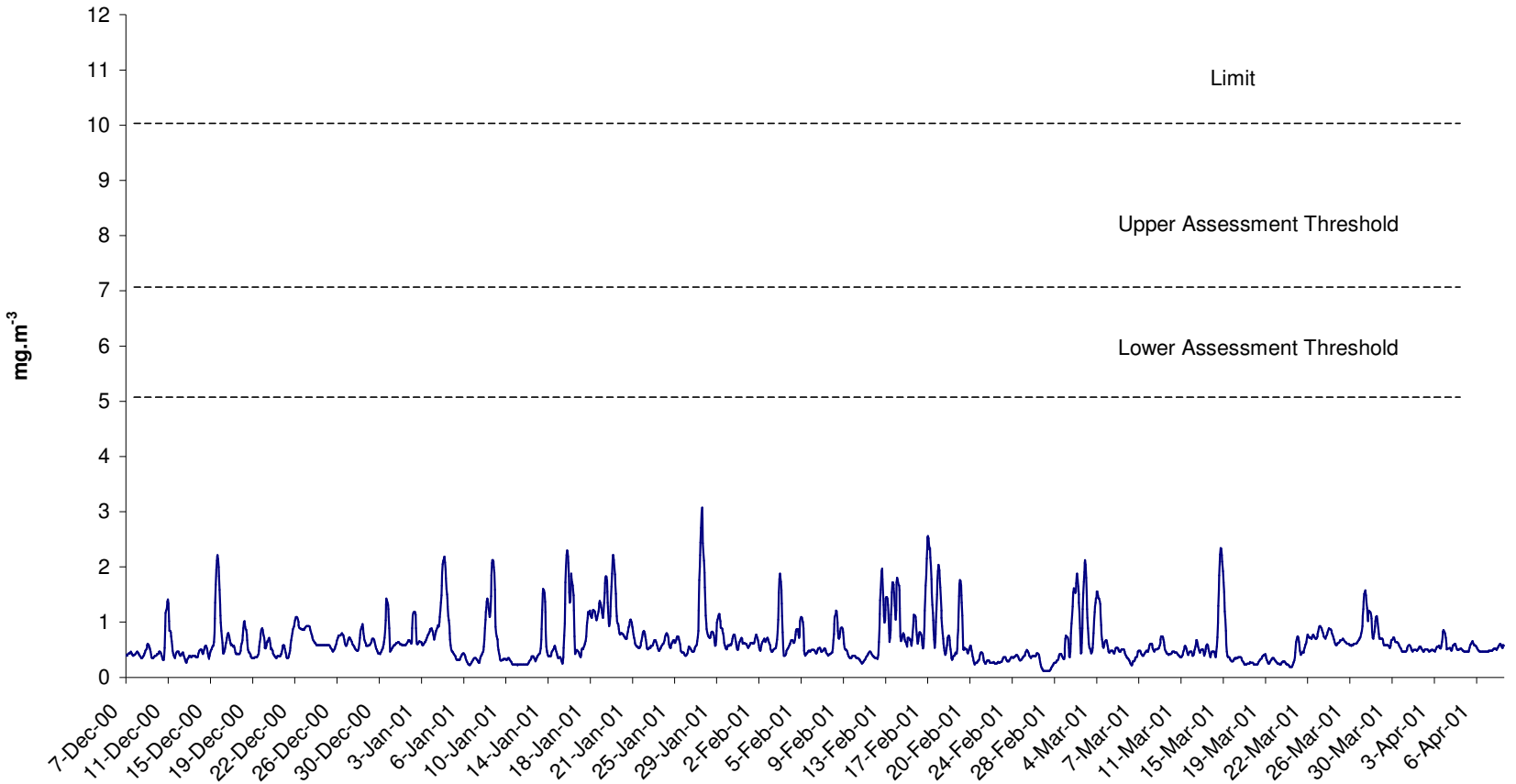
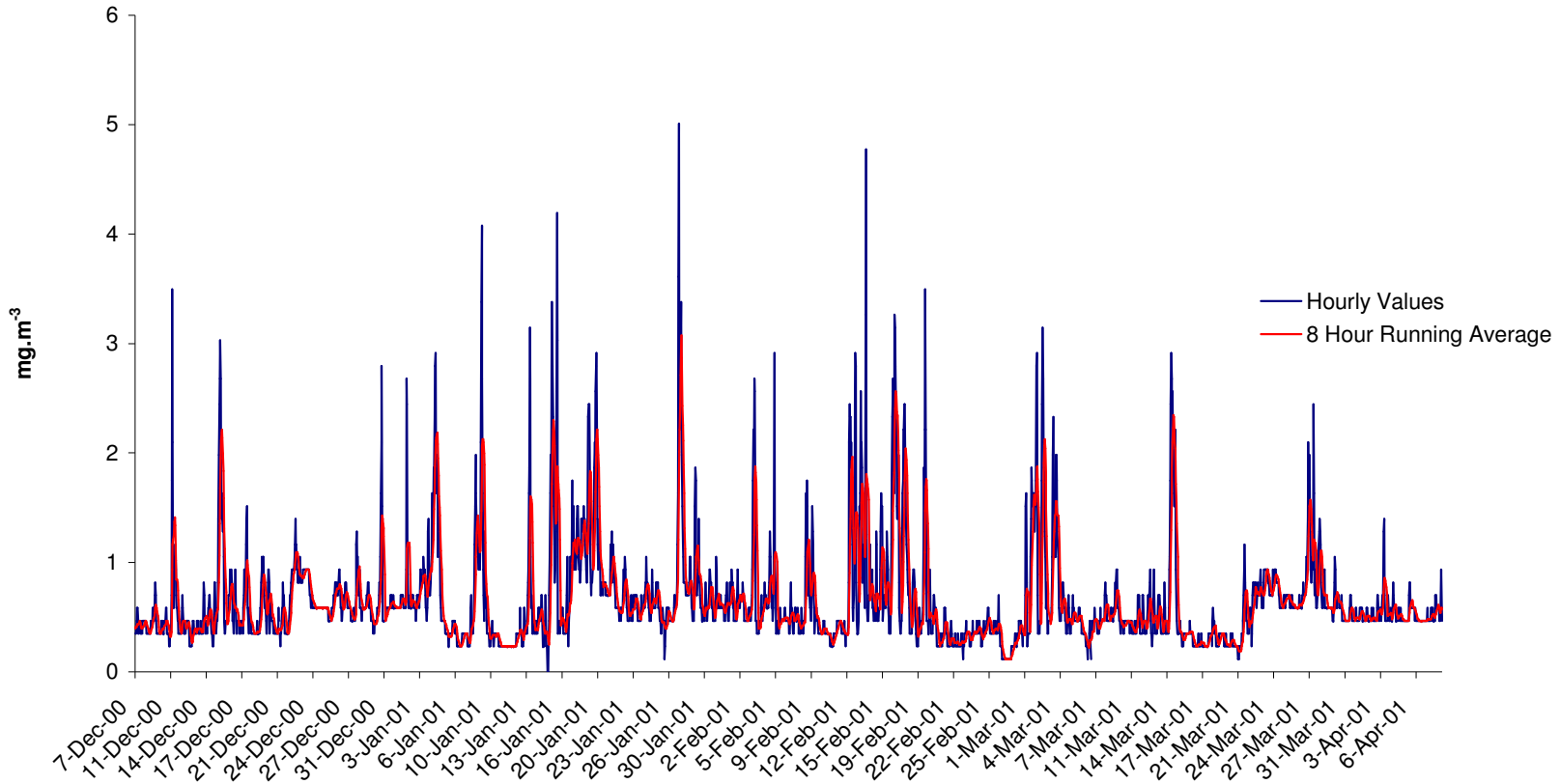


Fig. 3 Carbon Monoxide
Trailer 2 in Marino 5/12/00-9/4/01



Sulphur Dioxide

No. of hours	2946	
Missing values	28	
(including routine maintenance)	24	
No. of measured values	2918	
Percentage covered	99.0	
Maximum hourly value	232.1	$\mu g.m^{-3}$
98 percentile for hourly values	68.1	$\mu g.m^{-3}$
Mean hourly value	20.1	$\mu g.m^{-3}$
Maximum 24-hour value	50.3	$\mu g.m^{-3}$
98 percentile for 24-hour values	43.9	$\mu g.m^{-3}$

Directive Limits (1999/30/EC)

	Averaging Period	Limit Value	Date by which limit value is to be met
Hourly limit value for the protection of human health	1 hour	350 $\mu g\ m^{-3}$ not to be exceeded more than 24 times a calendar year	1 January 2005
Daily limit value for the protection of human health	24 hours	125 $\mu g\ m^{-3}$ not to be exceeded more than 3 times a calendar year	1 January 2005
Limit value for the protection of ecosystems	Calendar year and winter (1 October to 31 March)	20 $\mu g\ m^{-3}$	19 July 2001
Alert threshold		500 $\mu g\ m^{-3}$ over three consecutive hours	

Directive Limits (1999/30/EC) continued

	Averaging Period	Limit Value	Date by which limit value is to be met
Upper assessment threshold for the protection of human health	24 hours	75 μg m^{-3} not to be exceeded more than 3 times a calendar year	
Lower assessment threshold for the protection of human health	24 hours	50 μg m^{-3} not to be exceeded more than 3 times a calendar year	
Upper assessment threshold for the protection of ecosystems	Calendar year and winter (1 October to 31 March)	12 μg m^{-3}	
Lower assessment threshold for the protection of ecosystems	Calendar year and winter (1 October to 31 March)	8 μg m^{-3}	

The hourly limit value was not exceeded during the measurement period (Figure 5).There was one exceedence of the 50 μg.m^{-3} lower assessment threshold (Figure 4), this is the equivalent of three exceedences in a calendar year. The directive stipulates that the lower assessment threshold should not be exceeded more than three times in a calendar year.

The mean hourly value of 20.1 μg.m^{-3} exceeds the upper assessment threshold for the protection of ecosystems. However, this threshold may not be relevant to monitoring in an urban environment.

Fig. 4 Sulphur Dioxide 24 Hour Averages
Trailer 2 in Marino 5/12/00-9/4/01

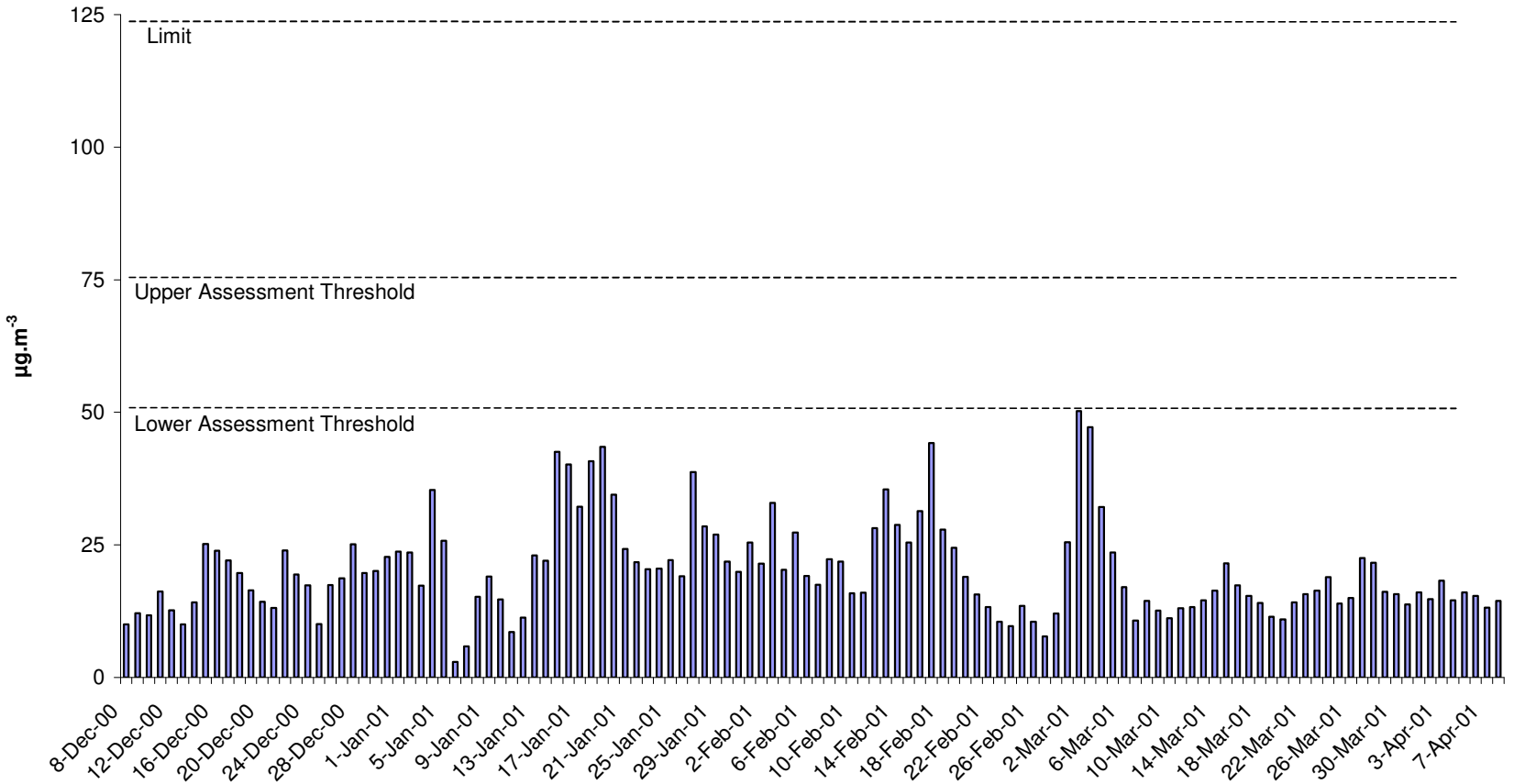
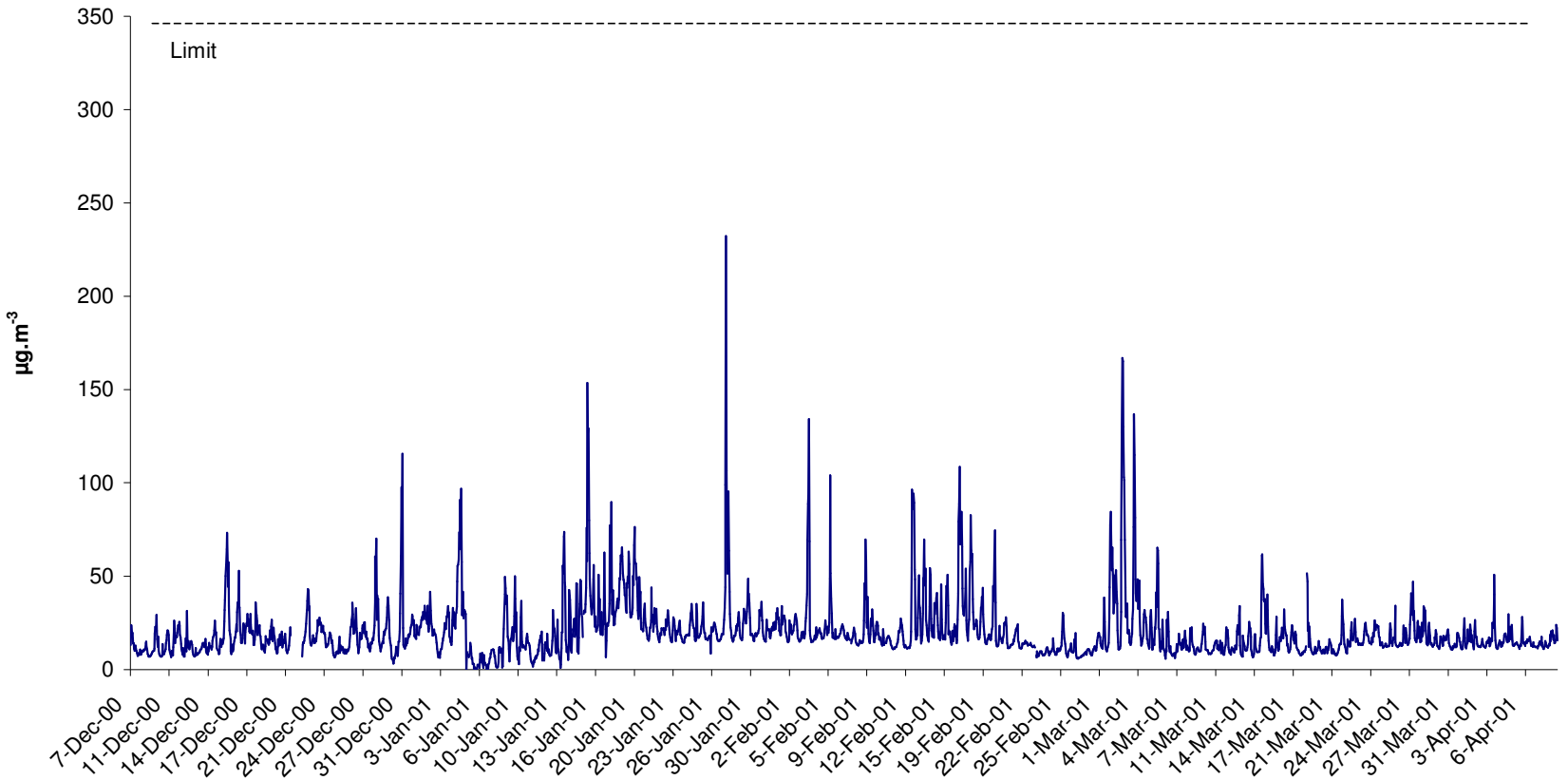


Fig. 5 Sulphur Dioxide Hourly Averages
Trailer 2 in Marino 5/12/00-9/4/01



Nitrogen Dioxide and Oxides of Nitrogen

No. of hours	2946	
Missing values	4	
(including routine maintenance)	2	
No. of measured values	2942	
Percentage covered	99.9	
Maximum hourly value (NO_2)	172.2	$\mu g.m^{-3}$
98 percentile for hourly values (NO_2)	84.6	$\mu g.m^{-3}$
Mean hourly value (NO_2)	32.6	$\mu g.m^{-3}$
Mean hourly value (NO_x)	59.2	$\mu g.m^{-3}$ NO_2

Directive Limits (1999/30/EC)

	Averaging Period	Limit Value	Date by which limit value is to be met
Hourly limit value for the protection of human health	1 hour	200 $\mu g\ m^{-3}$ NO_2 not to be exceeded more than 18 times a calendar year	1 January 2010
Annual limit value for the protection of human health	Calendar year	40 $\mu g\ m^{-3}$ NO_2	1 January 2010
Annual limit value for the protection of vegetation	Calendar year	30 $\mu g\ m^{-3}$ NO_x	19 July 2001
Alert threshold		400 $\mu g\ m^{-3}$ NO_2 over three consecutive hours	

Directive Limits (1999/30/EC) continued

	Averaging Period	Limit Value	Date by which limit value is to be met
Upper assessment threshold for the protection of human health	1 hour	140 μg m^{-3} NO_2 not to be exceeded more than 18 times a calendar year	
Upper assessment threshold for the protection of human health	Calendar year	32 μg m^{-3} NO_2	
Lower assessment threshold for the protection of human health	1 hour	100 μg m^{-3} NO_2 not to be exceeded more than 18 times a calendar year	
Lower assessment threshold for the protection of human health	Calendar year	26 μg m^{-3} NO_2	
Upper assessment threshold for the protection of vegetation	Calendar year	24 μg m^{-3} NO_x	
Lower assessment threshold for the protection of vegetation	Calendar year	19.5 μg m^{-3} NO_x	

There were nineteen hourly mean NO_2 values above the lower assessment threshold for the protection of human health and there was one hourly mean value in excess of the upper assessment threshold for the protection of health (Figure 6). The directive stipulates that each of the assessment thresholds should not be exceeded more than

eighteen times in a calendar year. With the exception of these nineteen values all other hourly mean NO_2 values were below the lower assessment threshold.

The mean hourly NO_2 value (32.6 $\mu g.m^{-3}$) during the measurement period was just above the upper assessment threshold for the protection of human health (32 $\mu g.m^{-3}$). Results from hourly measurements clearly put the data between the lower and upper assessment thresholds. Although the mean hourly NO_2 value just exceeded the upper assessment threshold, it was decided to classify NO_2 levels at Marino as being between the two assessment thresholds.

The mean hourly value of NO_X (59.2 $\mu g.m^{-3}$ NO_2) during the measurement period exceeded the annual limit value for the protection of vegetation (30 $\mu g.m^{-3}$). However, the applicability of this limit to urban air pollution monitoring is questionable.

Fig. 6 NO_2 Hourly Values
Trailer 2 in Marino 5/12/00-9/4/01

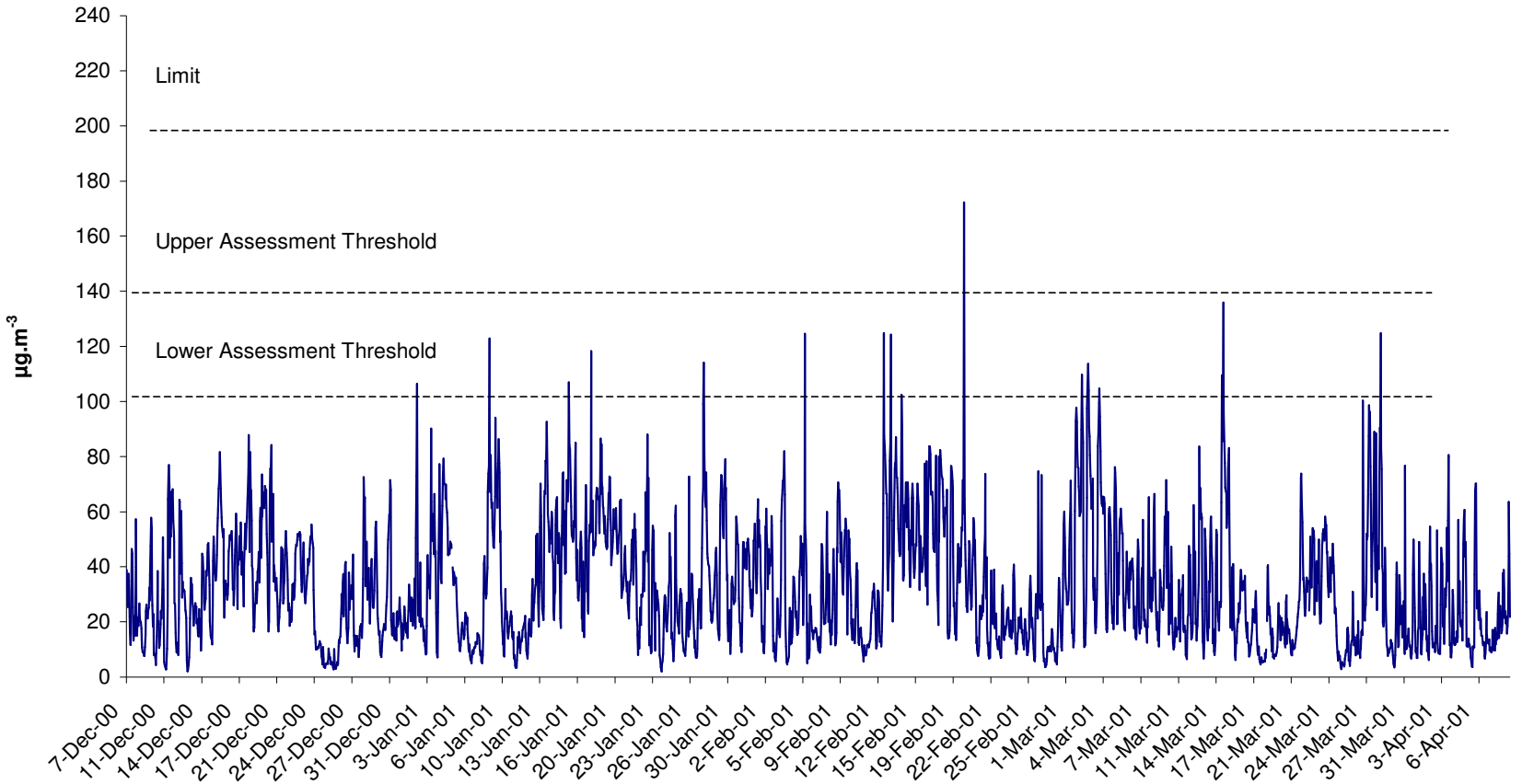
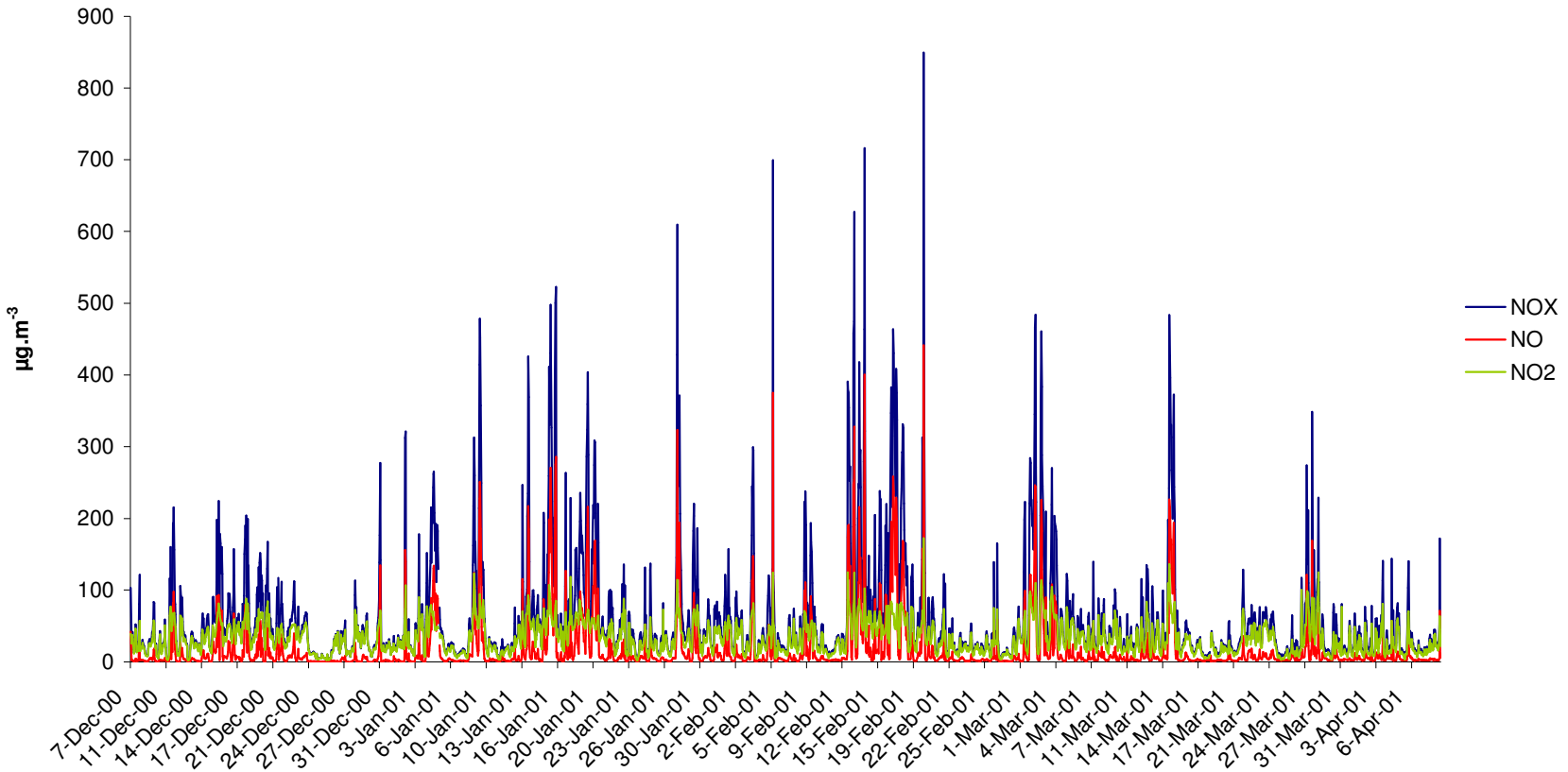


Fig. 7 NO_X Hourly Values
Trailer 2 in Marino 5/12/00-9/4/01



Particulate Matter

PM_{10} : gravimetric method

No. of days	124	
Missing values	49	
(including routine maintenance)	4	
No. of measured values	75	
Percentage covered	60.5	
Maximum daily value	61.6	$\mu g.m^{-3}$
98 percentile for daily values	57.3	$\mu g.m^{-3}$
Mean daily value	23.8	$\mu g.m^{-3}$

Directive Limits (1999/30/EC)

STAGE I

	Averaging Period	Limit Value	Date by which limit value is to be met
24-hour limit value for the protection of human health	24 hour	50 $\mu g\ m^{-3}$ PM_{10} not to be exceeded more than 35 times a calendar year	1 January 2005
Annual limit value for the protection of human health	Calendar year	40 $\mu g\ m^{-3}$ PM_{10}	1 January 2005
Upper assessment threshold for the protection of human health	24 hour	30 $\mu g\ m^{-3}$ PM_{10} not to be exceeded more than 7 times a calendar year	*based on the indicative limit values for 1 January 2010*
Upper assessment threshold for the protection of human health	Calendar year	14 $\mu g\ m^{-3}$ PM_{10}	*based on the indicative limit values for 1 January 2010*

Directive Limits (1999/30/EC) Stage I continued

	Averaging Period	Limit Value	Date by which limit value is to be met
Lower assessment threshold for the protection of human health	24 hour	20 μg m^{-3} PM_{10} not to be exceeded more than 7 times a calendar year	*based on the indicative limit values for 1 January 2010*
Lower assessment threshold for the protection of human health	Calendar year	10 μg m^{-3} PM_{10}	*based on the indicative limit values for 1 January 2010*

STAGE II

	Averaging Period	Limit Value	Date by which limit value is to be met
24-hour limit value for the protection of human health	24 hour	50 μg m^{-3} PM_{10} not to be exceeded more than 7 times a calendar year	1 January 2010
Annual limit value for the protection of human health	Calendar year	20 μg m^{-3} PM_{10}	1 January 2010

The 2005 limit value for the protection of human health was exceeded on four occasions (5.3% of measured values) during the measurement period (Figure 8). This is the equivalent of 12 exceedences in the calendar year. The limit plus a margin of tolerance of 40% (70 $\mu g.m^{-3}$) was not exceeded during the measurement period. The directive stipulates that the limit value should not be exceeded more than 35 times in a calendar year. The upper assessment threshold was exceeded on 18 days during the measurement period (24% of measured values), this is the equivalent of 53

exceedences in the calendar year. The lower assessment threshold was exceeded on 40 days during the measurement period (53.3% of measured values), this is the equivalent of 118 exceedences in the calendar year. The directive stipulates that each of the assessment thresholds should not be exceeded more than 7 times in a calendar year.

The mean of the daily values during the measurement period (23.8 $\mu g.m^{-3}$) is below the annual limit value for the protection of human health.

Particulate Matter : $PM_{2.5}$

Article 5 of Council Directive 1999/30/EC of 22 April 1999 states that

"Member States shall ensure that measuring stations to supply data on concentration of $PM_{2.5}$ are installed."

The concentration of $PM_{2.5}$ was measured with an OSIRIS Environmental Dust Monitor in the mobile laboratory. This instrument also measured total suspended particles (TSP), PM_{10} and PM_1. All measurements were hourly values.

The concentration of PM_{10} measured by the OSIRIS and that measured using the gravimetric method were compared to give a daily correction factor. The correction factor was used to estimate the concentration of $PM_{2.5}$ using the formula:

$$\text{24-hour average concentration of } PM_{2.5} = \text{OSIRIS 24-hour average concentration of } PM_{2.5} \times \frac{\text{gravimetric 24-hour average } PM_{10}}{\text{OSIRIS 24-hour average } PM_{10}}$$

Results:

No. of days	124	
Missing values	98	
(including routine maintenance)	0	
No. of measured values*	26	
Percentage covered	20.9%	
Maximum daily value	15.7	$\mu g.m^{-3}$
98 percentile for daily values	14.2	$\mu g.m^{-3}$
Mean daily value	4.7	$\mu g.m^{-3}$
Median daily value	3.7	$\mu g.m^{-3}$

* no. of days with measurements from both the OSIRIS monitor and the gravimetric method.

Fig. 8 PM_{10} Daily Values
Trailer 2 in Marino 5/12/00-9/4/01

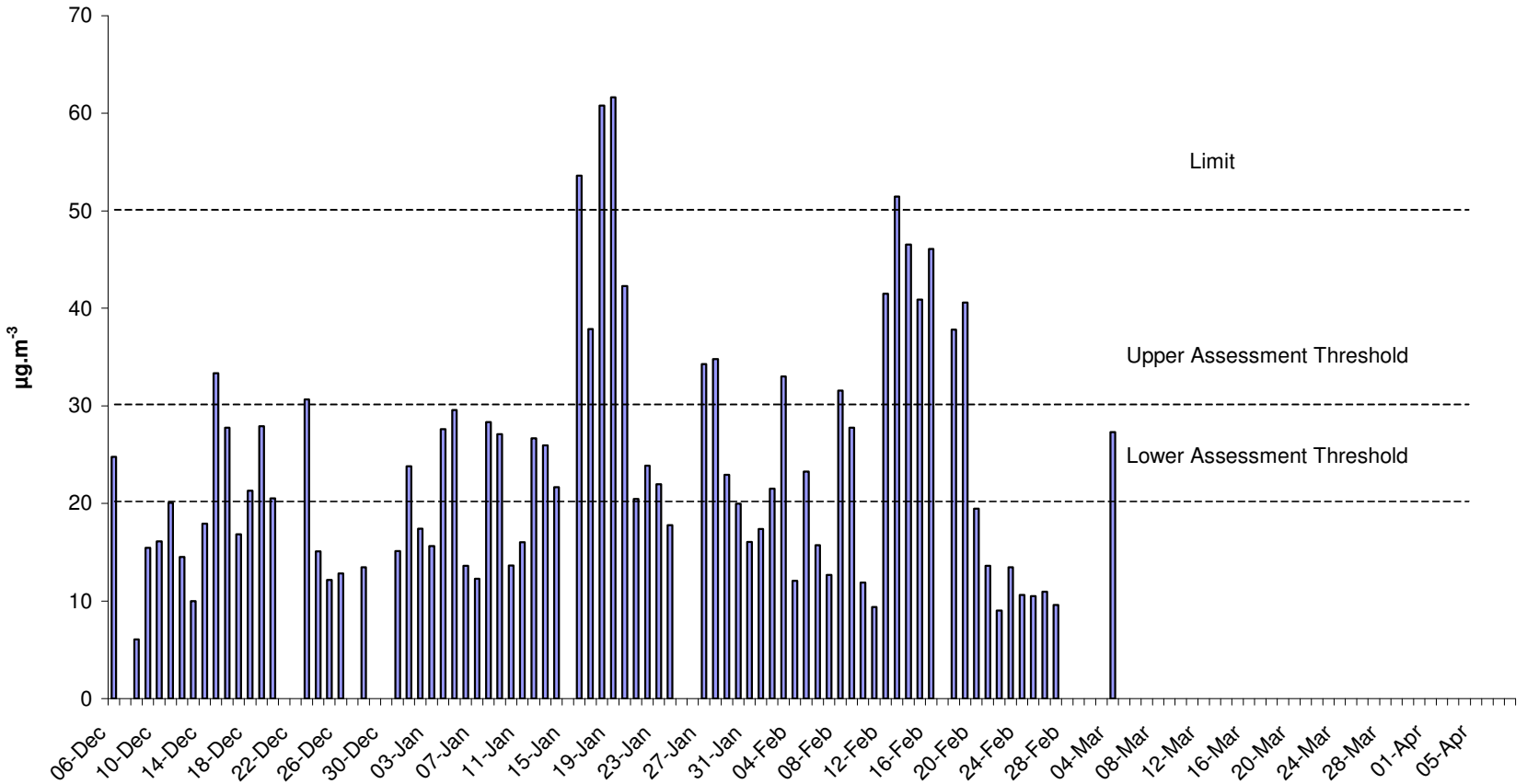
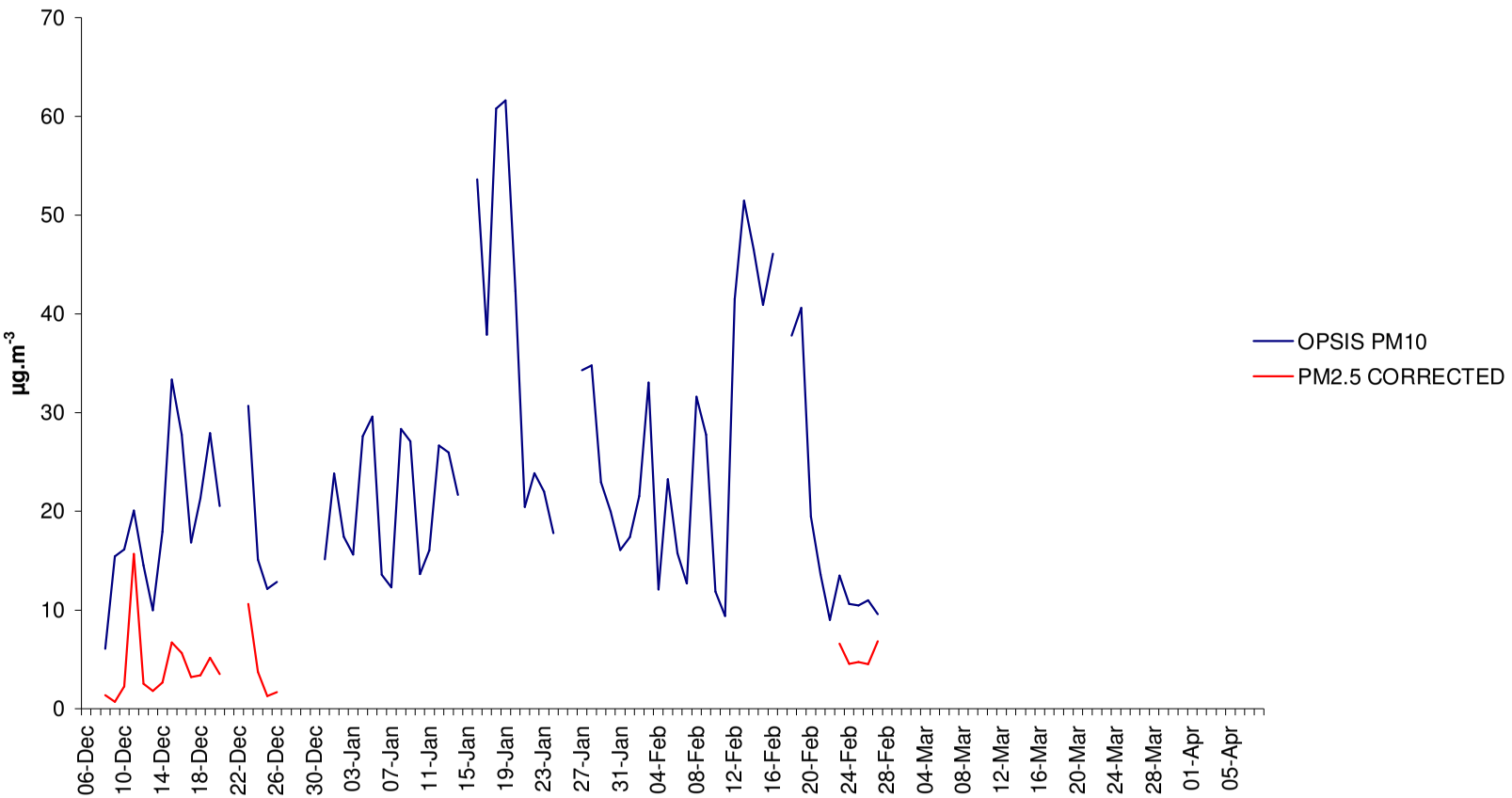


Fig. 9 PM_{10} and $PM_{2.5}$ Daily Values
Trailer 2 in Marino 5/12/00-9/4/01



Benzene

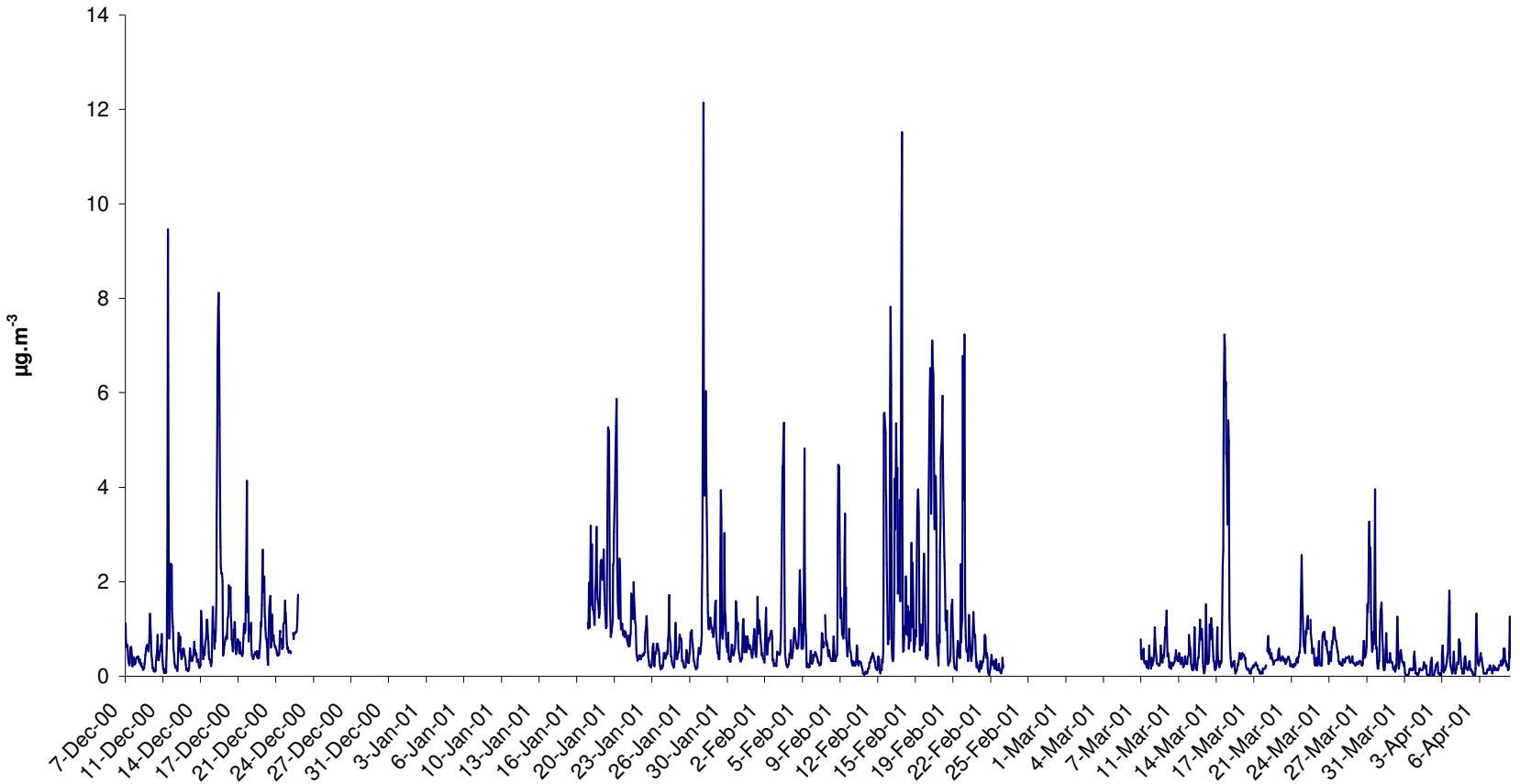
No. of hours	2946	
Missing values	916	
(including routine maintenance)	16	
No. of measured values	2030	
Percentage covered	68.9	
Maximum hourly value	12.1	$\mu g.m^{-3}$
98 percentile for hourly values	5.3	$\mu g.m^{-3}$
Mean hourly value	0.9	$\mu g.m^{-3}$

Proposed Directive Limits

	Averaging Period	Limit Value	Date by which limit value is to be met
Limit value for the protection of human health	Calendar year	5 $\mu g\ m^{-3}$	1 January 2010
Upper assessment threshold for the protection of human health	Calendar year	3.5 $\mu g\ m^{-3}$	
Lower assessment threshold for the protection of human health	Calendar year	2 $\mu g\ m^{-3}$	

The mean value for the measurement period (0.9 $\mu g.m^{-3}$) is below the lower assessment threshold for the protection of human health.

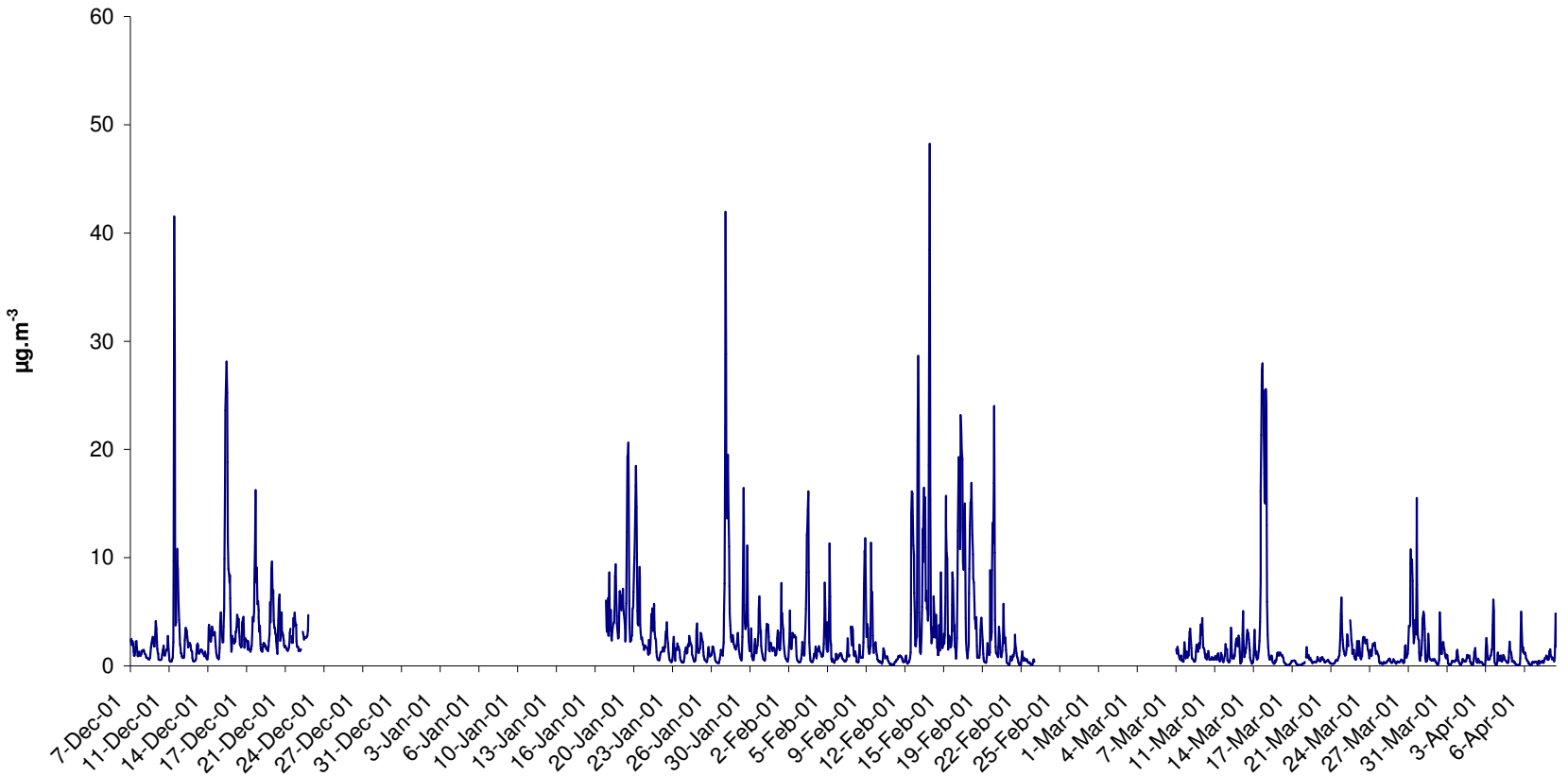
Fig. 10 Benzene Hourly Values
Trailer 2 in Marino 5/12/00-9/4/01



Toluene

No. of hours	2946	
Missing values	916	
(including routine maintenance)	16	
No. of measured values	2030	
Percentage covered	68.9	
Maximum hourly value	48.2	$\mu g.m^{-3}$
98 percentile for hourly values	16.7	$\mu g.m^{-3}$
Mean hourly value	2.6	$\mu g.m^{-3}$

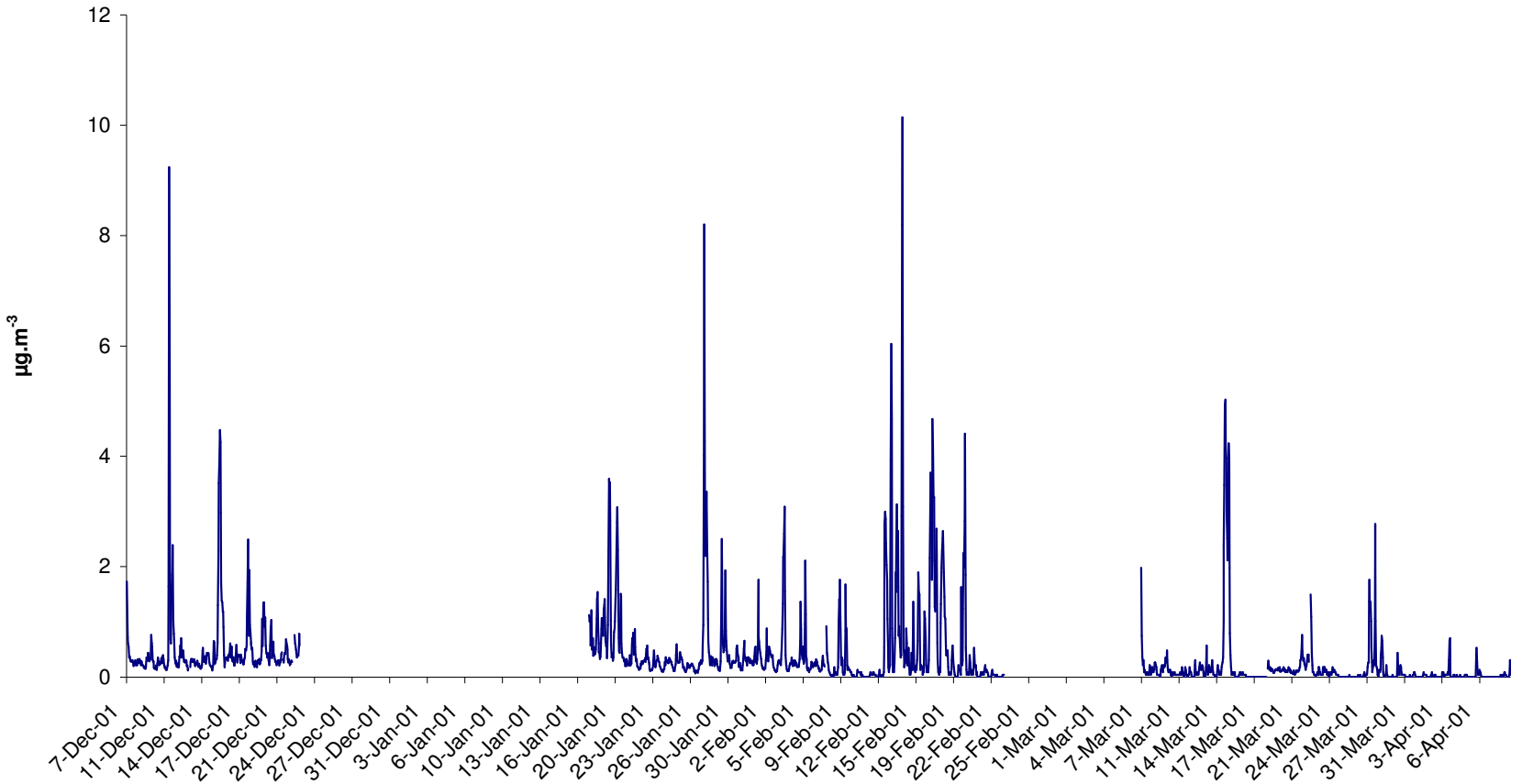
Fig. 11 Toluene Hourly Values
Trailer 2 in Marino 5/12/00-9/4/01



o-Xylene

No. of hours	2946	
Missing values	921	
(including routine maintenance)	16	
No. of measured values	2025	
Percentage covered	68.7	
Maximum hourly value	10.1	$\mu g.m^{-3}$
98 percentile for hourly values	2.9	$\mu g.m^{-3}$
Mean hourly value	0.4	$\mu g.m^{-3}$

Fig. 12 0-Xylene Hourly Values
Trailer 2 in Marino 5/12/00-9/4/01



Lead

No. of days	125	
Missing days	0	
(including routine maintenance)	0	
No. of measured days	125	
Percentage covered	100	
Concentration of Pb	0.003	$\mu g.m^{-3}$

Directive Limits (1999/30/EC)

	Averaging Period	Limit Value	Date by which limit value is to be met
Annual limit value for the protection of human health	Calendar year	0.5 $\mu g\ m^{-3}$	1 January 2005
Upper assessment threshold	Calendar year	0.35 $\mu g\ m^{-3}$	
Lower assessment threshold	Calendar year	0.25 $\mu g\ m^{-3}$	

The concentration of lead during the measurement period was well below the lower assessment threshold.

Other Metals:

Annex I of council directive 96/62/EC (Air Framework Directive) lists four metals other than lead to be taken into consideration in the assessment and management of ambient air quality. These are cadmium, arsenic, nickel and mercury. Limit values and measurement methods for these metals as well as certain polycyclic aromatic hydrocarbons will be set out in the fourth daughter directive.

An indicative method was used during this assessment to measure prevailing concentrations of cadmium, nickel and arsenic in air. This method is detailed above and essentially involves pumping air through a filter for several weeks before digesting the filter and analysing the digest for lead and other metals using ICP-MS. The problem with this method is that the detection limit is influenced by any traces of metal in the filter paper as well as by the volume of air passed through the filter.
The results, although indicative, do provide some indication of the concentrations of these metals in air.

During this assessment

The maximum concentration of cadmium in air was found to be 0.3 $ng.m^{-3}$

The maximum concentration of arsenic in air was found to be 0.9 $ng.m^{-3}$

The maximum concentration of nickel in air was found to be 1.8 $ng.m^{-3}$