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Environmental Protection Agency
An Ghníomhaireacht um Chaomhnú Comhshaoil

Ambient Air Monitoring

In

Waterford City

August 24th 2000 - 21st February 2001

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Summary

An assessment of air quality was carried out in Waterford city from 24th August 2000 until 21st February 2001. No limit values were exceeded during the measurement period.

Concentrations of carbon monoxide, nitrogen dioxide, benzene and lead were below their respective lower assessment thresholds. Levels of sulphur dioxide exceeded the lower assessment threshold but not the upper assessment threshold while concentrations of PM₁₀ exceeded the upper assessment threshold for this pollutant.

	Below Lower Assessment Threshold	Below Upper Assessment Threshold	Above Upper Assessment Threshold	Above Limit
PM₁₀				
NO₂				
CO				
SO₂				
Benzene				
Pb				

Waterford 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 PM₁₀ will need to be monitored continuously
- Levels of SO₂ can be assessed using a combination of measurement and modelling.
- Levels of CO, NO₂, 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 measurement and modelling is required if levels exceed the lower assessment threshold while 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 published 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 to determine 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 SO₂, 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, 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

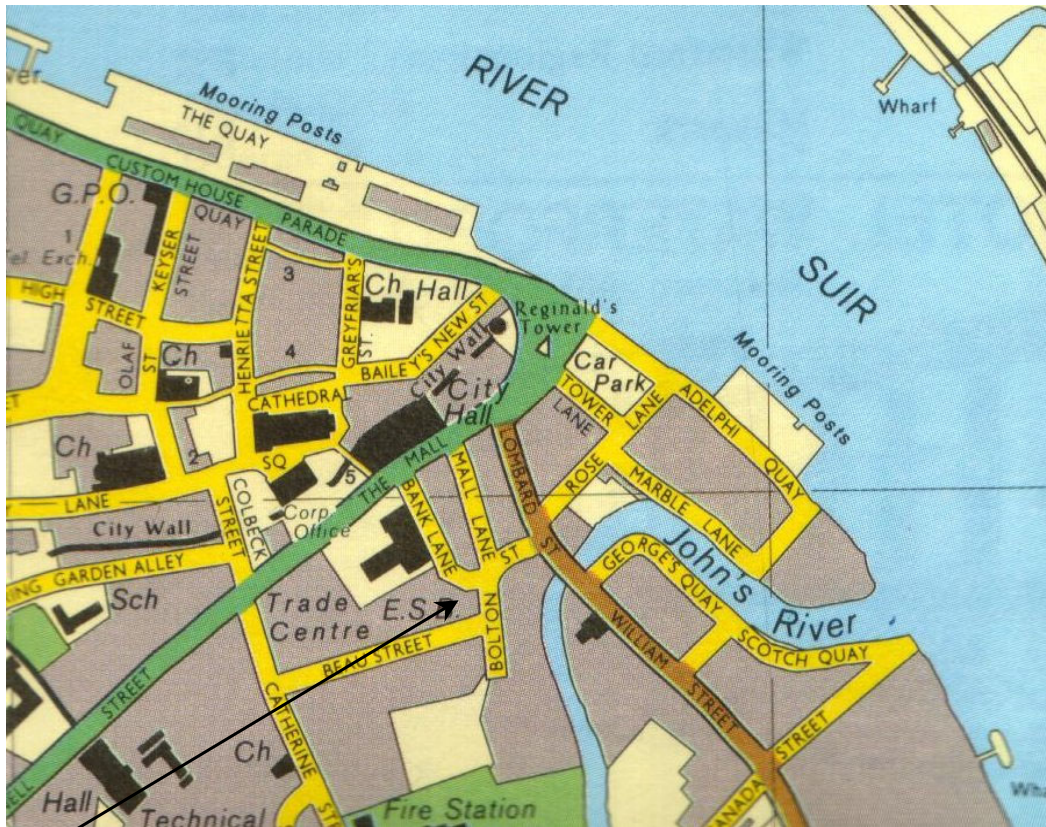
John Finnan, Barbara O' Leary or Ciaran O' Donnell.

Time Period

The mobile laboratory was in place from 24th August 2000 until 21st February 2001.

Siting

The mobile laboratory was situated in a yard owned by Waterford corporation. The yard is situated on Bolton Street and in this location the trailer was less than 100 metres from both William Street and from The Mall/Parnell Street, the latter being the principal thoroughfare through the city of Waterford. The area is a mixed residential/commercial district of Waterford city.



Location of mobile laboratory

Fig. 1 Map of site location

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 μ m.

Sulphur Dioxide

Sulphur dioxide was monitored using an Advanced Pollution Instrumentation SO₂ Fluorescent Analyser - Model 100A. This is a continuous analyser which measures the fluorescence of SO₂ molecules after excitation by ultraviolet radiation.

Nitrogen Dioxide and Oxides of Nitrogen

NO_x species were monitored using an Advanced Pollution Instrumentation Chemiluminescent NO/NO₂/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 the NO concentrations. Any NO₂ present is then reduced to NO by a molybdenum converter giving a second value for total NO_x concentration. The amount of NO₂ present is found by subtraction.

Particulate Matter

A gravimetric method was used to monitor PM₁₀ 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 10 μ 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 β 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, PM₁₀, PM_{2.5} and PM₁.

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 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, 0.8µm) situated in a calming chamber. The filters were changed every 1-2 weeks. They were digested in conc. HNO₃ and analysed for lead and other metals using ICP-MS (Inductively Coupled Plasma-Mass Spectrometry).

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.

Results

Carbon Monoxide

No. of hours	4345
Missing values (including routine maintenance)	731 27
No. of measured values	3614
Percentage covered	83.2%
Maximum hourly value	4.9 mg.m ⁻³
98 percentile for hourly values	2.2 mg.m ⁻³
Mean hourly value	0.6 mg.m ⁻³
Maximum 8-hour mean	2.6 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	

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

Fig.2 Carbon Monoxide 8-hour Running Average
Trailer 1 in Waterford 24/8/00-21/2/01

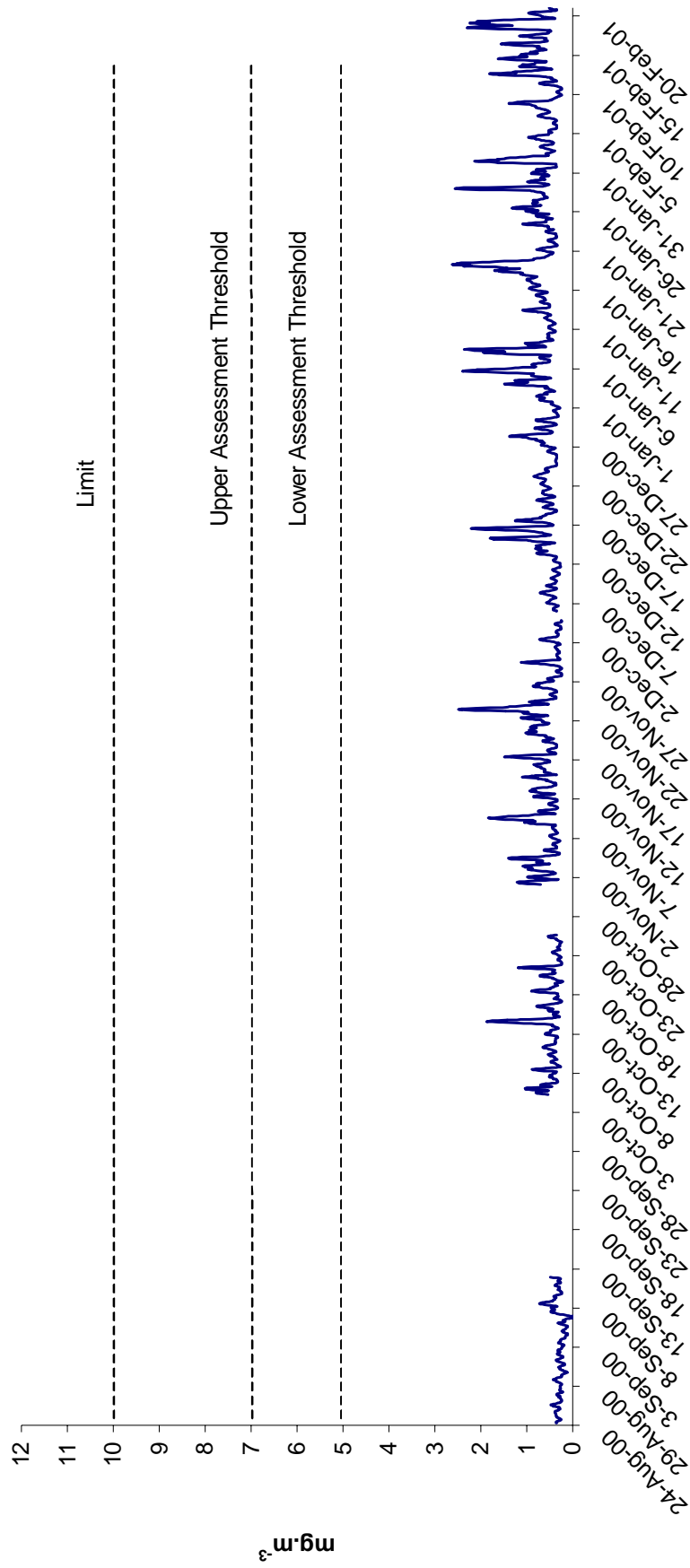
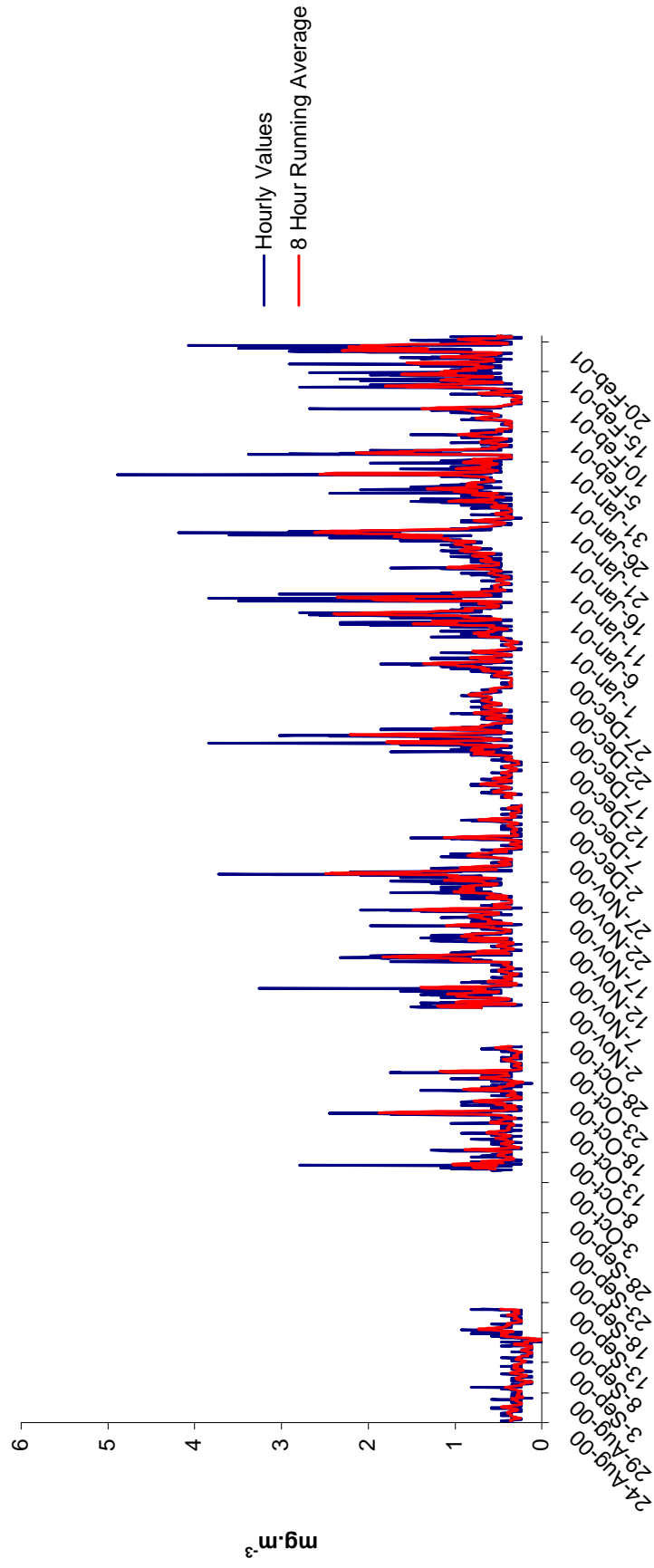


Fig. 3 Carbon Monoxide
Trailer 1 in Waterford 24/8/00-21/2/01



Sulphur Dioxide

No. of hours	4345
Missing values (including routine maintenance)	739 32
No. of measured values	3606
Percentage covered	83.0%
Maximum hourly value	310.4 $\mu\text{g}\cdot\text{m}^{-3}$
98 percentile for hourly values	103.5 $\mu\text{g}\cdot\text{m}^{-3}$
Mean hourly value	19.3 $\mu\text{g}\cdot\text{m}^{-3}$
Maximum 24-hour value	73.6 $\mu\text{g}\cdot\text{m}^{-3}$
98 percentile for 24-hour values	49.2 $\mu\text{g}\cdot\text{m}^{-3}$

Directive Limits (1999/30/EC)

	Averaging Period	Limit Value	Date by which limit value is to be met
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	

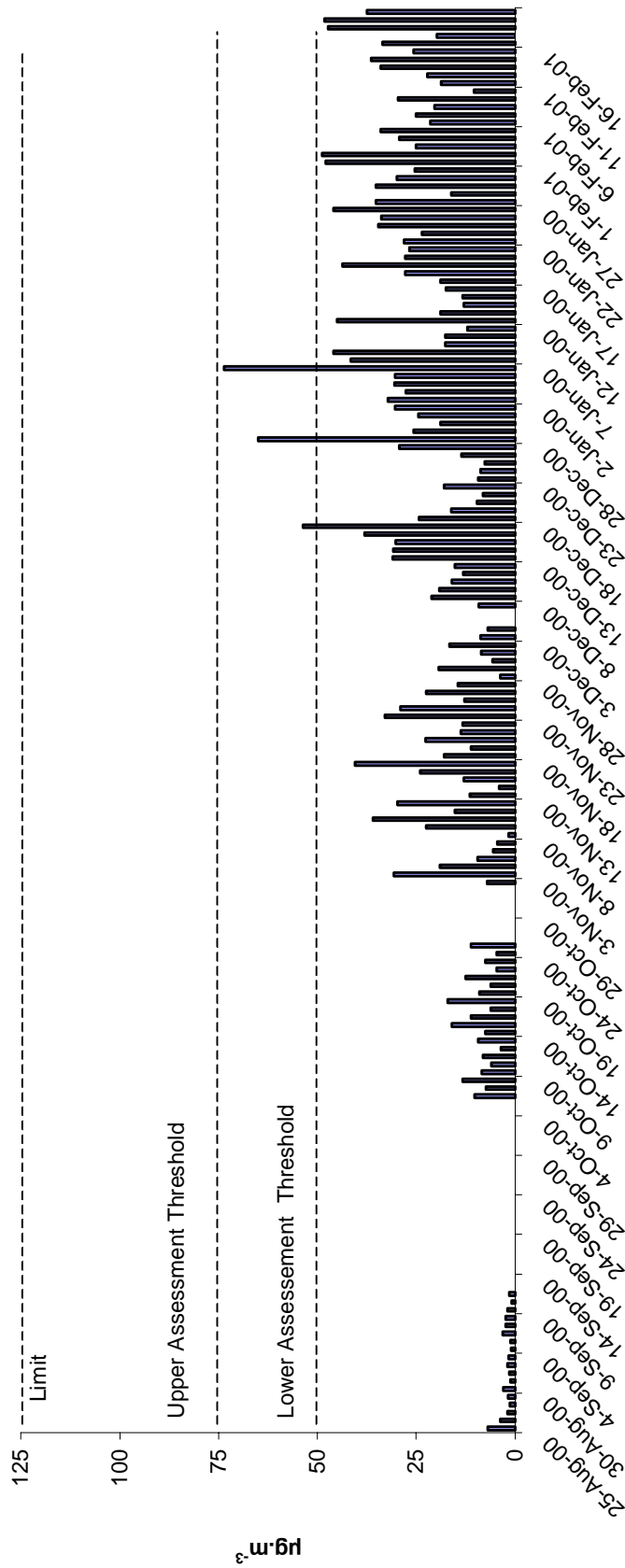
Directive Limits (1999/30/EC) continued

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

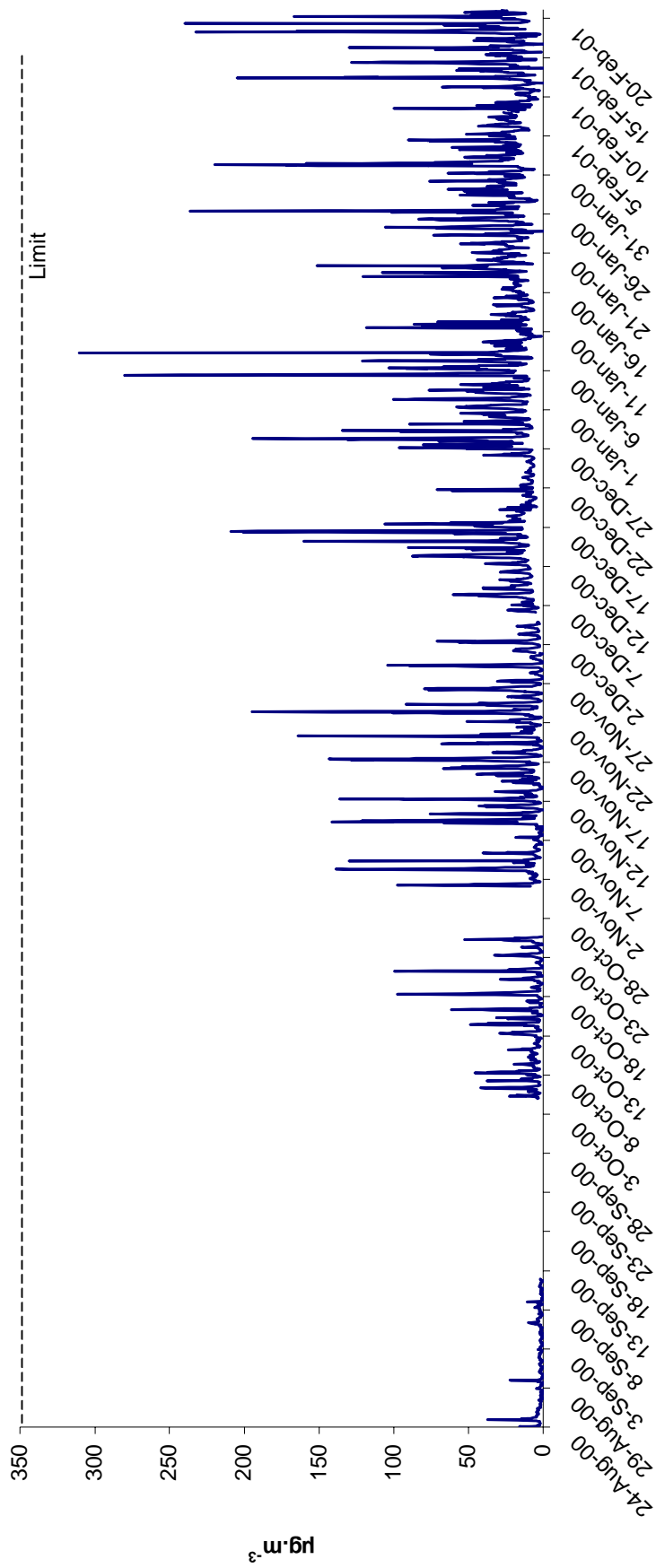
The hourly limit value was not exceeded during the measurement period (Figure 5). There were three exceedences of the 50 $\mu\text{g.m}^{-3}$ lower assessment threshold (Figure 4). The directive stipulates that the lower assessment threshold should not be exceeded more than three times in a calendar year.

The mean hourly value of 19.3 $\mu\text{g.m}^{-3}$ 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 1 in Waterford 24/8/00 - 21/2/01



**Fig. 5 Sulphur Dioxide Hourly Averages
Trailer 1 in Waterford 24/8/00-21/2/01**



Nitrogen Dioxide and Oxides of Nitrogen

No. of hours	4345
Missing values (including routine maintenance)	738 33
No. of measured values	3607
Percentage covered	83.0%
Maximum hourly value (NO ₂)	122.1 $\mu\text{g.m}^{-3}$
98 percentile for hourly values (NO ₂)	63.9 $\mu\text{g.m}^{-3}$
Mean hourly value (NO ₂)	23.5 $\mu\text{g.m}^{-3}$
Mean hourly value (NO _x)	42.2 $\mu\text{g.m}^{-3}$ 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 $\mu\text{g m}^{-3}$ 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 $\mu\text{g m}^{-3}$ NO ₂	1 January 2010
Annual limit value for the protection of vegetation	Calendar year	30 $\mu\text{g m}^{-3}$ NO _x	19 July 2001
Alert threshold		400 $\mu\text{g m}^{-3}$ 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 $\mu\text{g m}^{-3}$ 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 $\mu\text{g m}^{-3}$ NO ₂	
Lower assessment threshold for the protection of human health	1 hour	100 $\mu\text{g m}^{-3}$ 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 $\mu\text{g m}^{-3}$ NO ₂	
Upper assessment threshold for the protection of vegetation	Calendar year	24 $\mu\text{g m}^{-3}$ NO _x	
Lower assessment threshold for the protection of vegetation	Calendar year	19.5 $\mu\text{g m}^{-3}$ NO _x	

Four hourly mean NO₂ values were above the lower assessment for the protection of human health (Figure 6). The directive stipulates that the lower assessment threshold should not be exceeded more than 18 times in a calendar year. With the exception of

these four values all other hourly mean NO₂ values were below the lower assessment threshold.

The mean hourly NO₂ value (23.5 µg.m⁻³) during the measurement period was below the annual lower assessment threshold for the protection of human health (26 µg.m⁻³).

The mean hourly value of NO_x (42.2 µg.m⁻³ NO₂) during the measurement period exceeded the annual limit value for the protection of vegetation (30 µg.m⁻³). However, the applicability of this limit to urban air pollution monitoring is questionable.

NO, NO₂ and NO_x are measured as ppb (parts per billion) by volume. To convert to µg.m⁻³, a factor (1.25 for NO, 1.91 for NO₂) is used. No formula is specified for NO_x, the directive requires it to be expressed as NO₂ (i.e. ppb*1.91). This applies even when most of the NO_x is present as NO.

Fig. 6 NO₂ Hourly Values
Trailer 1 in Waterford 24/8/00-21/2/01

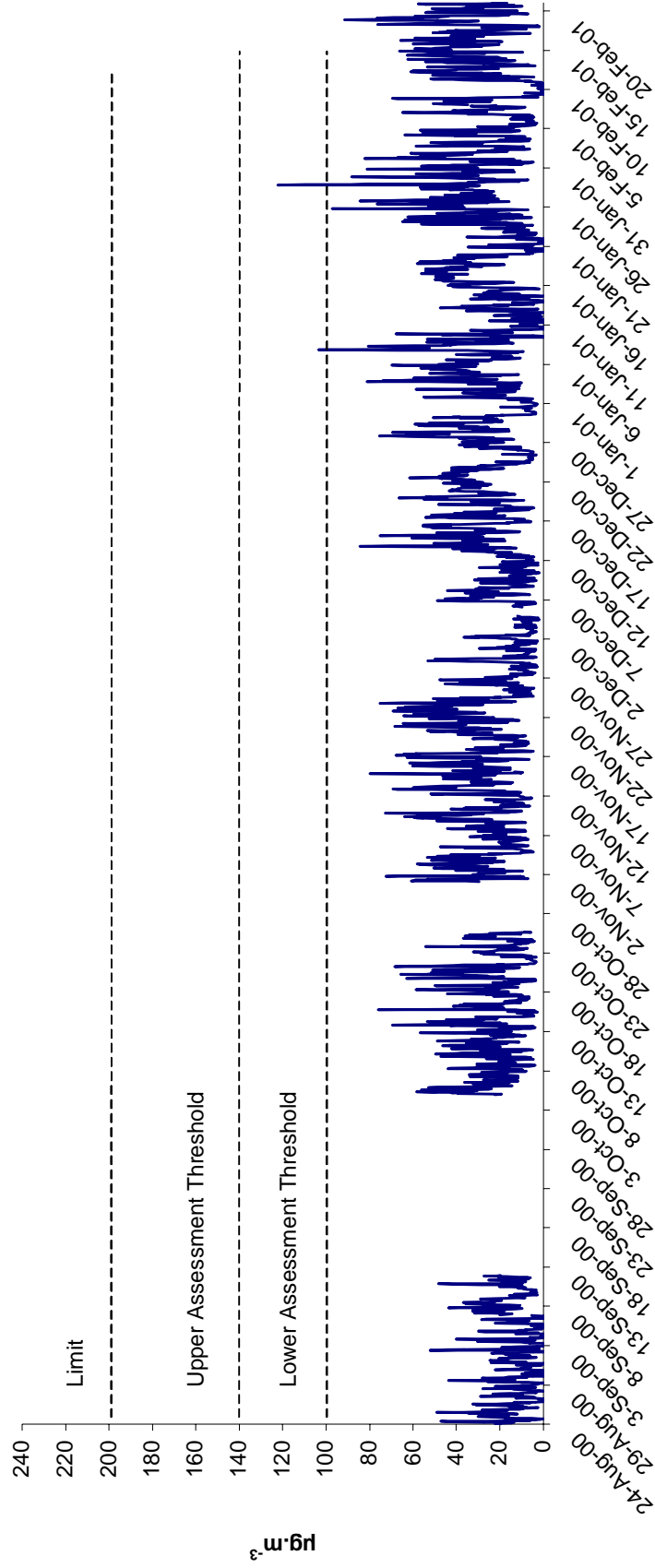
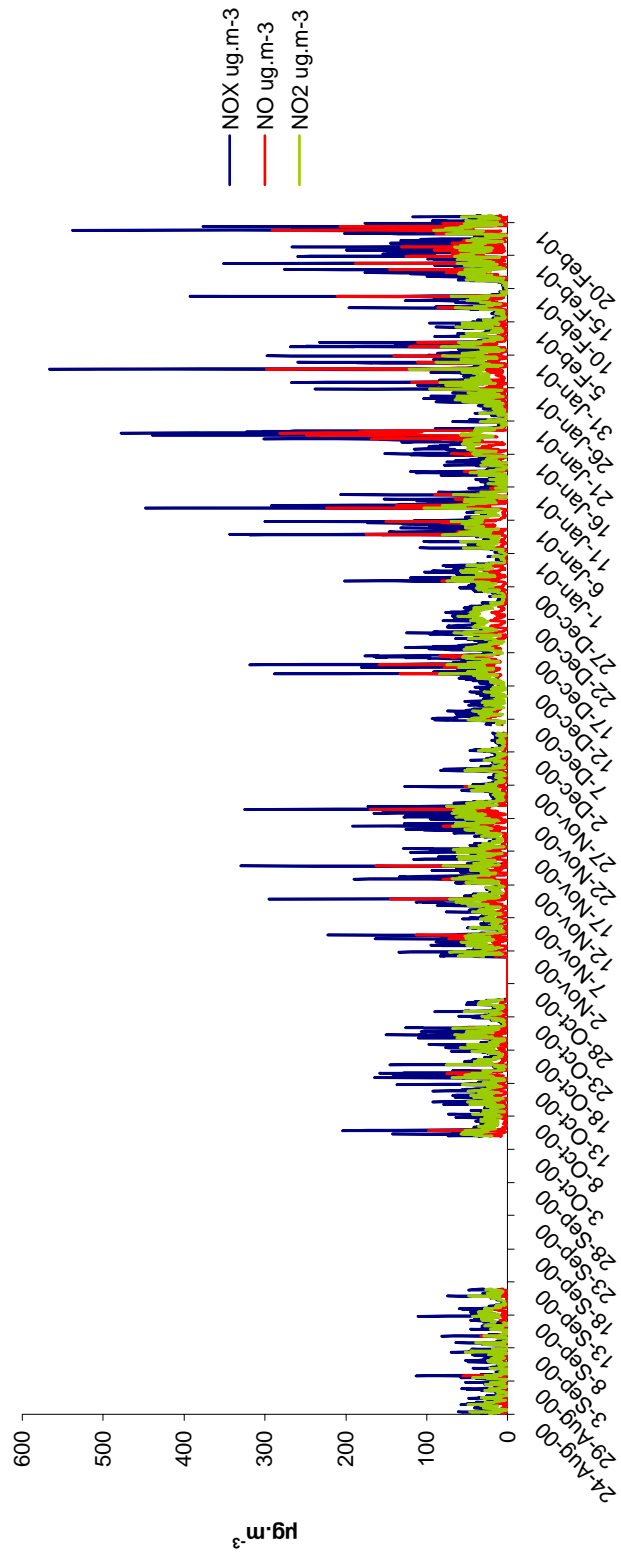


Fig. 7 NO_x Hourly Values
Trailer 1 in Waterford 24/8/00-21/2/01



Particulate Matter

PM₁₀ : gravimetric method

No. of days	180
Missing values (including routine maintenance)	80 3
No. of measured values	100
Percentage covered	55.6%
Maximum daily value	97.3 $\mu\text{g.m}^{-3}$
98 percentile for daily values	73.4 $\mu\text{g.m}^{-3}$
Mean daily value	32.4 $\mu\text{g.m}^{-3}$

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 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 $\mu\text{g m}^{-3}$ PM ₁₀	1 January 2005
Upper assessment threshold for the protection of human health	24 hour	30 $\mu\text{g m}^{-3}$ PM ₁₀ 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 ₁₀	<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 ₁₀ 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 ₁₀	<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 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 $\mu\text{g m}^{-3}$ PM ₁₀	1 January 2010

The 24 hour limit value for the protection of human health (50 $\mu\text{g.m}^{-3}$) was exceeded on ten occasions (10% of measured values) during the measurement period (Figure 8). The limit value plus a margin of tolerance of 50 % (75 $\mu\text{g.m}^{-3}$) was exceeded on 2 occasions during the measurement period while the limit value plus a margin of tolerance of 40% (70 $\mu\text{g.m}^{-3}$) was exceeded on three occasions 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 46 days (46% of measured values), the lower assessment threshold was exceeded on 87 days (87% of measured 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 ($32.4 \mu\text{g}\cdot\text{m}^{-3}$) is below the annual limit value for the protection of human health ($40 \mu\text{g}\cdot\text{m}^{-3}$).

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), PM₁₀ and PM₁. All measurements were hourly values.

The concentration of PM₁₀ 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:

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

Results:

No. of days	180
Missing values (including routine maintenance)	92
No. of measured values*	88
Percentage covered	48.9%
Maximum daily value	54.6 $\mu\text{g.m}^{-3}$
98 percentile for daily values	36.8 $\mu\text{g.m}^{-3}$
Mean daily value	14.6 $\mu\text{g.m}^{-3}$
Median daily value	11.8 $\mu\text{g.m}^{-3}$

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

Fig. 8 PM₁₀ Daily Values
Trailer 1 in Waterford 24/8/00-21/2/01

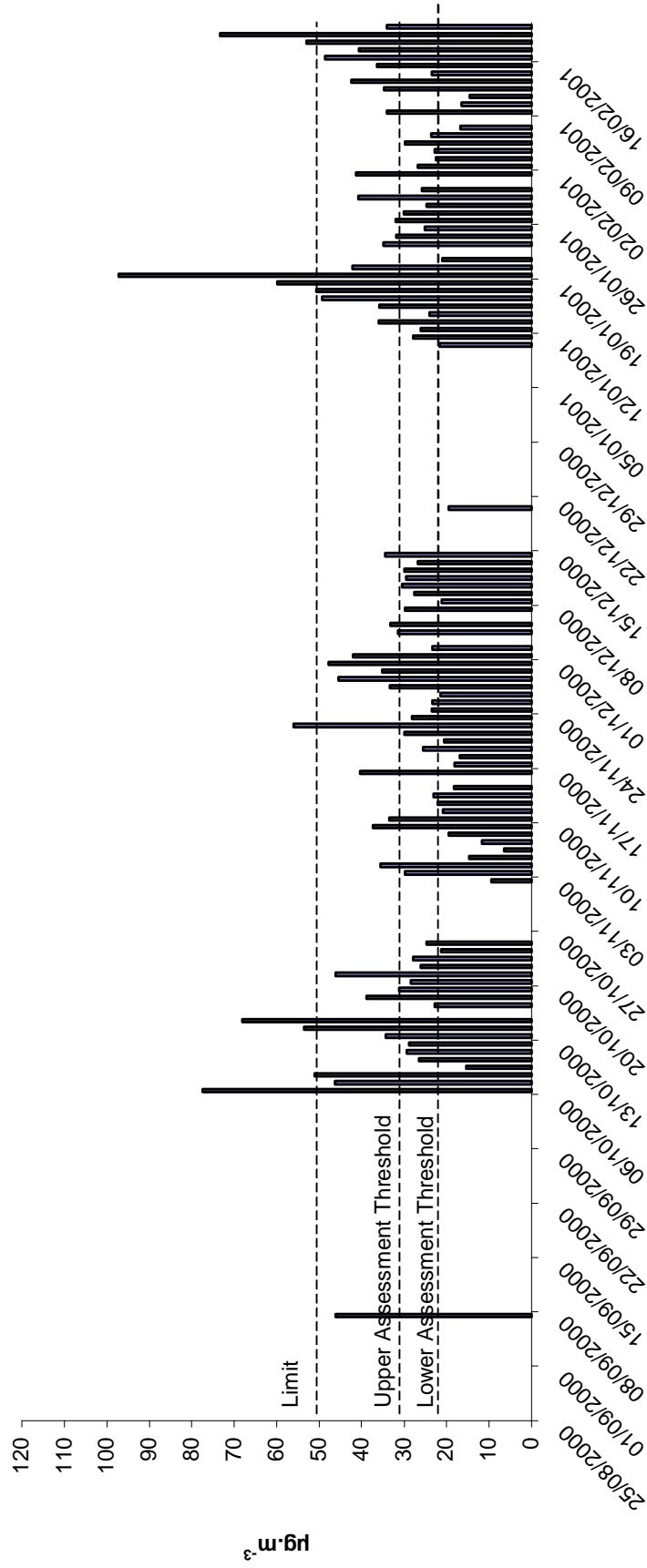
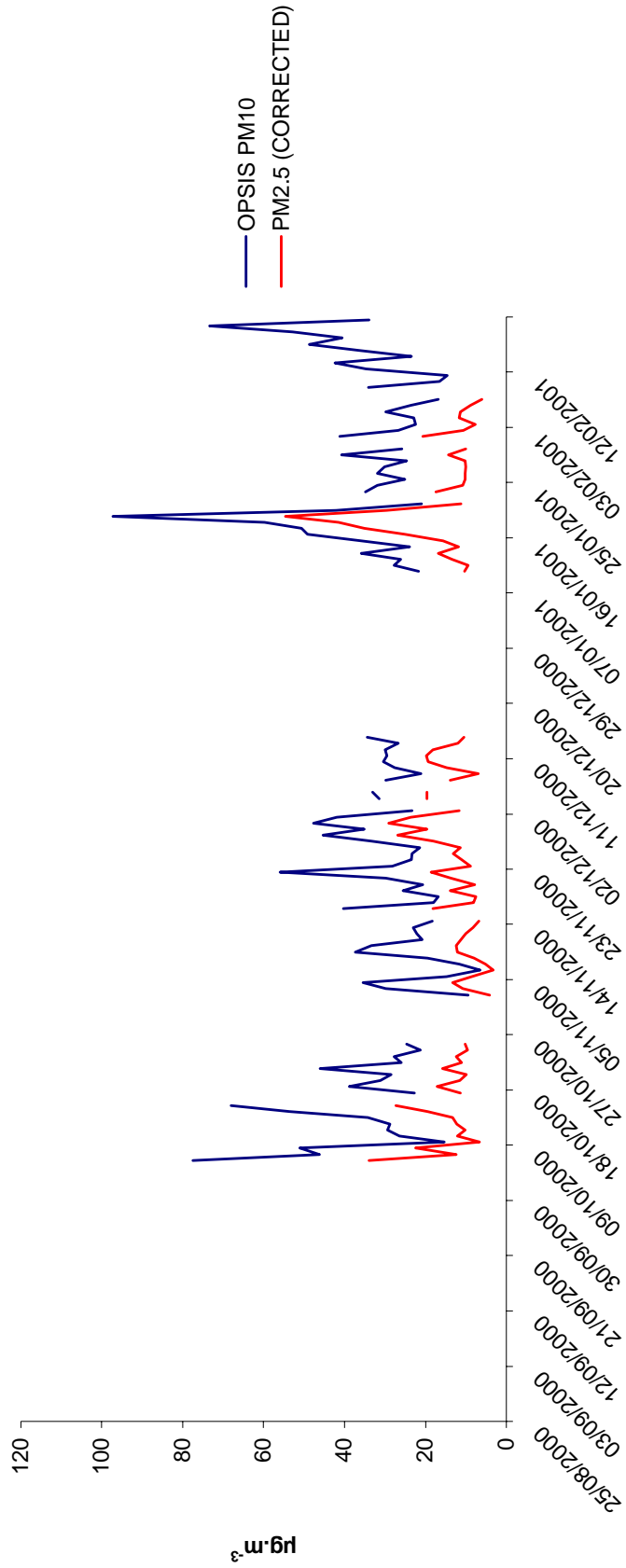


Fig. 9 PM₁₀ and PM_{2.5} Daily Values
Trailer 1 in Waterford 24/8/00-21/2/01



Benzene

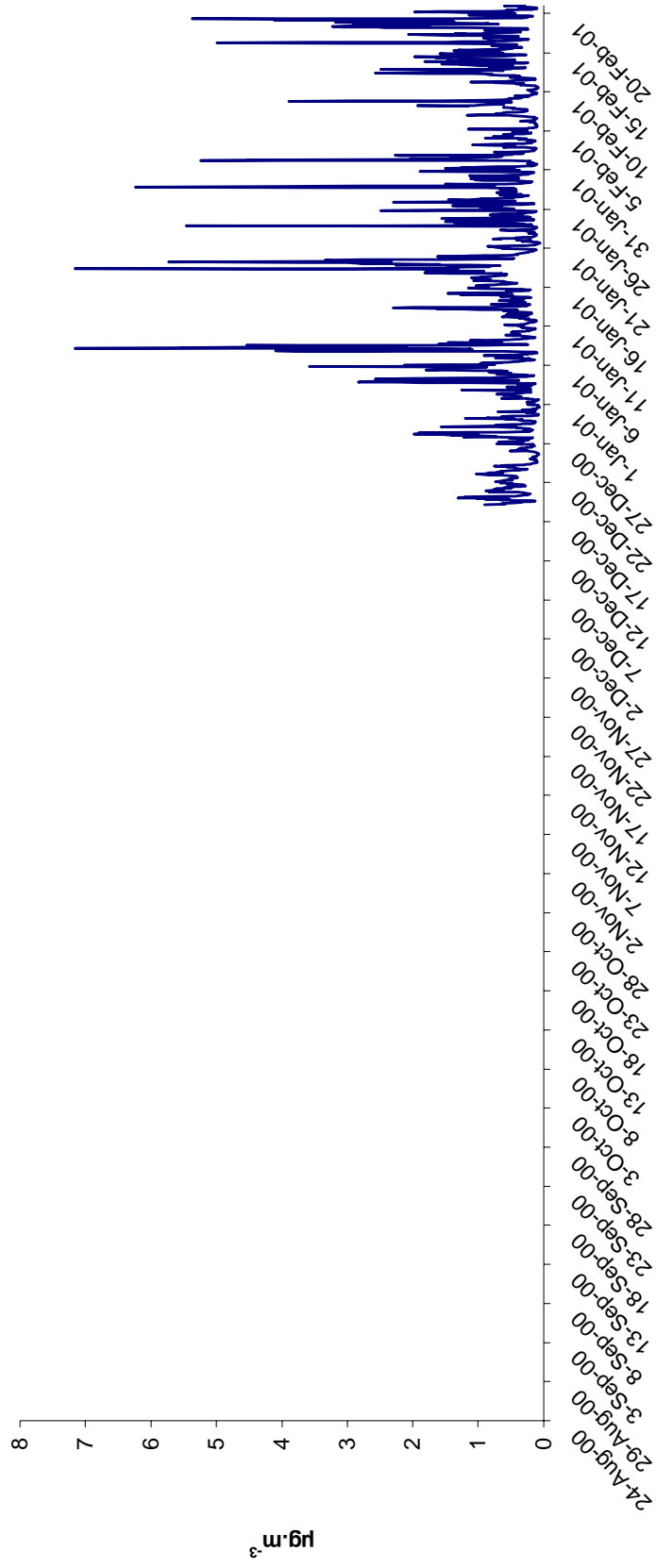
No. of hours	4345
Missing values (including routine maintenance)	2817 5
No. of measured values	1528
Percentage covered	35.2%
Maximum hourly value	7.2 $\mu\text{g.m}^{-3}$
98 percentile for hourly values	3.2 $\mu\text{g.m}^{-3}$
Mean hourly value	0.7 $\mu\text{g.m}^{-3}$

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 $\mu\text{g m}^{-3}$	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 (0.7 $\mu\text{g.m}^{-3}$) is below the lower assessment threshold for the protection of human health.

Fig. 10 Benzene Hourly Values
Trailer 1 in Waterford 24/8/00-21/2/01

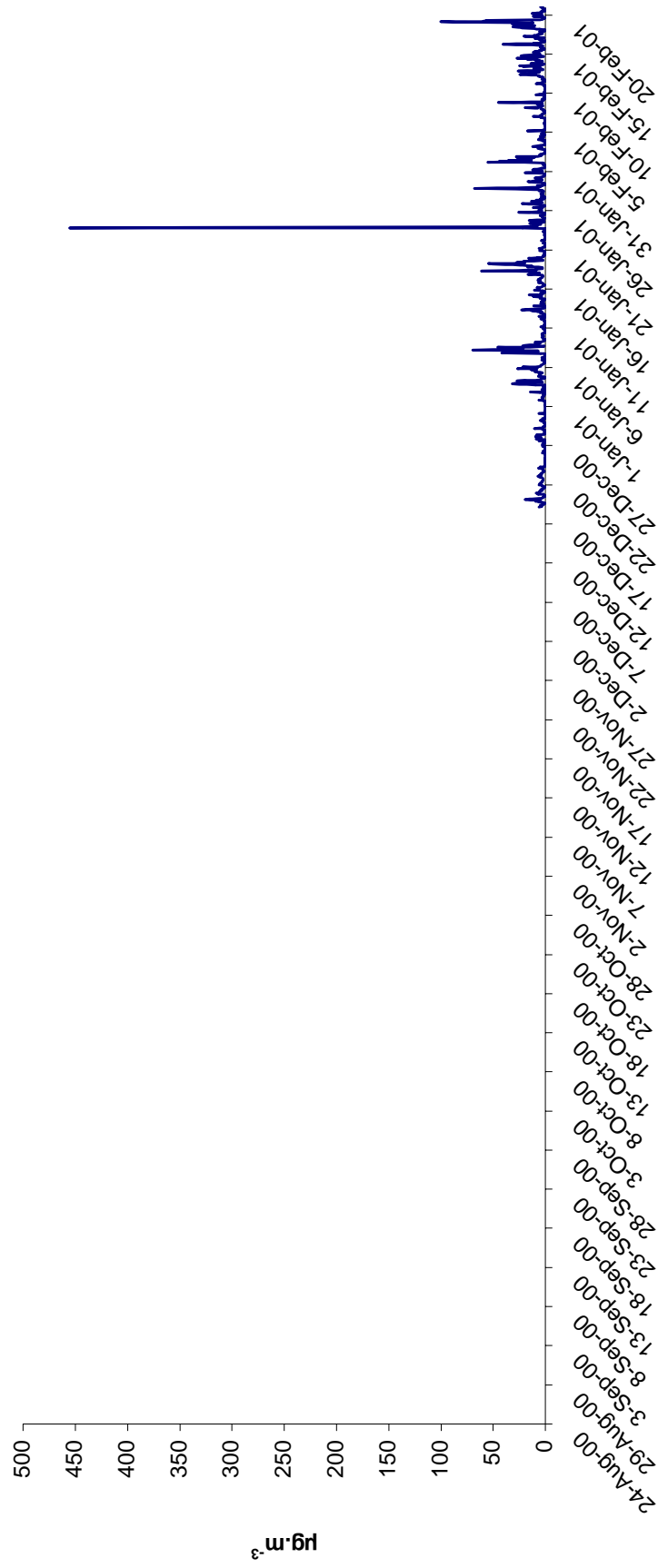


Toluene

No. of hours	4345
Missing values (including routine maintenance)	2817 5
No. of measured values	1528
Percentage covered	35.2%
Maximum hourly value	455.3 $\mu\text{g.m}^{-3}$
98 percentile for hourly values	36.2 $\mu\text{g.m}^{-3}$
Mean hourly value	6.3 $\mu\text{g.m}^{-3}$

Large concentrations of toluene were measured on the morning of 24th January. During a five hour period, toluene levels gradually rose to a maximum hourly average of 455 $\mu\text{g.m}^{-3}$ before declining

Fig. 11 Toluene Hourly Values
Trailer 1 in Waterford 24/8/00-21/2/01

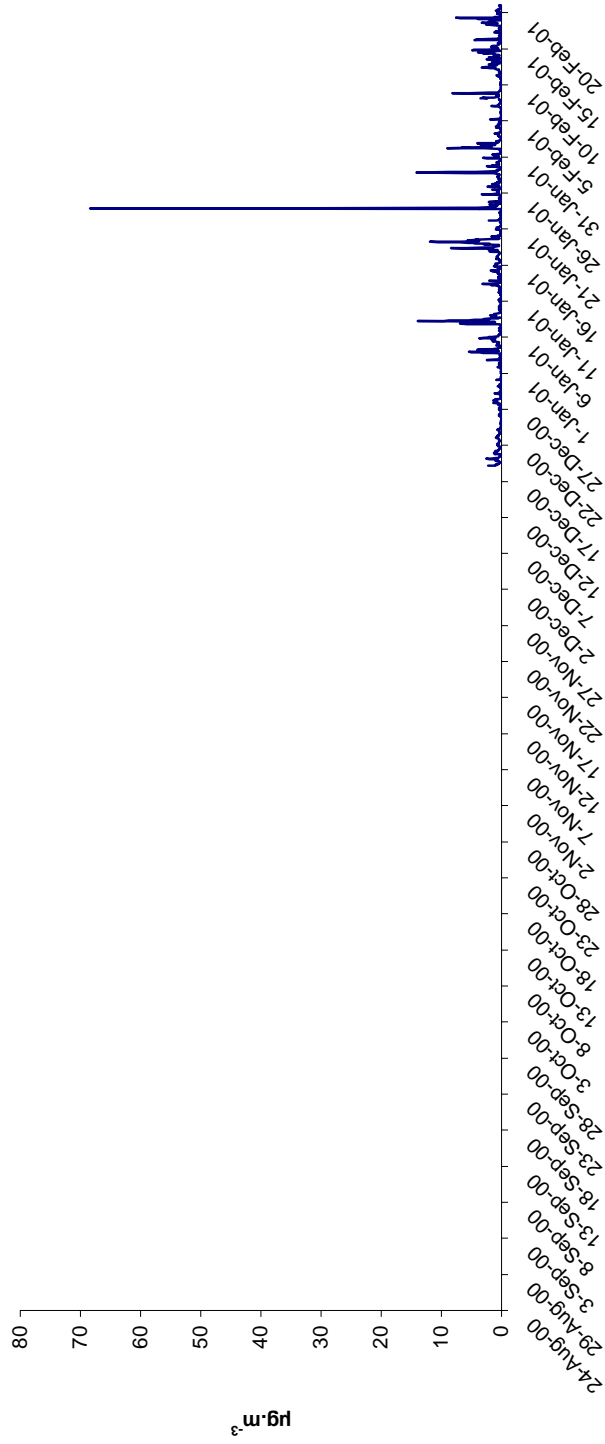


o-Xylene

No. of hours	4345
Missing values (including routine maintenance)	2817 5
No. of measured values	1528
Percentage covered	35.2%
Maximum hourly value	68.4 $\mu\text{g.m}^{-3}$
98 percentile for hourly values	5.2 $\mu\text{g.m}^{-3}$
Mean hourly value	0.8 $\mu\text{g.m}^{-3}$

High concentrations of xylene were recorded on the morning of the 24th January.

Fig. 12 0-Xylene Hourly Values
Trailer 1 in Waterford 24/8/00-21/2/01



Lead

No. of days	181
Missing days (including routine maintenance)	22 0
No. of measured days	159
Percentage covered	87.8%
Concentration of Pb	0.01 $\mu\text{g}\cdot\text{m}^{-3}$

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 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 both 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 nickel in the air was found to be 2.6 ng.m^{-3}

The maximum concentration of cadmium in the air was found to be 0.1 ng.m^{-3}

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

