



**Ambient Air Monitoring**

**At**

**Cork Harbour**

**August 31<sup>st</sup> 2007 – 15<sup>th</sup> March 2008**

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## Summary

An assessment of air quality was carried out at Monkstown, Cork Harbour from 31<sup>st</sup> August 2007 until 15<sup>th</sup> March 2008. No limit values were exceeded during the measurement period.

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

	<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>				

Monkstown is in Zone D of the country. The implications of this assessment are that within Zone D (rural background areas)

- Levels of PM<sub>10</sub> will need to be monitored continuously
- Levels of SO<sub>2</sub>, CO, 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. 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 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 third Daughter Directive relates to ozone (2002/3/EC) while the fourth Daughter Directive relates to heavy metals and polycyclic aromatic hydrocarbons (2004/107/EC). The first three Directives were transposed into Irish law as the Air Quality Standard Regulations 2002 (S.I. No 271 of 2002) and the Ozone in Ambient Air Regulations 2004 (S.I. No 53 of 2004).

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, carbon monoxide and PM<sub>10</sub>.
- 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

Micheál O'Dwyer, Lin Delaney, Kevin Delaney or Barbara O'Leary.

### ***Time Period***

The mobile laboratory was in place from the 31<sup>st</sup> August 2007 until the 15<sup>th</sup> March 2008.

### ***Siting***

The site was situated opposite 'The Bosun' public house, near the public car park on the quay in Monkstown, Cork.

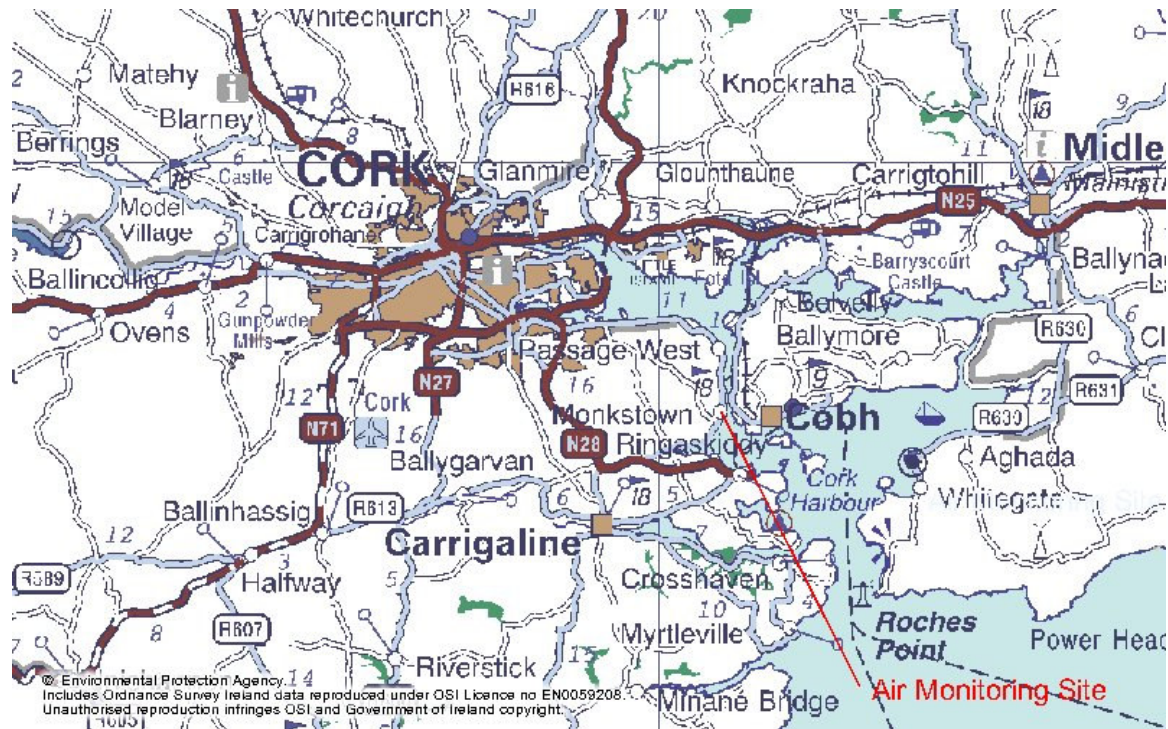


Figure 1. Map of site location

## ***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 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*

Concentrations of PM<sub>10</sub> were measured using an instrument, which employed tapered element oscillating microbalance technology with a Filter-Dynamic-Measurement-System (TEOM-FDMS, Rupprecht & Patashnick Co. Inc., 25 Corporate Circle, Albany, New York). This is a continuous method in which the air from the sampling head is passed through a filter placed on a tapered element. A mass transducer relates changes in the frequency of the tapered element to changes in particulate matter on the filter, the difference between the filter's current weight and its initial weight gives the total mass of collected particulate matter. An inertial impactor sampling head restricted the sampled particles to those with a diameter less than 10 $\mu$ m. The FDMS section of the TEOM-FDMS allows for the volatile organic component of the PM10.

### *Lead and Other Metals*

Ambient air was pumped through a Metricel 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	4398
Missing values (including routine maintenance)	292 20
No. of measured values	4086
Percentage covered	92.91%
Maximum hourly value	3.02 mg.m <sup>-3</sup>
98 percentile for hourly values	0.81 mg.m <sup>-3</sup>
Mean hourly value	0.26 mg.m <sup>-3</sup>
Maximum 8-hour mean	2.67 mg.m <sup>-3</sup>
98 percentile for 8-hour mean	0.68 mg.m <sup>-3</sup>

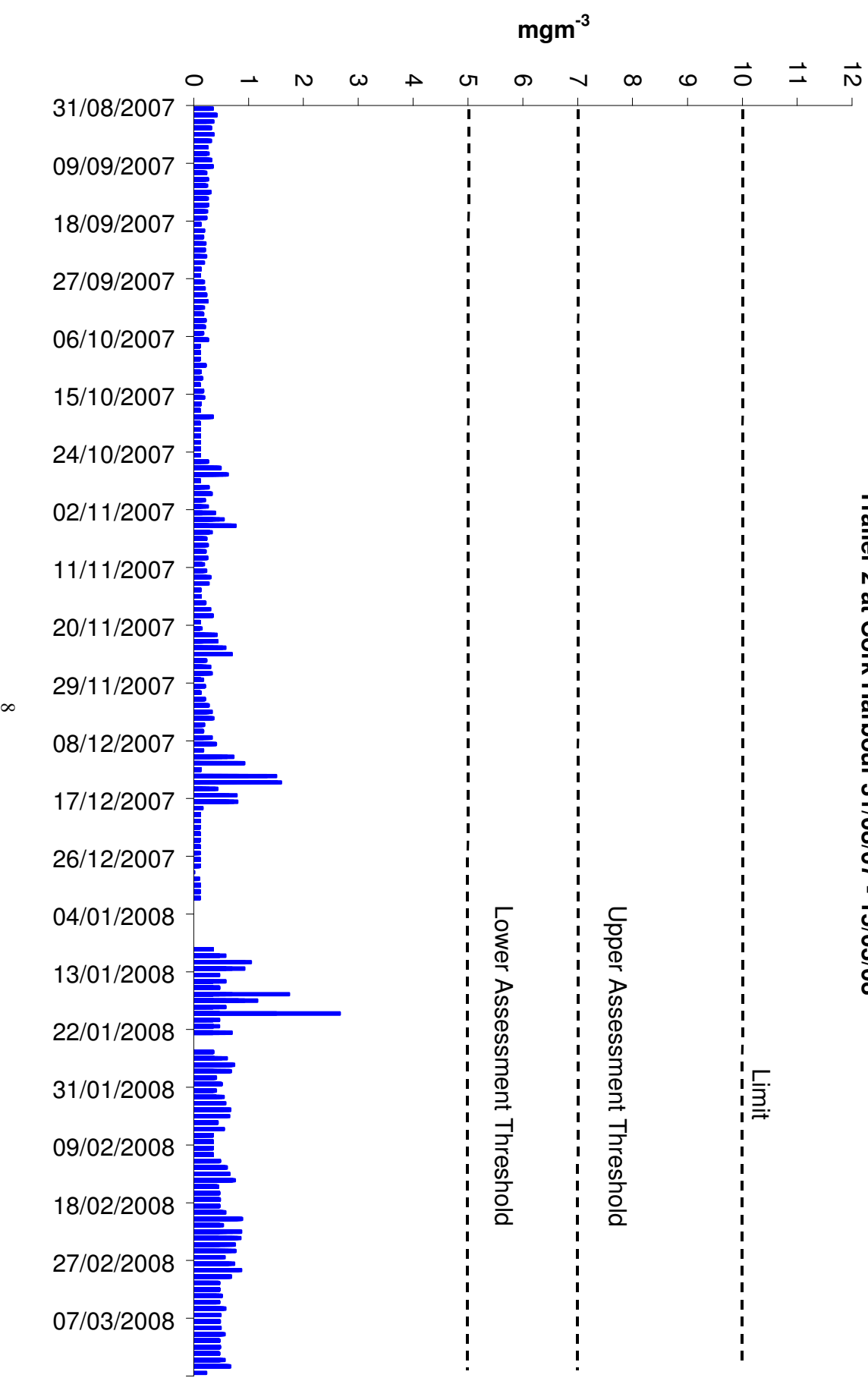
### Proposed Directive Limits

	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).



**Figure 2 Carbon Monoxide 8-Hour Running average  
Trailer 2 at Cork Harbour 31/08/07 - 15/03/08**



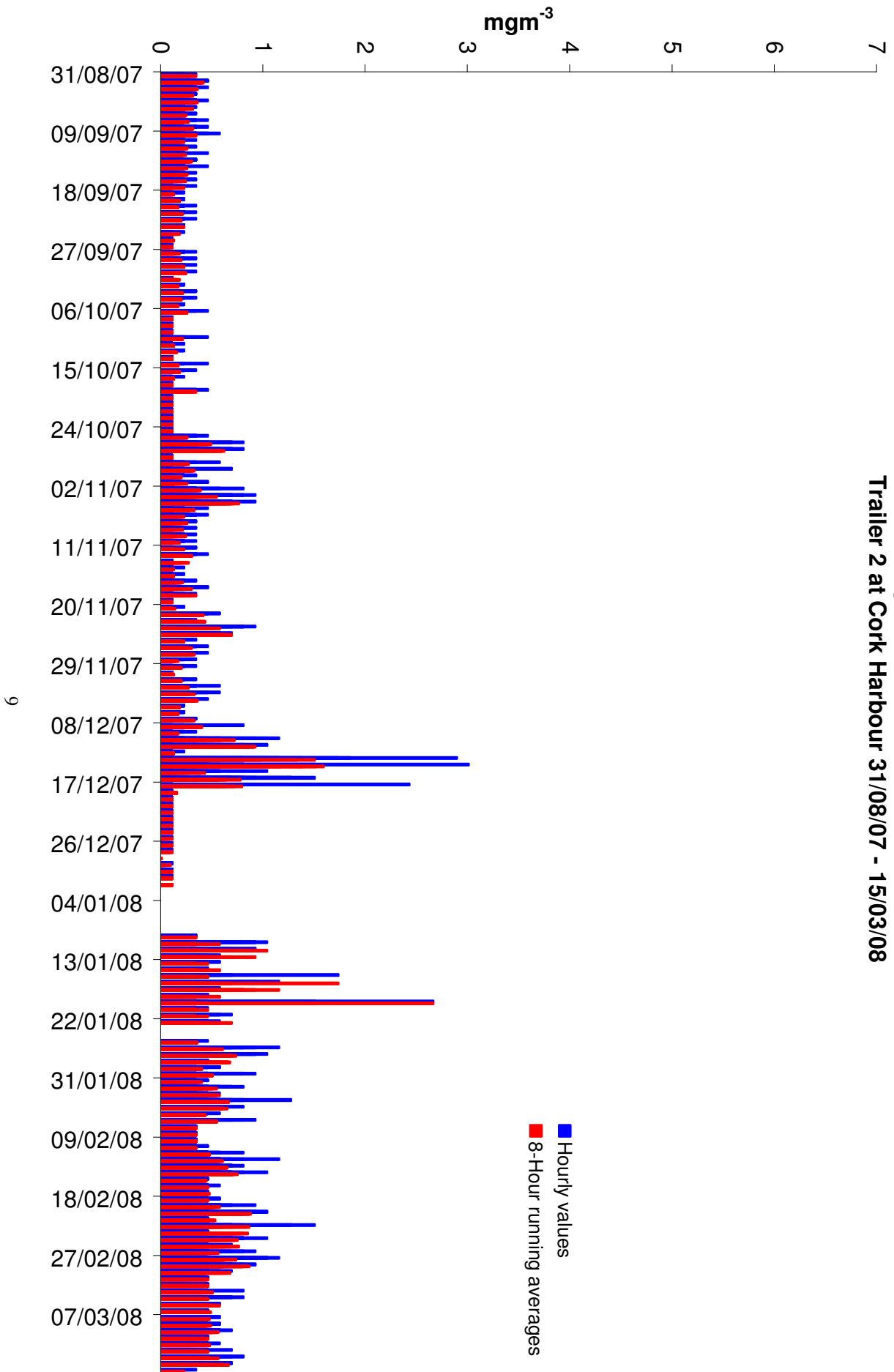


Figure 3 Carbon Monoxide  
Trailer 2 at Cork Harbour 31/08/07 - 15/03/08

## Sulphur Dioxide

No. of hours	4668
Missing values (including routine maintenance)	34 14
No. of measured values	4620
Percentage covered	98.97%
Maximum hourly value	32.7 $\mu\text{g.m}^{-3}$
98 percentile for hourly values	9.3 $\mu\text{g.m}^{-3}$
Mean hourly value	3.4 $\mu\text{g.m}^{-3}$
Maximum 24-hour value	11.6 $\mu\text{g.m}^{-3}$
98 percentile for 24-hour values	6.9 $\mu\text{g.m}^{-3}$

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

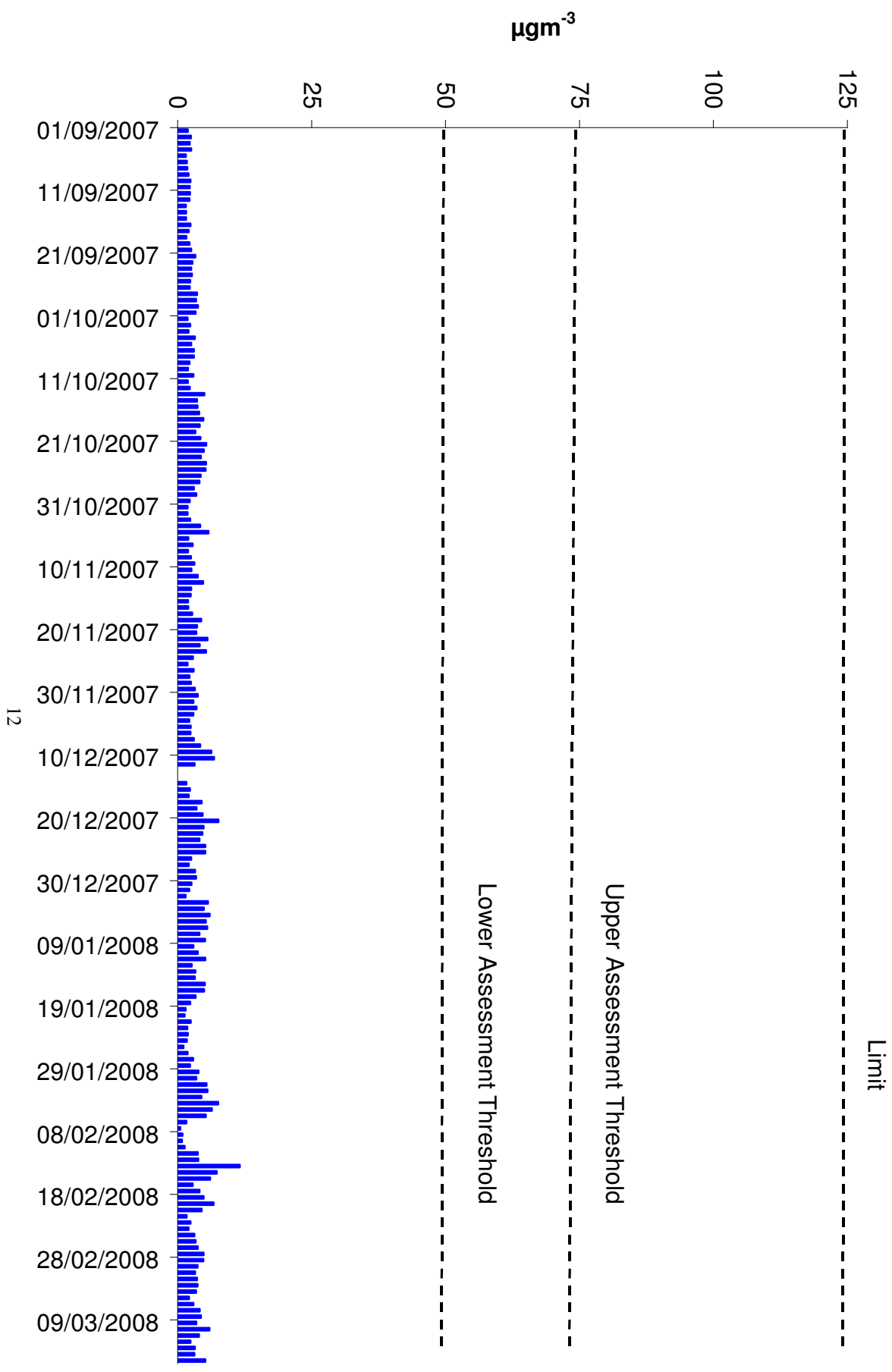
	Averaging Period	Limit Value	Date by which limit value is to be met
Hourly limit value for the protection of human health	1 hour	350 $\mu\text{g m}^{-3}$ not to be exceeded more than 24 times a calendar year	1 January 2005
Daily limit value for the protection of human health	24 hours	125 $\mu\text{g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

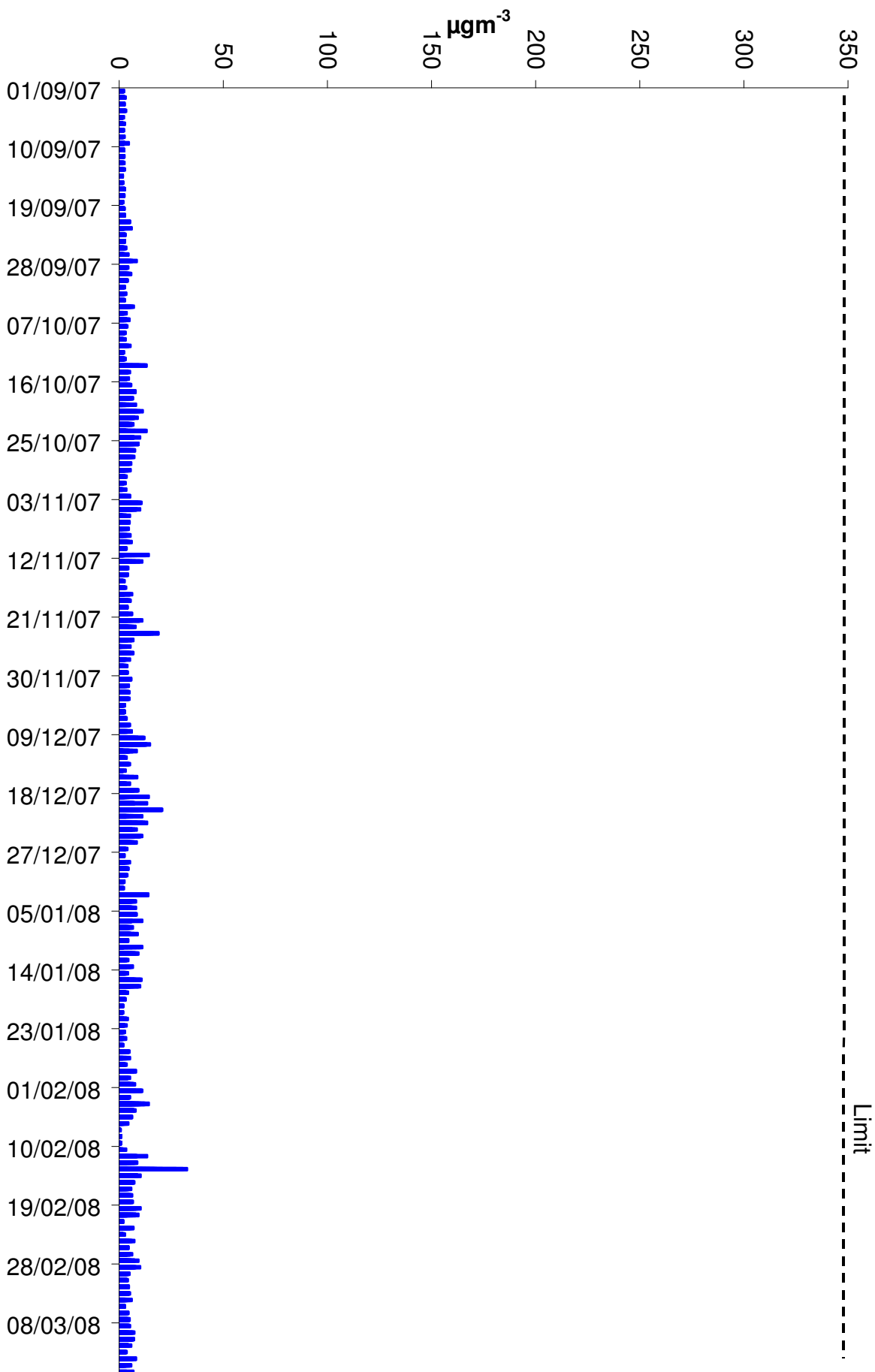
	Averaging Period	Limit Value	Date by which limit value is to be met
Upper assessment threshold for the protection of human health	24 hours	75 $\mu\text{g m}^{-3}$ not to be exceeded more than 3 times a calendar year	
Lower assessment threshold for the protection of human health	24 hours	50 $\mu\text{g m}^{-3}$ 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 were no 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.

**Figure 4 Sulphur Dioxide 24-Hour Averages  
Trailer 1 in Cork Harbour 31/08/07 - 15/03/08**



**Figure 5 Sulphur Dioxide Hourly Averages  
Trailer 1 in Cork Harbour 31/08/07 - 15/03/08**



## Nitrogen Dioxide and Oxides of Nitrogen

No. of hours	4642
Missing values (including routine maintenance)	43 20
No. of measured values	4579
Percentage covered	98.6%
Maximum hourly value (NO <sub>2</sub> )	62.8 $\mu\text{g}\cdot\text{m}^{-3}$
98 percentile for hourly values (NO <sub>2</sub> )	$\mu\text{g}\cdot\text{m}^{-3}$ 43.9
Mean hourly value (NO <sub>2</sub> )	10.4 $\mu\text{g}\cdot\text{m}^{-3}$
Mean hourly value (NO <sub>x</sub> )	15.4 $\mu\text{g}\cdot\text{m}^{-3}$ 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>	

No hourly mean NO<sub>2</sub> 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.

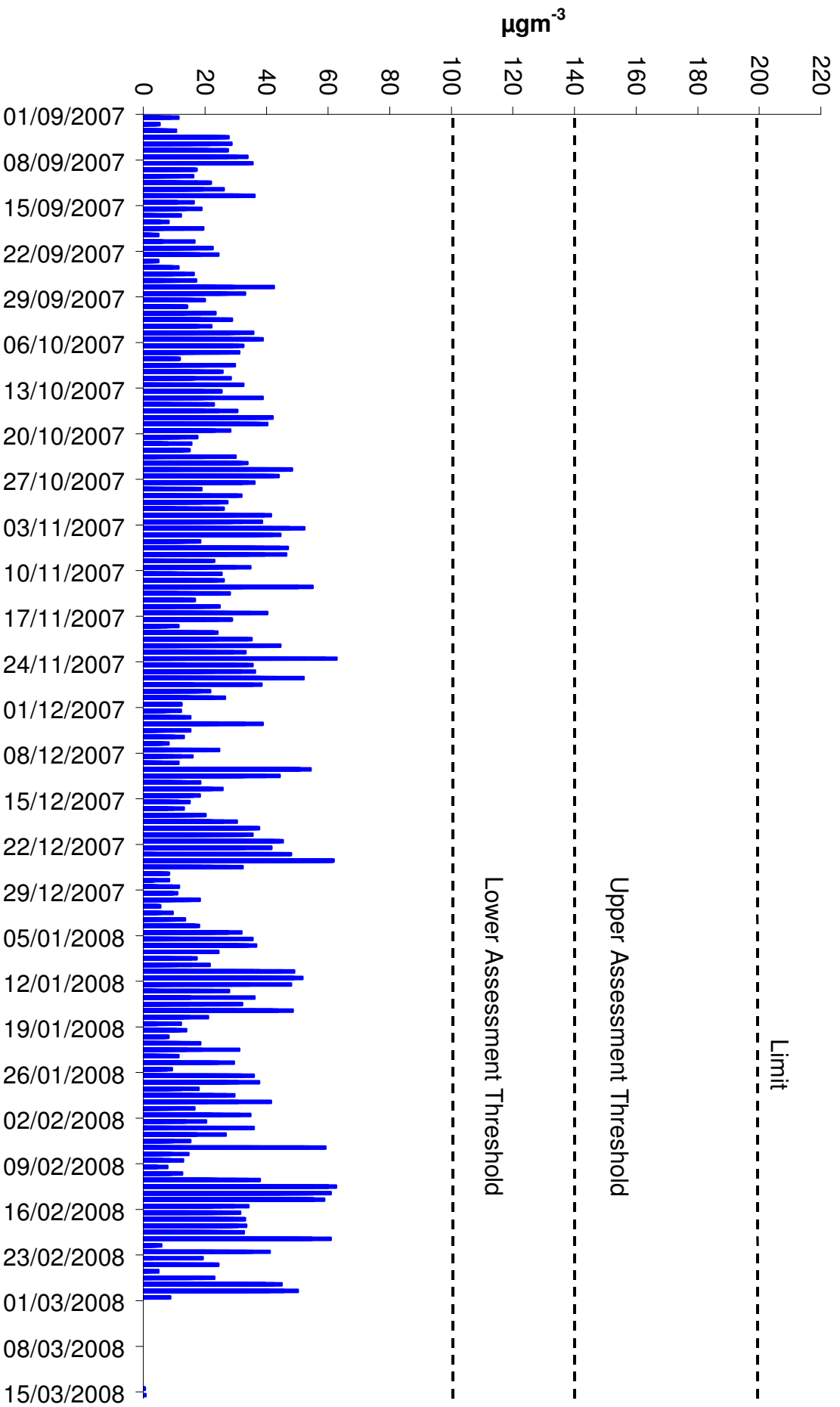
The mean hourly NO<sub>2</sub> value (10.4  $\mu\text{g.m}^{-3}$ ) during the measurement period was below the annual lower assessment threshold for the protection of human health (26  $\mu\text{g.m}^{-3}$ ).



The mean hourly value of  $\text{NO}_x$  ( $15.4 \mu\text{g}\cdot\text{m}^{-3} \text{NO}_2$ ) is just below the annual limit value for the protection of vegetation ( $30 \mu\text{g}\cdot\text{m}^{-3}$ ). However, the applicability of this limit to urban air pollution monitoring is questionable.

$\text{NO}$ ,  $\text{NO}_2$  and  $\text{NO}_x$  are measured as ppb (parts per billion) by volume. To convert to  $\mu\text{g m}^{-3}$ , a factor (1.25 for  $\text{NO}$ , 1.91 for  $\text{NO}_2$ ) is used. No formula is specified for  $\text{NO}_x$ , the directive requires it to be expressed as  $\text{NO}_2$  (i.e.  $\text{ppb}\cdot 1.91$ ). This applies even when most of the  $\text{NO}_x$  is present as  $\text{NO}$ .

**Figure 6 NO<sub>2</sub> Hourly Values  
Trailer 2 at Cork Harbour 01/09/07 - 15/03/08**



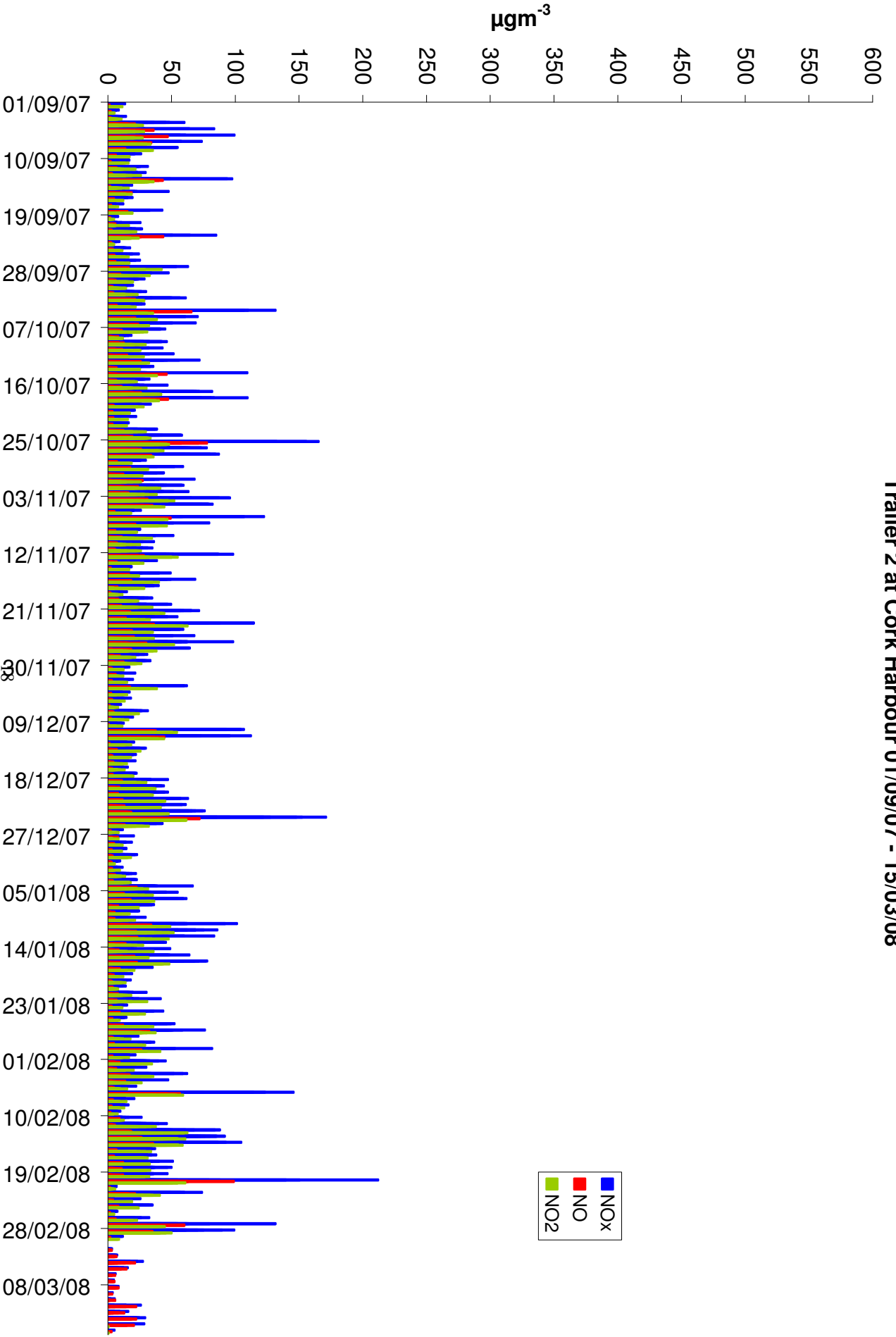


Figure 7 NO<sub>x</sub> Hourly Values  
Trailer 2 at Cork Harbour 01/09/07 - 15/03/08

## Particulate Matter

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

No. of days	207
Missing values (including routine maintenance)	126 0
No. of measured values	81
Percentage covered	39%
Maximum daily value	48.8 $\mu\text{g.m}^{-3}$
98 percentile for daily values	39.3 $\mu\text{g.m}^{-3}$
Mean daily value	16.7 $\mu\text{g.m}^{-3}$

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

	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) continued

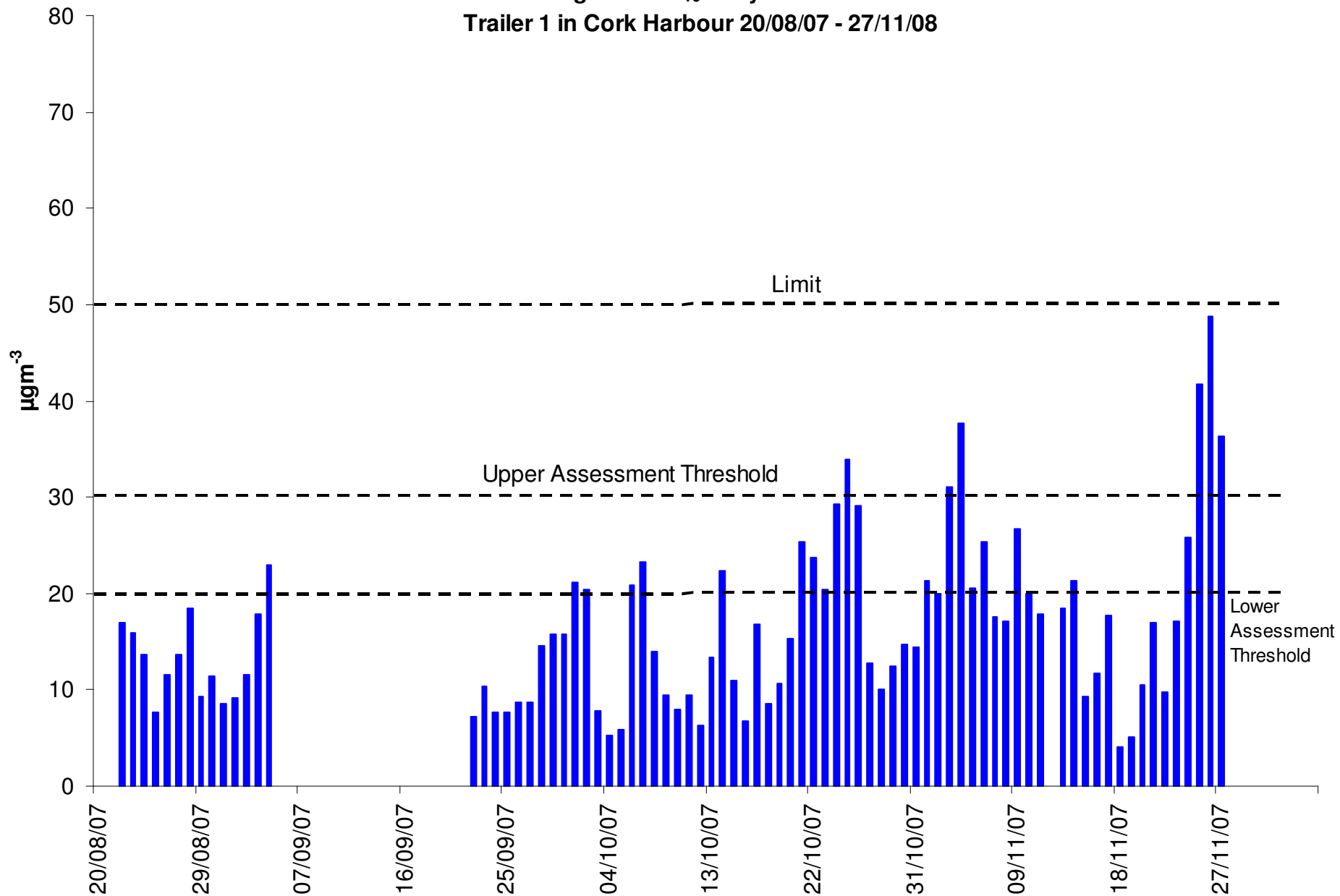
	Averaging Period	Limit Value	Date by which limit value is to be met
Lower assessment threshold for the protection of human health	24 hour	20 $\mu\text{g m}^{-3}$ PM <sub>10</sub> not to be exceeded more than 7 times a calendar year	<i>based on the indicative limit values for 1 January 2010</i>
Lower 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>

The 24 hour limit value for the protection of human health ( $50 \mu\text{g.m}^{-3}$ ) was not exceeded during the measurement period (Figure 8). 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 7 days, the lower assessment threshold was exceeded on 24 days. 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 ( $16.7 \mu\text{g.m}^{-3}$ ) is below the annual limit value for the protection of human health ( $40 \mu\text{g.m}^{-3}$ ).

Unfortunately we experienced technical difficulties with our TEOM FDMS sampler, which prevented full coverage for the measurement period.

**Figure 8 PM<sub>10</sub> Daily Values**  
**Trailer 1 in Cork Harbour 20/08/07 - 27/11/08**



## Lead

No. of days	182
Missing days (including routine maintenance)	0
No. of measured days	182
Percentage covered	100%
Concentration of Pb	0.004 $\mu\text{g}\cdot\text{m}^{-3}$

### 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 were subsequently set out in the fourth Daughter Directive (2004/107/EC).

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. With this method, 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.

The max concentration of arsenic measured in air was below the detection limit of the ICPMS.

The max concentration of cadmium measured in air was below the detection limit of the ICPMS.

The max concentration of nickel measured in air was below the detection limit of the ICPMS.

The target values of  $6 \text{ ng m}^{-3}$  for arsenic,  $5 \text{ ng m}^{-3}$  for cadmium and  $20 \text{ ng m}^{-3}$  for nickel have cross Europe attainment target dates of 31<sup>st</sup> of December 2012