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Environmental Protection Agency  
*An Ghníomhaireacht um Chaomhnú Comhshaoil*

**Ambient Air Monitoring**

**In**

**Limerick City**

**January 26<sup>th</sup> 2000 - 13<sup>th</sup> November 2000**

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## Summary

An assessment of air quality was carried out in Limerick city from 26<sup>th</sup> January until 13<sup>th</sup> November 2000. 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 for this parameter.

	<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>				

Limerick is in Zone C of the country. The implications of this assessment are that within Zone C (specified urban centres with populations in excess of 15,000)

- 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 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, toluene and xylene
- 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

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### ***Time Period***

The mobile laboratory was in place from 26<sup>th</sup> January 2000 until 13<sup>th</sup> November 2000.

### ***Siting***

The mobile laboratory was situated in the yard of a fire station owned by Limerick Corporation (Figure 1). The fire station is located on Mulgrave street with an entrance opening onto Cathedral Place, Limerick city centre is less than 1 km from the fire station. The laboratory was sited near the Cathedral Place entrance where it was approximately 40 metres distant from the kerbside of that street and approximately 80 metres distant from the kerbside on Mulgrave street. The area immediately surrounding the fire station is a predominantly commercial district with a high volume of traffic. Mulgrave street carries traffic from the city centre to the southern ring road and onto Waterford and Tipperary.

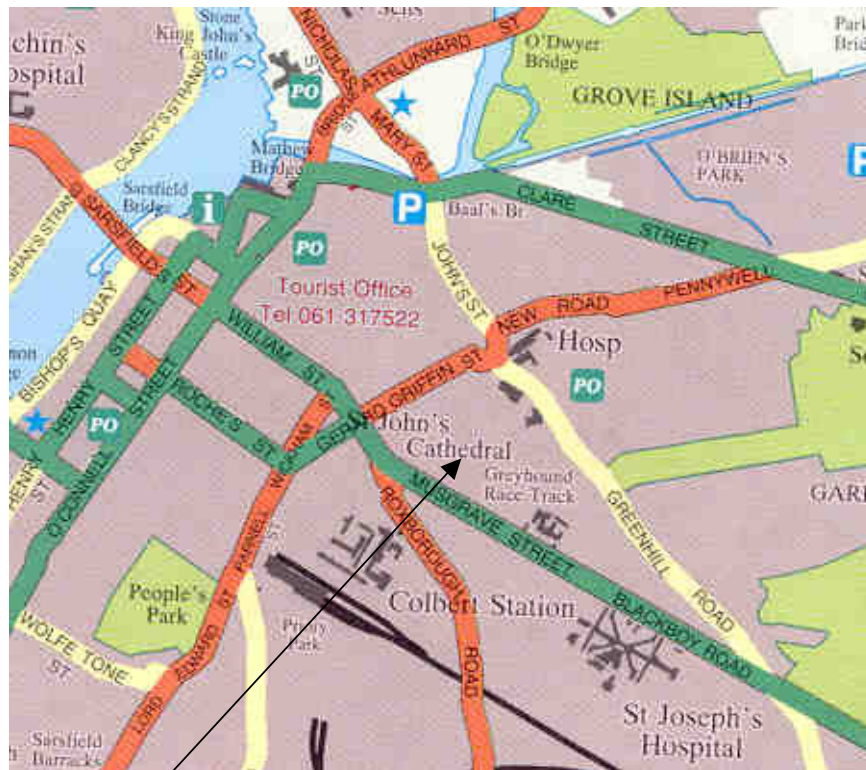


Fig. 1 Map of site location

Location of mobile laboratory

## ***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 4.7 $\mu$ 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> due to absorption of 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 of nitric oxide in the sample and ozone to measure the 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, prEN12341, July 1998, Central Secretariat, rue de Stassart, 36, B-1050 Brussels). The air was sampled by an Ambient Dust Automatic Monitor (Model SM200CD with  $\beta$  source removed, OPSIS, S-24402, Furulund, Sweden) which changed the filters daily at midnight. 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.

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 every 15 minutes and is equipped with a photoionisation detector.

*Lead and Other Metals*

Ambient air was pumped through a Metrical 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<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	6840
Missing values (including routine maintenance)	11 0
No. of measured values	6829
Percentage covered	99.8%
Maximum hourly value	2.3 mg.m <sup>-3</sup>
98 percentile for hourly values	0.9 mg.m <sup>-3</sup>
Mean hourly value	0.3 mg.m <sup>-3</sup>
Maximum 8-hour mean	1.8 mg.m <sup>-3</sup>
98 percentile for 8-hour mean	0.9 mg.m <sup>-3</sup>

### 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 <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>	

There were no exceedences of the lower assessment threshold during the measurement period (Figure 2).

Fig. 2 Carbon Monoxide 8-hour Running Average  
Trailer 2 in Limerick, 2/2/00-13/11/00

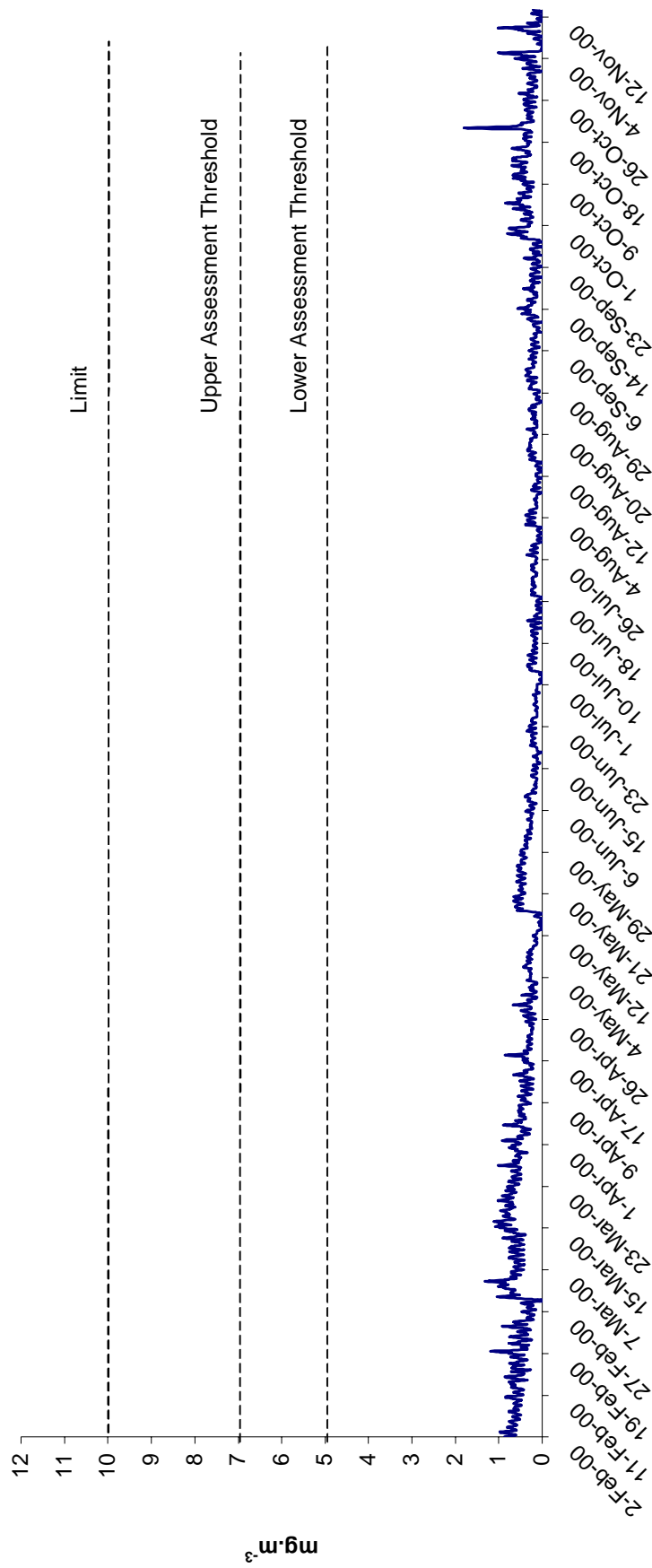
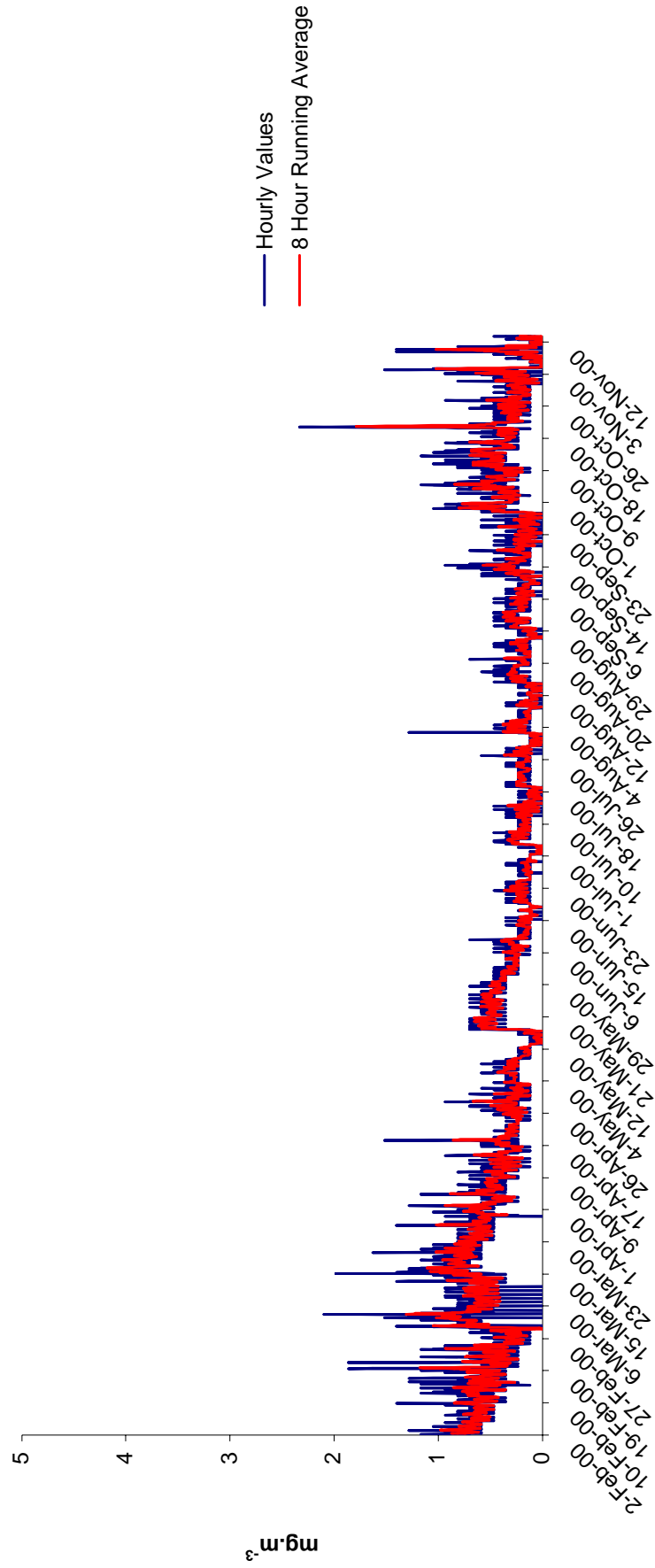


Fig. 3 Carbon Monoxide  
Trailer 2 in Limerick, 2/2/00-13/1/00



## Sulphur Dioxide

No. of hours	6840
Missing values (including routine maintenance)	28 12
No. of measured values	6812
Percentage covered	99.6%
Maximum hourly value	235.1 $\mu\text{g.m}^{-3}$
98 percentile for hourly values	50.5 $\mu\text{g.m}^{-3}$
Mean hourly value	10.4 $\mu\text{g.m}^{-3}$
Maximum 24-hour value	51.2 $\mu\text{g.m}^{-3}$
98 percentile for 24-hour values	29.5 $\mu\text{g.m}^{-3}$

### 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 limit value was not exceeded during the measurement period (Figure 5). There was one exceedence of the 50  $\mu\text{g.m}^{-3}$  lower assessment threshold (Figure 4). 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 10.4  $\mu\text{g.m}^{-3}$  exceeds the lower 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 Limerick 2/2/00-13/11/00

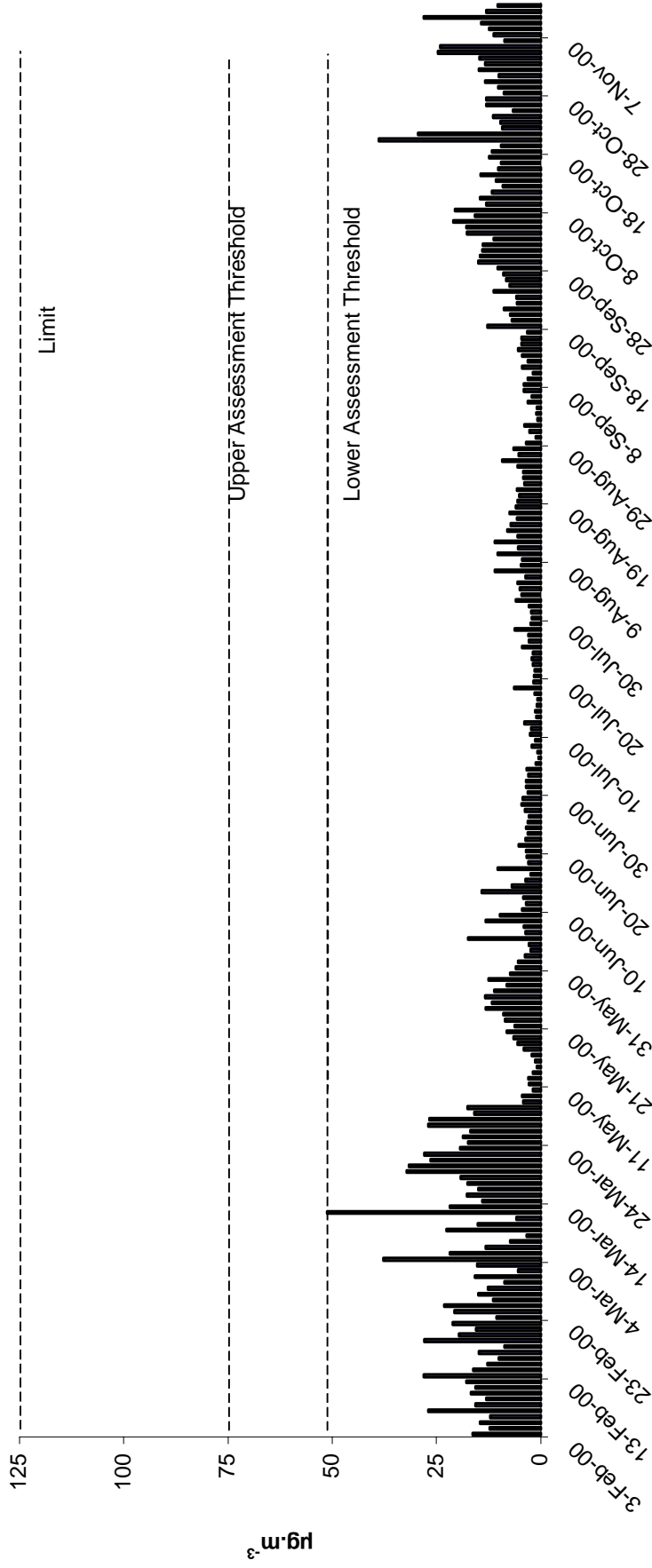
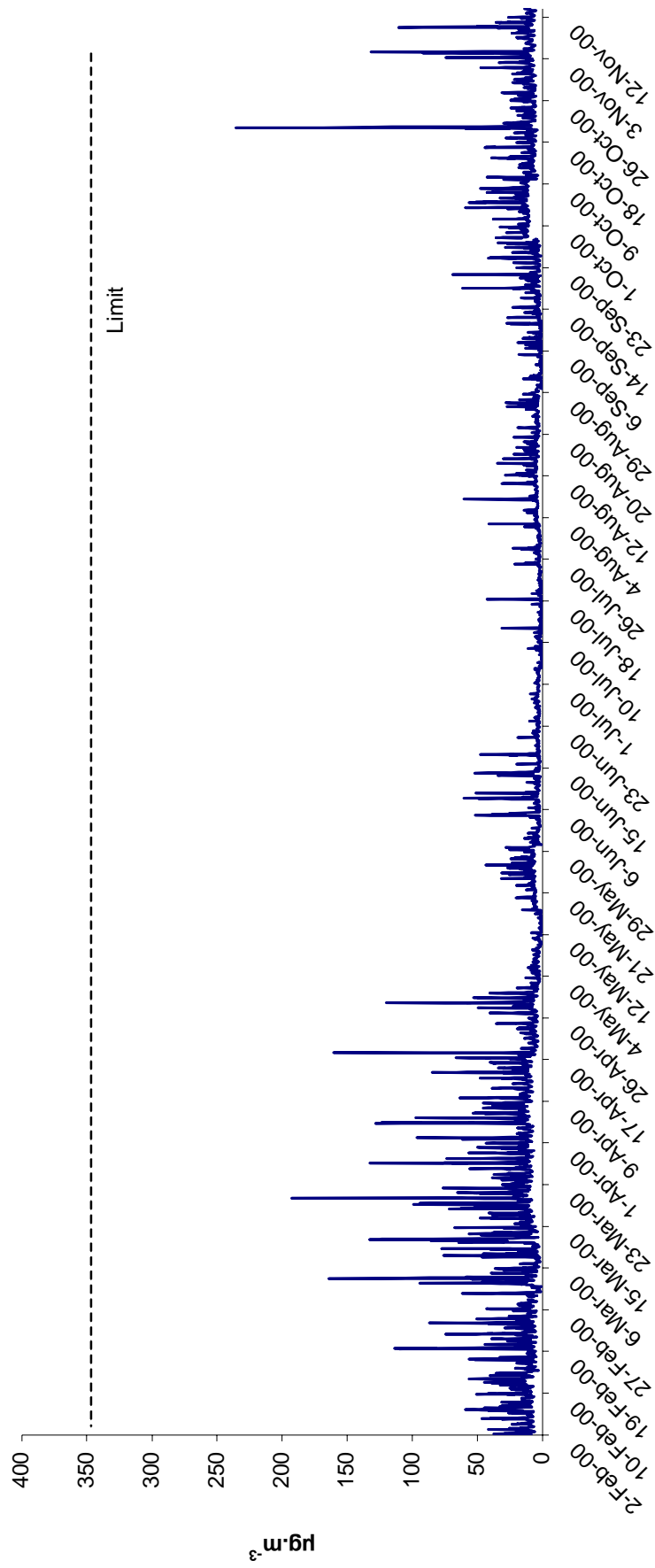


Fig.5 Sulphur Dioxide Hourly Averages  
Trailer 2 in Limerick 2/2/00-13/11/00



## Nitrogen Dioxide and Oxides of Nitrogen

No. of hours	6840
Missing values (including routine maintenance)	31 13
No. of measured values	6809
Percentage covered	99.5%
Maximum hourly value (NO <sub>2</sub> )	243.2 µg.m <sup>-3</sup>
98 percentile for hourly values (NO <sub>2</sub> )	57.6 µg.m <sup>-3</sup>
Mean hourly value (NO <sub>2</sub> )	22.0 µg.m <sup>-3</sup>
Mean hourly value (NO <sub>x</sub> )	34.1 µg.m <sup>-3</sup>

### 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 µg m <sup>-3</sup> 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 µg m <sup>-3</sup> NO <sub>2</sub>	1 January 2010
Annual limit value for the protection of vegetation	Calendar year	30 µg m <sup>-3</sup> NO <sub>x</sub>	19 July 2001
Alert threshold		400 µg m <sup>-3</sup> 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>	

Three hourly mean NO<sub>2</sub> values are above the lower assessment threshold for the protection of human health (Figure 6). Two hourly mean NO<sub>2</sub> values, both of which were recorded on March 23<sup>rd</sup>, are above the upper assessment threshold and above the limit value. The directive stipulates that the lower and upper assessment thresholds and

the limit value should not be exceeded more than 18 times in a calendar year. With the exception of these three values all other hourly mean NO<sub>2</sub> values are below the lower assessment threshold.

The mean hourly NO<sub>2</sub> value (22.0 µg.m<sup>-3</sup>) during the measurement period is below the annual lower assessment threshold for the protection of human health (26 µg.m<sup>-3</sup>).

The mean hourly value of NO<sub>x</sub> (34.1 µg.m<sup>-3</sup> NO<sub>2</sub>) during the measurement period exceeds the annual limit value for the protection of vegetation (30 µg.m<sup>-3</sup>). However, the applicability of this limit to urban air pollution monitoring is questionable.

NO, NO<sub>2</sub> and NO<sub>x</sub> are measured as ppb (parts per billion) by volume. To convert to µg.m<sup>-3</sup>, 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 Limerick 2/2/00-13/11/00**

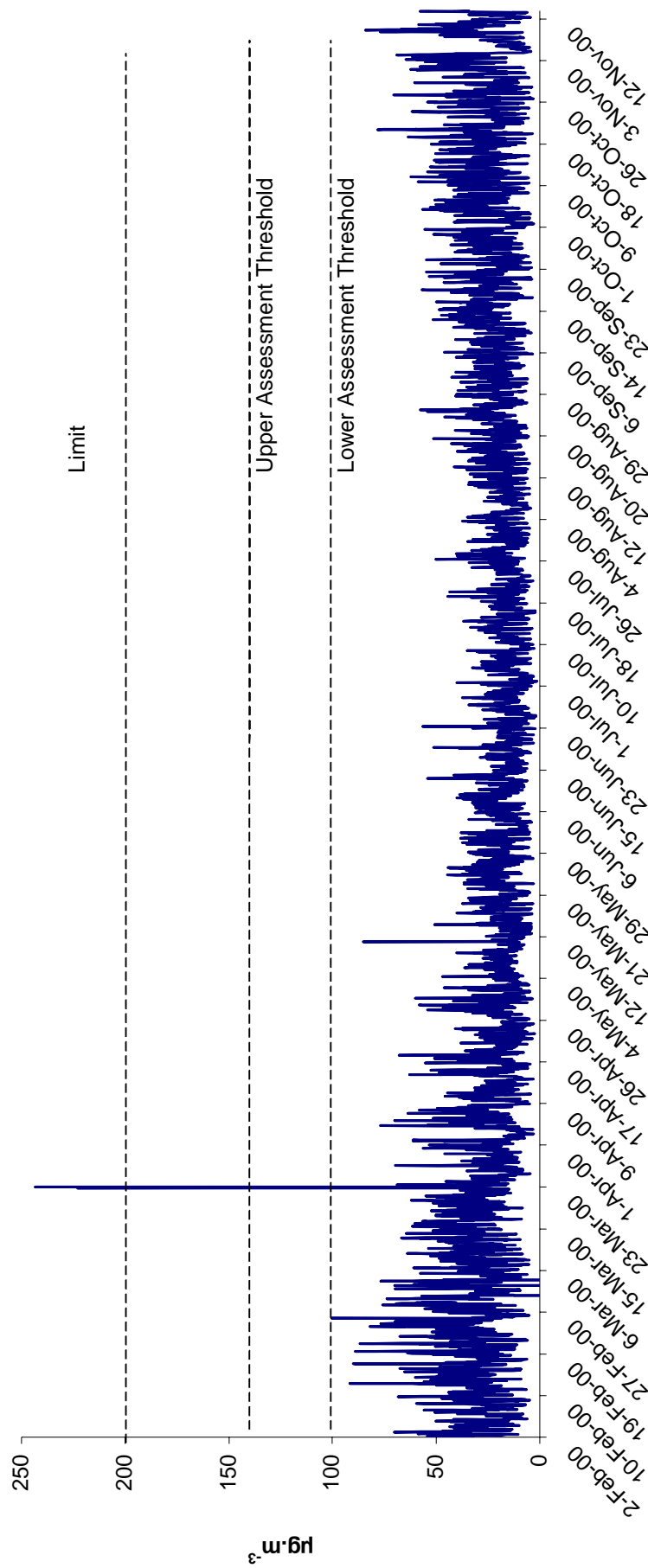
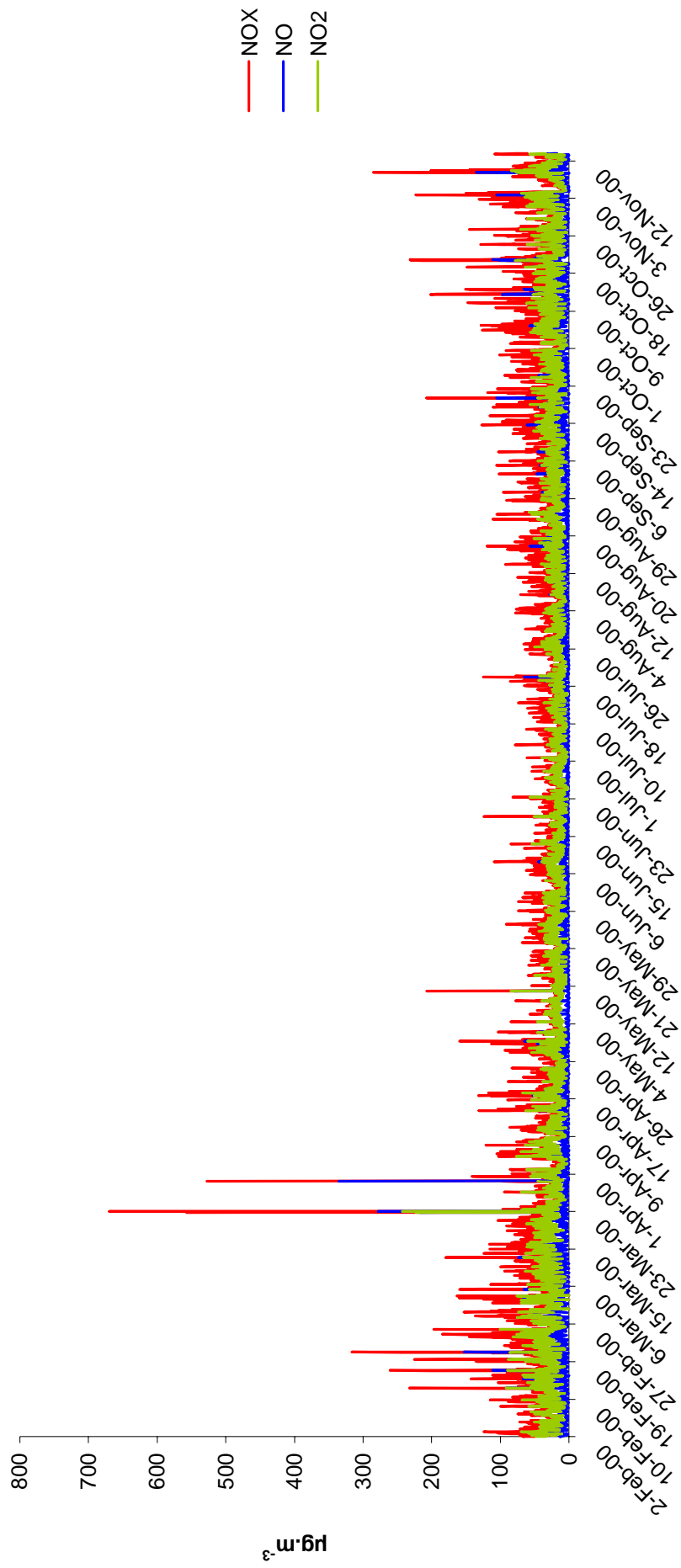


Fig. 7 NO<sub>x</sub> Hourly Values  
Trailer 2 in Limerick 2/2/00-13/11/00



## Particulate Matter

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

No. of days	291
Missing values (including routine maintenance)	84 0
No. of measured values	207
Percentage covered	71.1%
Maximum daily value	49.5 $\mu\text{g.m}^{-3}$
98 percentile for daily values	46.6 $\mu\text{g.m}^{-3}$
Mean daily value	24.0 $\mu\text{g.m}^{-3}$

### 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

The 24-hour limit value for the protection of human health was not breached during the measurement period (Figure 8). The upper assessment threshold was exceeded on 52 days (25.1% of values) while the lower assessment threshold was exceeded on 122 occasions (58.9% of values). 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 ( $24.0 \mu\text{g.m}^{-3}$ ) is below the annual limit value for the protection of human health ( $40 \mu\text{g.m}^{-3}$ ).

### **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.”*

In the mobile laboratory the concentration of PM<sub>2.5</sub> was measured with an OSIRIS Environmental Dust Monitor. 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	291
Missing values	86
(including routine maintenance)	0
No. of measured values*	205
Percentage covered	70.4%
Maximum daily value	18.9 $\mu\text{g.m}^{-3}$
98 percentile for daily values	10.6 $\mu\text{g.m}^{-3}$
Mean daily value	4.1 $\mu\text{g.m}^{-3}$
Median daily value	3.3 $\mu\text{g.m}^{-3}$

\* 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 Limerick 27/1/00-13/11/00

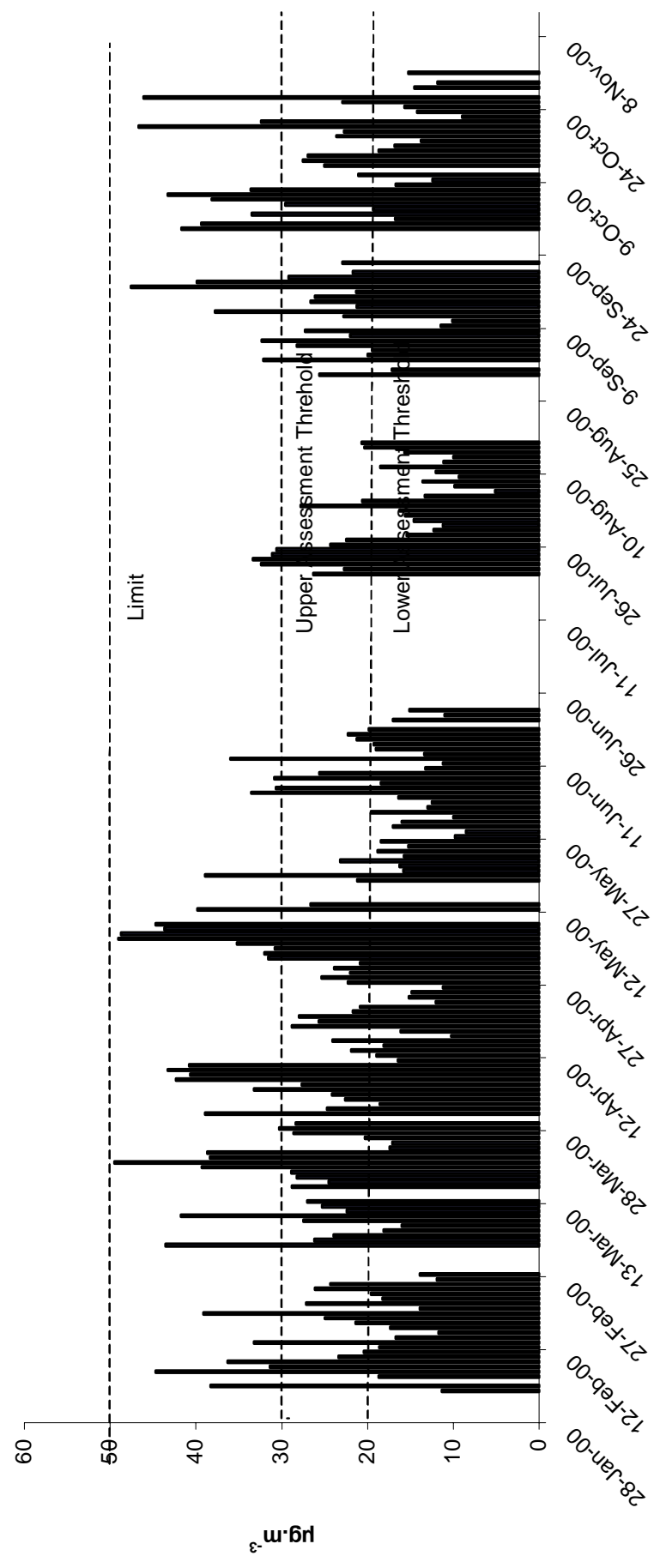
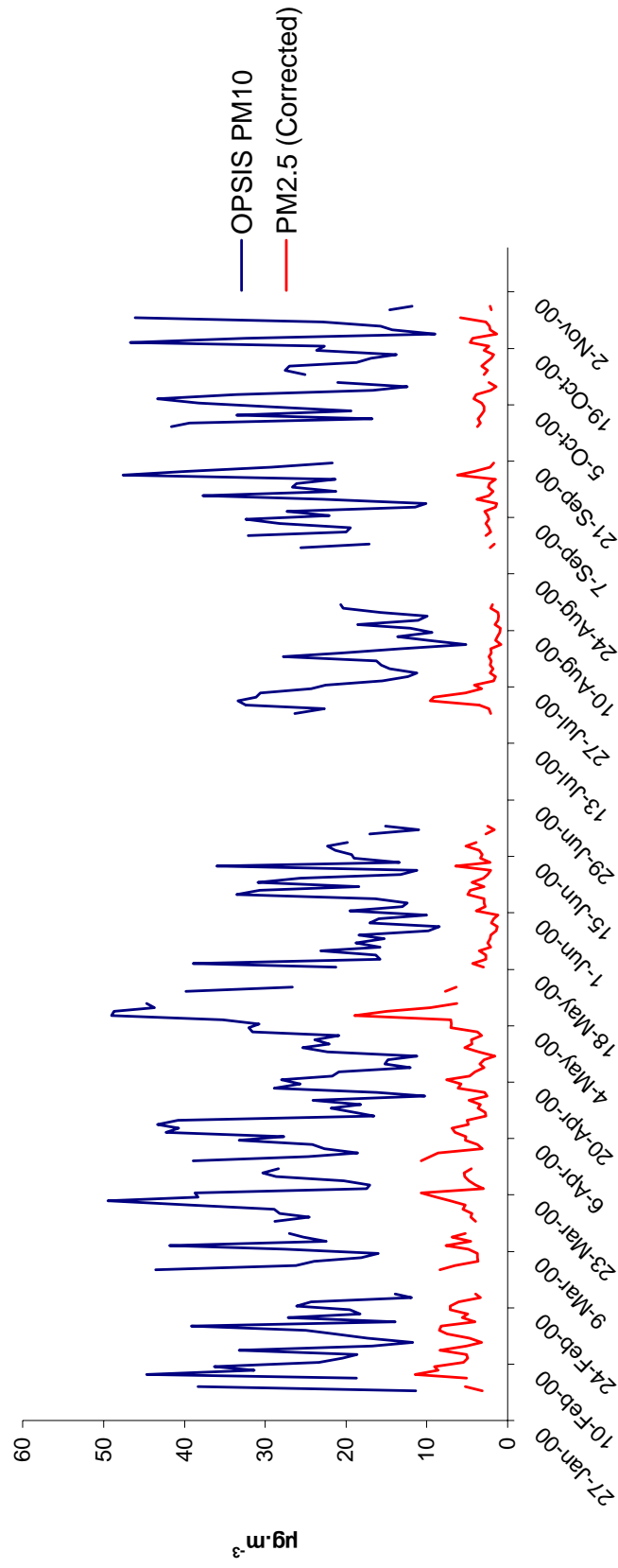




Fig. 9 PM10 and PM2.5 Daily Values  
Trailer 2 in Limerick 27/1/00-13/11/00



## Benzene

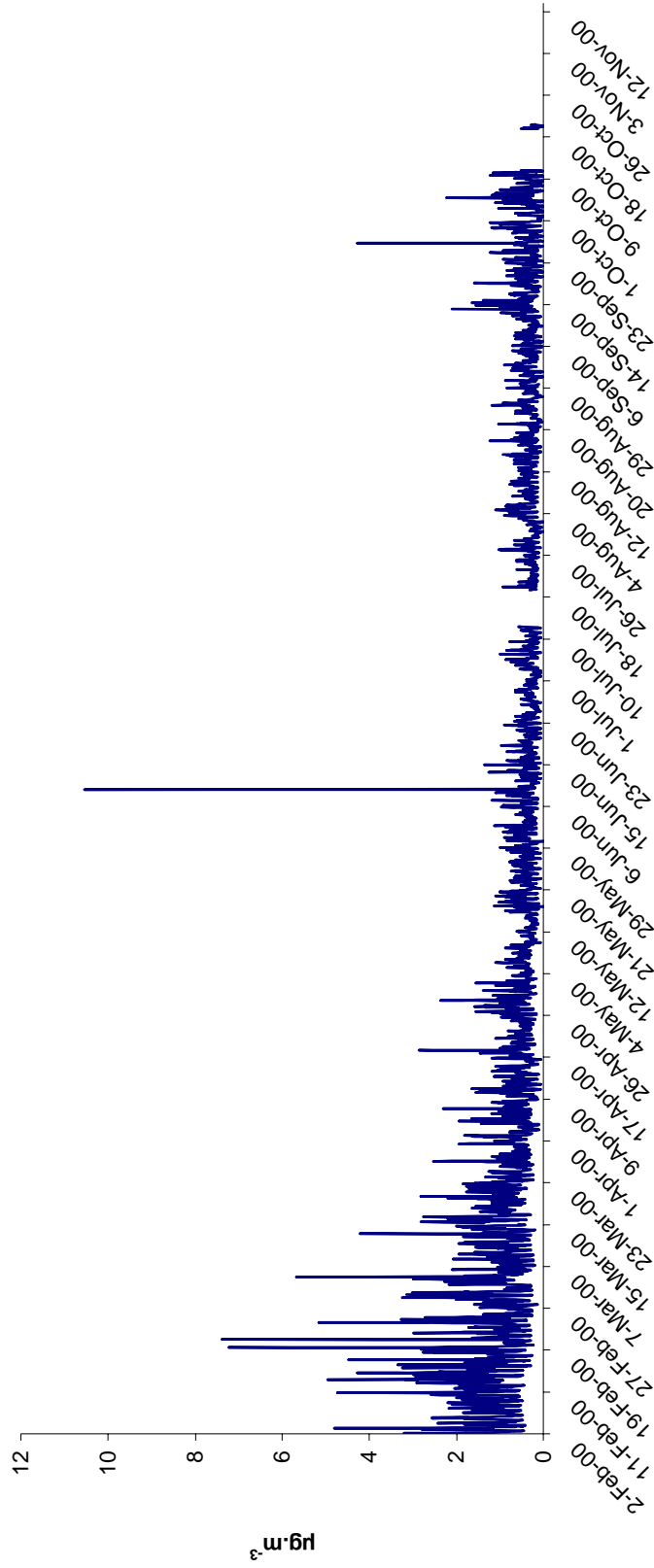
No. of hours	6840
Missing values (including routine maintenance)	997 55
No. of measured values	5843
Percentage covered	85.4%
Maximum hourly value	10.5 $\mu\text{g}\cdot\text{m}^{-3}$
98 percentile for hourly values	2.0 $\mu\text{g}\cdot\text{m}^{-3}$
Mean hourly value	0.5 $\mu\text{g}\cdot\text{m}^{-3}$

### 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 $\mu\text{g m}^{-3}$	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 $\mu\text{g m}^{-3}$	

The mean hourly value for the measurement period (0.5  $\mu\text{g}\cdot\text{m}^{-3}$ ) is below the lower assessment threshold for the protection of human health. (Figure 10).

**Fig. 10 Benzene Hourly Values  
Trailer 2 in Limerick 2/2/00-13/1/00**



## Lead

No. of days	292
Missing days (including routine maintenance)	13 0
No. of measured days	279
Percentage covered	95.6%
Concentration of Pb	0.006 $\mu\text{g}\cdot\text{m}^{-3}$

### 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 during the measurement period is 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 levels of arsenic in air were lower than trace levels of arsenic known to exist on the filter papers

The maximum concentration of nickel in air was found to be  $7.6 \text{ ng.m}^{-3}$

The maximum concentration of cadmium in air was found to be  $0.2 \text{ ng.m}^{-3}$