



## **Ambient Air Monitoring**

**In**

**Carlow**

**12<sup>th</sup> July 2004 – 14<sup>th</sup> March 2005**



## *Contents*

Summary . . . . .	3
Introduction . . . . .	4
Time Period . . . . .	5
Siting . . . . .	5
Monitoring Methods . . . . .	6
Results. . . . .	8
Carbon Monoxide . . . . .	8
Sulphur Dioxide . . . . .	11
Nitrogen Dioxide and Oxides of Nitrogen . . . . .	15
Particulate Matter . . . . .	20
Benzene . . . . .	26
Toluene . . . . .	28
Lead . . . . .	30
Cadmium . . . . .	31
Arsenic . . . . .	31
Nickel . . . . .	31

## ***List of Figures***

Fig.1 Map of Site Location . . . . .	5
Fig.2 Carbon Monoxide 8-hour Running Average . . . . .	9
Fig.3 Carbon Monoxide . . . . .	10
Fig.4 Sulphur Dioxide 24-hour Averages . . . . .	13
Fig.5 Sulphur Dioxide Hourly Averages . . . . .	14
Fig.6 NO <sub>2</sub> Hourly Values . . . . .	18
Fig.7 NO <sub>x</sub> Hourly Values . . . . .	19
Fig.8 PM <sub>10</sub> Daily Values . . . . .	24
Fig 9. PM <sub>10</sub> and PM <sub>2.5</sub> Daily Values . . . . .	25
Fig.10 Benzene Hourly Values . . . . .	27
Fig. 11 Toluene Hourly Values . . . . .	29

### **Summary**

An assessment of air quality was carried out in Carlow town from July 12<sup>th</sup> 2004 until March 14<sup>th</sup> 2005. No limit values were exceeded during the measurement period.

Concentrations of carbon monoxide, sulphur dioxide, nitrogen dioxide, benzene and lead were below their respective lower assessment thresholds. Levels of PM<sub>10</sub> exceeded the upper assessment threshold.

	<b>Below Lower Assessment Threshold</b>	<b>Below Upper Assessment Threshold</b>	<b>Above Upper Assessment Threshold</b>	<b>Above Limit</b>
<b>PM<sub>10</sub></b>				
<b>NO<sub>2</sub></b>				
<b>CO</b>				
<b>SO<sub>2</sub></b>				
<b>Benzene</b>				
<b>Pb</b>				

Carlow is in Zone C of the country, this zone is made up of 15 cities and towns around the country all with populations in excess of 15,000. The implications of this assessment are that within Zone C

- Levels of PM<sub>10</sub> will need to be monitored continuously
- Levels of CO, SO<sub>2</sub>, NO<sub>2</sub>, 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. Continuous monitoring is required if levels exceed the upper assessment threshold.

## ***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, 2<sup>nd</sup> 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<sub>2</sub>, NO<sub>x</sub>, 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 quality measurements. These trailers contain 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).

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 trailer was brought to the fire station in Carlow on 12<sup>th</sup> July 2004. It remained in position until 13<sup>th</sup> March 2005.

### ***Siting***

The trailer was located at Carlow fire station in a mixed residential/commercial area. In this site the trailer was approximately 200m from the town centre.

Fig. 1 Map of site location (kind permission of Ordnance Survey Ireland)



Location of trailer

## ***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 whose measurement technique is based on the absorption of infrared radiation by CO molecules at wavelengths near 4.7 $\mu$ m.

### *Sulphur Dioxide*

Sulphur dioxide was monitored using an Advanced Pollution Instrumentation SO<sub>2</sub> Fluorescent Analyser - Model 100A. This is a continuous analyser which measures the fluorescence of SO<sub>2</sub> molecules after excitation by ultraviolet radiation.

### *Nitrogen Dioxide and Oxides of Nitrogen*

NO<sub>x</sub> species were monitored using an Advanced Pollution Instrumentation Chemiluminescent NO/NO<sub>2</sub>/NO<sub>x</sub> Analyser - Model 200A. This is a continuous analyser which utilises the chemiluminescent reaction between nitric oxide in the sample and ozone to measure NO concentrations. Any NO<sub>2</sub> present is then reduced to NO by a molybdenum converter giving a second value for total NO<sub>x</sub> concentration. The amount of NO<sub>2</sub> present is found by subtraction.

### *Particulate Matter*

A gravimetric method was used to monitor PM<sub>10</sub> particles (as defined in European Standard, EN12341, 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 10 $\mu$ m. The particles were collected on preweighed glassfibre filters (Whatman GF/A, 47mm). The filters were equilibrated at constant temperature and humidity (T = 293 $\pm$ 1 $^{\circ}$ K, R.H. = 50 $\pm$ 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  $\beta$  source removed, OPSIS, S-24402, Furulund, Sweden) was used to change the filters daily at midnight.

Particulate matter was also measured using an OSIRIS Environmental Dust Monitor (Turnkey Instruments, 1&2 Dalby Court, Gadbrook Business Centre, Northwich, 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<sub>10</sub>, PM<sub>2.5</sub> and PM<sub>1</sub>.

### *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 fifteen minute cycle and is equipped with a photoionisation detector.

### *Lead and Other Metals*

Ambient air was pumped through a Metrical membrane filter (Gelman, 37mm, 0.8 $\mu$ m) situated in a calming chamber. The filters were changed every 3-4 weeks. They were digested in conc. HNO<sub>3</sub> and analysed for lead and other metals using ICP-MS (Inductively Coupled Plasma-Mass Spectrometry).

All results for CO, SO<sub>2</sub>, NO<sub>x</sub> and the continuous particulate monitor were integrated to give 1-hour average values as required for comparison with the Directive limit values.



## Results

### Carbon Monoxide

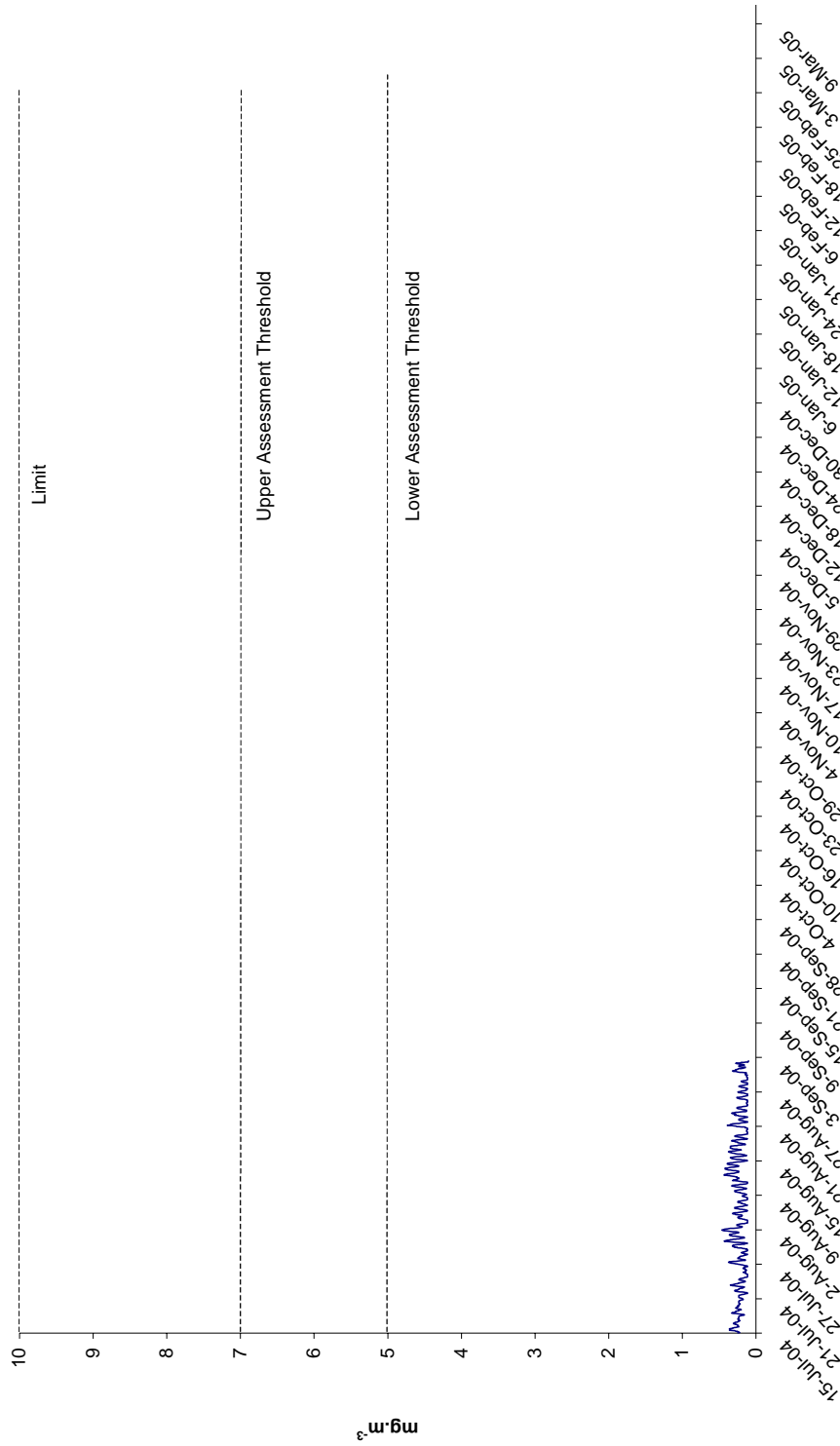
No. of hours	5823	
Missing values (including routine maintenance)	4630	0
No. of measured values	1193	
Percentage covered	20.5	
Maximum hourly value	0.6	mg.m <sup>-3</sup>
98 percentile for hourly values	0.5	mg.m <sup>-3</sup>
Mean hourly value	0.2	mg.m <sup>-3</sup>
Maximum 8-hour mean	0.5	mg.m <sup>-3</sup>
98 percentile for 8-hour mean	0.4	mg.m <sup>-3</sup>

### Directive Limits (2000/69/EC)

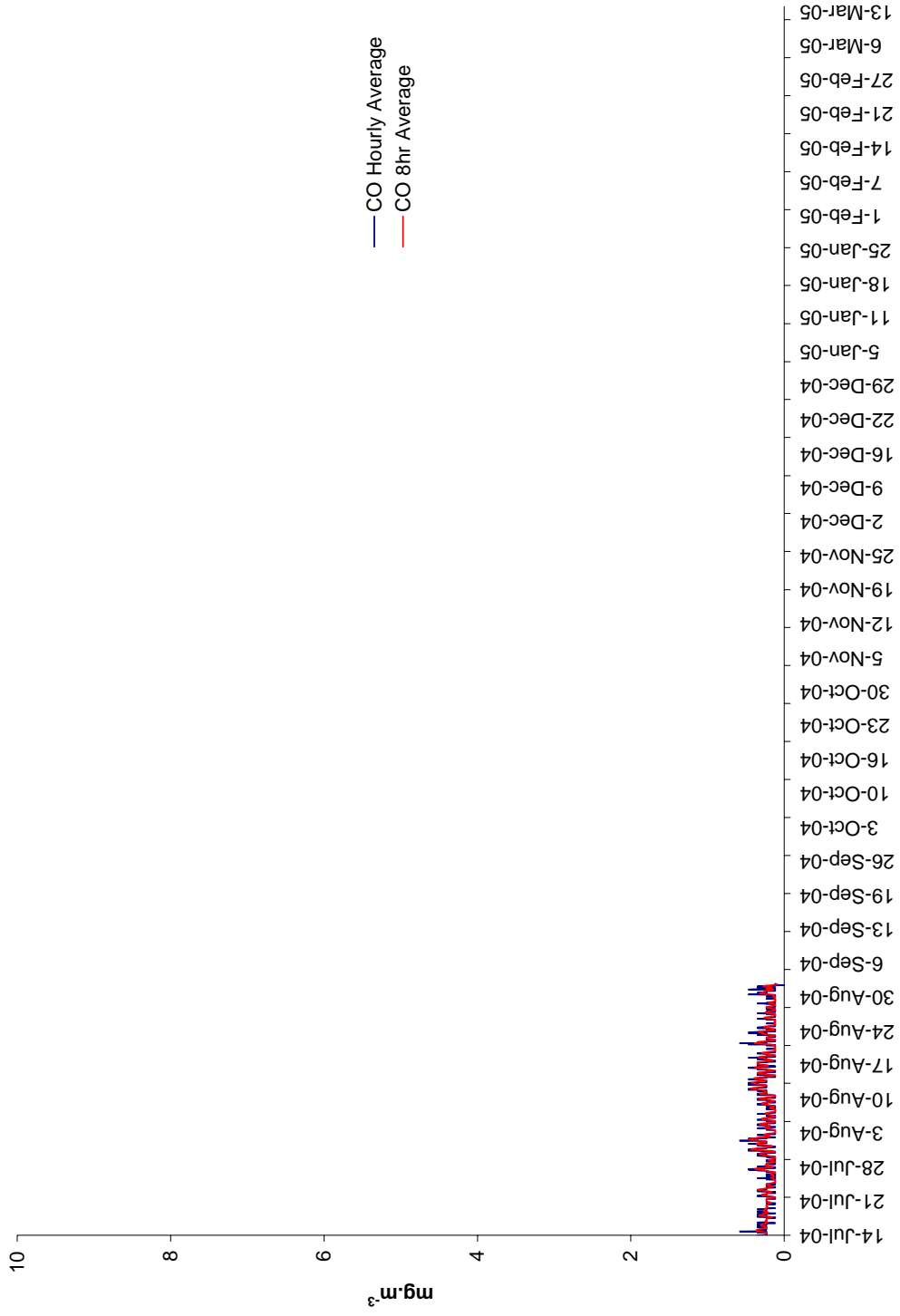
	Averaging Period	Limit Value	Date by which limit value is to be met
Limit Value for the protection of human health	8-hour running average	10 mg m <sup>-3</sup>	1 January 2005
Upper assessment threshold	8-hour running average	7 mg m <sup>-3</sup>	
Lower assessment threshold	8-hour running average	5 mg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

Carbon monoxide monitoring took place between July 12<sup>th</sup> and September 2<sup>nd</sup> 2004. The lower assessment threshold was not exceeded during the monitoring period (Figure 2).

**Fig. 2 Carbon Monoxide 8hr Running Average  
Trailer 2 in Carlow 12/7/04 - 14/3/05**



**Fig. 3 Carbon monoxide  
Trailer 2 in Carlow 12/7/04 - 14/3/05**



## Sulphur Dioxide

No. of hours	5823
Missing values (including routine maintenance)	646 32
No. of measured values	5177
Percentage covered	88.9
Maximum hourly value	48.4 $\mu\text{g.m}^{-3}$
98 percentile for hourly values	18.1 $\mu\text{g.m}^{-3}$
Mean hourly value	4.7 $\mu\text{g.m}^{-3}$
Maximum 24-hour value	22.1 $\mu\text{g.m}^{-3}$
98 percentile for 24-hour values	16.1 $\mu\text{g.m}^{-3}$

### Directive Limits (1999/30/EC)

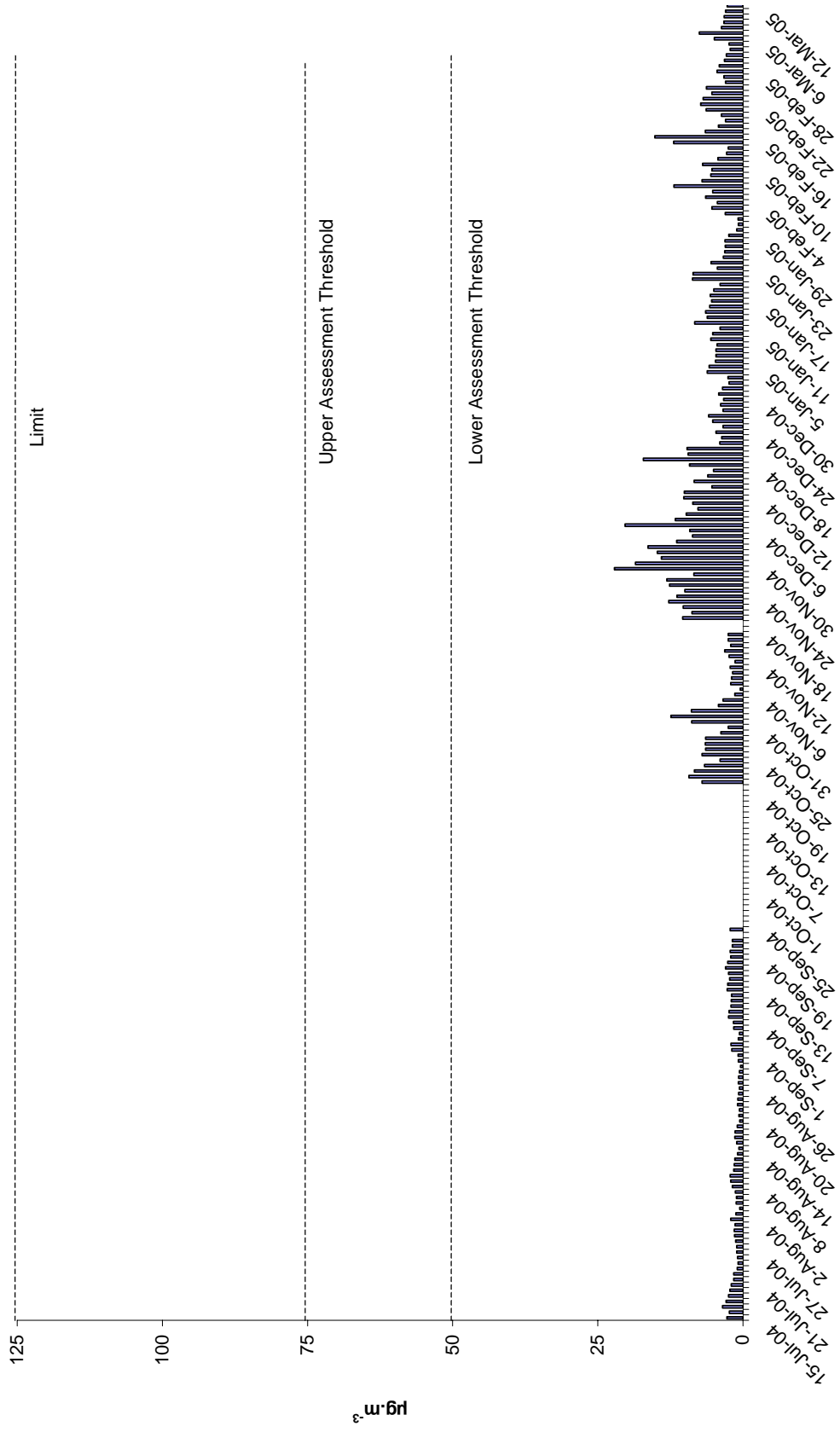
	Averaging Period	Limit Value	Date by which limit value is to be met
Hourly limit value for the protection of human health	1 hour	350 $\mu\text{g m}^{-3}$ not to be exceeded more than 24 times a calendar year	1 January 2005
Daily limit value for the protection of human health	24 hours	125 $\mu\text{g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

**Directive Limits (1999/30/EC) continued**

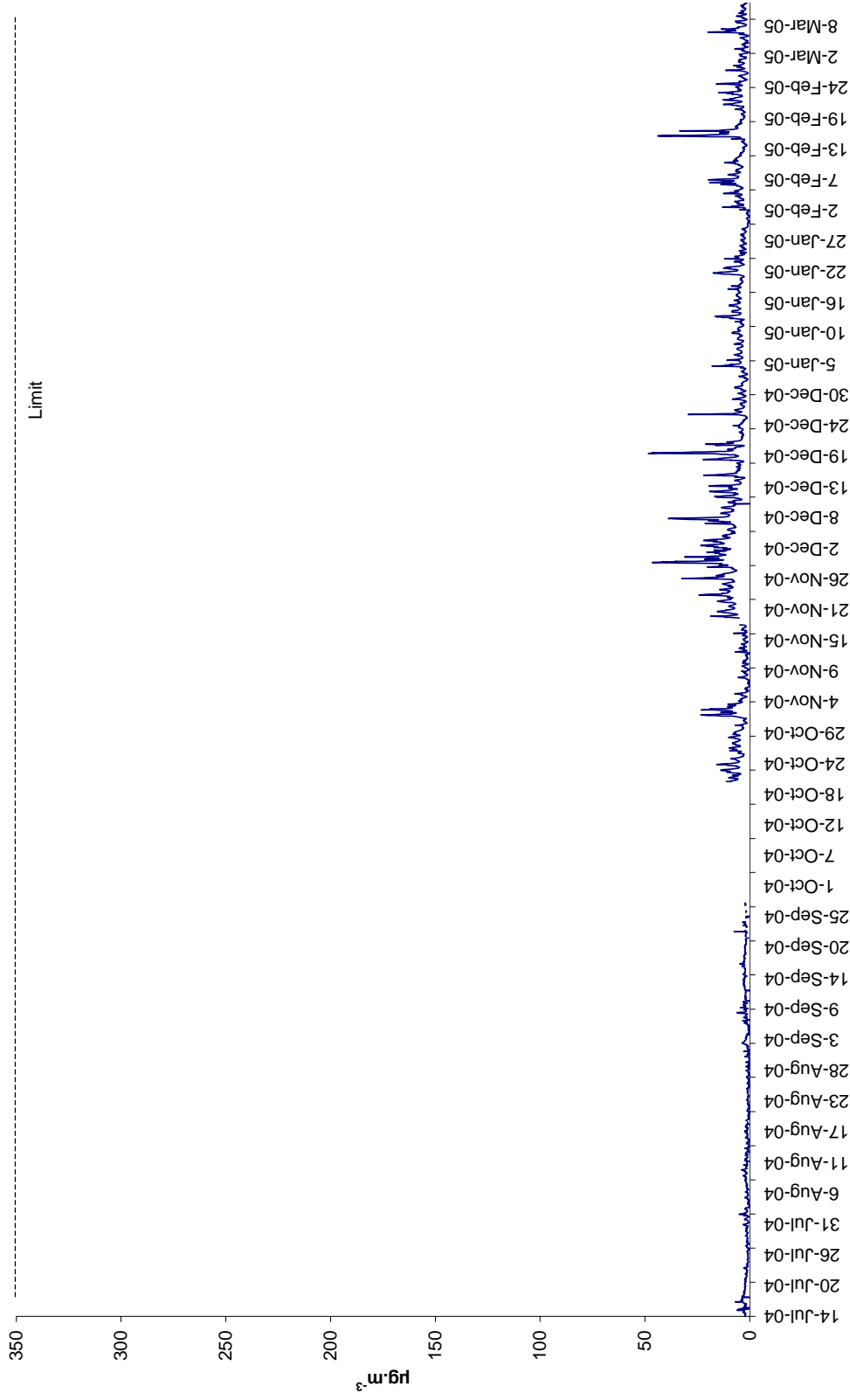
	Averaging Period	Limit Value	Date by which limit value is to be met
Upper assessment threshold for the protection of human health	24 hours	75 $\mu\text{g m}^{-3}$ not to be exceeded more than 3 times a calendar year	
Lower assessment threshold for the protection of human health	24 hours	50 $\mu\text{g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

The hourly and daily limit values for the protection of human health were not exceeded during the measurement period. Similarly, the lower assessment thresholds for the protection of human health and for the protection of ecosystems were not exceeded.

**Fig. 4 Sulphur Dioxide 24 Hour Averages  
Trailer 2 in Carlow 12/7/04-14/3/05**



**Fig. 5 Sulphur Dioxide Hourly Values  
Trailer 2 in Carlow 12/7/04 - 14/3/05**



## Nitrogen Dioxide and Oxides of Nitrogen

No. of hours	5823
Missing values (including routine maintenance)	534 32
No. of measured values	5289
Percentage covered	90.8
Maximum hourly value (NO <sub>2</sub> )	90.5 $\mu\text{g}\cdot\text{m}^{-3}$
98 percentile for hourly values (NO <sub>2</sub> )	50 $\mu\text{g}\cdot\text{m}^{-3}$
Mean hourly value (NO <sub>2</sub> )	15.8 $\mu\text{g}\cdot\text{m}^{-3}$
Mean hourly value (NO <sub>x</sub> )	27.4 $\mu\text{g}\cdot\text{m}^{-3}$ NO <sub>2</sub>

### 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 $\mu\text{g m}^{-3}$ NO <sub>2</sub> 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 $\mu\text{g m}^{-3}$ NO <sub>2</sub>	1 January 2010
Annual limit value for the protection of vegetation	Calendar year	30 $\mu\text{g m}^{-3}$ NO <sub>x</sub>	19 July 2001
Alert threshold		400 $\mu\text{g m}^{-3}$ NO <sub>2</sub> over three consecutive hours	



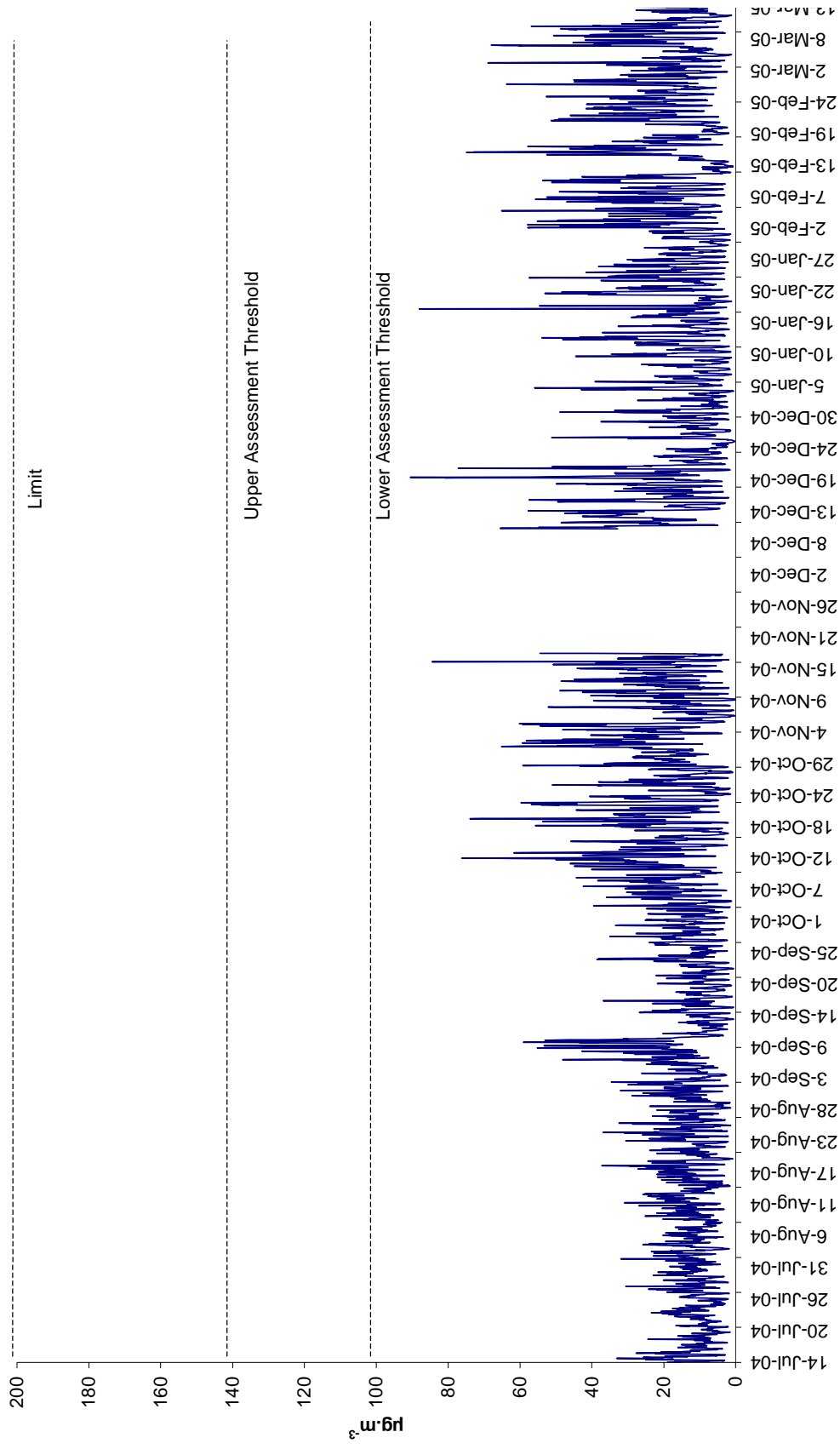
**Directive Limits (1999/30/EC) continued**

	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 $\mu\text{g m}^{-3}$ NO <sub>2</sub> not to be exceeded more than 18 times a calendar year	
Upper assessment threshold for the protection of human health	Calendar year	32 $\mu\text{g m}^{-3}$ NO <sub>2</sub>	
Lower assessment threshold for the protection of human health	1 hour	100 $\mu\text{g m}^{-3}$ NO <sub>2</sub> not to be exceeded more than 18 times a calendar year	
Lower assessment threshold for the protection of human health	Calendar year	26 $\mu\text{g m}^{-3}$ NO <sub>2</sub>	
Upper assessment threshold for the protection of vegetation	Calendar year	24 $\mu\text{g m}^{-3}$ NO <sub>x</sub>	
Lower assessment threshold for the protection of vegetation	Calendar year	19.5 $\mu\text{g m}^{-3}$ NO <sub>x</sub>	

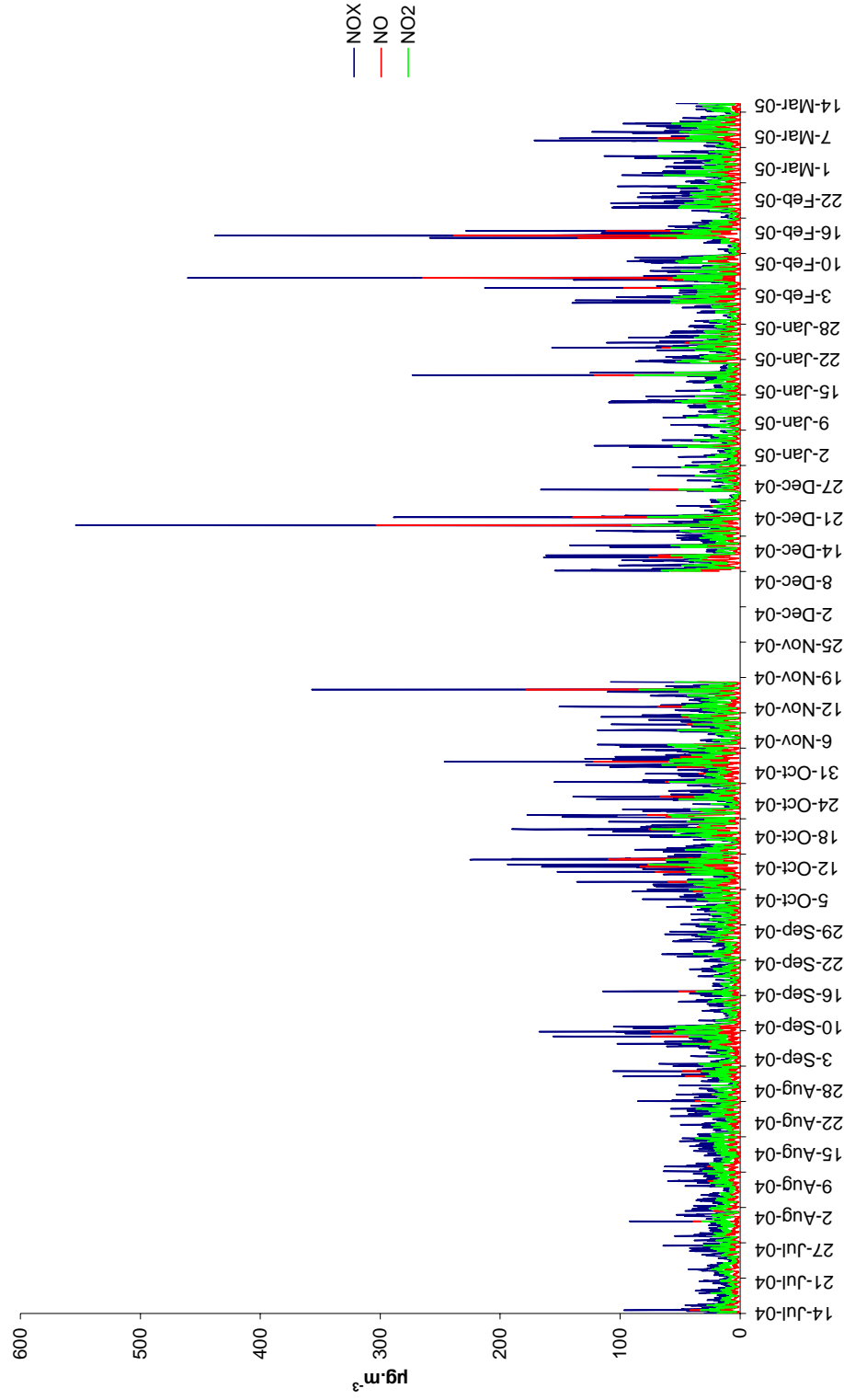
The hourly and annual limit values for the protection of human health were not exceeded during the assessment. Similarly, the lower assessment threshold for the protection of human health was not exceeded. Although the upper assessment threshold for vegetation protection was exceeded, the applicability of this standard to urban air quality monitoring is uncertain.

NO, NO<sub>2</sub> and NO<sub>x</sub> are measured as ppb (parts per billion) by volume. To convert to  $\mu\text{g}\cdot\text{m}^{-3}$ , a factor (1.25 for NO, 1.91 for NO<sub>2</sub>) is used. No formula is specified for NO<sub>x</sub>, the directive requires it to be expressed as NO<sub>2</sub> (i.e. ppb\*1.91). This applies even when most of the NO<sub>x</sub> is present as NO.

**Fig.6 NO<sub>2</sub> Hourly Values  
Trailer 2 in Carlow 12/7/04 - 14/3/05**



**Fig. 7 NO<sub>x</sub> Hourly Values  
Trailer 2 in Carlow 12/7/04 - 14/3/05**



## Particulate Matter

### PM<sub>10</sub> : gravimetric method

No. of days	244
Missing values (including routine maintenance)	97 1
No. of measured values	147
Percentage covered	60.2
Maximum daily value	57.4 $\mu\text{g.m}^{-3}$
98 percentile for daily values	47.6 $\mu\text{g.m}^{-3}$
Mean daily value	16.6 $\mu\text{g.m}^{-3}$

### 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 $\mu\text{g m}^{-3}$ PM <sub>10</sub> 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 $\mu\text{g m}^{-3}$ PM <sub>10</sub>	1 January 2005
Upper assessment threshold for the protection of human health	24 hour	30 $\mu\text{g m}^{-3}$ PM <sub>10</sub> not to be exceeded more than 7 times a calendar year	<i>based on the indicative limit values for 1 January 2010</i>
Upper assessment threshold for the protection of human health	Calendar year	14 $\mu\text{g m}^{-3}$ PM <sub>10</sub>	<i>based on the indicative limit values for 1 January 2010</i>

**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 $\mu\text{g m}^{-3}$ PM <sub>10</sub> not to be exceeded more than 7 times a calendar year	<i>based on the indicative limit values for 1 January 2010</i>
Lower assessment threshold for the protection of human health	Calendar year	10 $\mu\text{g m}^{-3}$ PM <sub>10</sub>	<i>based on the indicative limit values for 1 January 2010</i>

**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 $\mu\text{g m}^{-3}$ PM <sub>10</sub> 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 $\mu\text{g m}^{-3}$ PM <sub>10</sub>	1 January 2010

There was one daily value greater than the 2004 limit value ( $55 \mu\text{g}\cdot\text{m}^{-3}$ ) and two values greater than the 2005 limit value ( $50 \mu\text{g}\cdot\text{m}^{-3}$ ). Neither the daily or the annual limits for the protection of human health were exceeded. The lower assessment threshold was exceeded on 35 occasions (23.8% of measured values) while the upper assessment threshold was exceeded on 13 occasions (8.8% of measured values). Carlow is classified as being above the upper assessment threshold for  $\text{PM}_{10}$  as the directive stipulates that assessment thresholds can only be exceeded 7 times in a calendar year.

## Particulate Matter : PM<sub>2.5</sub>

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<sub>2.5</sub> are installed.”*

The concentration of PM<sub>2.5</sub> was measured with an OSIRIS Environmental Dust Monitor in the mobile laboratory. This also measured total suspended particles (TSP), PM<sub>10</sub> and PM<sub>1</sub>. All measurements were hourly values.

The concentration of PM<sub>10</sub> 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<sub>2.5</sub> using the formula:

$$\begin{array}{l} \text{24-hour average} \\ \text{concentration} \\ \text{of PM}_{2.5} \end{array} = \begin{array}{l} \text{OSIRIS 24-hour} \\ \text{average concentration} \\ \text{of PM}_{2.5} \end{array} \times \frac{\text{gravimetric 24-hour average PM}_{10}}{\text{OSIRIS 24-hour average PM}_{10}}$$

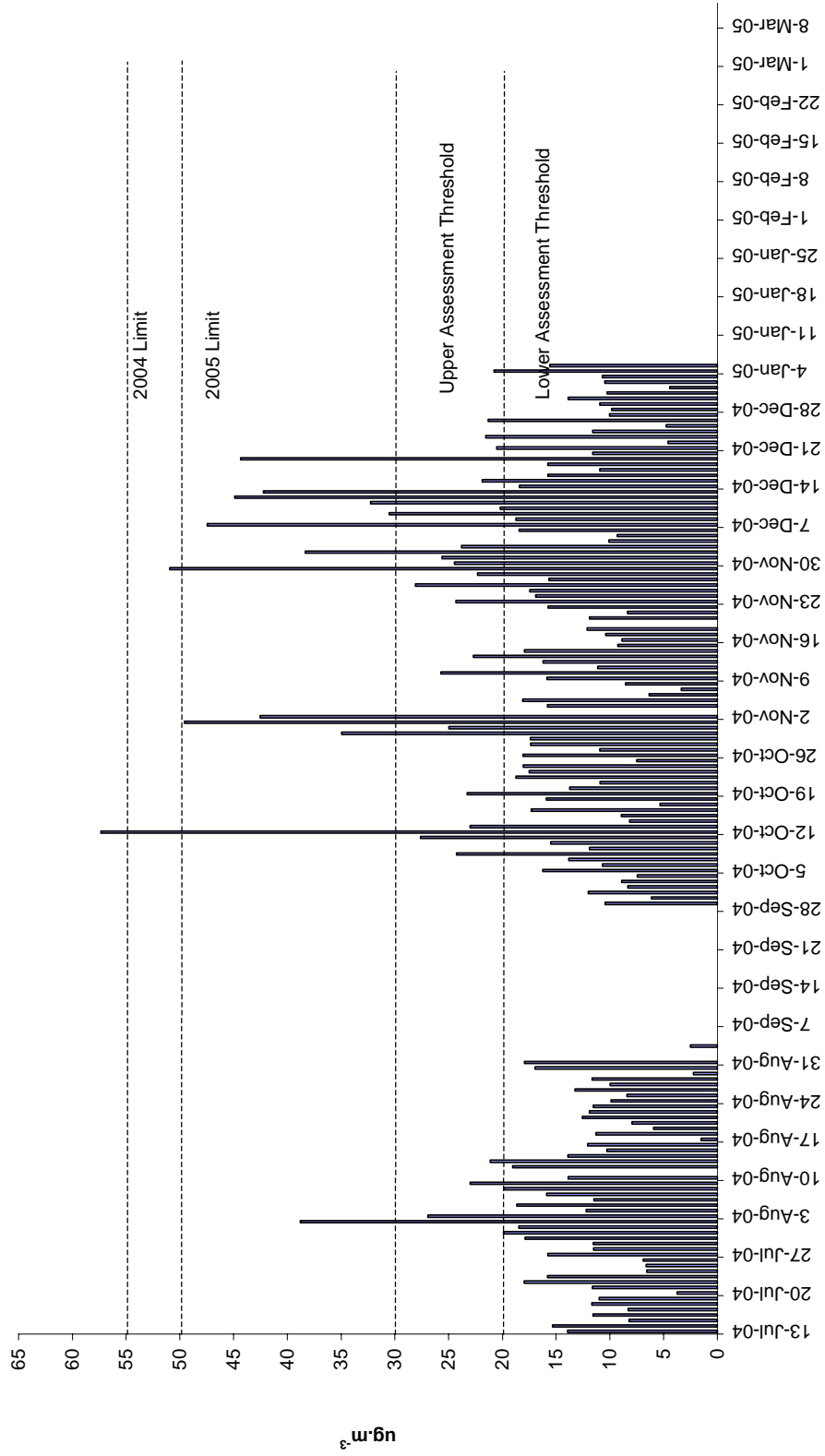
### Results:

No. of days	244
Missing values (including routine maintenance)	138 0
No. of measured values*	106
Percentage covered	43.4
Maximum daily value	28.4 $\mu\text{g.m}^{-3}$
98 percentile for daily values	25.6 $\mu\text{g.m}^{-3}$
Mean daily value	7.4 $\mu\text{g.m}^{-3}$
Median daily value	6.1 $\mu\text{g.m}^{-3}$

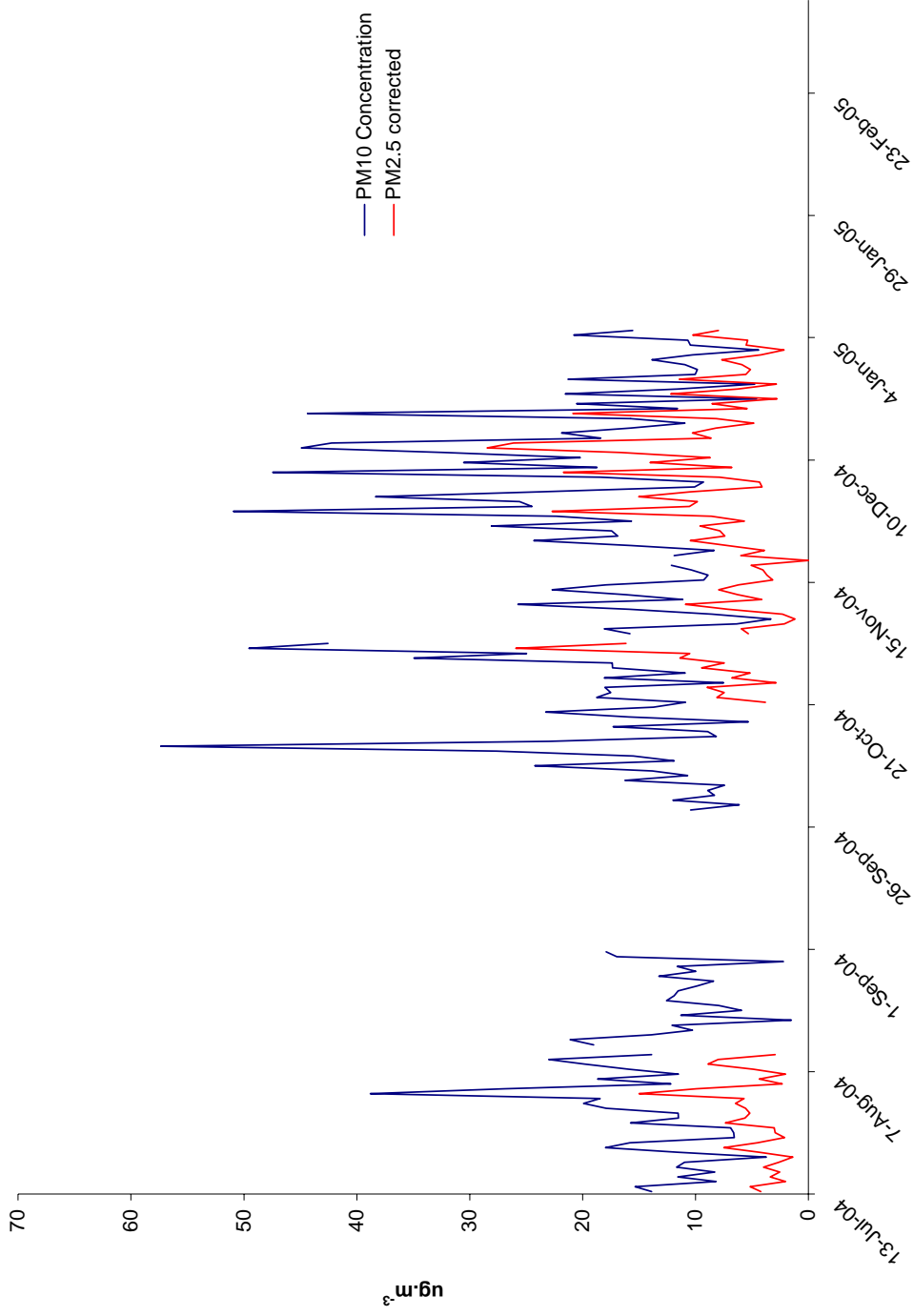
\* no. of days with measurements from both the OSIRIS monitor and the gravimetric method.



**Fig. 8 PM<sub>10</sub> Daily Values  
Trailer 2 in Carlow 12/7/04 - 14/3/05**



**Fig. 9 PM<sub>10</sub> and PM<sub>2.5</sub> Daily Values  
Trailer 2 in Carlow 12/7/04 - 14/3/05**



## Benzene

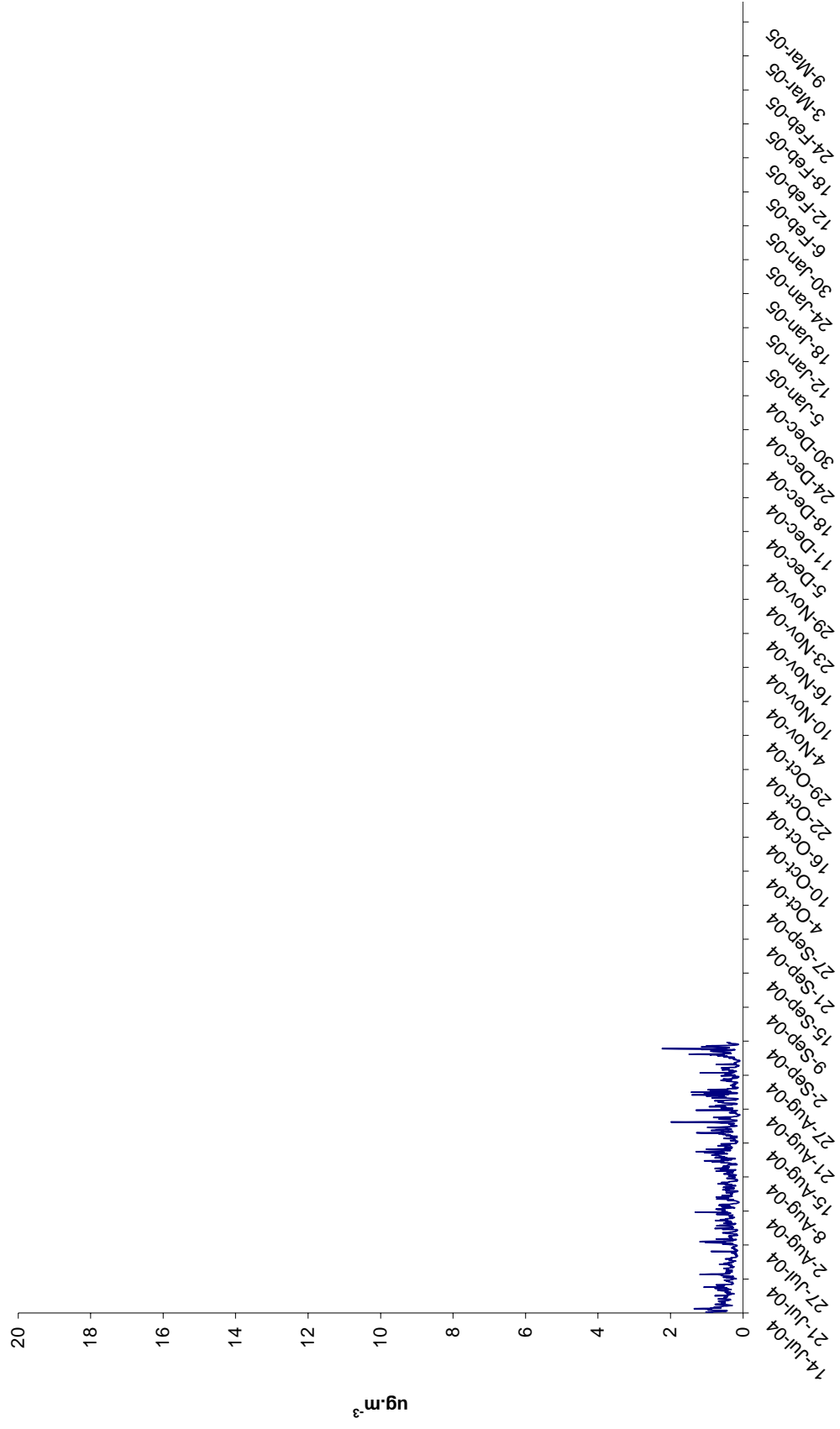
No. of hours	5823
Missing values (including routine maintenance)	4630 1
No. of measured values	1193
Percentage covered	20.5
Maximum hourly value	2.2 $\mu\text{g.m}^{-3}$
98 percentile for hourly values	1.1 $\mu\text{g.m}^{-3}$
Mean hourly value	0.4 $\mu\text{g.m}^{-3}$

### Directive Limits (2000/69/EC)

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

Benzene monitoring took place between July 12<sup>th</sup> and September 2<sup>nd</sup> 2004. The lower assessment threshold was not exceeded during this monitoring period (Figure 10).

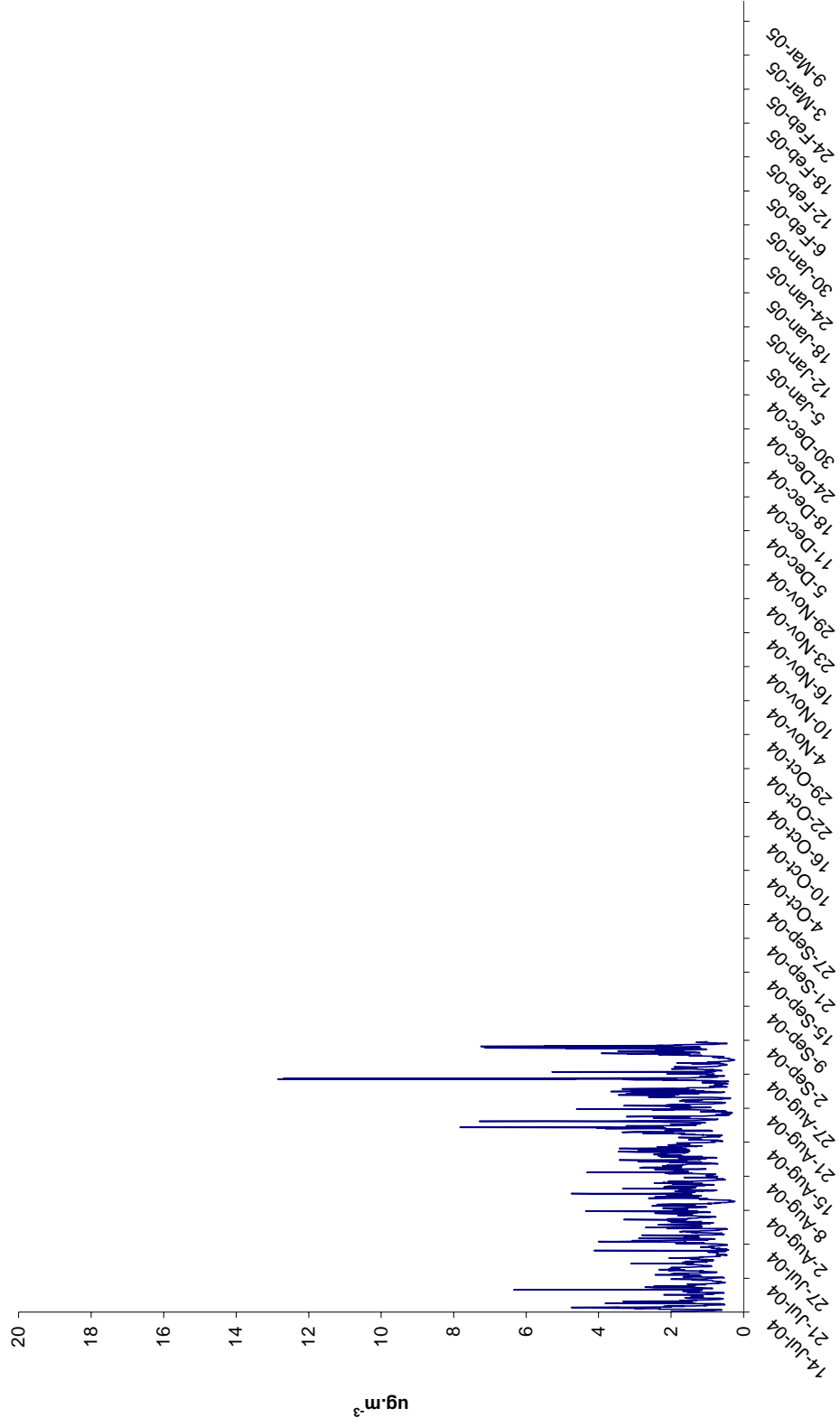
**Fig. 10 Benzene Hourly Values  
Trailer 2 in Carlow 12/7/04 - 14/3/05**



## Toluene

No. of hours	5823	
Missing values (including routine maintenance)	4630	1
No. of measured values	1193	
Percentage covered	20.5	
Maximum hourly value	12.8	$\mu\text{g.m}^{-3}$
98 percentile for hourly values	4.0	$\mu\text{g.m}^{-3}$
Mean hourly value	1.5	$\mu\text{g.m}^{-3}$

**Fig. 11 Toluene Hourly Values  
Trailer 2 in Carlow 12/7/04 - 14/3/05**



## Lead

No. of days	245
Missing days (including routine maintenance)	30 0
No. of measured days	215
Percentage covered	87.7
Concentration of Pb	0.02 $\mu\text{g}\cdot\text{m}^{-3}$

### 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 $\mu\text{g m}^{-3}$	1 January 2005
Upper assessment threshold	Calendar year	0.35 $\mu\text{g m}^{-3}$	
Lower assessment threshold	Calendar year	0.25 $\mu\text{g m}^{-3}$	

The concentration of lead 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 have subsequently been set out in the fourth daughter directive (2004/107/EC). The fourth daughter directive requires metals to be determined in the PM<sub>10</sub> fraction.

The method used in this assessment to measure lead and other metals essentially involved pumping air through a filter for several weeks before digesting the filter and analysing the digest for lead and other metals using ICP-MS. This method only provides an indication of metal concentrations in air and is not the proper method as specified in the fourth daughter directive

The results, although indicative, do provide some indication of metal concentrations in air.

During this assessment

The maximum concentration of arsenic in the air were lower than trace levels of arsenic known to exist on the filter papers.

The maximum level of nickel in the air was found to be 72.1 ng.m<sup>-3</sup>

The maximum level of cadmium in the air was found to be 24.6 ng.m<sup>-3</sup>

<b>Sampling Date</b>	<b>As</b>	<b>Cd</b>	<b>Ni</b>
11/8/04-28/9/04	BDL	3.7 ng.m <sup>-3</sup>	1.7 ng.m <sup>-3</sup>
28/9/04-20/10/04	BDL	24.6 ng.m <sup>-3</sup>	BDL
20/10/04-10/12/04	BDL	BDL	47.1 ng.m <sup>-3</sup>
10/12/04-6/1/05	BDL	BDL	BDL
6/1/05-25/1/05	BDL	BDL	72.1 ng.m <sup>-3</sup>
25/1/05-14/3/05	BDL	BDL	21.5 ng.m <sup>-3</sup>

BDL : Below detection limit



