

# Operation of EMEP 'supersites' in the United Kingdom



## Annual Report for 2007

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Ratified data from the AURN and Hydrocarbons Network were downloaded from the  
UK Air Quality website (<http://www.airquality.co.uk/>).

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## Executive Summary

As part of its commitment to the UN-ECE Convention on Long-range Transboundary Air Pollution the United Kingdom will operate two 'supersites' reporting data to the Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP).

This report provides the annual summary for 2007, the first full calendar year of operation of the first EMEP 'supersite' to be established in the United Kingdom. Detailed operational reports have been submitted to Defra every 3 months, with unratified data. This annual report contains a summary of the ratified data for 2007.

The EMEP 'supersite' is located in central southern Scotland at Auchencorth (3.2 °W, 55.8°N), a remote rural moorland site ~20 km south-west of Edinburgh. Monitoring operations started formally on 1 June 2006.

In addition to measurements made specifically under this contract, the Centre for Ecology & Hydrology also acts as local site operator for measurements made under other UK monitoring networks: the Automated Urban and Rural Network (AURN), the UK Precipitation Network, the UK Hydrocarbons Network, and the UK Heavy Metals Rural Network. Some measurements were also made under the auspices of the 'Acid Deposition Processes' contract. All these associated networks are funded by Defra.

This report summarises the measurements made between January and December 2007, and presents summary statistics on average concentrations.

The site is dominated by winds from the south-west, but wind direction data highlight potential sources of airborne pollutants (power stations, conurbations).

The average diurnal patterns of gases and particles are consistent with those expected from a remote rural site.

The frequency distributions are presented for data where there was good data capture throughout the whole period. Some components (e.g. black carbon) show log-normal frequency distributions, while other components (e.g. ozone) have more nearly normal frequency distributions.

A case study is presented showing the influence of regional pollution on measurements at Auchencorth, from a period in mid-June 2007 when there was a consistent northerly air flow to the site.

All the data reported under the contract are shown graphically in the Appendix.

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## 1. Overview

This project covers the operation of one of two 'supersites' in the UK for monitoring air pollutants. It is part of the UK's contribution to a Europe-wide programme of air monitoring under the UN Economic Commission for Europe's Convention on Long Range Transboundary Air Pollution. The monitoring is done under the auspices of EMEP (Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe), and contributes data to a central European database. The results are used to evaluate the levels of air pollution across Europe, to identify trends, and for comparison with computer model outputs.

The measurements under this project were started in June 2006 at Auchencorth Moss, approximately 20 km south of Edinburgh, in east central Scotland. The site is remote from sources of air pollutants, and provides a large flat area of uniform vegetation (moss, grass and heather) which is ideally suited to long-term monitoring. The site is classified as remote rural.

Measurements included a range of trace gases (ozone, nitrogen oxides, sulphur dioxide, nitric acid, ammonia, volatile organic compounds), and particles in two size fractions: diameters up to 2.5 micrometre (PM<sub>2.5</sub>) and up to 10 micrometre (PM<sub>10</sub>). Particle mass in the two size fractions was measured, as well as water-soluble particulate material (salts) and black carbon (soot). Occasional 'intensive' monitoring activity, coordinated at several sites across Europe to provide a more detailed picture of air quality for two months out of every year, is reported separately.

Data collected under this project are archived and made available via the internet through a central database.

## 2. Background

### 2.1 Policy context

The UNECE Convention on Long Range Transboundary Air Pollutants operates a number of measurement and monitoring programmes, including EMEP – the Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (see [http://www.emep.int/index\\_facts.html](http://www.emep.int/index_facts.html)).

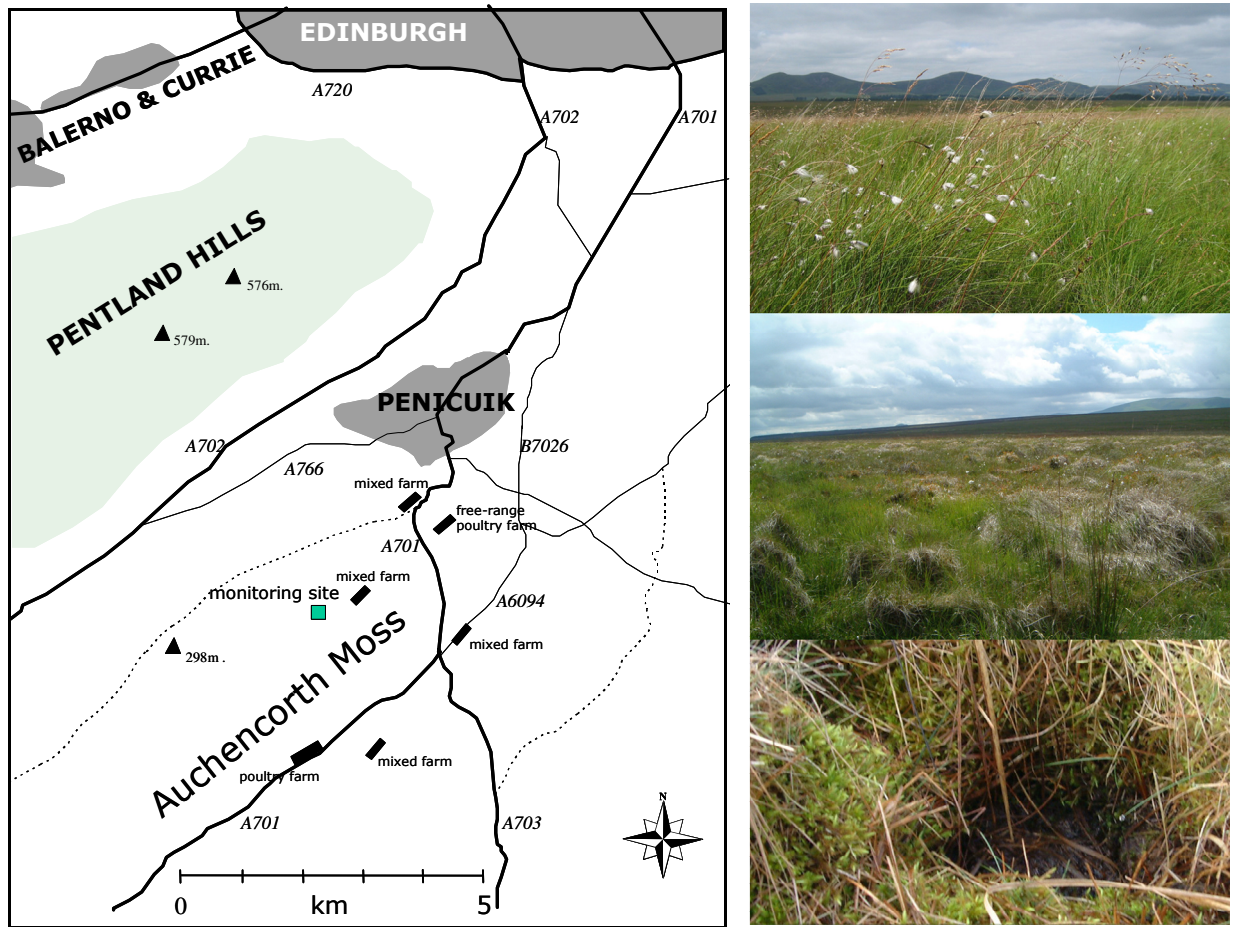
The Norwegian Institute for Air Research (NILU) arranged an EMEP Task Force on Measurements and Modelling (TFMM) workshop on the implementation of the EMEP monitoring strategy (EB.AIR/GE.1/2004/5) in Oslo on 22-24 November 2004 (see also <http://www.nilu.no/projects/ccc/reports/cccr9-2003.pdf>). The objective of the workshop was to discuss methodologies and technical requirements needed to implement the level 2 and level 3 activities defined by the EMEP monitoring strategy. Subsequently a meeting was held in Zagreb, Croatia in April 2005 (<http://www.nilu.no/projects/ccc/tfmm/index.html>) which also considered implementation of the EMEP monitoring strategy. Details of the EMEP monitoring strategy and measurement programme for 2004-9 are available at [http://www.unece.org/env/emep/Monitoring%20Strategy\\_full.pdf](http://www.unece.org/env/emep/Monitoring%20Strategy_full.pdf).

The United Kingdom contribution to the EMEP monitoring strategy is based on the creation of two Level 2 ‘supersites’, one in the north of the UK and one in the south, at which additional measurements are, or can be, made to qualify as an EMEP Level 3 site. Data from these sites at hourly or daily frequency will be supplemented by long-term integrating measurements from existing Defra-funded monitoring networks across the UK (<http://www.nilu.no/projects/ccc/network/index.html>). The northern site is identified as Auchencorth Moss in eastern Scotland (UK OS grid reference NT220562; [http://www.heavymetals.ceh.ac.uk/sites/site\\_auc.htm](http://www.heavymetals.ceh.ac.uk/sites/site_auc.htm)) which has been used by the Centre for Ecology & Hydrology for several years as an intensive monitoring site for trace gas and particle concentrations and fluxes. The site is based in an area of upland peat, with heather and grass cover, and has an extensive fetch to the south-west. The southern site is at Harwell, in Oxfordshire (OS grid reference SU468860), operated by Netcen over many years for sampling trace gases and aerosols.

The Auchencorth site was inaugurated as a ‘supersite’ in June 2006, although it had been used by CEH for 10 years previously for gas concentration and flux measurements. It has been operating continuously since then for continuous monitoring activities and the ‘intensive’ periods of more detailed measurements which are coordinated by EMEP across Europe for two months each year. The first ‘intensive’ period was in June 2006, with the second ‘intensive’ period in January/February 2007. The suite of measurements includes data which are currently being collected as part of existing Defra UK monitoring networks. However, all data from the site are recorded and stored on a single database at CEH Edinburgh, so that the measurements from the different UK networks operating at the site can be compared.

## 2.2 Site details

The Auchencorth site is located ~20 km south-west of Edinburgh on open moorland at 255 m asl, 3.2 °W, 55.8°N (OS grid reference NT220562). There are no major sources of pollution nearby, although there are some large towns to the north-east and intensive farming to the south and south-east, as indicated on the maps in Figure 1a. There is an extensive uniform fetch of blanket bog to the south, west and north (Figure 1b) comprising mixed grass species, heather and substantial areas of moss species *Sphagnum spp.* and *Polytrichum spp.* (Figure 1c).



a.  
b.

c.

**Figure 1: a. Map showing the location of Auchencorth Moss, b view of the fetch from the SW to NW (panorama generated from several individual photos hence some discontinuities and distortion), c. the vegetation during summer months.**

### 2.3 Outline of work at Auchencorth

The measurements made during 2007 are listed below. A summary overview is given in Table 1, which also shows the measurements that were being made as part of other research and monitoring programmes. Measurements made under this contract are shown in **bold** type. Additional measurements from the site with data reported here are shown in *italic* type.

**Table 1. Summary of measurements made in 2007**

<b>Measurement</b>	<b>EMEP Level</b>	<b>Status (Funding)</b>
<i>Meteorological data (30 min)</i>	I	CEH
Weekly bulk deposition of inorganic ions	I	Defra RMP2258– Acid Deposition Processes
<i>Daily wet-only deposition</i>	I	Defra/AEA Technology RMP2901 - Acid Deposition Monitoring Network
Monthly trace gases and particle concentrations	I	Defra/AEA Technology RMP2901 - Nitric Acid Network – Acid Deposition Monitoring
<b>Trace gas and particle concentrations at PM<sub>2.5</sub> and PM<sub>10</sub> (hourly)</b>	II	This contract – MARGA
<i>Daily particle mass (PM<sub>2.5</sub> and PM<sub>10</sub>)</i>	I	Defra - AURN
<b>Black carbon PM<sub>2.5</sub> (30 min)</b>	II	This contract - Aethalometer
Ammonia (monthly)	II	Defra RMP1906 -Ammonia in UK
<i>Ozone (hourly)</i>	I	Defra - AURN
<i>VOCs</i>	II	Defra RMP1833 - VOC network
<i>Heavy metals in precipitation (weekly)</i>	I	Defra CPEA32 - Heavy Metals
<i>Heavy metals in PM<sub>10</sub> (weekly)</i>	II	
<i>Mercury in precipitation (weekly)</i>	II	
<i>Speciated mercury in air (hourly)</i>	II	
Trace gas (O <sub>3</sub> , NO <sub>x</sub> , SO <sub>2</sub> ) fluxes (hourly) ( <i>concentrations only</i> )		Defra RMP2258 – Acid Deposition Processes
Monthly trace gas and particle fluxes		Defra RMP2258 – Acid Deposition Processes

#### **2.4 Site modifications during 2007**

A new 3-phase power supply was installed in November 2007. This provides additional power (up to 100A) and a permanent earth circuit – the lack of a suitable earth was part of the cause of an air conditioning failure which led to loss of some VOC data. New additional boardwalk and fixing construction was installed in preparation for new high-volume instruments for sampling polycyclic aromatic hydrocarbons (PAHs) and toxic organic micro-pollutants (TOMPs).

#### **2.5 Site management and operation to meet EMEP Level II requirements**

Effective operation of a ‘supersite’ over a period of several years requires that there is in place a management structure to ensure that access to the different instruments used for calibration, maintenance etc. does not compromise the operation of other measurements at the site. A designated site manager (Mr Robert Storeton-West) was appointed to oversee and coordinate all measurements at the site (including those



made by CEH not under this or any other Defra contract). In most cases, routine maintenance of all the equipment, and standard calibrations and tests, was done by CEH staff. However, network protocols also required external maintenance and/or calibration visits for quality assurance, and such visits were coordinated as required.

In addition, the operation of a long-term site requires liaison with land owners and other users of the land, and ongoing maintenance of access routes and communications systems. This is particularly a problem at Auchencorth, where there is no road access. Heavy instruments, gas cylinders and water tanks (60 litres per week for the MARGA) must be transported to the site by an all-terrain vehicle. Health and safety requirements mean that lone working at the site is not usually permitted, particularly in winter.

CEH acted as local site operator for the following measurements (see also Table 1), which were operated under a separate Defra contract or as part of a UK monitoring network:

### 2.5.1 *Wet deposition*

The weekly bulk sampling of precipitation continued as part of the Defra-funded Acid Deposition Processes contract (RMP 2258). The site at Auchencorth acts as the 'lowland' site for comparison with the cloud and rain sampling conducted at Bowbeat.

Daily samples from a wet-only collector were collected every week and shipped to Netcen for analysis as part of the UK Acid Deposition Monitoring Project (RMP2901), under sub-contract agreement 14709935, following the protocols laid down for that network. Samples were analysed by ion chromatography for the concentrations of major anions and cations, pH and conductivity. The wet-only collector developed a fault with the opening mechanism, and had to be left open for most of the first 3 months of the year, so the data from this period are not technically 'wet-only' but 'bulk' deposition.

### 2.5.2 *Trace gas and aerosol concentrations*

The integrated monthly concentration measurements of  $\text{NH}_3$ ,  $\text{SO}_2$ ,  $\text{HNO}_3$ ,  $\text{HCl}$  gases and  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  in aerosol continued under the Defra-funded Acid Deposition Monitoring contract with Netcen (RMP2901), sub-contracted to CEH as part of the Nitric Acid Network (Agreement 14709935). Measurements were made using coated denuders and filter packs (CEH DELTA samplers).

The integrated monthly flux measurements of  $\text{NH}_3$ ,  $\text{SO}_2$ ,  $\text{HNO}_3$ ,  $\text{HCl}$  gases and  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  in aerosol also continued under the Defra-funded Acid Deposition Processes contract with CEH (RMP 2258). Measurements were made using the CEH COTAG (COnditional Time-Averaged Gradient) technique.

### 2.5.3 *Particle mass (PM)*

Automated particle samplers (Partisols) for measuring the daily integrated mass of both  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  were already in operation as part of the Defra Particulate Monitoring Network, part of the Automated Urban and Rural Network (AURN). These were operated by CEH on behalf of the contractor Bureau Veritas (1/3/191). Exposed filters (daily integrated sampling) were removed two-weekly and shipped to

the contractor for analysis. A problem with the PM<sub>10</sub> sampler, which was identified in 2007, means that valid data are only available from 14 August.

After some difficulties with the electrical supply, the two new TEOM/FDMS samplers (PM<sub>2.5</sub> and PM<sub>10</sub>) were installed and have been operating since the beginning of the year. Data are collected by mobile phone by the AURN operators.

#### 2.5.4 Trace gases

Measurements of vertical gradients of O<sub>3</sub>, NO<sub>x</sub> and SO<sub>2</sub> by CEH are used to infer fluxes of these trace gases to/from the surface. Concentration measurements are cycled through 3 different heights, with 3 minutes at each measurement height. The SO<sub>2</sub> measurements were part of the Acid Deposition Processes contract held by CEH (RMP2258). Data from the top height (2.5m) are reported here.

Ozone – a continuous UV-photometric instrument was operated by Bureau Veritas as part of the AURN (1/3/191). Data are recorded as hourly averages.

Volatile Organic Compounds (VOC) – an automated sampler/gas chromatograph was operated by AEATechnology at Auchencorth as part of the UK Hydrocarbons Monitoring Network (RMP1883). Data are recorded hourly. The long downtimes caused by power failures at the site, which required manual intervention to restart the sampler, have been overcome, and the whole system can now be restarted using the web access.

Carbonyls (aldehydes and ketones) – automated samplers were constructed in 2006 for installation at Auchencorth and at Harwell. Following the EMEP protocol, two 8-hour integrated samples are scheduled to be taken in daylight hours every week. The exposed sampling tubes (commercially available packed cartridges containing dinitrophenylhydrazine, DNPH) are shipped to Netcen weekly for analysis under the UK Hydrocarbons Monitoring Network (RMP1883). More frequent (manual) operation of the devices is possible during 'intensive' periods. Field testing of the samplers and analysis showed continuing problems with contamination which were not resolved during 2007 despite several field trials.

#### 2.5.5 Heavy metals

The Defra contract with CEH (CPEA32) includes Auchencorth as one of the UK Heavy Metal Network sites. Measurements include:

- Weekly sampling of precipitation for heavy metals (excluding mercury)
- Separate weekly sampling of precipitation for mercury
- Weekly integrated sampling of PM<sub>10</sub> aerosol for heavy metals
- Semi-continuous sampling of speciated airborne mercury (elemental mercury, reactive gaseous mercury, and particulate mercury) using an automated Tekran system. Data are reported as hourly averages every 2 hours; elemental mercury data are available every 5 minutes during every alternate hour, if required.

Precipitation and filter samples are sent weekly to CEH Lancaster for chemical analysis using ICP-MS (Inductively-coupled plasma mass spectrometry) for all heavy metals except mercury, and cold vapour atomic fluorescence for mercury. EMEP protocols are used for all heavy metal and mercury measurements.

From mid-February, there was an issue with the 1135P Particulate Unit, in which the RCD was tripping intermittently. The instrument was returned to the supplier on 15th March for repair, and reinstated on 28<sup>th</sup> May. The mercury analyzer pump failed in October, leading to some loss of data.

### **3. Operation of instruments under this contract**

Summaries of the start dates (for new instruments) and data capture during 2007 are given in Table 2. Brief descriptions of the instrumentation and explanations of periods with missing data are given below.

#### **3.1 Meteorological measurements**

Measurements were made continuously of the following variables: wind speed, wind direction, air temperature, relative humidity, barometric pressure; precipitation amount, timing and duration. Data were stored as 30-minute averages. Wind direction data were averaged as vectors. Wind speed and direction data are missing from the latter part of December because of instrument faults.

#### **3.2 Trace gas and aerosol concentrations (MARGA)**

The automated continuous-flow denuder and steam-jet aerosol sampler (MARGA) samples water-soluble trace gases and aerosol particles with hourly resolution, using a rotating wet denuder to remove gases from the sampled air stream before the residual particles (which pass through the denuder) are activated by steam into droplets, which are subsequently captured and analysed. The solutions of dissolved gases and dissolved particles are analysed on-line by ion chromatography, using parallel systems for cations and anions. A dual sampler was installed, with separate analysis of PM<sub>10</sub> and PM<sub>2.5</sub> aerosols. Internal standards of Li<sup>+</sup> (cations) and Br<sup>-</sup> (anions) are used for calibration checks.

A field visit to Auchencorth by the Dutch manufacturers led to some improvements in the performance of the instrument: change of the original collection solution (weak formaldehyde solution) to de-ionised water has greatly improved the instrument performance for NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup>. In addition, a ground loop was fixed, which means that the communication within the instrument is much more stable. However, the addition of an improved cation pre-concentrator column was unsuccessful, leading to low data capture in Feb 2007. Gaps in the MARGA data were mainly due to awaiting the mass flow controller replacement at the start of August and a UPS failure in September. The software (MARGA2s, Applikon B. V. Schiedeam, Netherlands) used to operate the instrument was also upgraded from MARGA2s v1.1.0.0 to version MARGA2s v1.1.3.0 on the 27/09/07. A new UPS was added to the MARGA at the start of November 2007, allowing the software alarms to be enabled again.

#### **3.3 Particulate carbon (Aethalometer)**

The monitor for the continuous measurement of black carbon in air (aethalometer) was operated, recording data as 30-minute averages. The data for 2007 represent PM<sub>3.3</sub> rather than PM<sub>2.5</sub> because of an error in the prescribed flow rate to the instrument. It is not expected that this will make a large difference in the reported air concentrations relative to PM<sub>2.5</sub> because at this site, remote from particle sources, the long-range transported aerosols are likely to be in the size range of < 1 micrometre. The instrument developed a fault on 23<sup>rd</sup> July and was returned to the supplier for repair; monitoring restarted on 21<sup>st</sup> August.

### 3.4 Trace gases (ANNOX)

Nitrogen oxides: a high-sensitivity automated NO/NO<sub>2</sub> analyzer (ANNOX) was installed and commissioned at the site in May, but was subject to several initial problems, and ongoing problems with over-heating which were partially solved by installation of additional air-conditioning. The lack of a stable ozone analyzer (used for automatic calibration) meant that no data are reported for 2007. This chemiluminescent instrument uses UV photolysis to convert NO<sub>2</sub> to NO prior to analysis, as specified by the EMEP protocol. It is therefore specific for NO<sub>2</sub>, and does not respond to other oxidised N species such as PAN and HNO<sub>3</sub>, which are positive artefacts when using a thermal convertor.

**Table 2. Data capture for instrumentation operated and reporting under this contract.**

<b>Instrument</b>	<b>% data capture for 2007</b>
Wind speed and direction	83%
Air temperature	100%
Relative humidity	94%
Barometric pressure	100%
Surface wetness	100%
Precipitation (30-minute)	100%
Precipitation (daily)	100%
MARGA PM <sub>10</sub>	49% (at least one ion > l.o.d)
MARGA PM <sub>2.5</sub>	38% (at least one ion > l.o.d)
MARGA gases	51% (at least one gas > l.o.d)
Aethalometer	80%
VOCs	65% (at least one VOC > l.o.d.)
Ozone (CEH)	86%
Sulphur dioxide	99%
Nitrogen oxides	98%
Daily PM <sub>10</sub> and PM <sub>2.5</sub>	36% (PM <sub>10</sub> ), 89% (PM <sub>2.5</sub> )
Ozone (AURN)	99%
Hourly PM <sub>10</sub> and PM <sub>2.5</sub>	98%(PM <sub>10</sub> ), 97%(PM <sub>2.5</sub> )
Mercury: Hg <sup>0</sup> , RGM, part	75%, 67%, 48%

## 4. Data collation and QA/QC

During 2007 a broadband link was established which permits most of the analytical instruments to be interrogated and controlled via the internet. This has led to improvements in detecting malfunctions, and a consequent improvement in data capture rates. All continuously-monitored data are recorded on a 'mirrored' server on site, and downloaded to a backed-up data store at CEH Edinburgh every night. Once data have been initially checked for instrument malfunction or obvious errors by dedicated CEH staff, the 'raw' data are uploaded to a web-accessible database, and available to any user with password access. Data are then ratified after identification of any long-term drifts in instrument response and recalibration (if necessary). The datasets are updated as required and marked in the database as 'ratified'. Data from other UK networks which sample at Auchencorth are downloaded (after ratification) from the Air Quality database (<http://www.airquality.co.uk/index.php>), or directly

from the network operators, and uploaded into the 'Auchencorth EMEP' database at CEH Edinburgh. This means that all data collected at the site can be accessed simply, and can be reported to EMEP using the standard prescribed format.

The recommended maximum time scales for the release of non-quality-assured data that are collected as part of the operations of other networks or projects are as follows:

<u>Measurement</u>	<u>Data released within (period) after sampling</u>
Daily wet-only sample volumes	1 month
Daily wet-only ion concentrations	3 months
Monthly trace gas/aerosol concentrations (DELTA)	3 months
Monthly trace gas/aerosol concentrations (COTAG)	3 months
Hourly trace gas/aerosol concentrations (MARGA)	1 month
PM10/PM2.5 concentrations	1 month
Aethalometer	2 weeks
VOCs	2 weeks
Ozone, NO/NO <sub>2</sub>	2 weeks
Heavy metal concentrations (precipitation or air)	3 months
Mercury in precipitation	3 months
Mercury in air	2 weeks

Note that these data are to be used for quality assurance purposes only.

## **5. Reports on site operations and data**

Formal reports are provided every 3 months to Defra, and take the form of short progress reports (form SID4), noting operational matters (e.g. data capture) and any problems with instrumentation or the site, and a summary of the data during the reporting period. This annual report brings together the information in the quarterly reports, and provides ratified data and summaries for the preceding calendar year (in this case 2007).

## **6. Summary data results**

Plots for each of the data sets in Table 2 are presented in the Appendix. Statistical summary data are presented below in Table 3. These data should be read in conjunction with the % data capture and start dates in Table 2 to indicate how representative they are for the period. In all cases, the minimum concentrations recorded were at or below the limit of detection of the instrument. Note that for VOCs, only those compounds that exceeded the limit of detection (l.o.d.) are reported.

Data may be viewed and downloaded from the website <http://emepdata.ceh.ac.uk/> after application for a password from CEH ([jnc@ceh.ac.uk](mailto:jnc@ceh.ac.uk)). The database will become 'live' during 2009.

**Table 3. Summary data for the period 1 January to 31 December 2007**

<b>Instrument</b>	<b>mean</b>	<b>median</b>	<b>min/max</b>
Wind speed, m s <sup>-1</sup> (30 min)	4.29	3.86	0.06/18.1
Air temperature, °C (30 min)	7.9	7.8	-9.7/22.1
Relative humidity, % (30 min)	83.0	86.1	38/94
Bar. pressure, kPa (30 min)	98.1	98.2	93.7/100.8
Precipitation (mm/30 min)	0.064	0	0/6.5
Precipitation (daily wet-only)	2.56	0.10	0/28.1
Daily rain concentrations: H <sup>+</sup> (µequivalent L <sup>-1</sup> )	17.1	13.5	0.4/110
NH <sub>4</sub> <sup>+</sup>	24.7	14.6	0/302
Na <sup>+</sup>	74.5	26.6	0/707
K <sup>+</sup>	2.5	1.3	0/29
Ca <sup>2+</sup>	7.1	4	0/58
Mg <sup>2+</sup>	14.7	4.8	0/154
Cl <sup>-</sup>	83.0	4.8	2/749
NO <sub>3</sub> <sup>-</sup>	15.3	30.7	0/253
SO <sub>4</sub> <sup>2-</sup>	24.2	15.6	1/212
Non-sea SO <sub>4</sub> <sup>2-</sup>	15.3	12.4	0/127
Conductivity (µS cm)	18.0	9.5	11/93
Daily rain deposition: H <sup>+</sup> (µequivalent m <sup>-2</sup> )	86	28	621
NH <sub>4</sub> <sup>+</sup>	73	44	628
Na <sup>+</sup>	336	87	10500
K <sup>+</sup>	9	5	211
Ca <sup>2+</sup>	29	15	408
Mg <sup>2+</sup>	67	18	2060
Cl <sup>-</sup>	376	99	11500
NO <sub>3</sub> <sup>-</sup>	55	23	623
SO <sub>4</sub> <sup>2-</sup>	95	48	1280
Non-sea SO <sub>4</sub> <sup>2-</sup>	55	37	631
Rain wtd. concentrations: H <sup>+</sup> (µequivalent L <sup>-1</sup> )	15.9		
NH <sub>4</sub> <sup>+</sup>	13.4		
Na <sup>+</sup>	62.1		
K <sup>+</sup>	1.7		
Ca <sup>2+</sup>	5.3		
Mg <sup>2+</sup>	12.3		
Cl <sup>-</sup>	69.4		
NO <sub>3</sub> <sup>-</sup>	10.2		
SO <sub>4</sub> <sup>2-</sup>	17.6		
Non-sea SO <sub>4</sub> <sup>2-</sup>	10.1		
MARGA PM <sub>10</sub> : NH <sub>4</sub> <sup>+</sup> (µg m <sup>-3</sup> )	0.98	0.33	17
Na <sup>+</sup>	0.62	0.36	9.6
Ca <sup>2+</sup>	0.12	0.09	0.8
Mg <sup>2+</sup>	0.09	0.06	2.1
Cl <sup>-</sup>	0.95	0.55	11.6
NO <sub>3</sub> <sup>-</sup>	1.55	0.56	32
SO <sub>4</sub> <sup>2-</sup>	1.19	0.61	34
MARGA PM <sub>2.5</sub> : NH <sub>4</sub> <sup>+</sup> (µg m <sup>-3</sup> )	0.72	0.21	8.3
Na <sup>+</sup>	0.37	0.26	7.3
Ca <sup>2+</sup>	0.09	0.07	1.6

Instrument		mean	median	min/max
	Mg <sup>2+</sup>	0.07	0.06	1.6
	Cl <sup>-</sup>	0.59	0.38	9.7
	NO <sub>3</sub> <sup>-</sup>	1.21	0.36	16
	SO <sub>4</sub> <sup>2-</sup>	0.81	0.45	34
MARGA gases: (µg m <sup>-3</sup> )	NH <sub>3</sub>	1.14	0.64	24
	HCl	0.13	0.07	4.6
	HNO <sub>3</sub>	0.12	0.07	3.7
	HNO <sub>2</sub>	0.14	0.10	2.9
	SO <sub>2</sub>	0.37	0.13	23
Aethalometer (µg C m <sup>-3</sup> )		0.26	0.17	5.0
VOCs (µg m <sup>-3</sup> )	1,3-butadiene	0.013	0.02	0.29
	1-butene	0.008	0	0.16
	cis-2-butene	0.005	0	0.16
	trans-2-butene	0.014	0.02	0.30
	ethane	0.40	0.38	3.19
	ethene	0.055	0.04	1.22
	ethyne	0.047	0.04	0.36
	isoprene	0.049	0.03	0.99
	propane	0.289	0.24	19
	propene	0.036	0.02	1.24
	n-butane	0.17	0.12	17
	iso-butane	0.10	0.07	7.2
	n-pentane	0.058	0.03	6.1
	iso-pentane	0.077	0.06	5.9
Ozone (CEH) (ppb)		25.9	26.1	55
Sulphur dioxide (ppb)		0.30	0.13	20
Nitrogen oxides: NO (ppb)		0.21	0	52
	NO <sub>2</sub> (ppb)	2.3	1.5	44
Mass daily (µg m <sup>-3</sup> )	PM <sub>2.5</sub>	7.4	5.0	46
	PM <sub>10</sub>	10.2	8.5	30
Mass hourly (µg m <sup>-3</sup> )	PM <sub>2.5</sub>	4.1	2	64
	PM <sub>10</sub>	6.4	4	82
	Involatile PM <sub>2.5</sub>	3.5	2	67
	Involatile PM <sub>10</sub>	5.8	4	73
	Volatile PM <sub>2.5</sub>	0.57	1	25
	Volatile PM <sub>10</sub>	0.61	0	21
Ozone (AURN) (µg m <sup>-3</sup> )		58.2	58	118
Mercury: Elemental (ng m <sup>-3</sup> )		1.10	1.09	0.6/6.8
	Reactive gaseous (pg m <sup>-3</sup> )	0.11	0	29
	Particulate (pg m <sup>-3</sup> )	0.86	0	116
Heavy metals in air (weekly) (ng m <sup>-3</sup> )	As	0.25	0.19	1.4
	Cd	0.05	0.03	0.24
	Cr	0.63	0.60	1.7
	Cu	1.04	0.90	3.5
	Ni	1.16	0.18	35
	Pb	2.45	1.80	11
	Se	0.35	0.29	1.2
	V	0.65	0.41	2.4

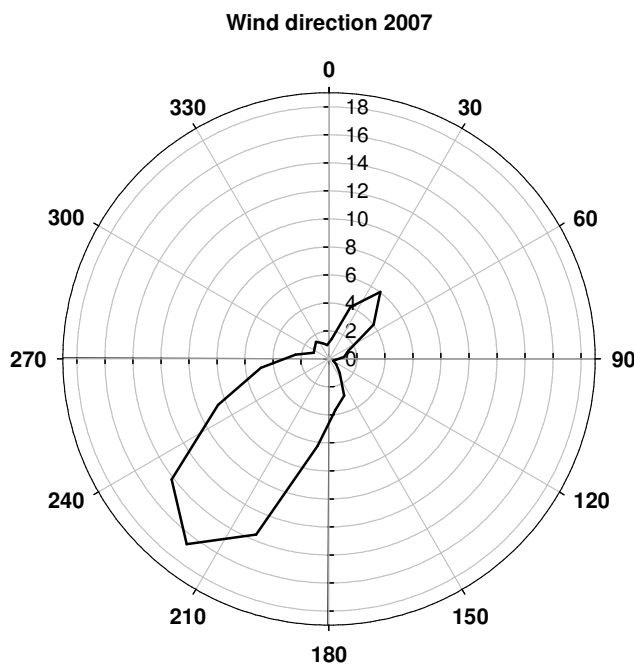
<b>Instrument</b>		<b>mean</b>	<b>median</b>	<b>min/max</b>
(two weekly)	Zn	5.03	2.99	23
	Hg	1.47	1.52	0.91/1.84
Heavy metals in rain (weekly)				
(ng L <sup>-1</sup> )				
	As	0.12	0.08	0.31
	Cd	0.013	0.006	0.113
	Cr	0.10	0.07	0.43
	Cu	0.32	0.3	0.96
	Ni	0.12	0.09	0.41
	Pb	0.25	0.16	1.4
	Se	0.14	0.10	0.53
	V	0.19	0.13	0.71
(monthly)	Zn	3.0	2.2	19
	Hg	4.6	3.6	5.7



## 7. Discussion

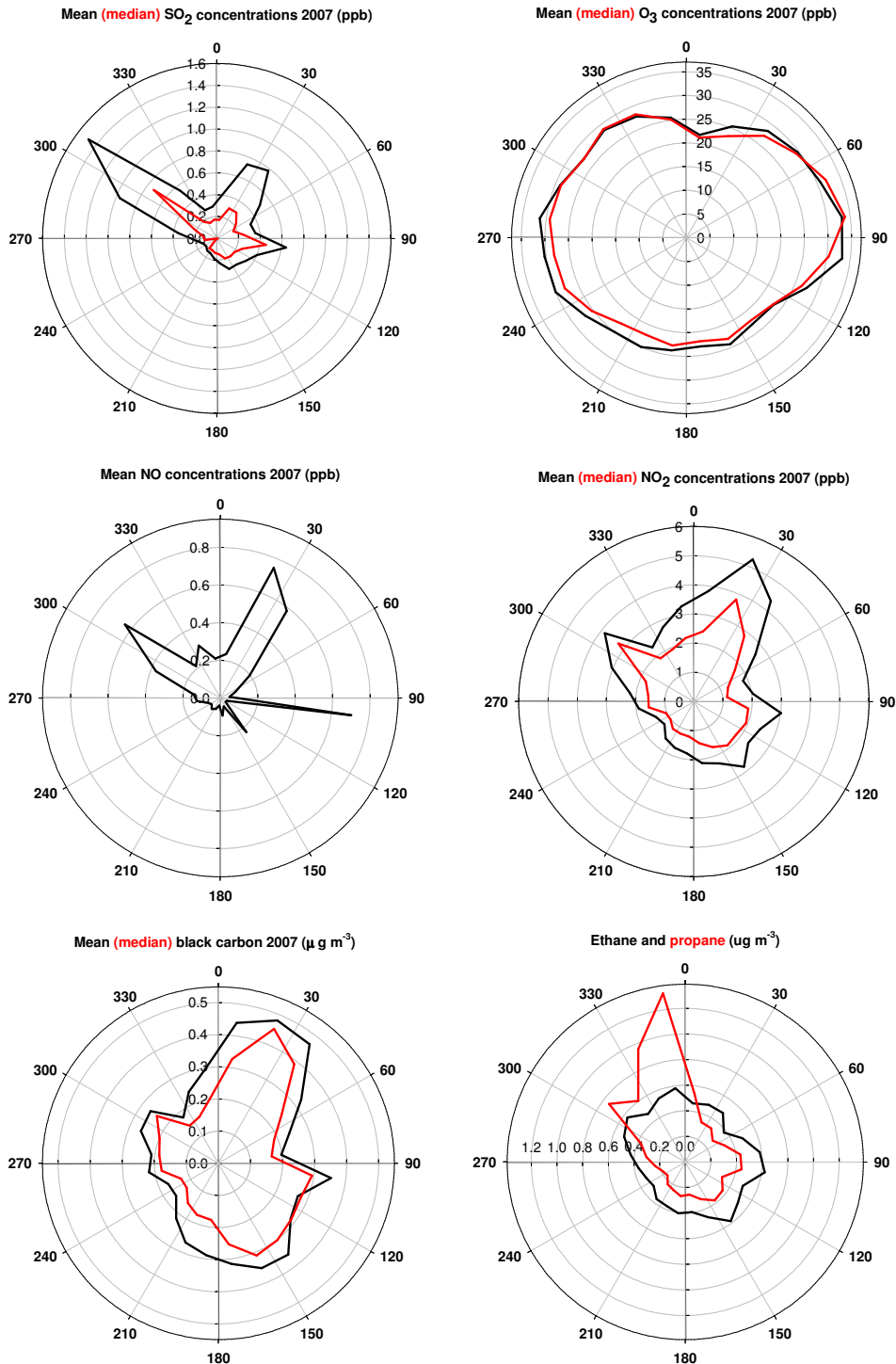
### 7.1 Influence of wind direction

The site at Auchencorth is dominated by winds from the south-west, but in contrast to the second half of 2006, there was a greater frequency of winds from the north-east, as shown in Figure 2. The wind sector distribution of trace gases and particles gives a crude indication of potential sources that influence the air quality at the site. Examples are shown in Figures 3a-e below.



**Figure 2: Distribution of wind direction frequency during 2007, expressed as % time**

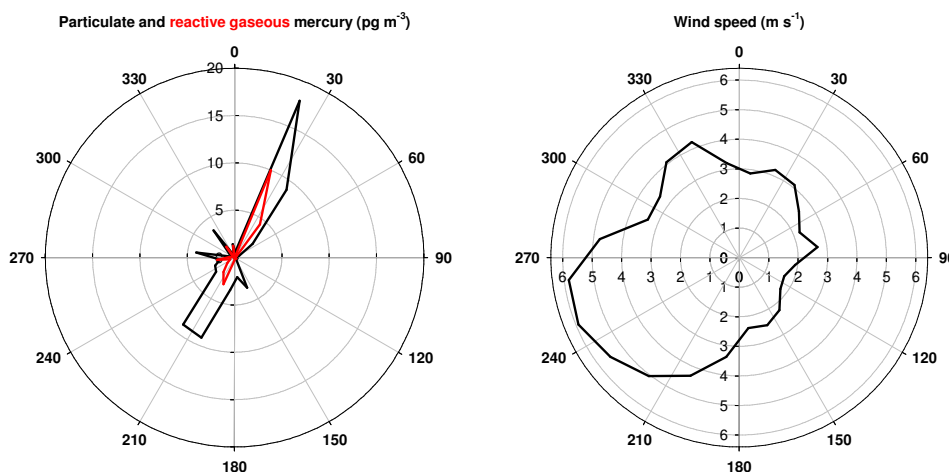
Concentrations of sulphur dioxide ( $\text{SO}_2$ ) were low (median 0.13 ppb) and for much of the time close to the detection limit of the UV photometric analyzer deployed by CEH. Median concentrations were much smaller than the mean concentrations, because of the log-normal distribution of the concentration data (see 7.3 below). Figure 3a shows the directional dependence – the highest concentrations to the NW probably originate from power stations at Grangemouth oil refinery and Longannet (coal-fired), while the smaller peak to the NE probably derives from the Midlothian town of Dalkeith (popn.12,000) and the coal-burning power station at Cockenzie. The city of Edinburgh (popn. 470,000) lies closer to the north, in the same direction as the town of Penicuik (popn. 15,000). The directional dependence of ozone ( $\text{O}_3$ ) concentrations is much less marked, with higher concentrations to the E, possibly reflecting the influence of continental air masses. The median and mean are very similar, showing an approximately normal distribution of the ozone concentration data (see 7.3 below). Nitric oxide (NO) concentrations were at or below the detection limit of the analyzer (0.5 ppb) for most of the time, so the directional data (Figure 3c)



**Figure 3: Directional dependence of air concentrations, from top left (a) sulphur dioxide, (b) ozone, (c) nitric oxide, (d) nitrogen dioxide, (e) black carbon, (f) ethane and propane.**

reflect occasional peak concentrations when NO exceeded O<sub>3</sub> and so was not removed by reaction, usually at night. The influence of Grangemouth/Longannet and Edinburgh/Penicuik can be seen in the directional peaks to the NW and NE, respectively. For nitrogen dioxide (NO<sub>2</sub>) the pattern (Figure 3d) is quite different from that for SO<sub>2</sub>, with broad peaks to the NW and NE, particularly in the median values,

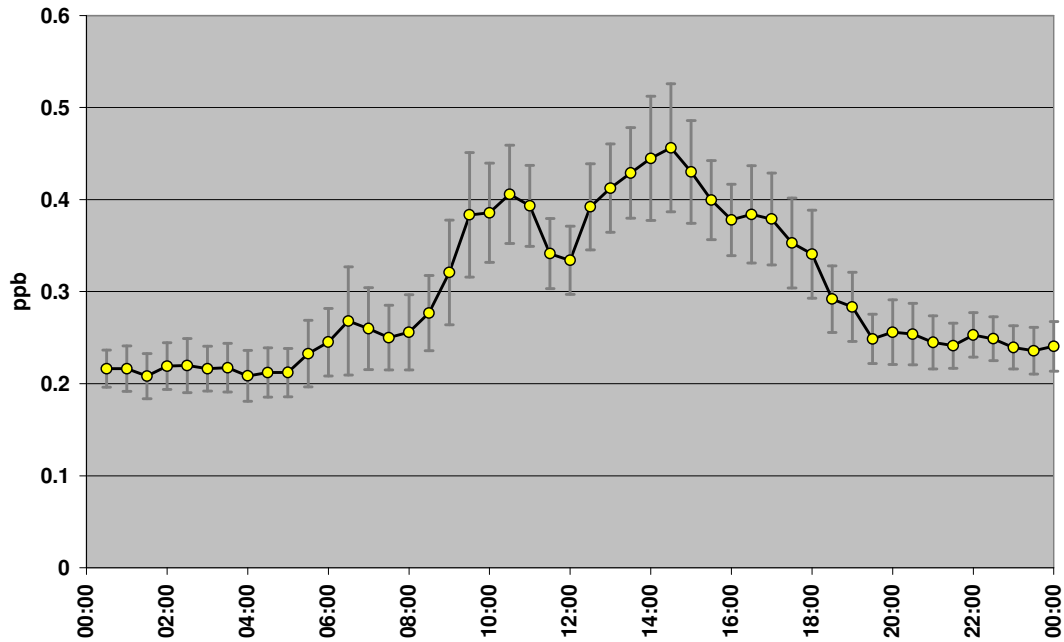
and an additional peak in the mean value just to the south of east, which may reflect local sources from the hamlet of Leadburn, 2 km away. The whole SW sector has very low concentrations, with no major conurbations or industry upwind. Unlike  $\text{SO}_2$ , however, there is no direction which has concentrations of  $\text{NO}_2$  approaching zero. The increased frequency in winds from the NE compared with 2006 is also reflected in increased  $\text{NO}_2$  concentrations from this direction. Black carbon concentrations, as measured by the aethalometer, show a similar spatial pattern to those for  $\text{NO}_2$ , suggesting a similar (combustion) source (Figure 3e) to the north and east, but no influence from the industrial emissions to the NW. This implies that the sources of black carbon are more likely to be vehicle emissions and low-level sources of combustion, rather than power stations. The distribution of ethane shows no major directional dependence, reflecting its long atmospheric lifetime, however there is a sharp peak in propane concentrations to the north, possibly reflecting emissions from the liquid petroleum gas handling facility at Dalmeny or the gas processing plant at Mossmoran in Fife (Figure 3f). Concentrations of elemental mercury show no strong directional dependence, but particulate and reactive gaseous mercury show a very strong directional dependence (Figure 3g, below), with the peak towards Edinburgh – possibly from local domestic coal burning in Midlothian, the coal-fired power station at Cockenzie, or the crematoria in Edinburgh, which are all to the NE. The influence of relatively local sources may also be enhanced by the much lower average wind speed from the NE, approximately half of that from the SW (Figure 3h, below).



**Figure 3 (contd.): Directional dependence of air concentrations of particulate and reactive gaseous mercury (g, to left), and of mean wind speed (h, to right) in 2007**

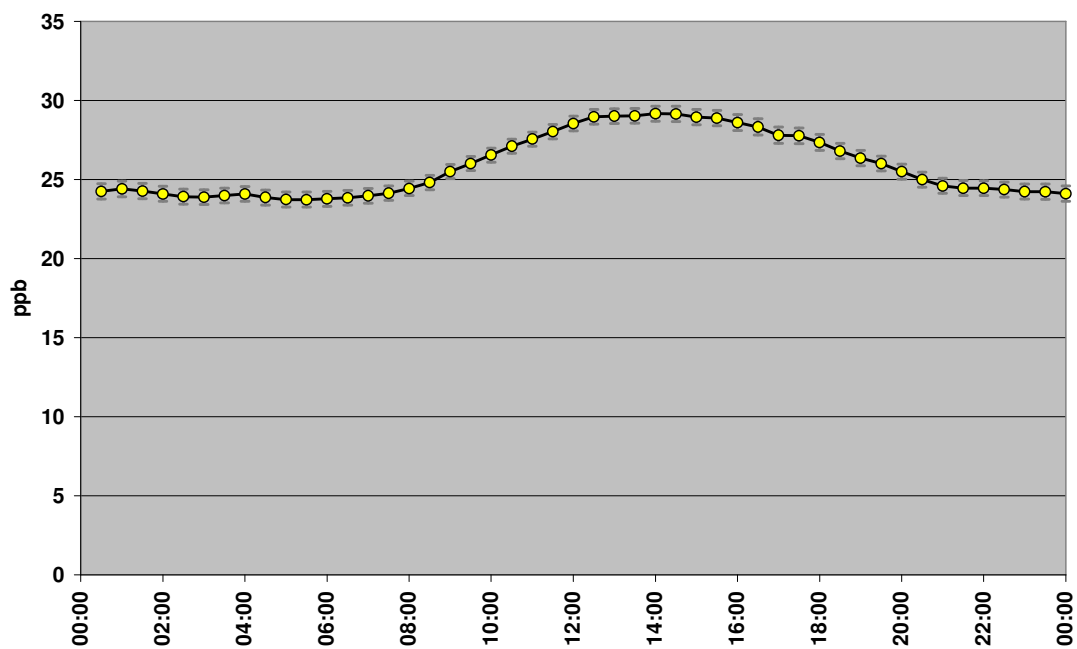
## 7.2 Diurnal cycles

Throughout the day, gas and particle concentrations vary systematically, as shown in Figure 4a-e, where averages for each 30-minute period during the day are presented over the whole year. The diurnal variations in concentration are very similar to those for 2006 (June-December).

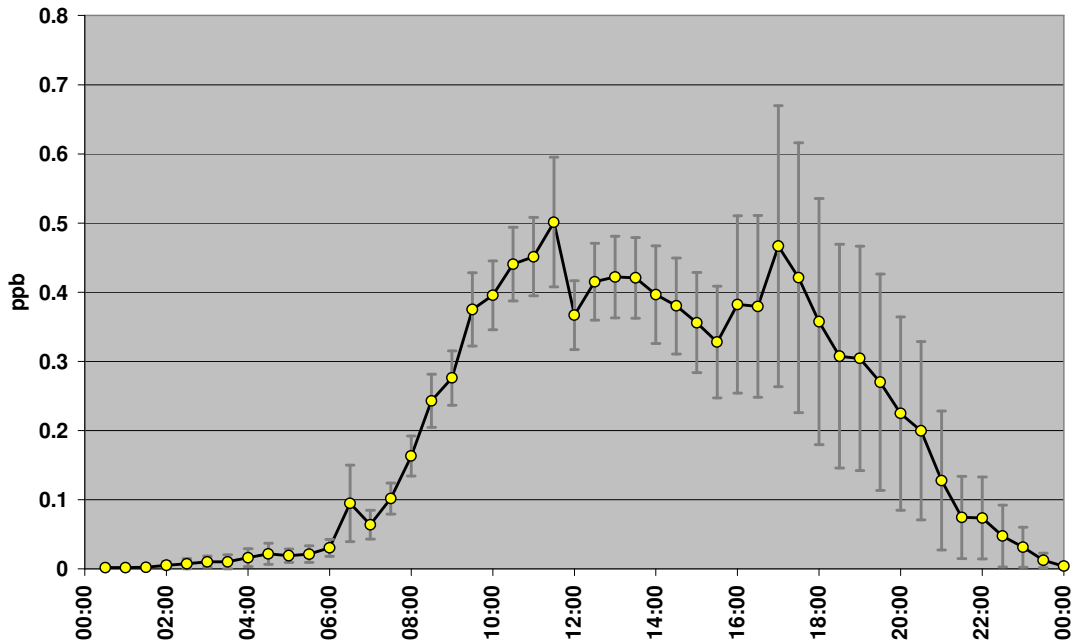


**Figure 4a: Average diurnal variation of sulphur dioxide concentrations at Auchencorth in 2007.**

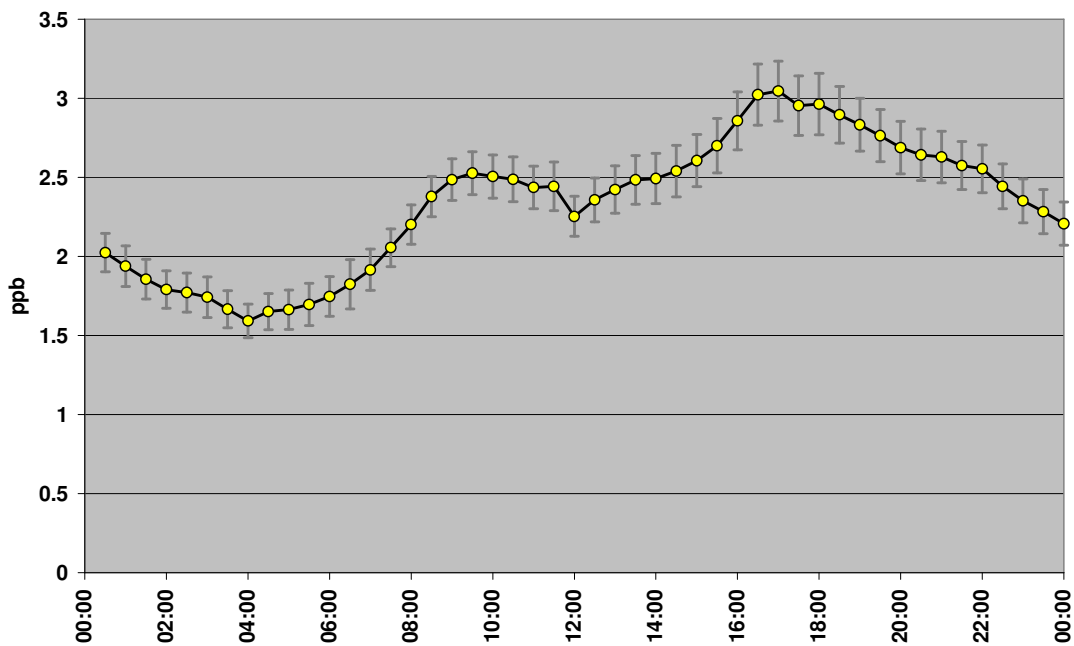
Sulphur dioxide concentrations (Figure 4a) were very low overnight, with a slow rise from around 07:00 GMT, and a broad peak in the middle of the day, then decreasing slowly after 19:00. By contrast, ozone concentrations (Figure 4b) show a typical diurnal trend for rural air, with a clear diurnal cycle peaking in mid afternoon, and a minimum in the early morning. The small diurnal amplitude is consistent with a windy site, with a well-mixed boundary layer and little night-time depletion through dry deposition or reaction with nitric oxide. Nitric oxide concentrations fall to zero at night (Figure 4c) because of reaction with ozone. During the daytime, this reaction is reversed by the photolysis of NO<sub>2</sub> to give a small but consistent daytime peak in nitric oxide concentrations. The late evening data are very variable.



**Figure 4b: Average diurnal variation of ozone concentrations at Auchencorth in 2007.**



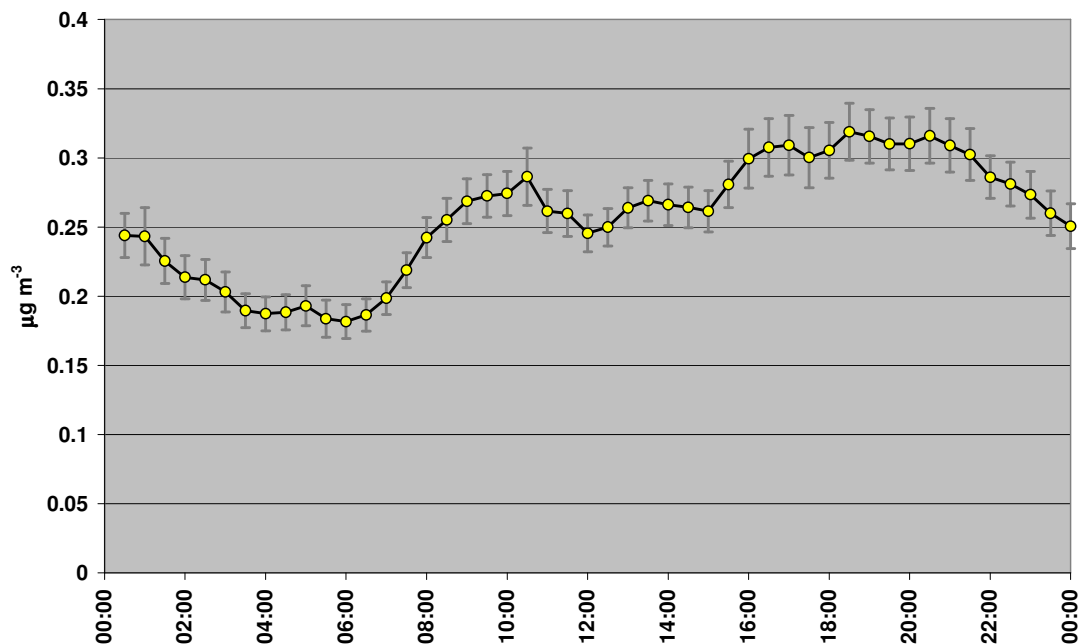
**Figure 4c: Average diurnal variation of nitric oxide concentrations at Auchencorth in 2007.**



**Figure 4d: Average diurnal variation of nitrogen dioxide concentrations at Auchencorth in 2007.**

The diurnal variation of nitrogen dioxide (Figure 4d) is much smaller than for nitric oxide and shows an evening peak and little diurnal change. This pattern may simply reflect changes in boundary layer depth throughout the day, with the largest concentrations developing as the nocturnal boundary layer forms, with subsequent

slow depletion before a steeper rise in the morning, caused by a combination of morning traffic emissions and the breakdown of the nocturnal boundary layer.

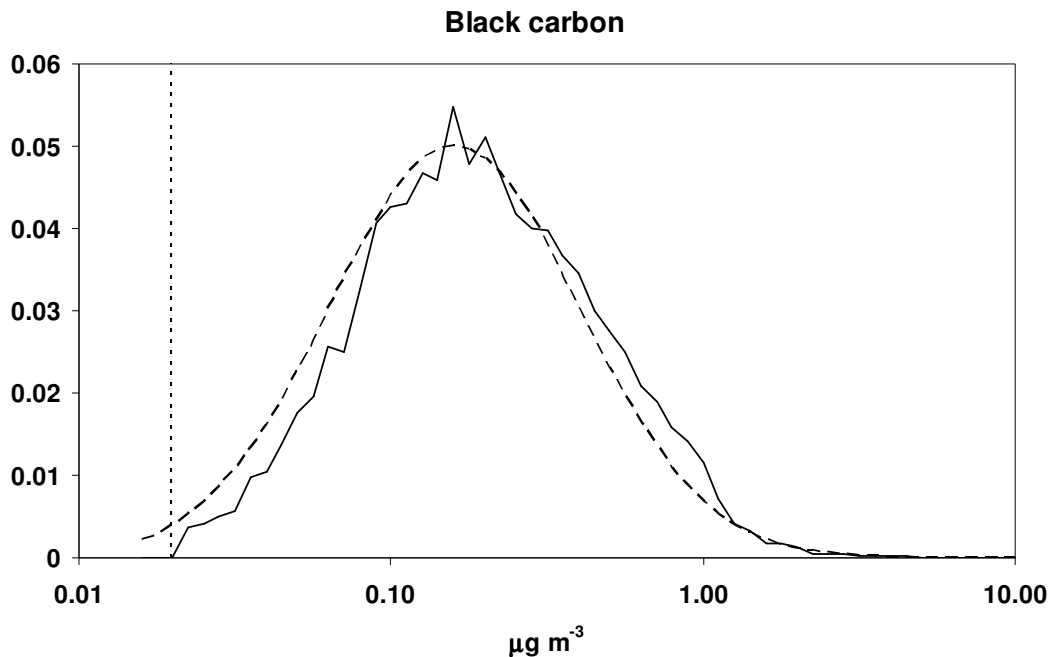


**Figure 4e: Average diurnal variation of black carbon concentrations at Auchencorth in 2007.**

An almost identical pattern is observed for black carbon (Figure 4e), again suggesting very similar sources for nitrogen oxides and black carbon.

### 7.3 Frequency distributions

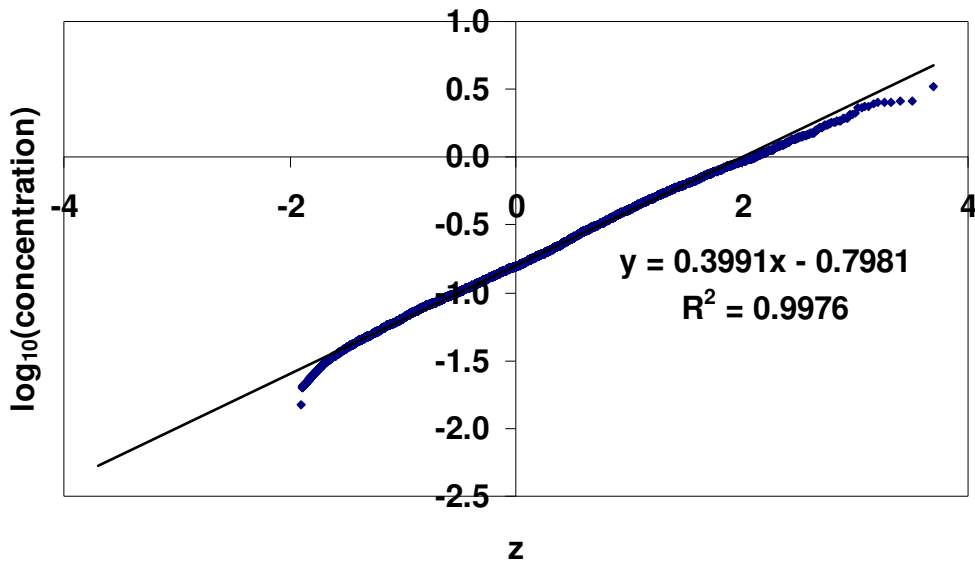
As discussed above, the air concentrations of gases and particles measured in 2007 at Auchencorth show rather different frequency distributions. Many gases and particles show a 'classical' log-normal distribution (Figure 5a), which can be used to predict the probability of particular concentrations being observed.



**Figure 5a: Frequency distribution of 30-minute black carbon concentrations during 2007. Note the log scale on the x-axis. The dotted line shows the lower limit of detection, and the dashed line shows the best-fit to a log-normal distribution (see Figure 5b).**

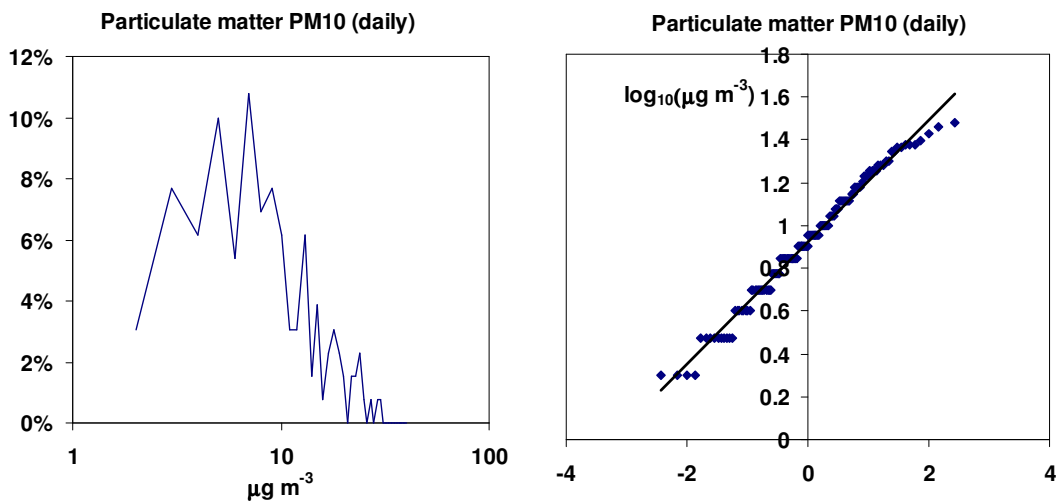
In order to investigate the form of the distribution in more detail it can be helpful to plot the data as a (log)-normal probability plot, where the x-axis is the standard normal variate ( $z$ ); the (geometric) mean of the distribution is given when  $z=0$ , and unit differences from zero ( $z = 1$  or  $-1$ ) give the concentrations at 1 standard deviation either side of the mean. The slope of the plot therefore gives an estimate of the standard deviation, and the intercept with the vertical axis gives the mean. For black carbon the normal probability plot for the data above is shown in Figure 5b. A perfect log-normal distribution would give a straight-line plot. For black carbon, the points deviate from a straight line at higher concentrations, implying that high concentrations occur less frequently than would be expected for a perfect log-normal distribution. The effective limit of detection is at or below  $0.02 \mu\text{g m}^{-3}$  ( $\log_{10} = -1.7$ ). The best-fit line from Figure 5b is shown on Figure 5a as the equivalent frequency distribution, as a dashed line. Note that the slope of this plot for 2007 is identical to that for 2006, although the geometric mean ( $0.16 \mu\text{g m}^{-3}$ ) is somewhat smaller than in 2006 ( $0.21 \mu\text{g m}^{-3}$ ).

**Log-normal probability: black carbon 2007**

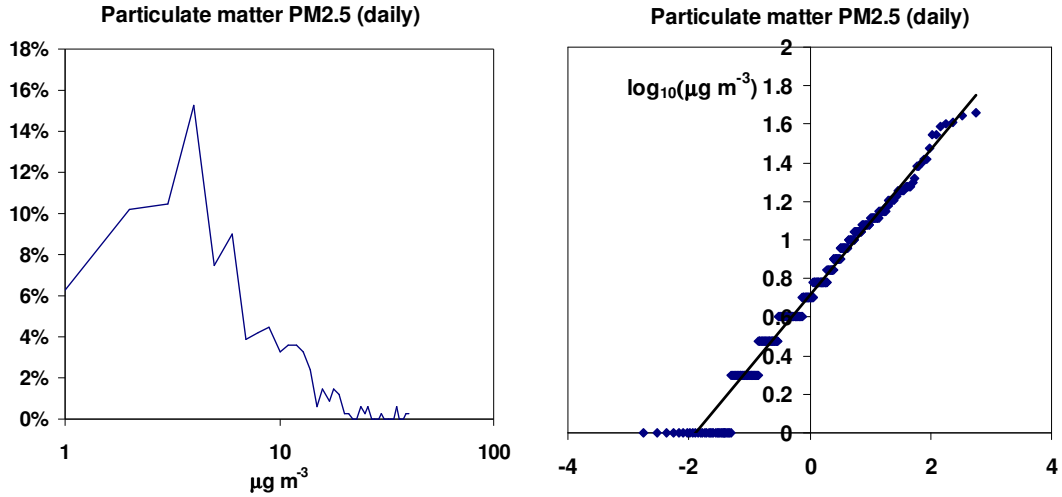


**Figure 5b: Log-normal probability plot of black carbon concentrations during 2007. The horizontal axis shows the standard normal variate ( $z$ ), and the vertical axis the  $\log_{10}$  concentration of black carbon in  $\mu\text{g m}^{-3}$ . The geometric mean is given by the intercept after conversion from logarithms ( $-0.7981 \Rightarrow 0.159 \mu\text{g m}^{-3}$ ), and the geometric standard deviation is given from the slope ( $0.3991 \Rightarrow 2.51 \mu\text{g m}^{-3}$ )**

The frequency distributions and normal probability plots are shown below for some of the other gases and particles measured in 2007. Figure 6 shows the daily data for particulate matter (PM).  $\text{PM}_{10}$  data are only available after mid-August 2007. The smaller number of valid data points than for hourly sampling give a less smooth pattern than for the black carbon data, but the PM data can be seen to follow an approximately log-normal distribution.

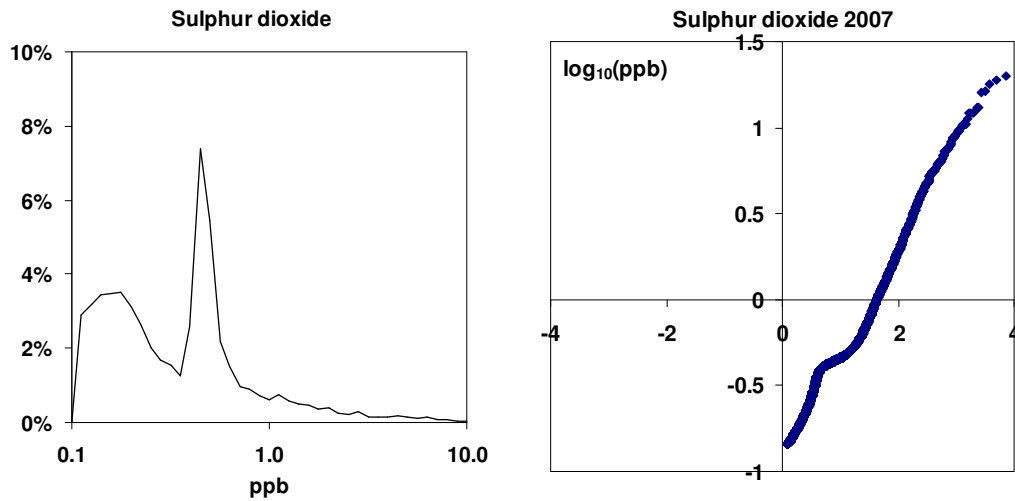






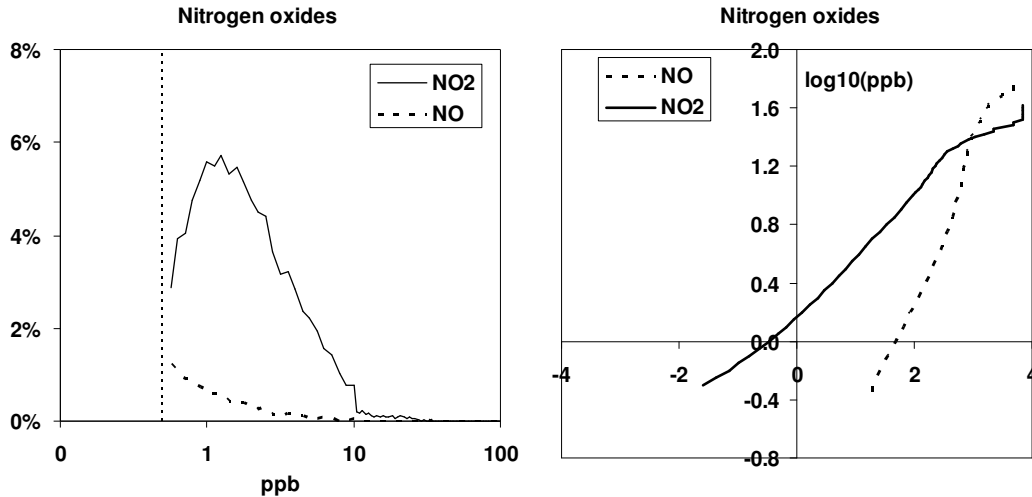
**Figure 6: Frequency distribution and log-normal probability plot for daily PM<sub>10</sub> and PM<sub>2.5</sub> mass concentrations during 2007.**

Figure 7 shows data for sulphur dioxide. The data are fairly well described by a log-normal distribution (RH plot), but almost half the data set occurs below the instrumental detection limit (no data points for  $z < 0$  in RH plot). The peak in the frequency distribution at 0.35 ppb may represent an artefact of making measurements close to the instrumental detection limit.



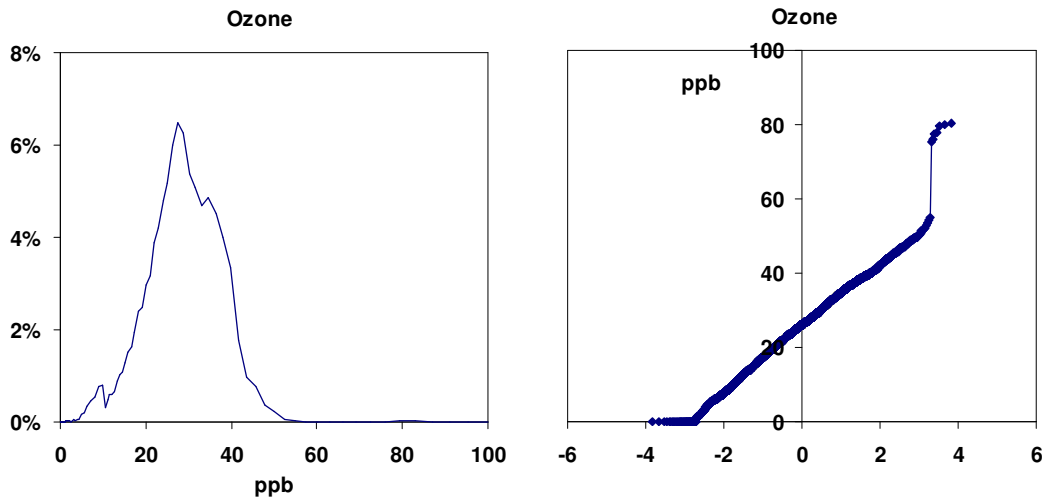
**Figure 7: Frequency distribution and log-normal probability plot for sulphur dioxide during 2007**

The frequency distribution of nitrogen dioxide also follows a log-normal pattern (Figure 8). There are too few data for nitric oxide above the instrumental detection limit (0.5 ppb) to determine the form of the distribution from the frequency plot alone, but the few measurable data suggest a log-normal distribution (dashed line in the normal-probability plot).



**Figure 8: Frequency distribution and log-normal probability plot for nitrogen oxides during 2007**

The frequency distribution for ozone is different from those above, in that most of the time at this site, the ozone frequency distribution is approximately normal (rather than log-normal), with only a small proportion of time when the ozone concentrations were greater than 50 ppb and higher than predicted from the overall distribution – these might be regarded as ozone ‘episodes’ (Figure 9.)



**Figure 9: Frequency distribution and normal probability plot for ozone, 2007**

Similar patterns of behaviour are also seen for elemental mercury ( $Hg^0$ ), where the distribution of concentrations is approximately normal about the mean, and with a small proportion of the time where larger concentrations are observed (Figure 10). However particulate mercury shows a distribution more similar to log-normal, even though only 30% of the data are above the limit of detection (Figure 11). The picture for reactive gaseous mercury is even less clear, with only 10% of data above the limit of detection (Figure 12).

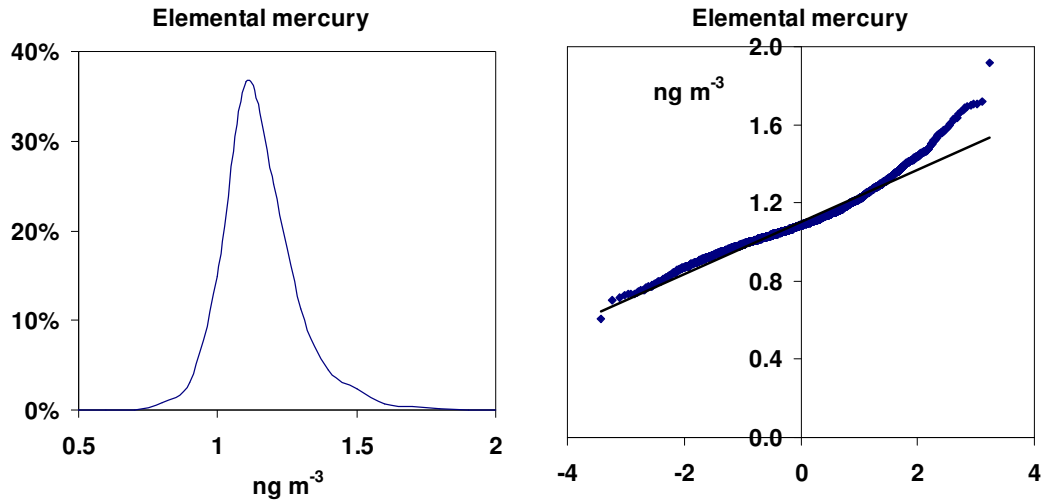


Figure 10: Frequency distribution and normal probability plot for elemental mercury, 2007

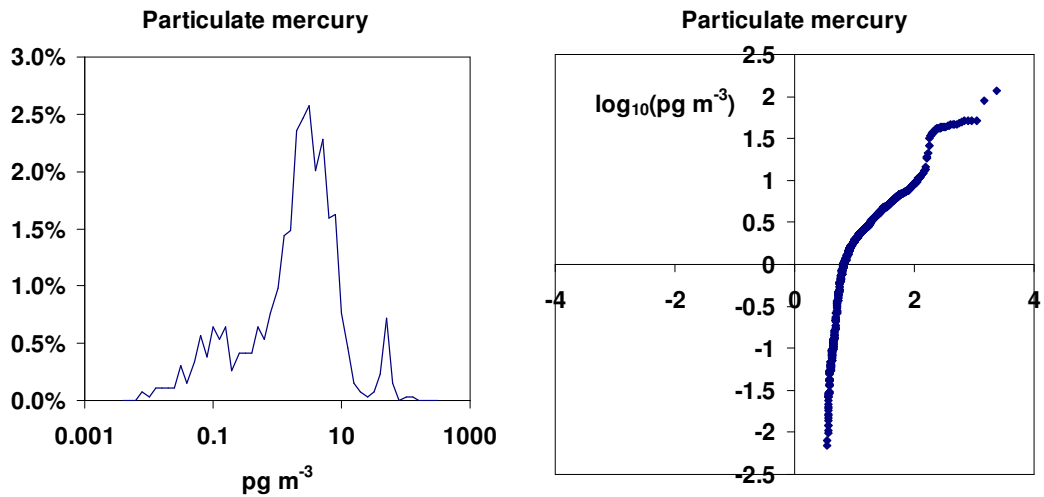


Figure 11: Frequency distribution and log-normal probability plot for particulate mercury, 2007

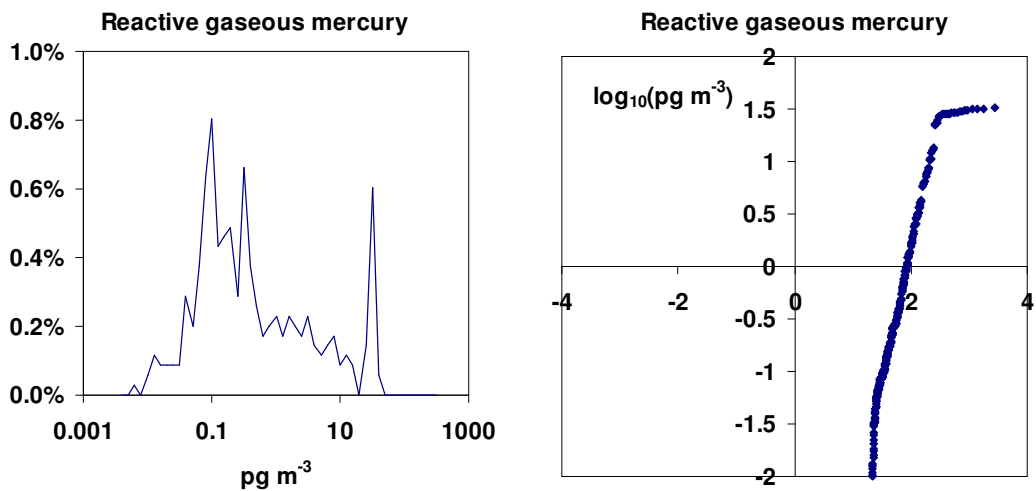
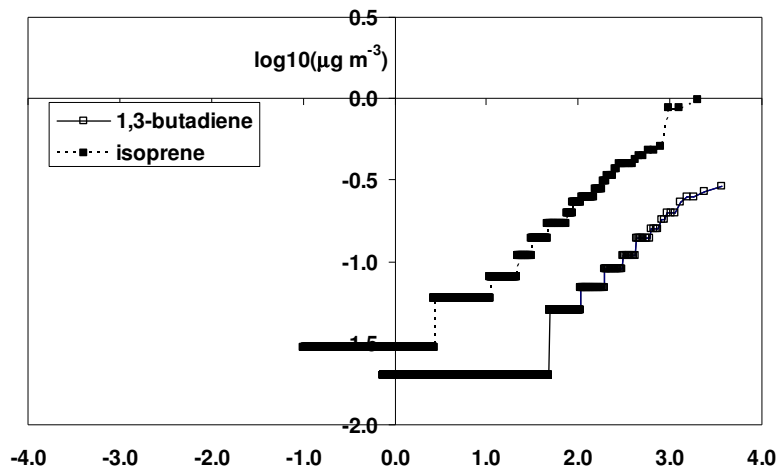


Figure 12: Frequency distribution and log-normal probability plot for reactive gaseous mercury, 2007

In 2007 for the first time there are data for a full year for VOCs. The frequency distributions for these compounds provide an insight into their sources and transport in the atmosphere. For example, the log-normal probability plots for 1,3-butadiene and isoprene show similar slopes (standard deviation), even though the absolute concentrations are very different (Figure 13). Both are compounds that are relatively rapidly oxidised in the atmosphere – typical lifetimes with respect to oxidation by the OH radical (assuming a concentration of  $10^6 \text{ molec cm}^{-3}$ ) are 4.1h and 2.8h respectively. Lifetimes with respect to ozone reaction (at 25 ppb) are much longer, 60h and 47h respectively.

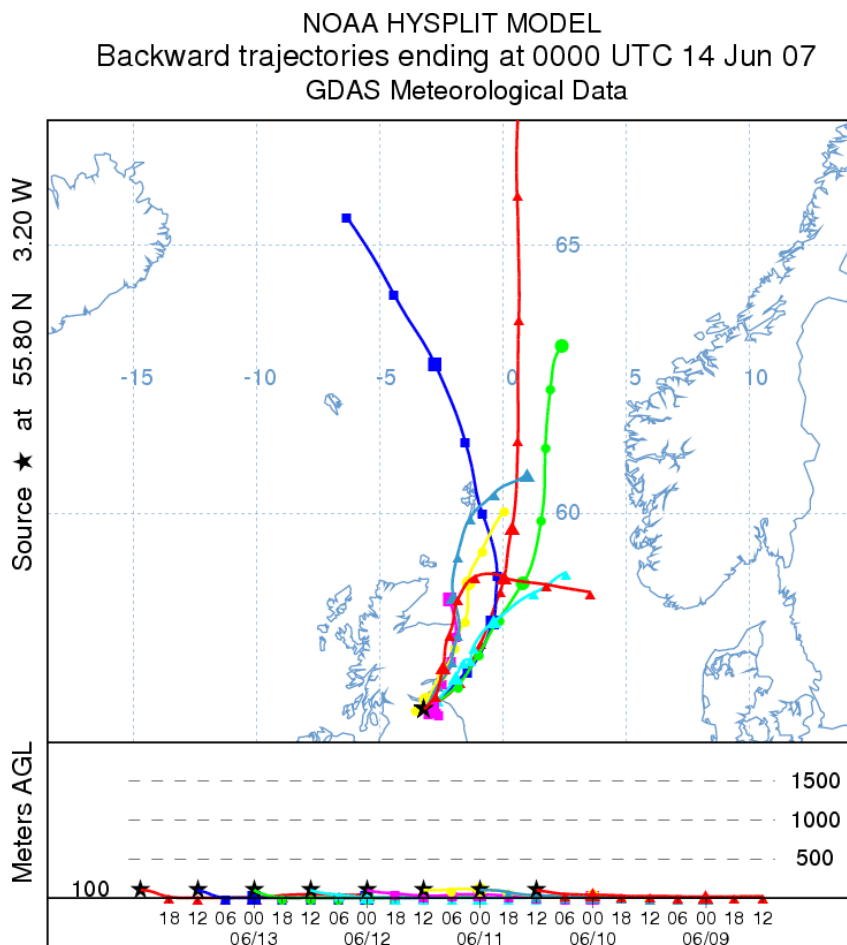


**Figure 13. Log-probability distribution of 1,3-butadiene and isoprene, 2007.**

## 8. Case studies

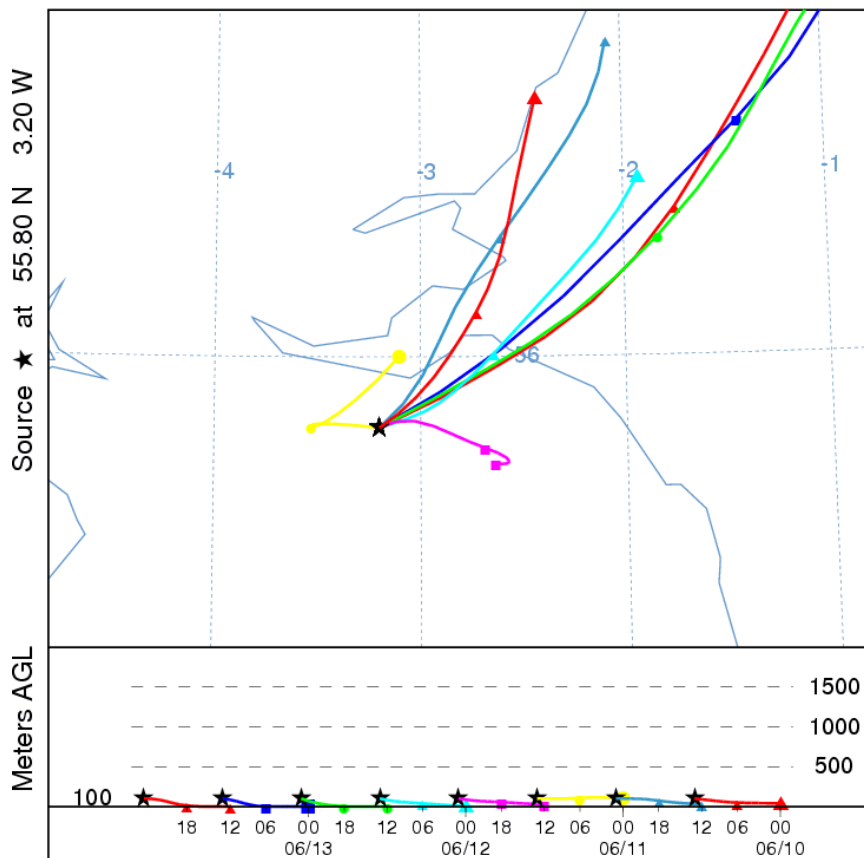
### 10-13 June 2007

During this period there was a consistent northerly air flow bringing surface air across the site. Wind speeds were initially low, increasing through the 12<sup>th</sup> and 13<sup>th</sup> June; local surface winds were north-easterly, with occasional movement to the north. The 48h air mass back-trajectories are shown in Figure 14, showing air flowing from the north-east, with periods of very low wind speed, particularly on 11<sup>th</sup> June (Figure 15) when local wind directions were variable.



**Figure 14a:** HYSPLIT ([www.ready.noaa.gov](http://www.ready.noaa.gov)) trajectory maps for arrival times between 1200 on 10 June 2007 and 0000 on 14 June, showing the paths air parcels took during the 48h before arriving at the site. Symbols are shown every 6h. The lower figure shows the vertical path of the air parcels. Trajectories shown above start (red – origin N.Sea) with those arriving at 1200 on 10 June, and finish (red – origin Arctic) with those arriving at midnight on 13 June, and are shown at 6h intervals. The later air parcels (green, blue, red) are shown as more rapidly moving (longer).

NOAA HYSPLIT MODEL  
 Backward trajectories ending at 0000 UTC 14 Jun 07  
 GDAS Meteorological Data



**Figure 14b:** As Figure 14a but showing only the last 12 h of each trajectory before arriving at the site, showing the air passing over Edinburgh, and the very low wind speeds (stagnation) during 11<sup>th</sup> June (yellow and pink lines).

The transport of slow-moving air over the city and upwind areas of Midlothian is reflected in the locally high SO<sub>2</sub> concentrations (Figure 16), and also HCl, associated with coal combustion. Sulphate particle and nitrate particle concentrations were also high, while sea-salt concentrations were very low, as would be expected in low-wind conditions, despite the trajectories from across the North Sea (Figure 17). Gas concentrations decreased rapidly as wind speed increased on 12<sup>th</sup>, even though the overall wind direction was unchanged, but particle concentrations, particularly for sulphate, remained high throughout 12<sup>th</sup> June, possibly reflecting long-distance transport of continental air (see Figure 14a, turquoise trajectory). Throughout the period, the nitrate and sulphate content of particulate matter was approximately balanced by ammonium ions.

This episode illustrates that even ‘remote rural’ sites occasionally experience the influence of regional air pollution, albeit at air concentrations that are still well below the short-term air quality standards for human exposure (1-hour mean concentration of SO<sub>2</sub> of 350 µg m<sup>-3</sup>). The maximum hourly SO<sub>2</sub> concentration recorded in the city of Edinburgh (St. Leonards) was 67 µg m<sup>-3</sup>, at 10:00 on 11<sup>th</sup> June (AURN data).

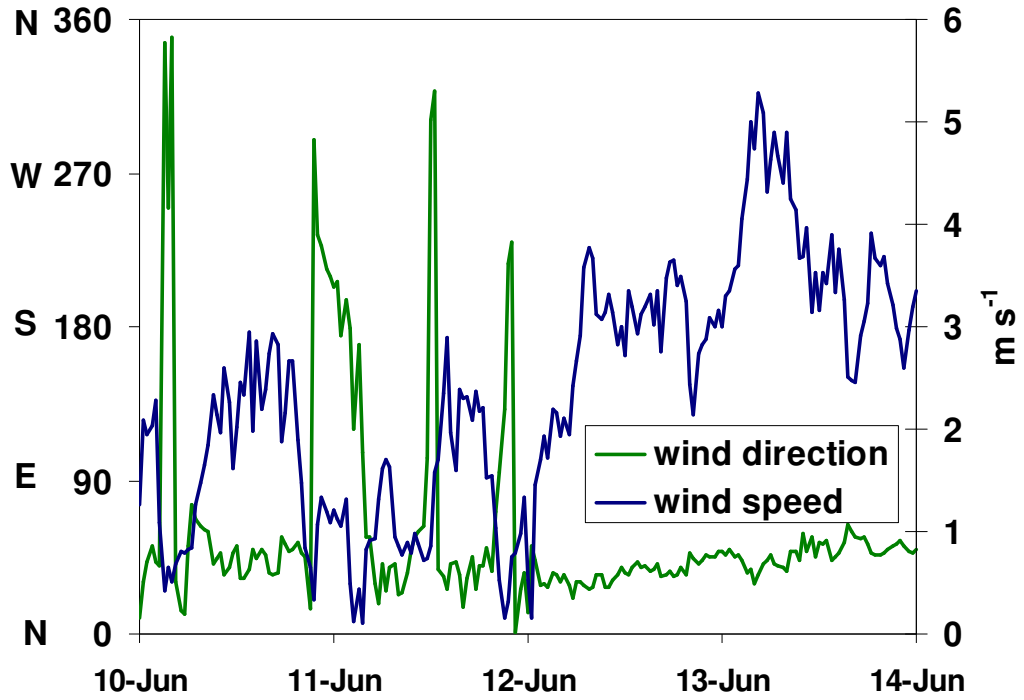


Figure 15: Wind direction and wind speed measured at the site between 10 and 14 June 2007.

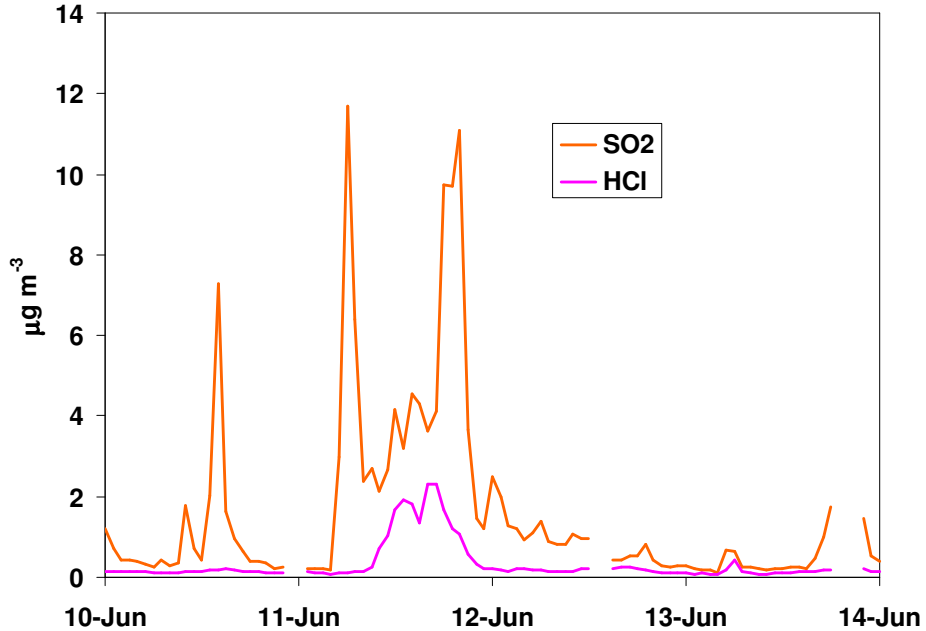
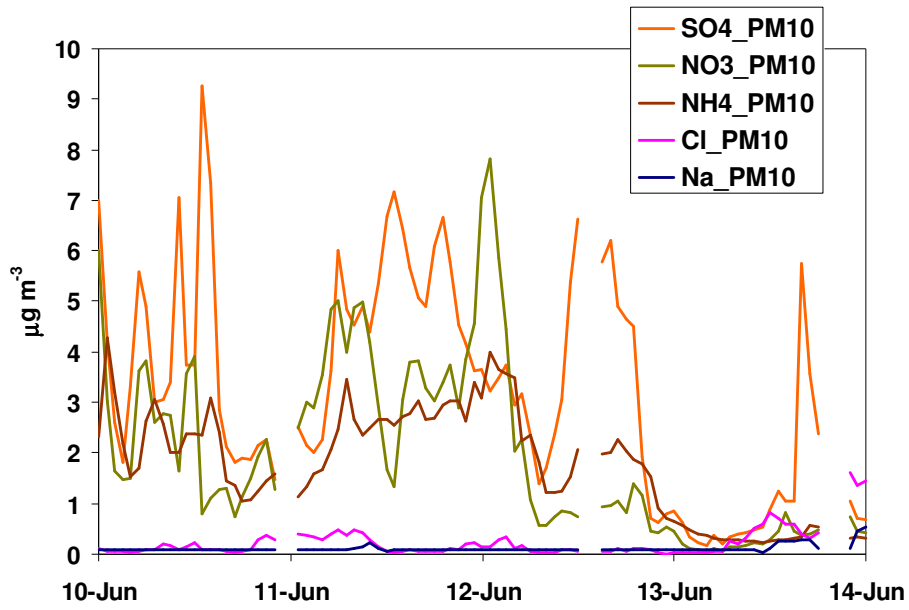


Figure 16: Concentrations of sulphur dioxide and hydrogen chloride sampled by the MARGA between 10 and 14 June 2007.



**Figure 17: Concentrations of particulate matter (PM<sub>10</sub>) sampled by the MARGA between 10 and 14 June 2007**



## **APPENDIX – Data recorded during 2007**

### **Meteorological data**

- Air temperature
- Relative humidity
- Atmospheric pressure
- Surface wetness
- 30 minute rainfall
- Wind speed
- Wind direction

### **MARGA data (PM<sub>10</sub>, PM<sub>2.5</sub> and gases)**

- Ammonium
- Ammonia
- Sodium
- Calcium
- Magnesium
- Chloride
- Sulphur dioxide and Hydrogen chloride
- Nitrate
- Nitric and nitrous acid
- Sulphate

### **Hydrocarbon data**

- 1,3-butadiene and 1-butene
- Ethene and ethyne
- Ethane and propane
- Isoprene and propene
- iso-butane and iso-pentane
- n-butane and n-pentane
- 2-butenes

### **AURN data**

- Ozone
- PM<sub>10</sub> and PM<sub>2.5</sub> (hourly)
- PM<sub>10</sub> (volatile and non-volatile)
- PM<sub>2.5</sub> (volatile and non-volatile)
- PM<sub>10</sub> and PM<sub>2.5</sub> (daily)

### **Mercury data**

- Elemental mercury (Hg<sup>0</sup>)
- Reactive gaseous and particulate mercury

### **CEH flux gases**

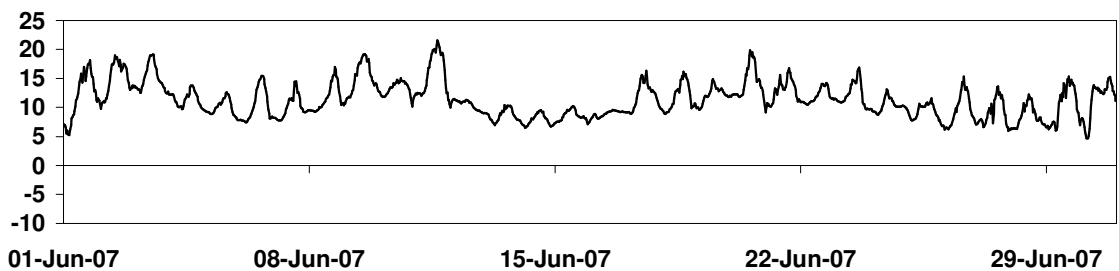
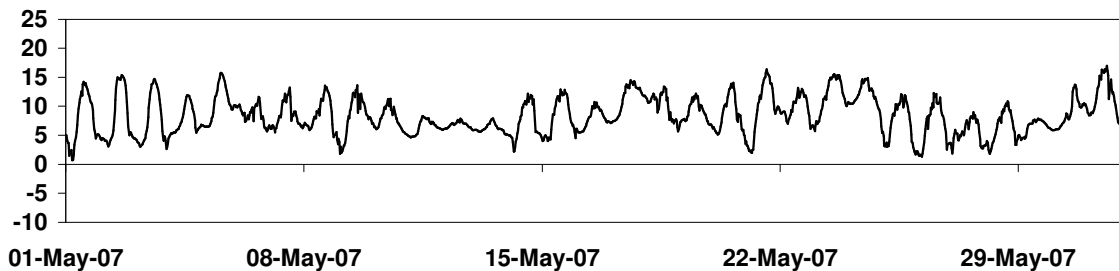
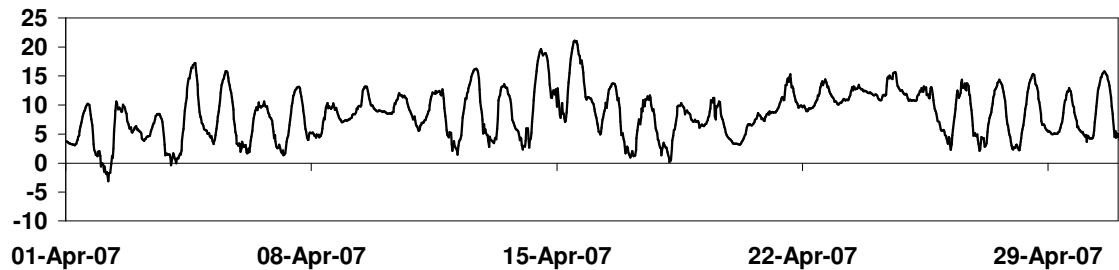
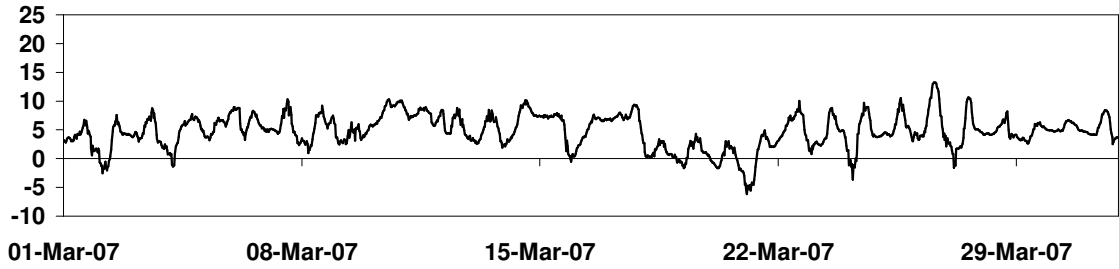
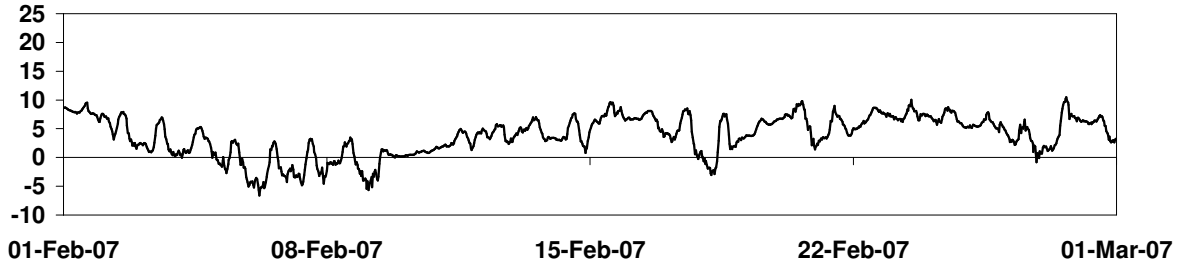
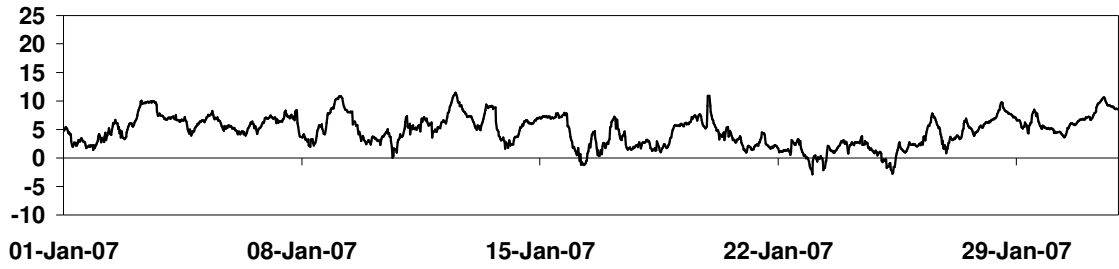
- Nitrogen oxides
- Ozone
- Sulphur dioxide

### **Black carbon**

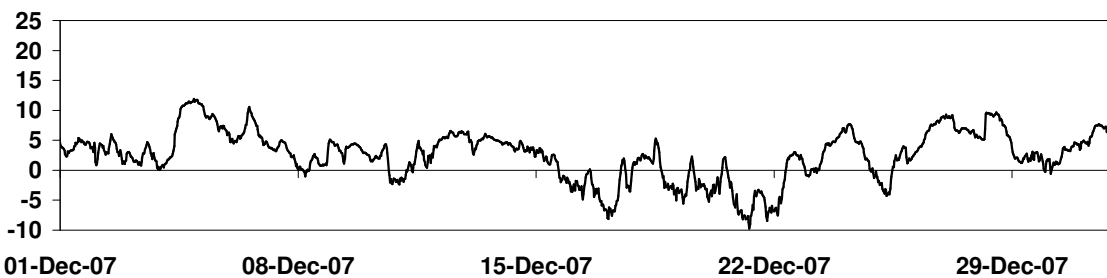
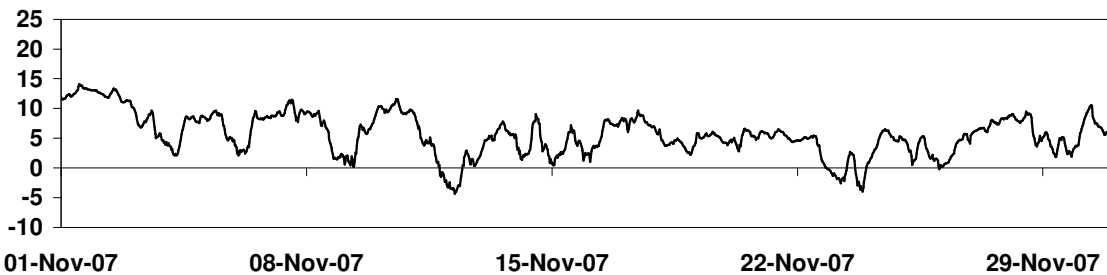
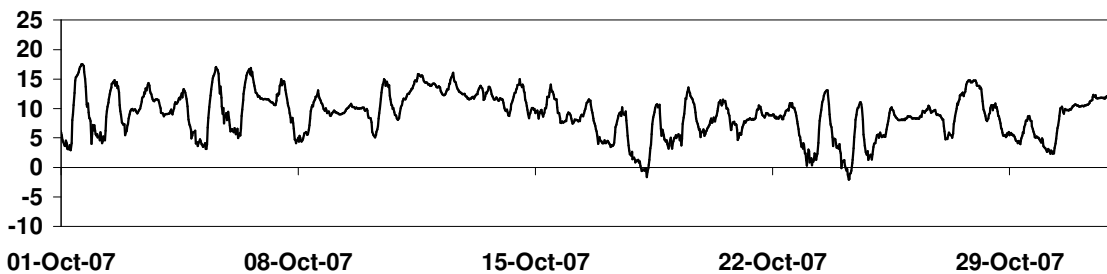
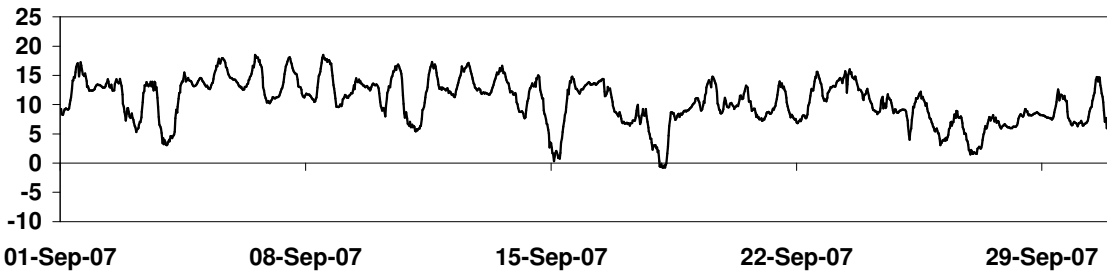
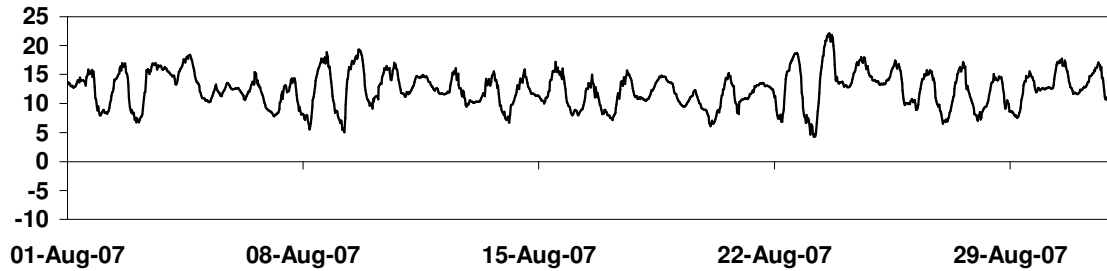
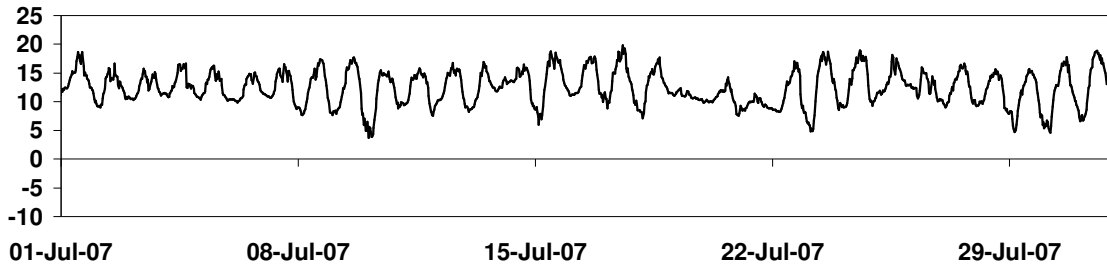
### **Wet-only precipitation**

- Daily rainfall
- Concentrations of NH<sub>4</sub><sup>+</sup>, H<sup>+</sup>; Na<sup>+</sup>, Cl<sup>-</sup>; Mg<sup>2+</sup>, Ca<sup>2+</sup>; SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>

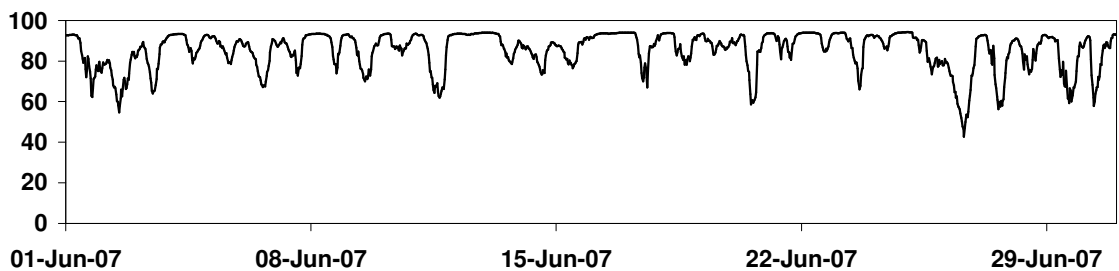
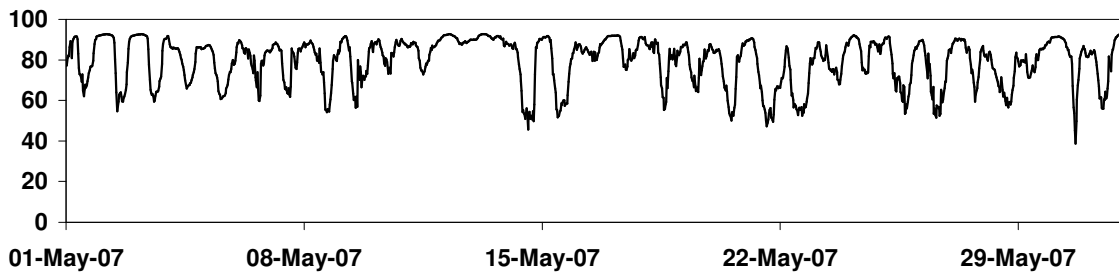
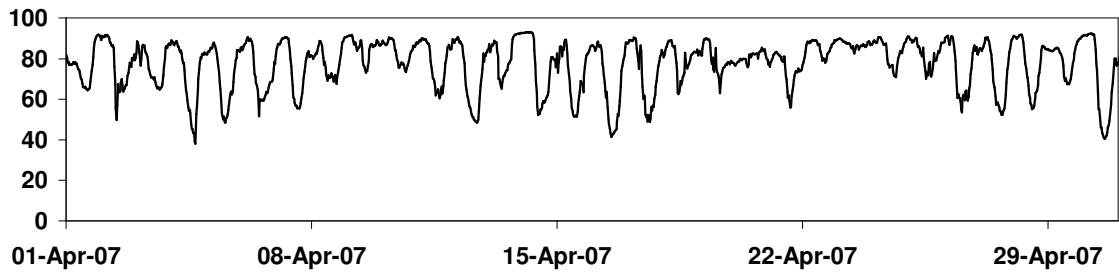
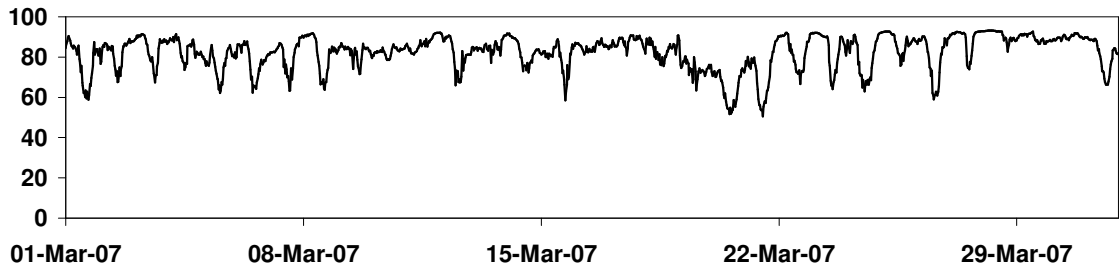
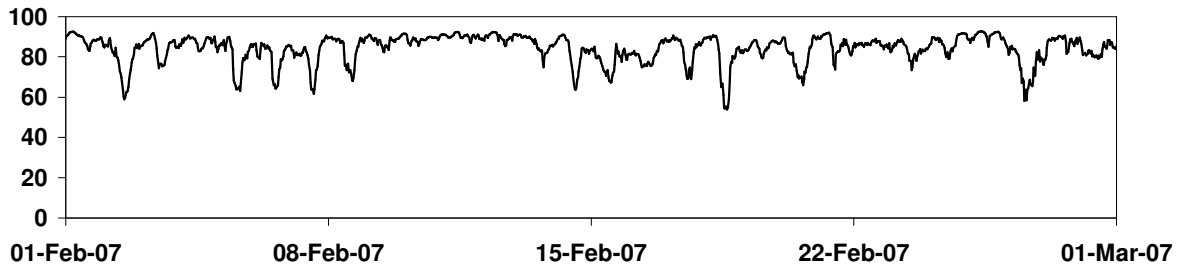
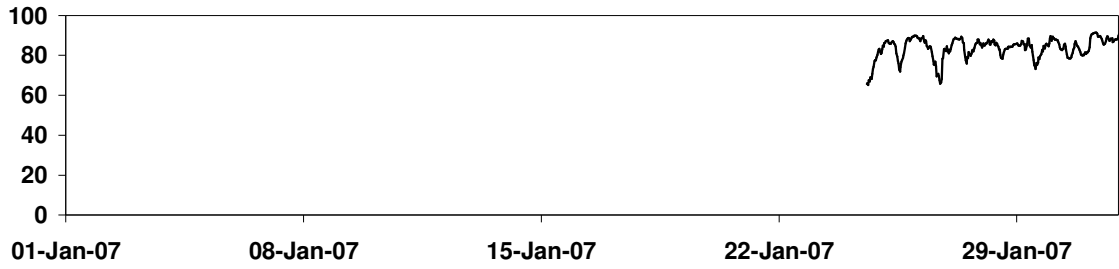
## Air temperature °C



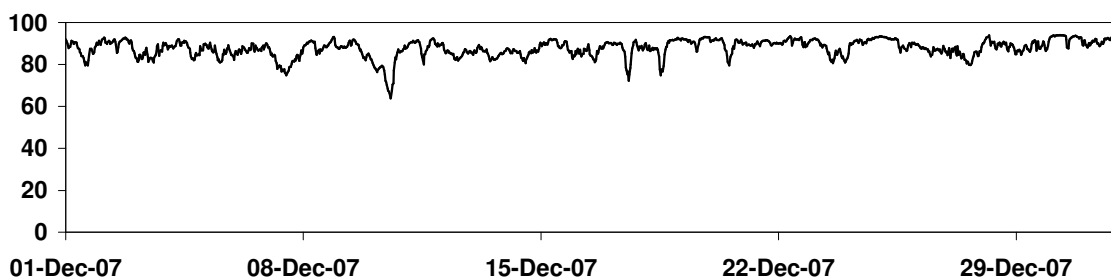
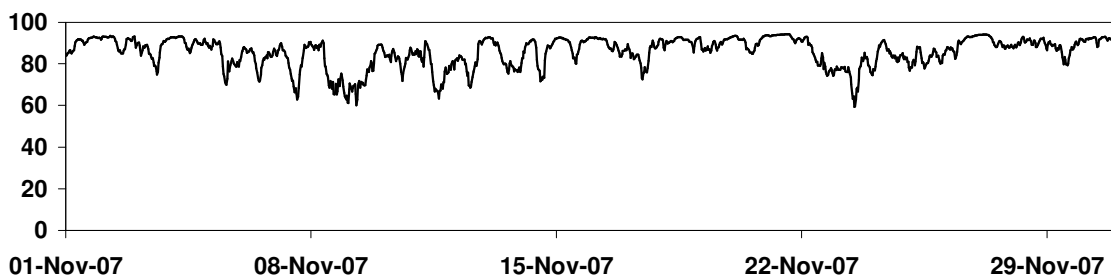
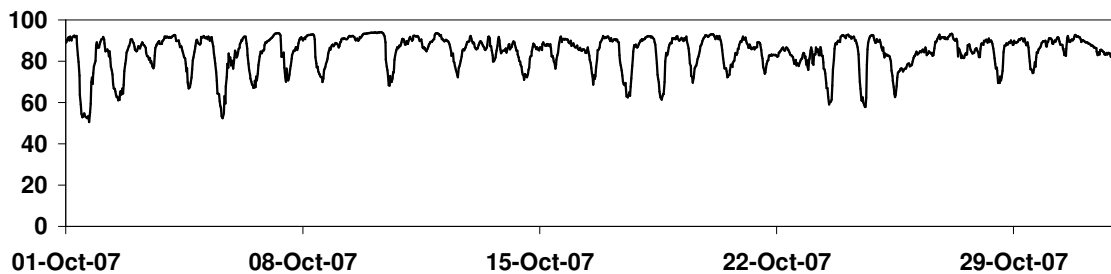
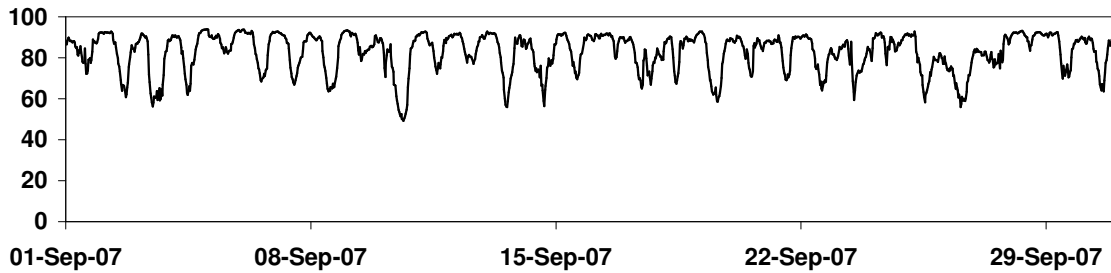
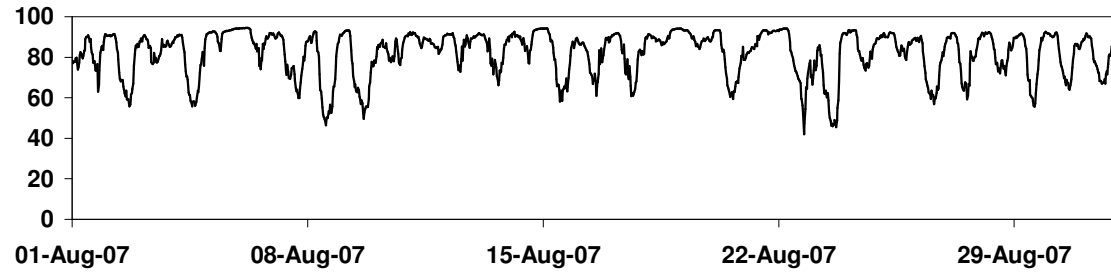
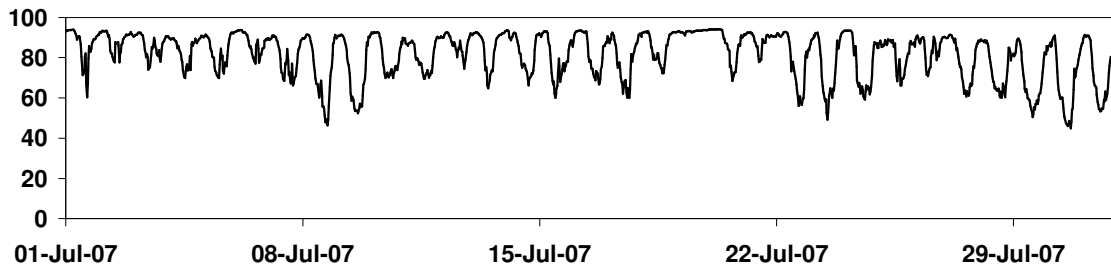
## Air temperature °C



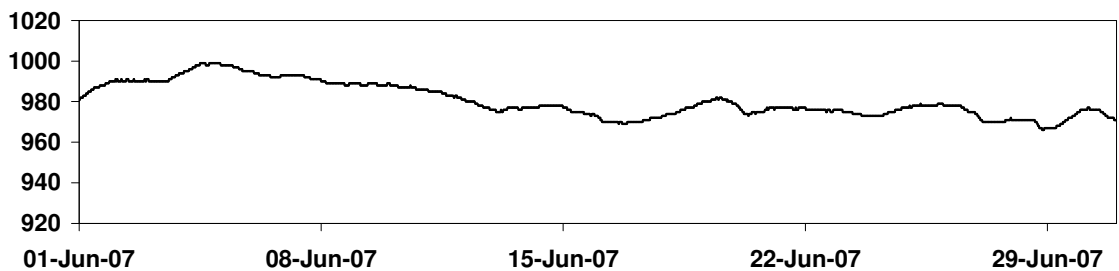
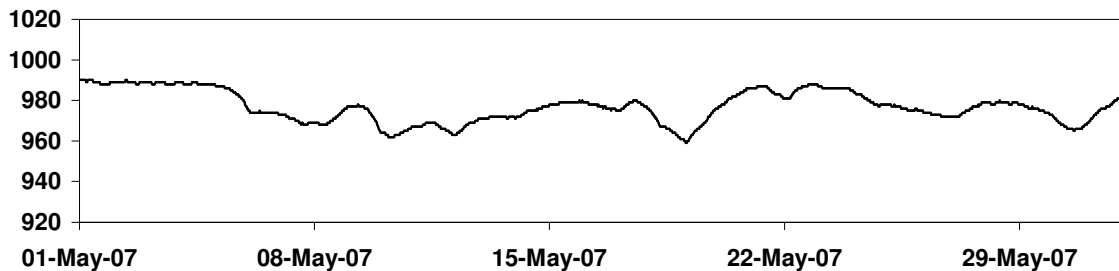
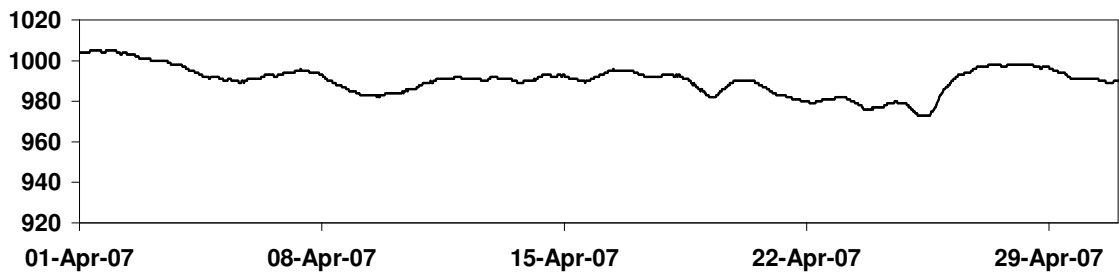
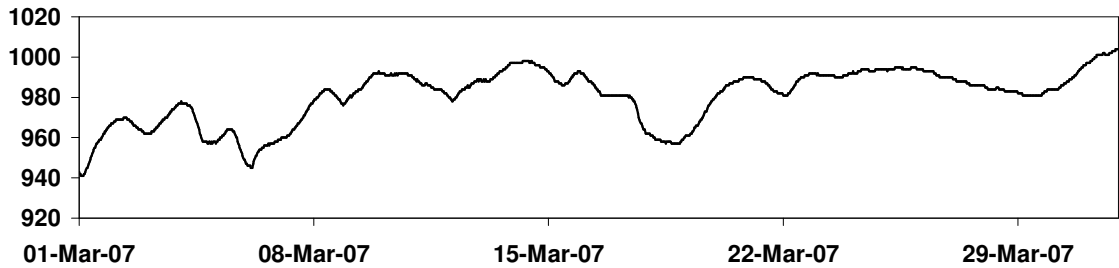
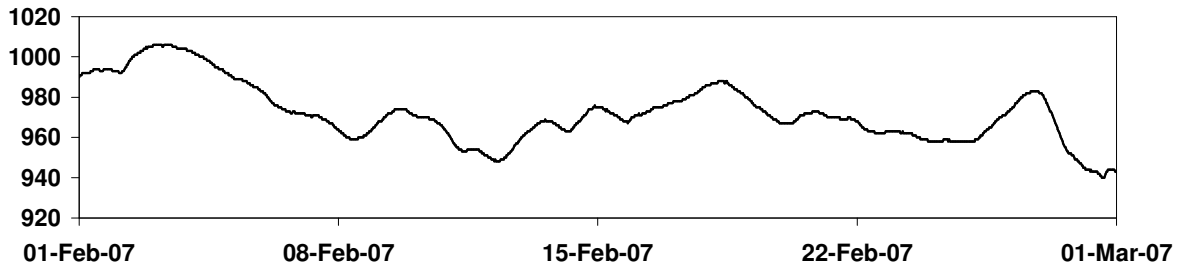
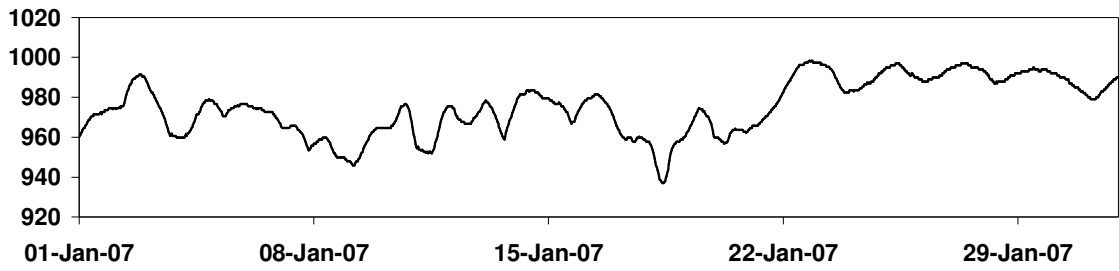
## Relative humidity %



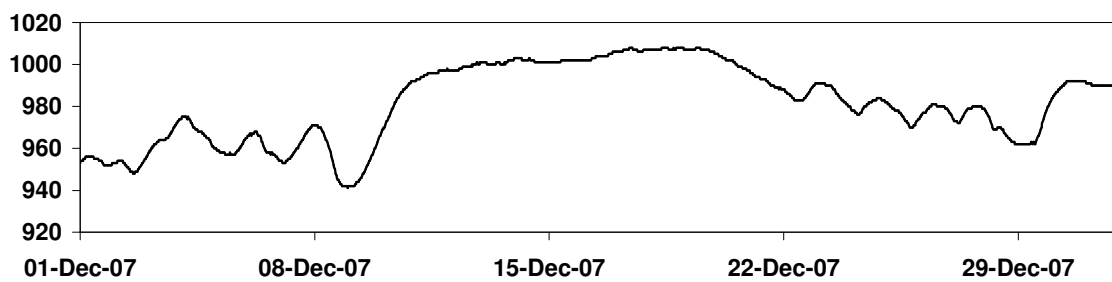
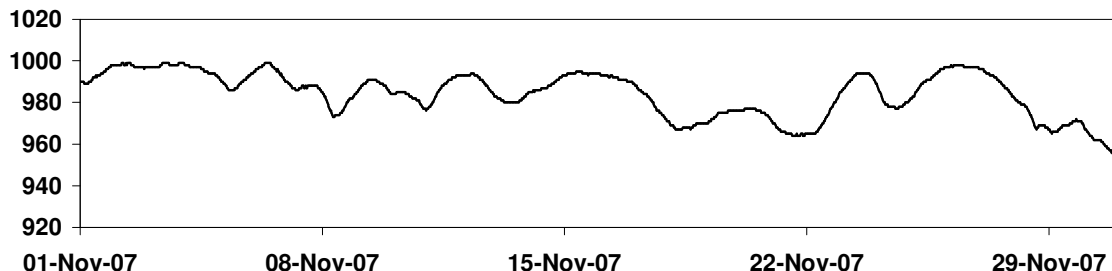
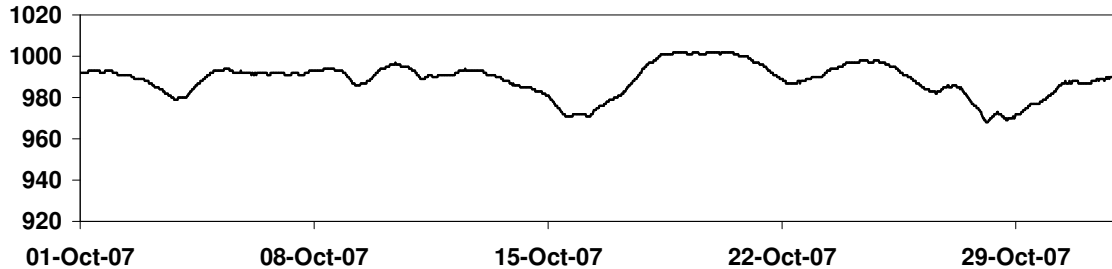
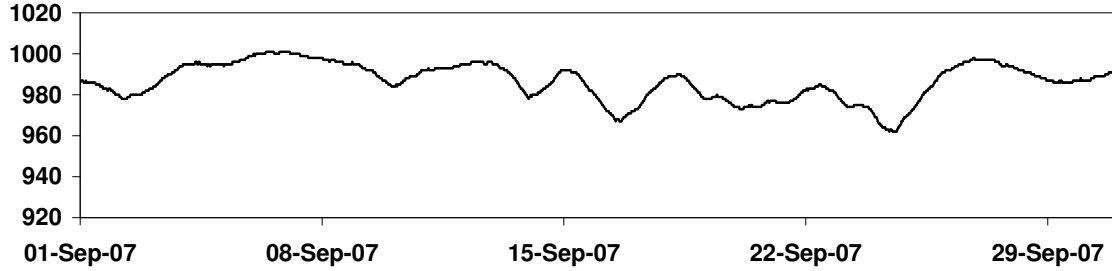
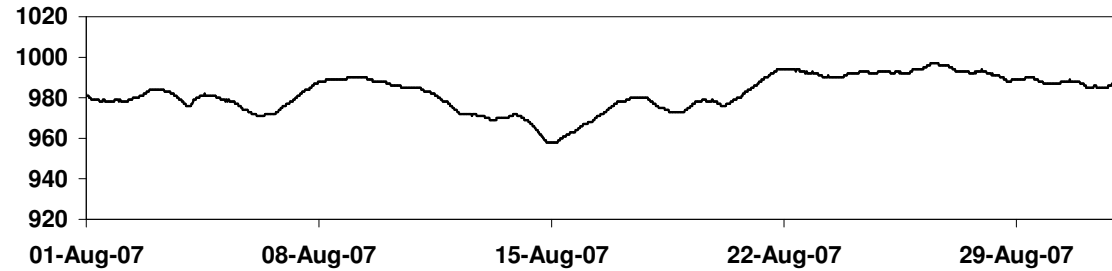
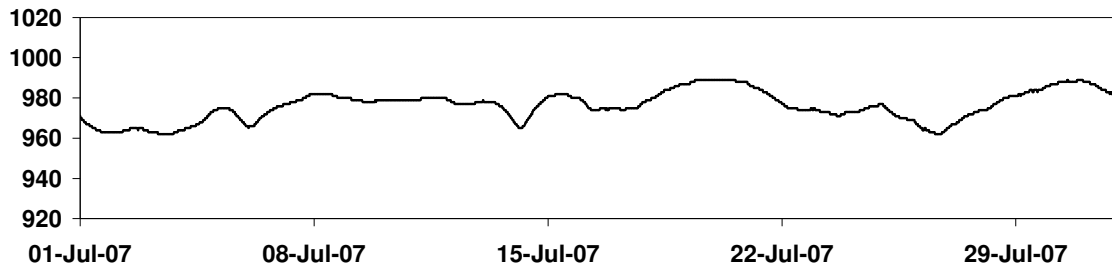
## Relative humidity %



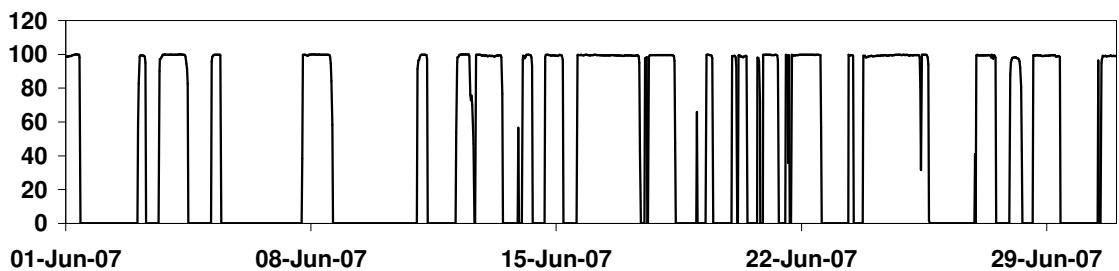
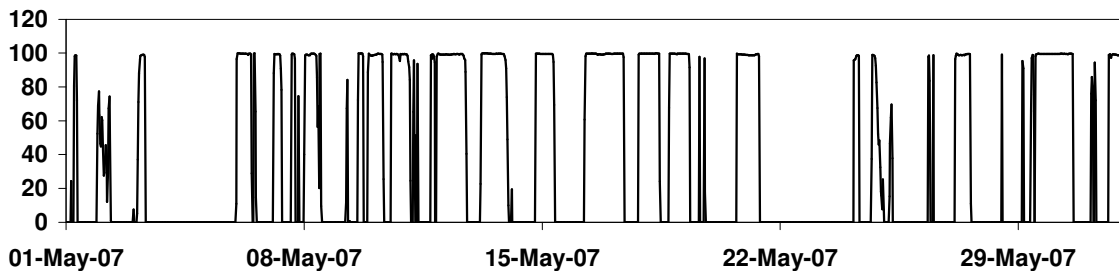
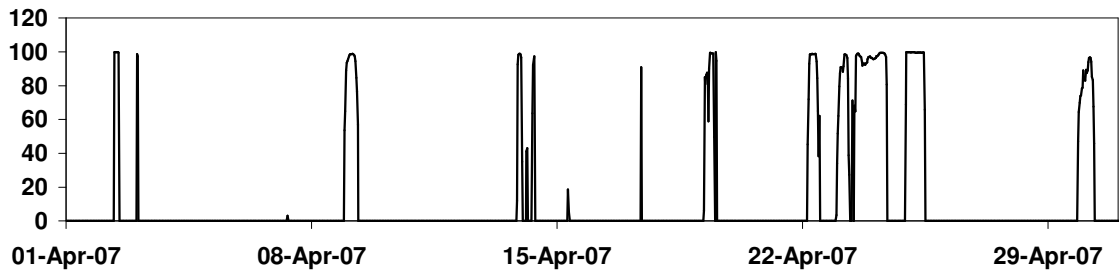
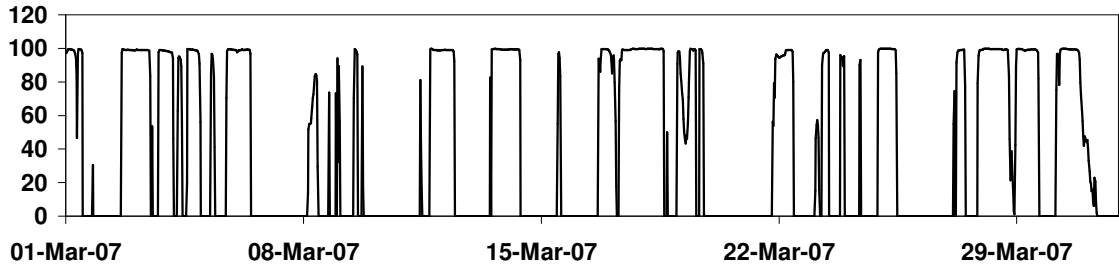
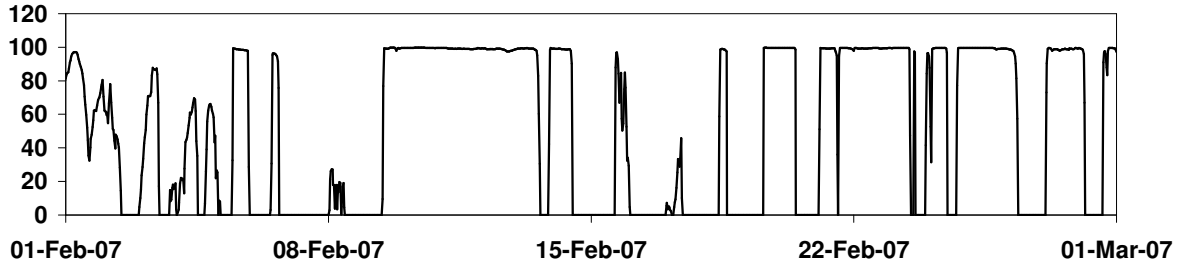
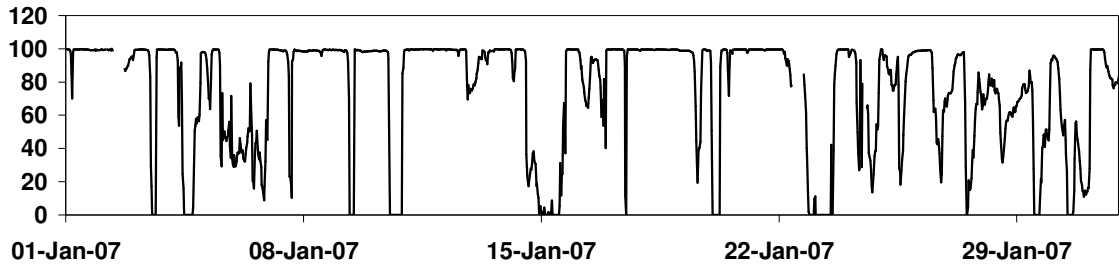
## Atmospheric pressure kPa



## Atmospheric pressure kPa

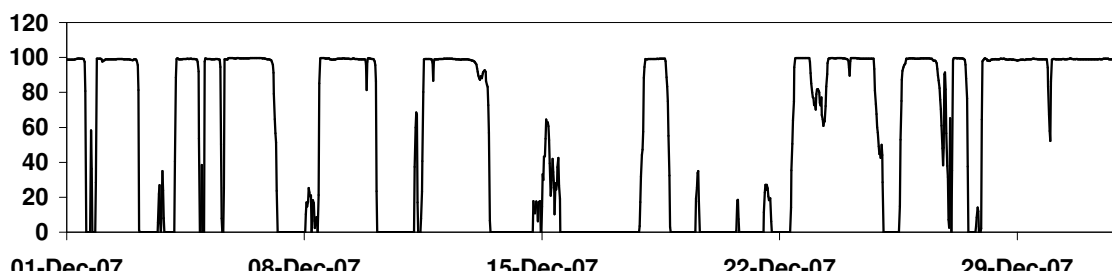
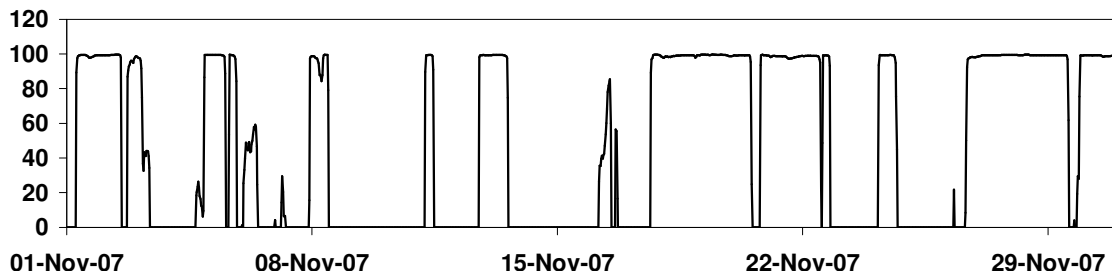
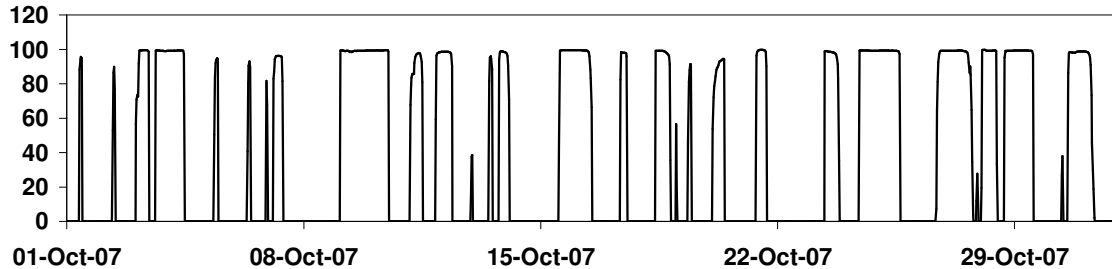
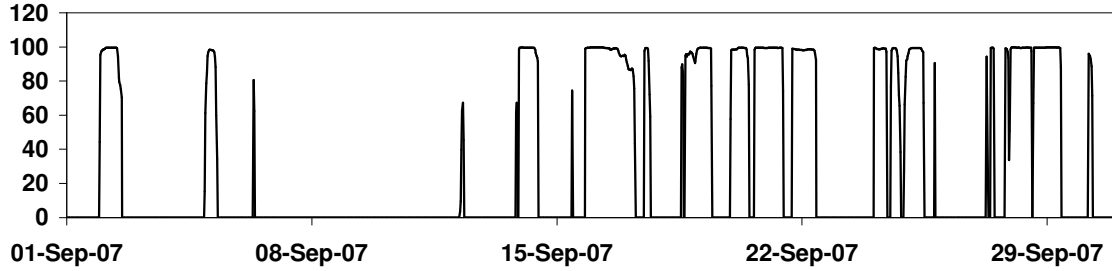
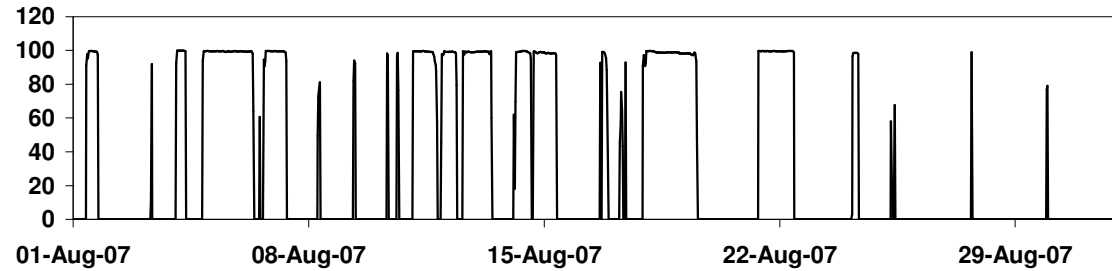
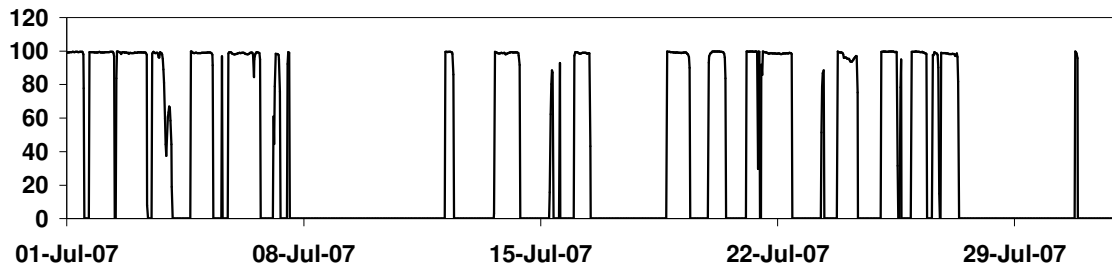


## Wetness %

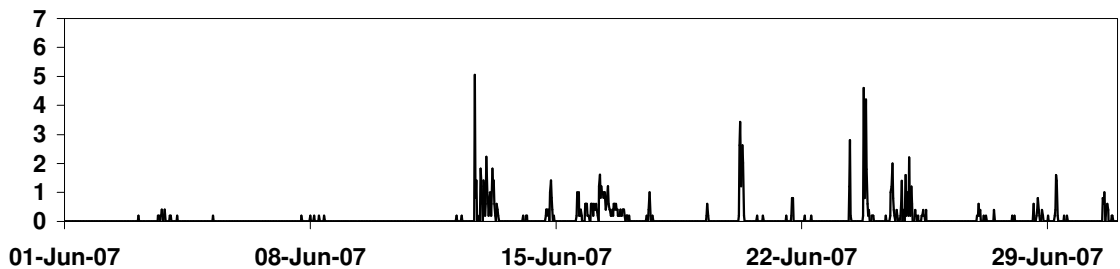
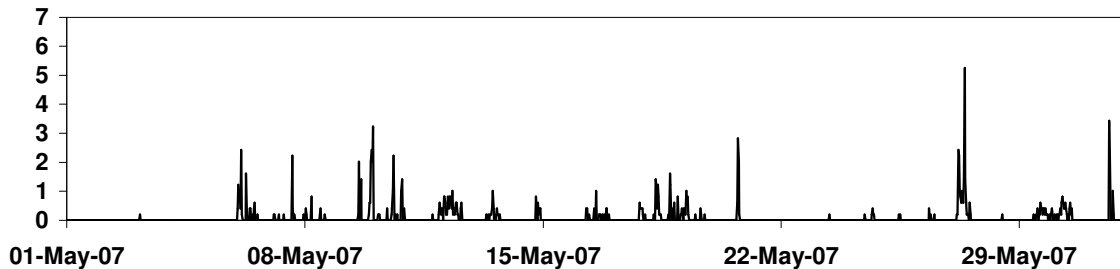
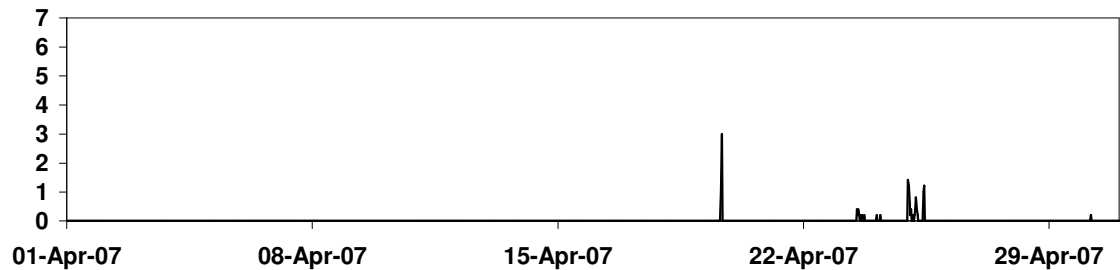
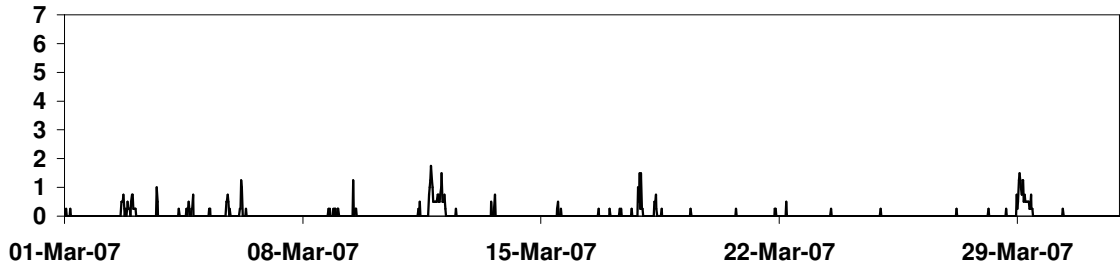
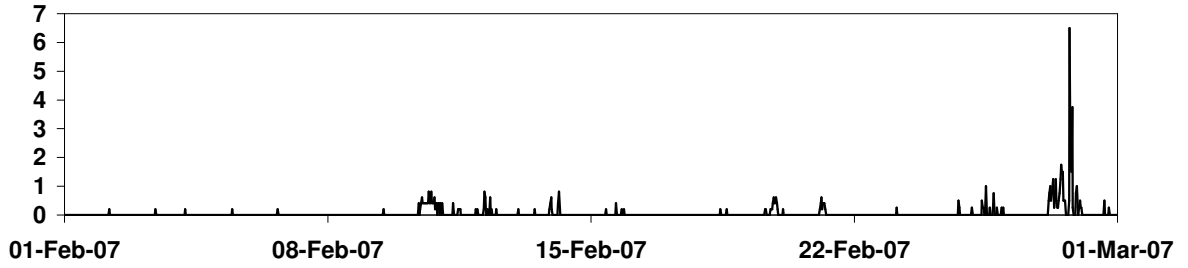
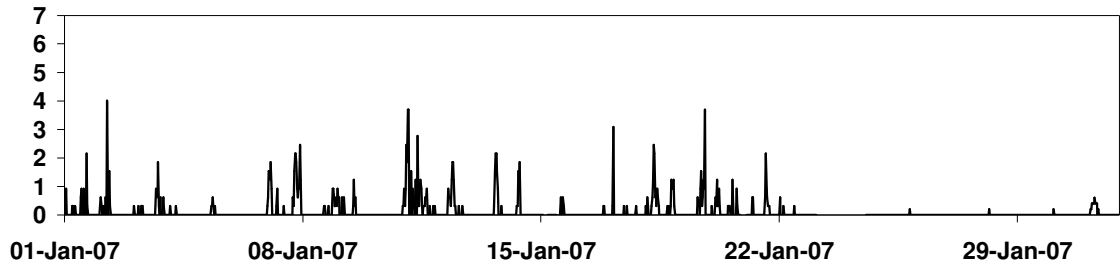




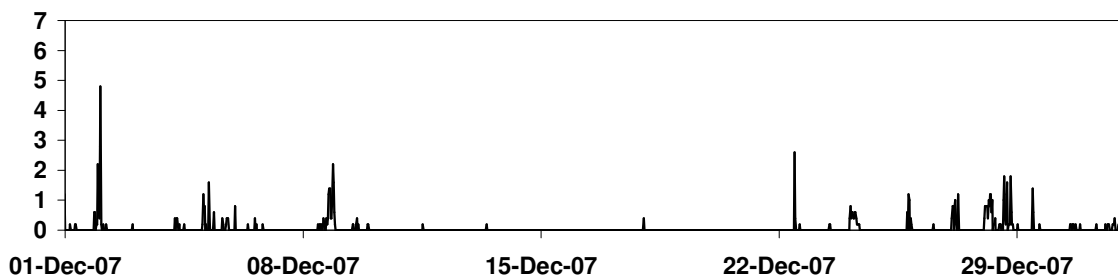
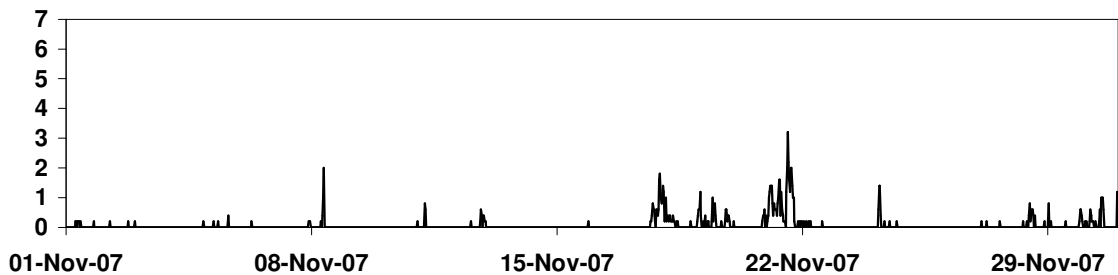
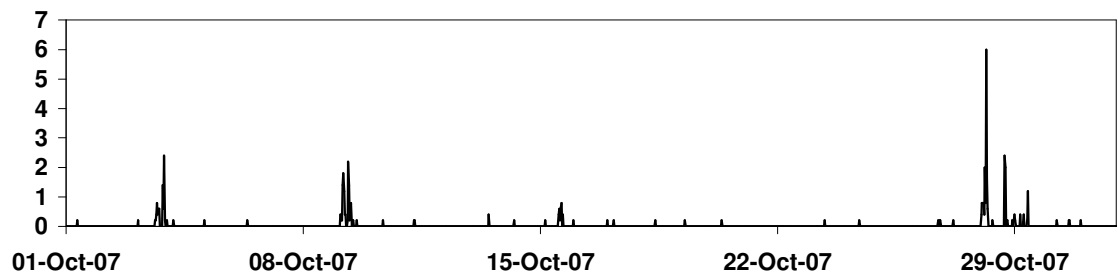
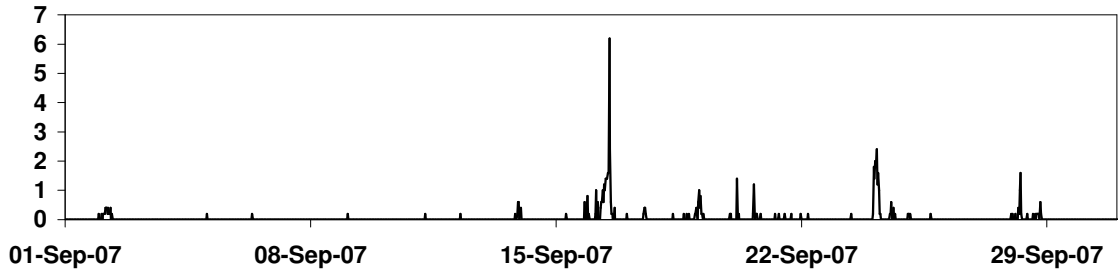
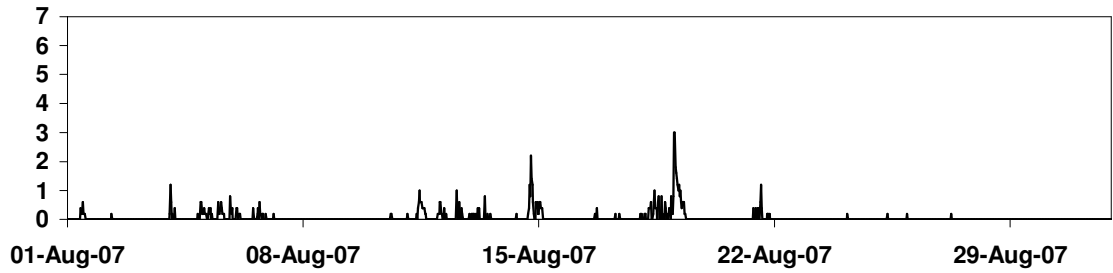
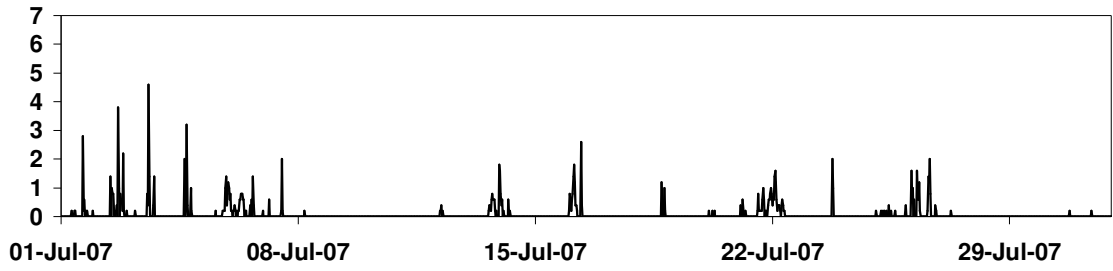
## Wetness %



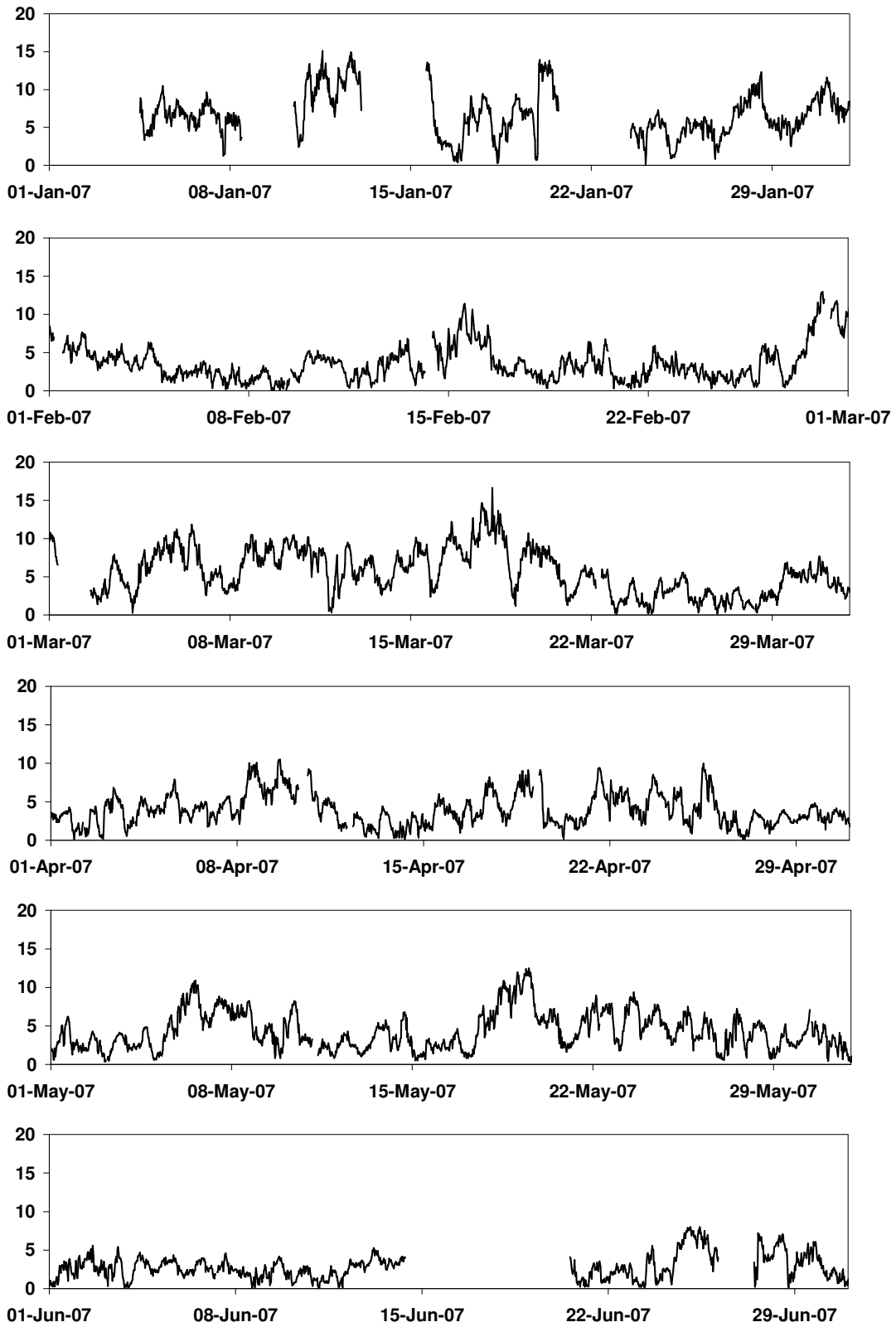
### 30-minute rainfall mm



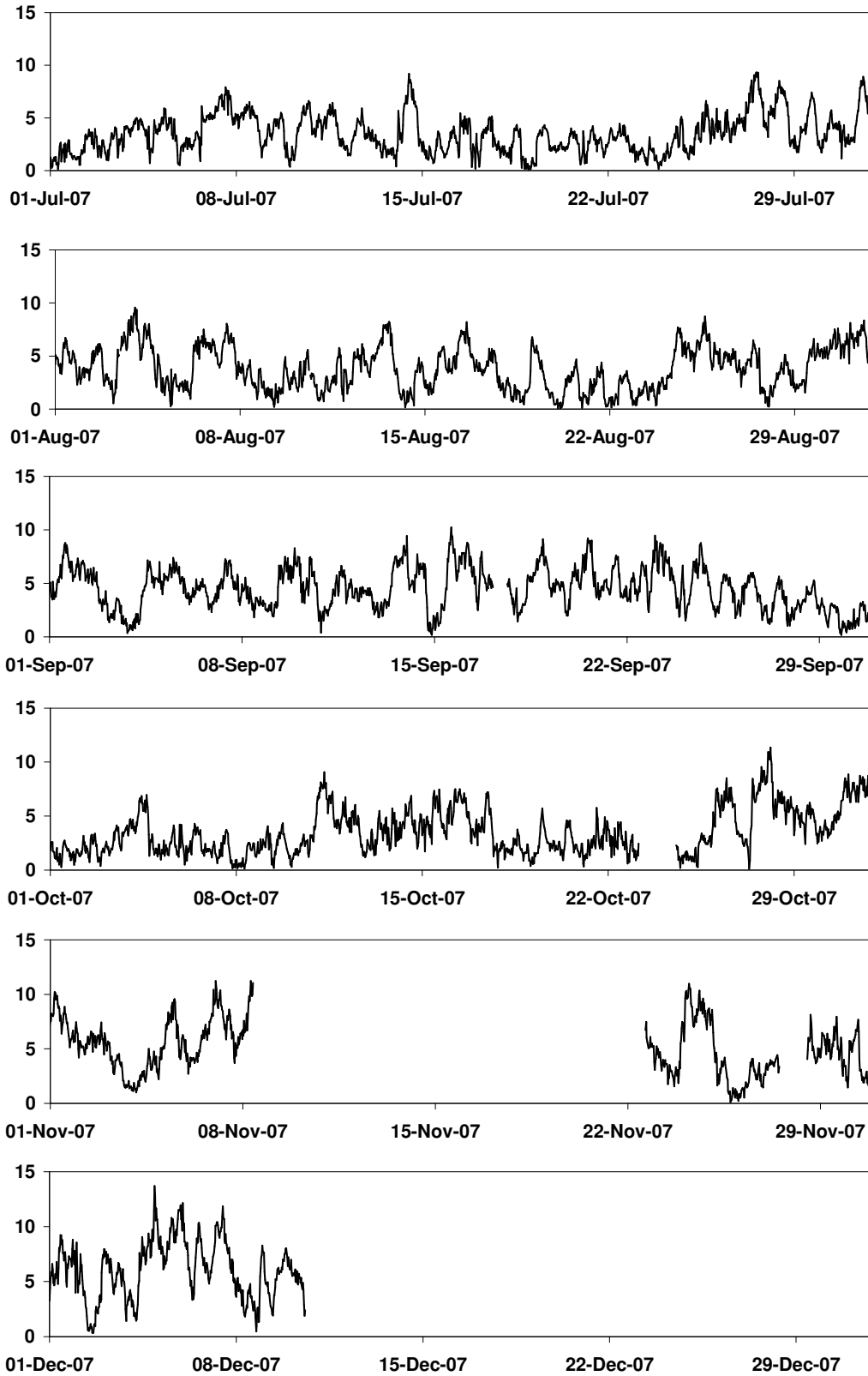
### 30-minute rainfall



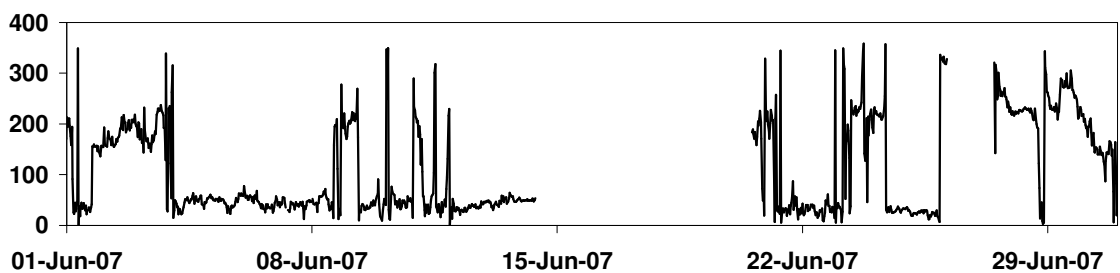
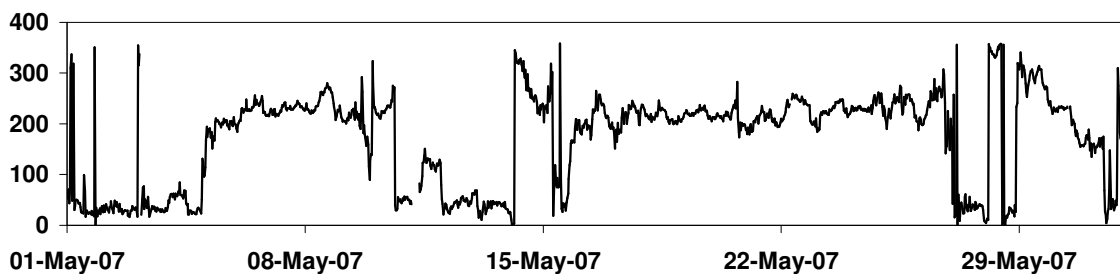
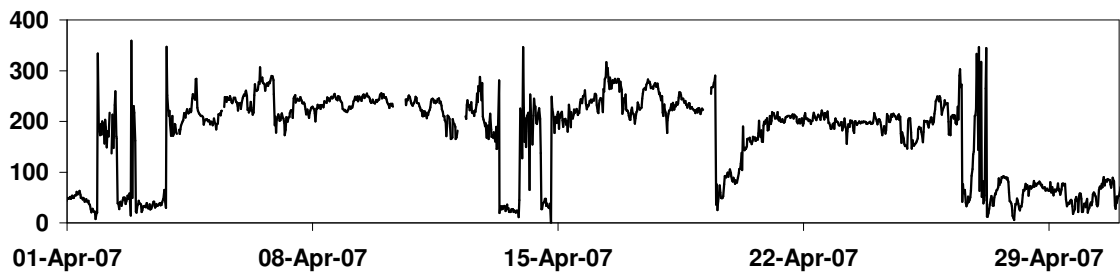
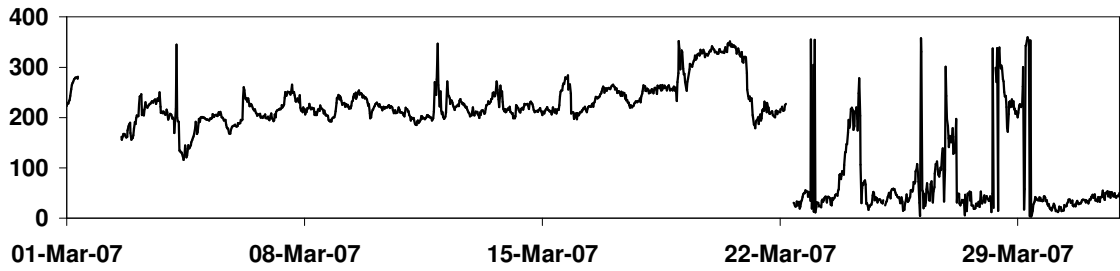
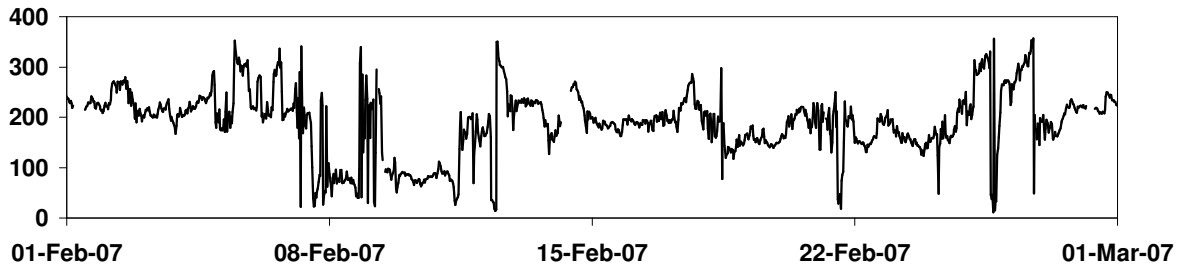
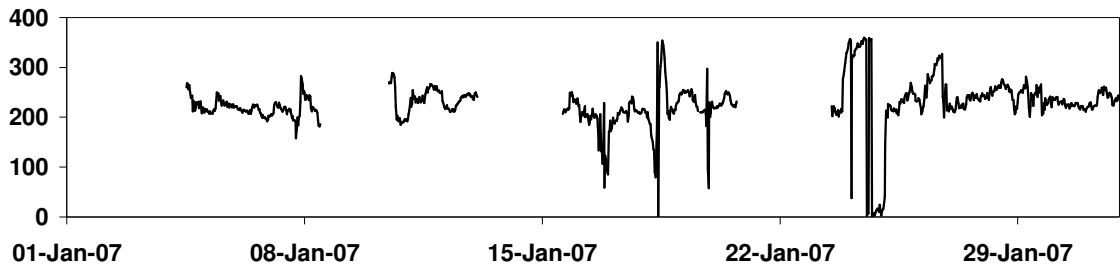
### Wind speed $\text{m s}^{-1}$



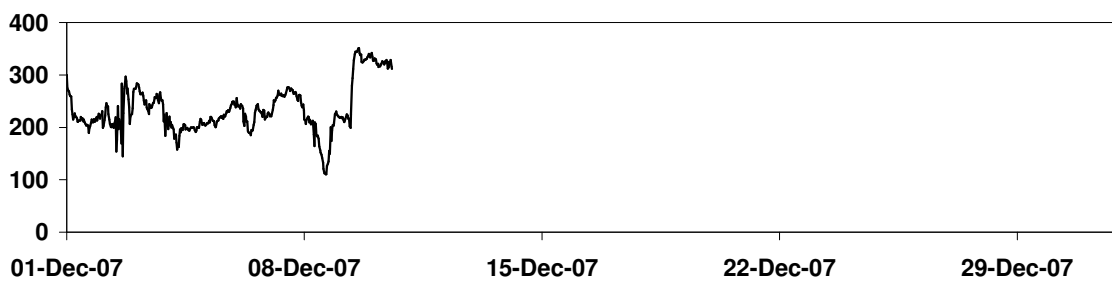
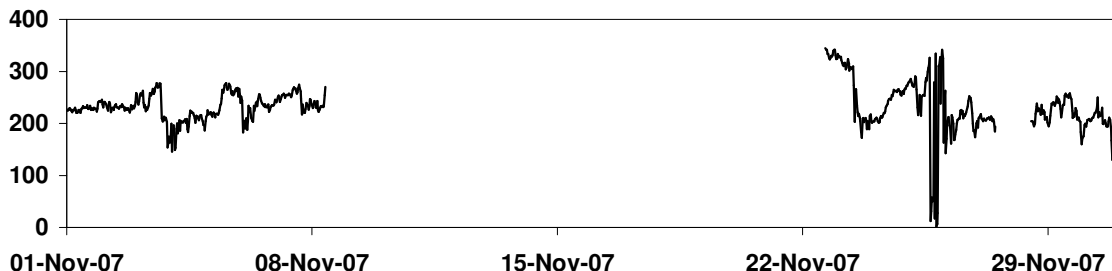
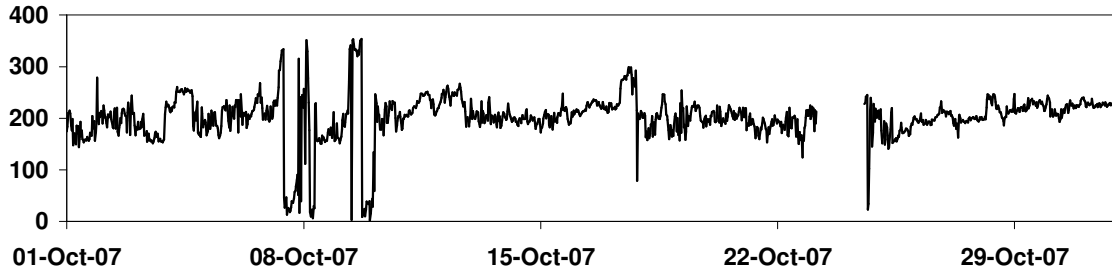
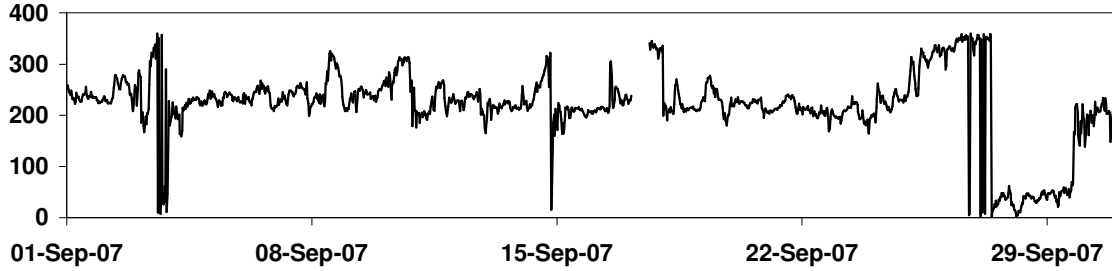
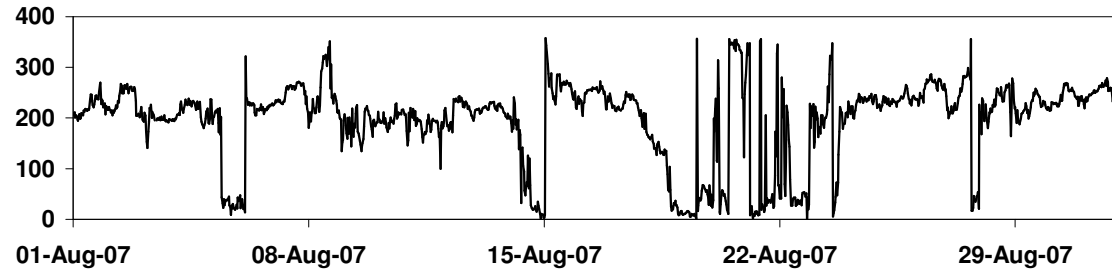
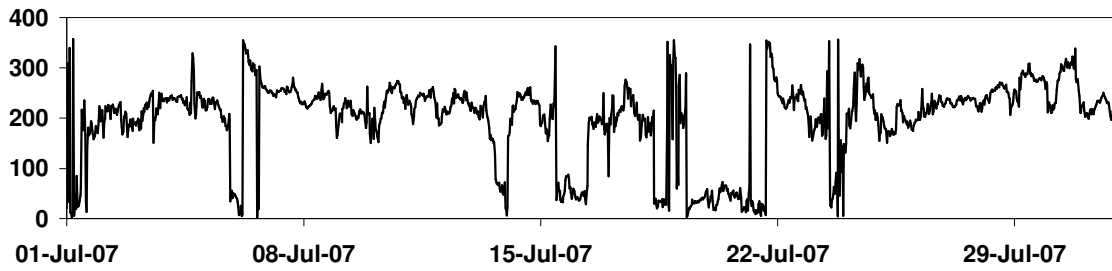
### Wind speed $\text{m s}^{-1}$



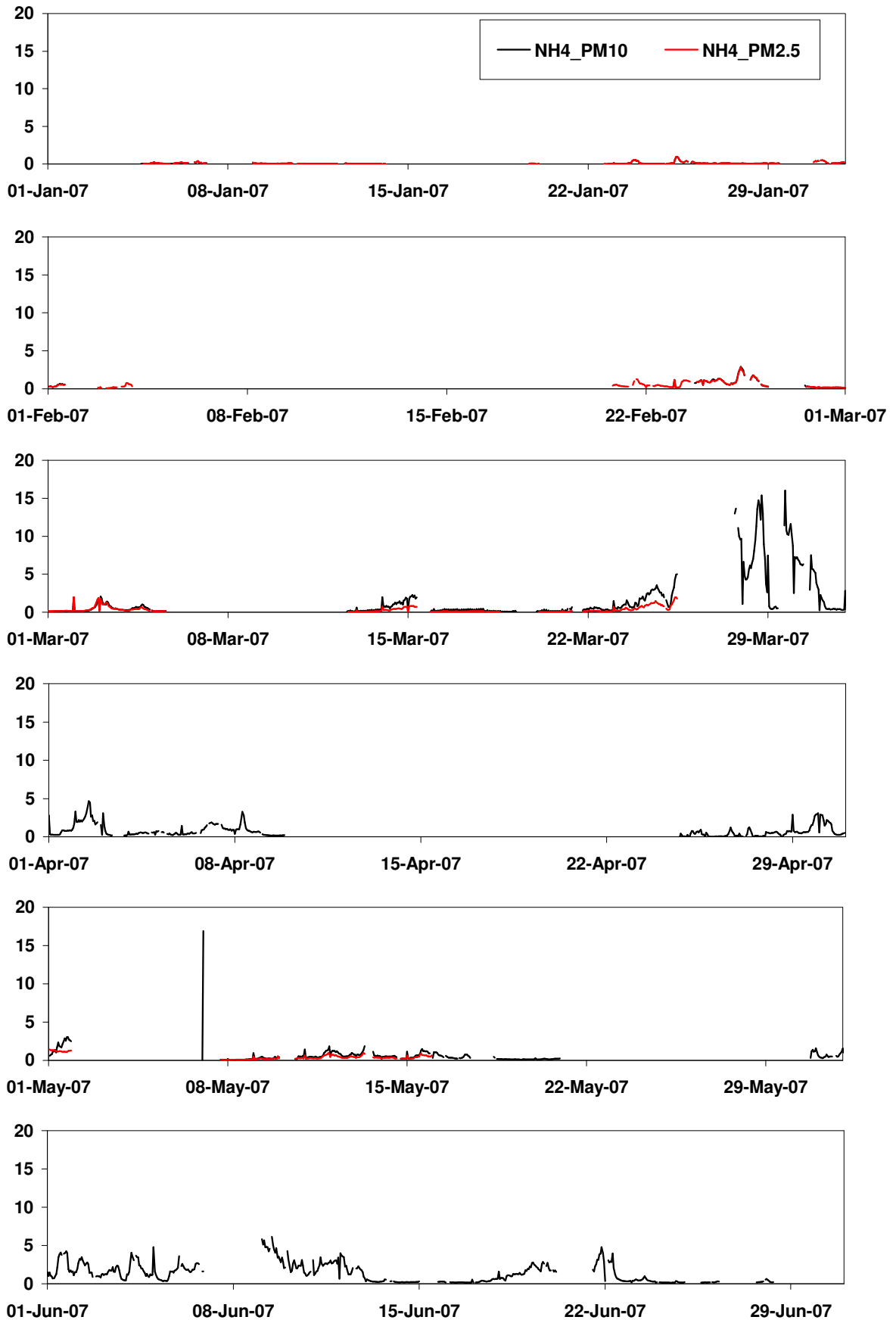
## Wind direction degrees



## Wind direction degrees

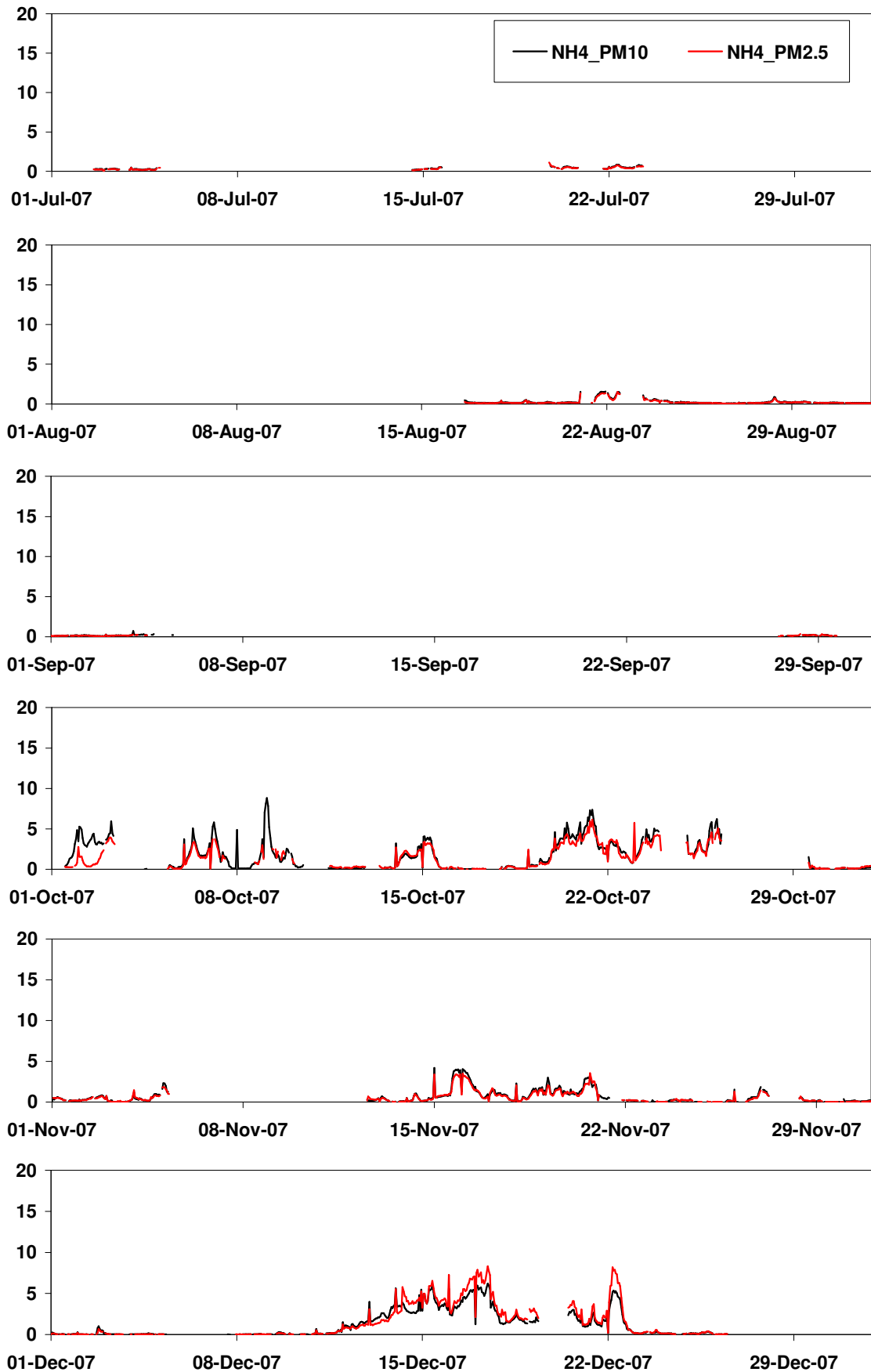


## PM10 ammonium/PM2.5 ammonium $\mu\text{g m}^{-3}$

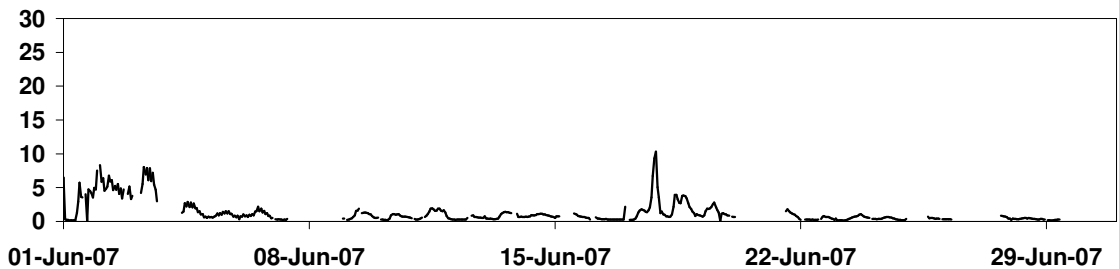
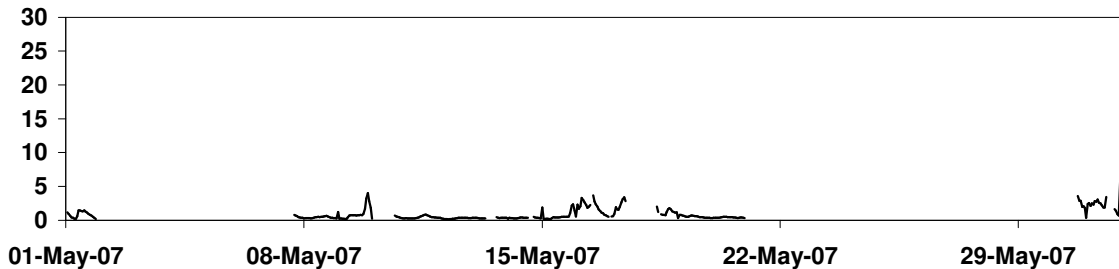
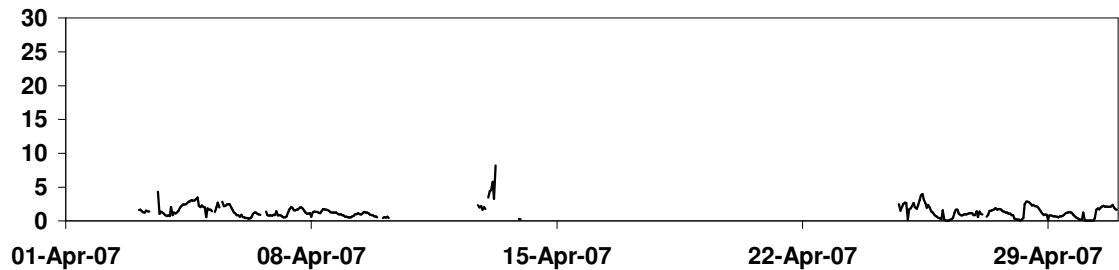
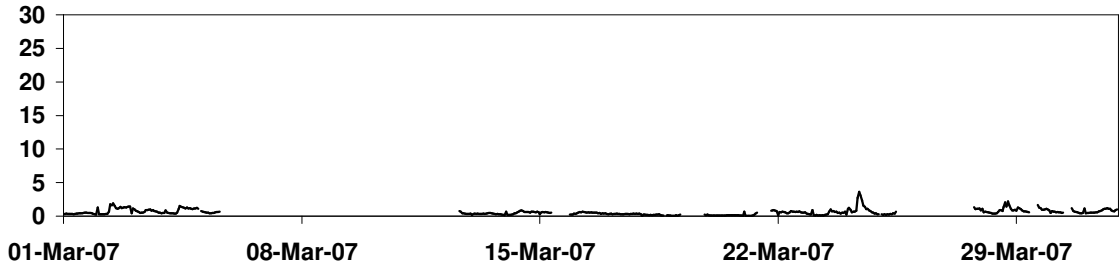
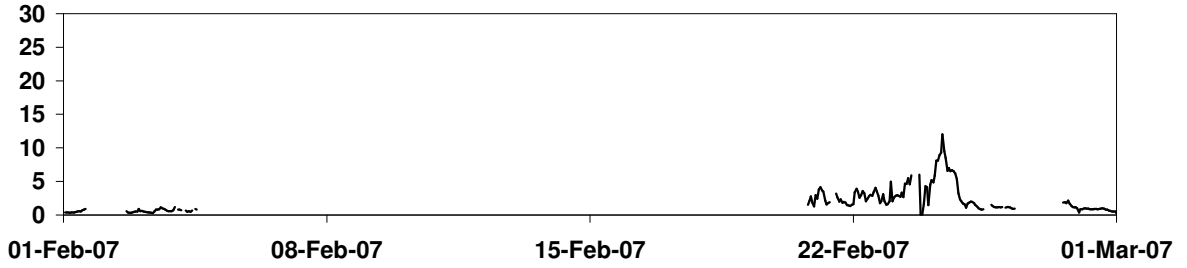
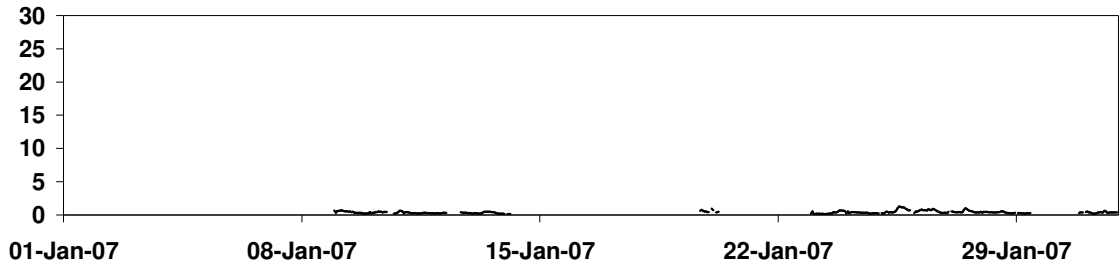




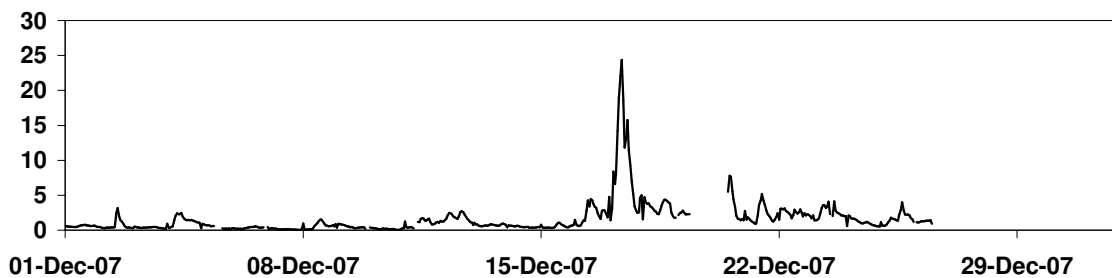
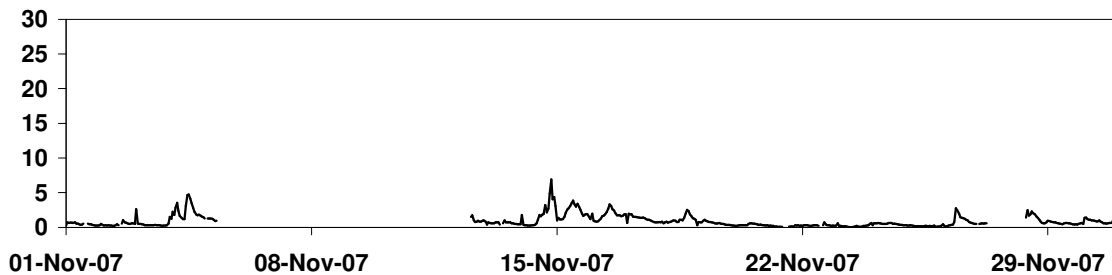
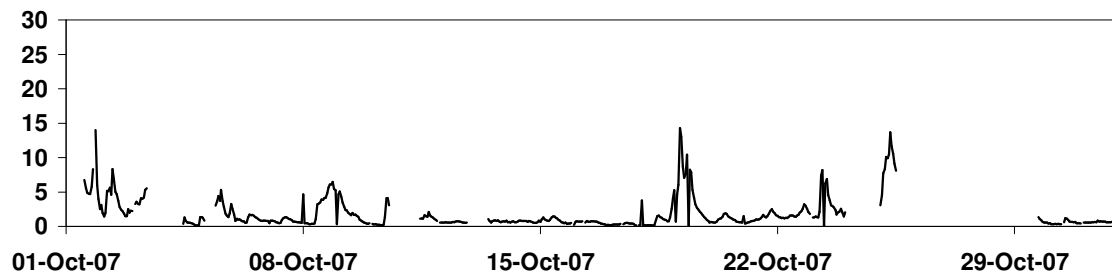
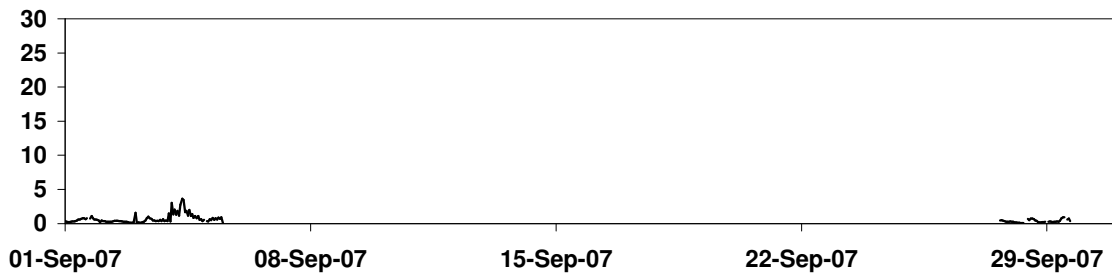
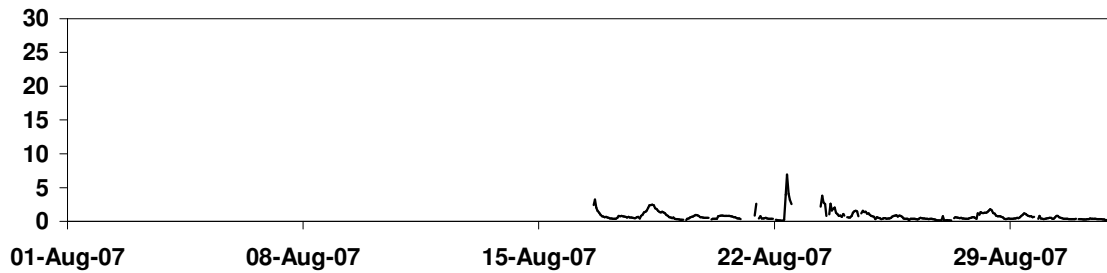
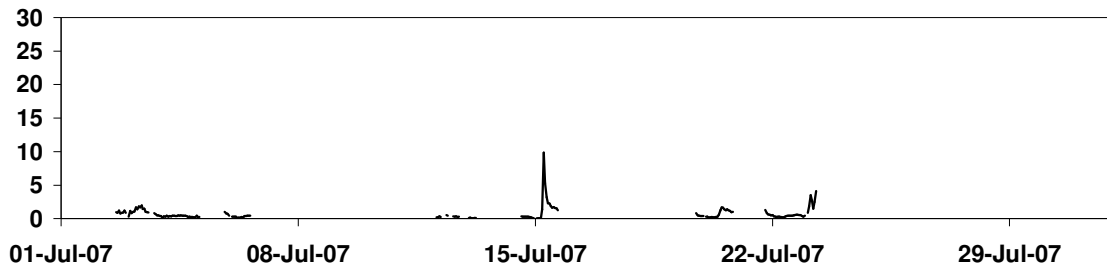
## PM10 ammonium/PM2.5 ammonium $\mu\text{g m}^{-3}$



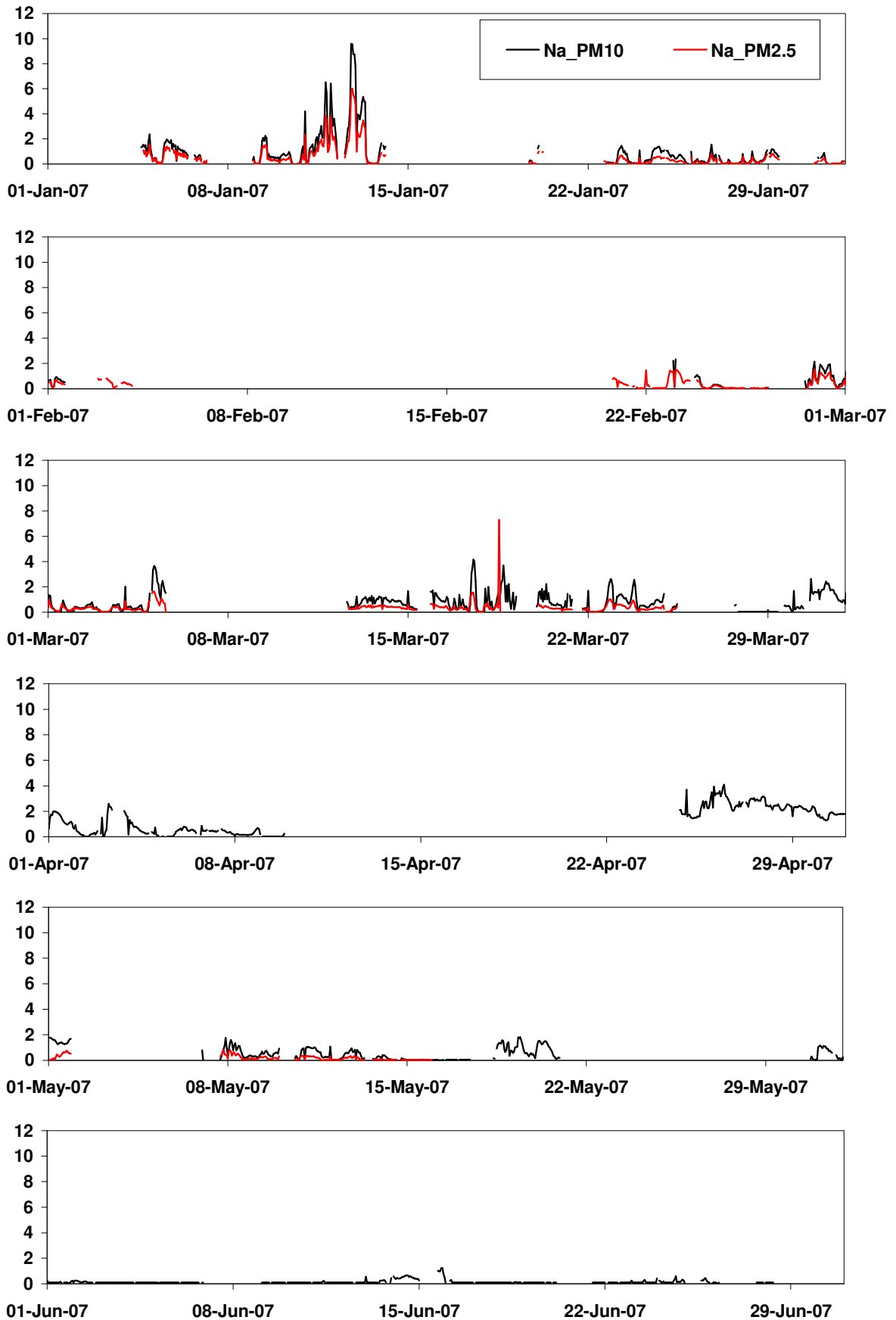
# Ammonia $\mu\text{g m}^{-3}$



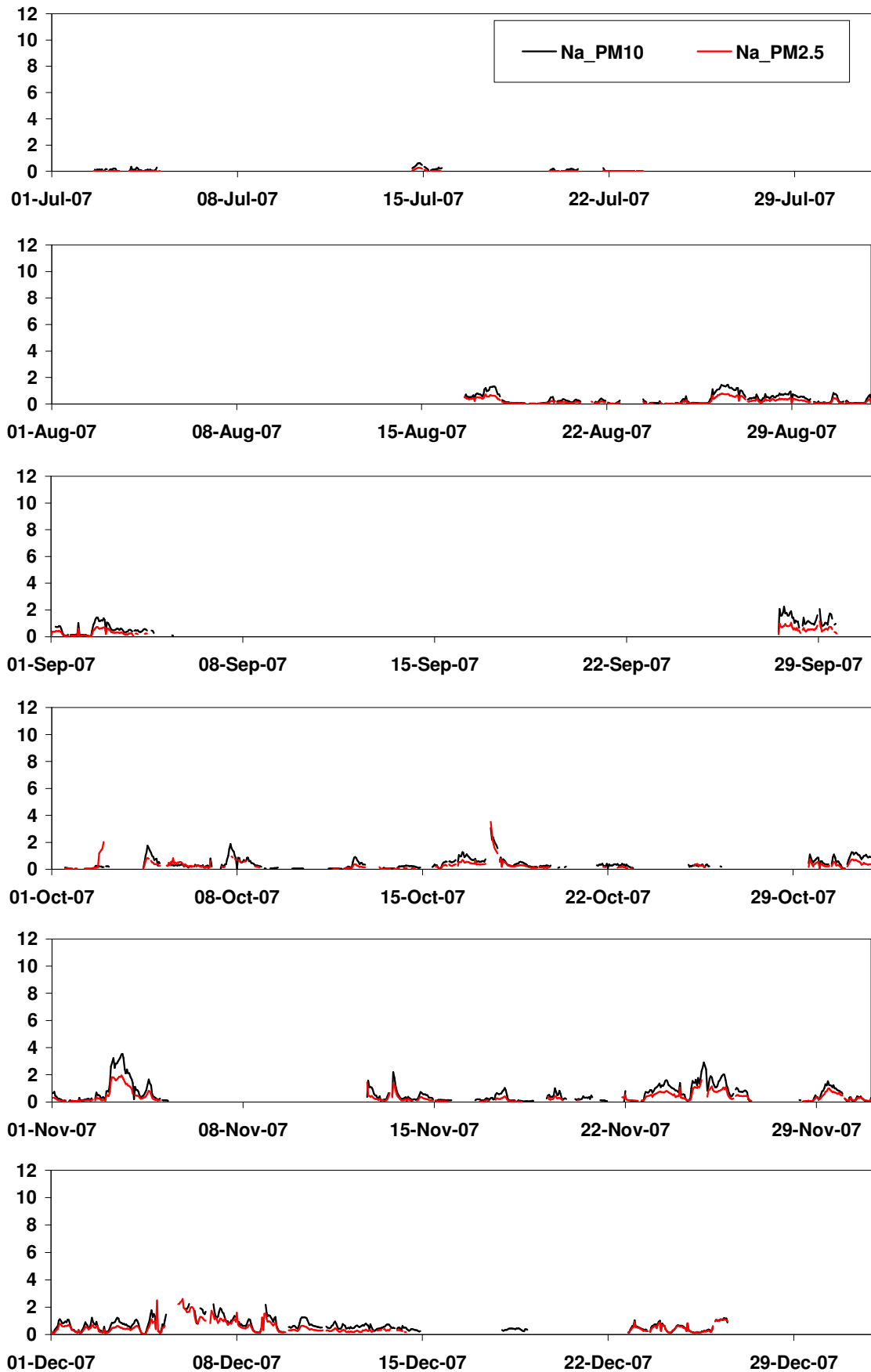
## Ammonia $\mu\text{g m}^{-3}$



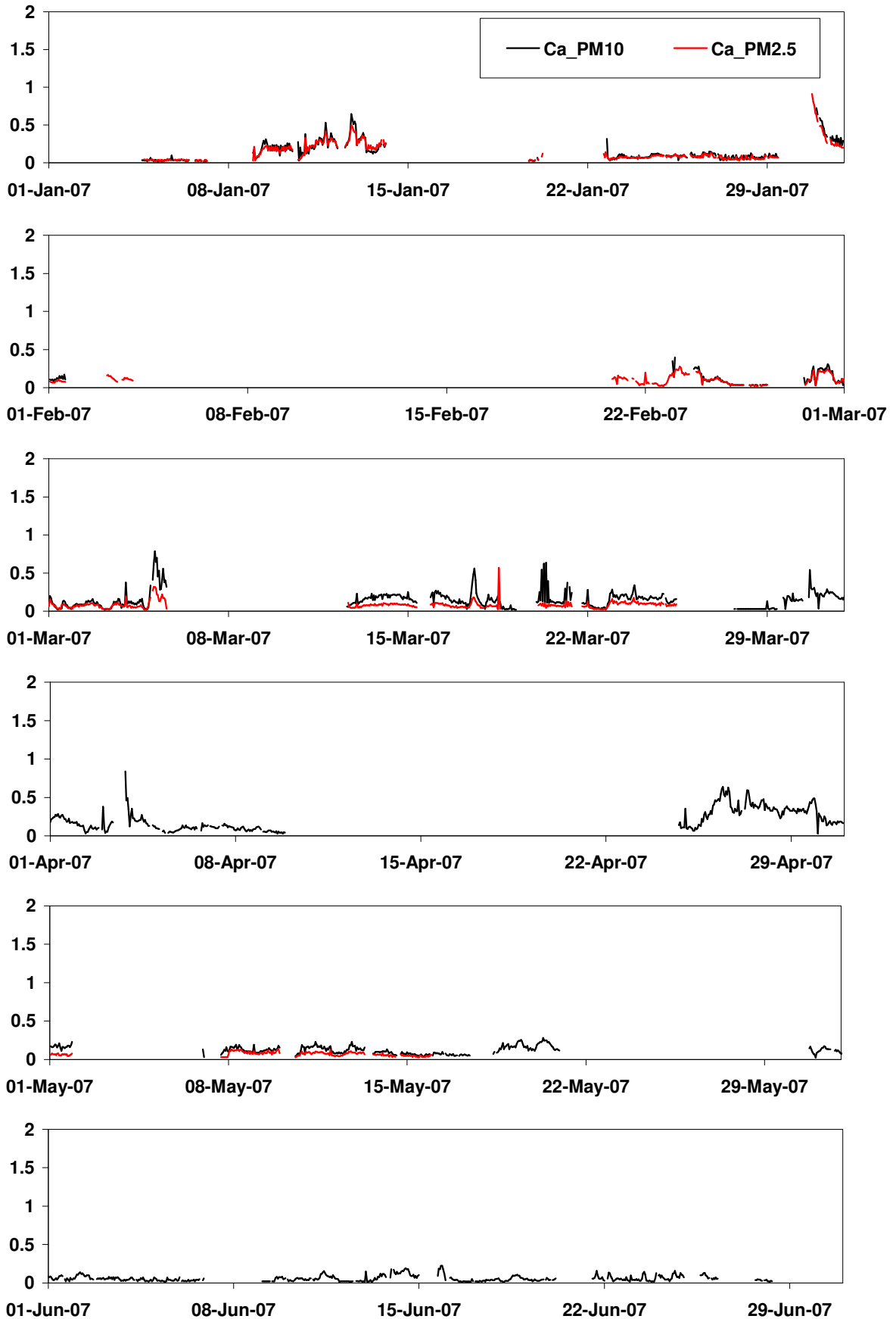
### PM10 sodium/PM2.5 sodium $\mu\text{g m}^{-3}$



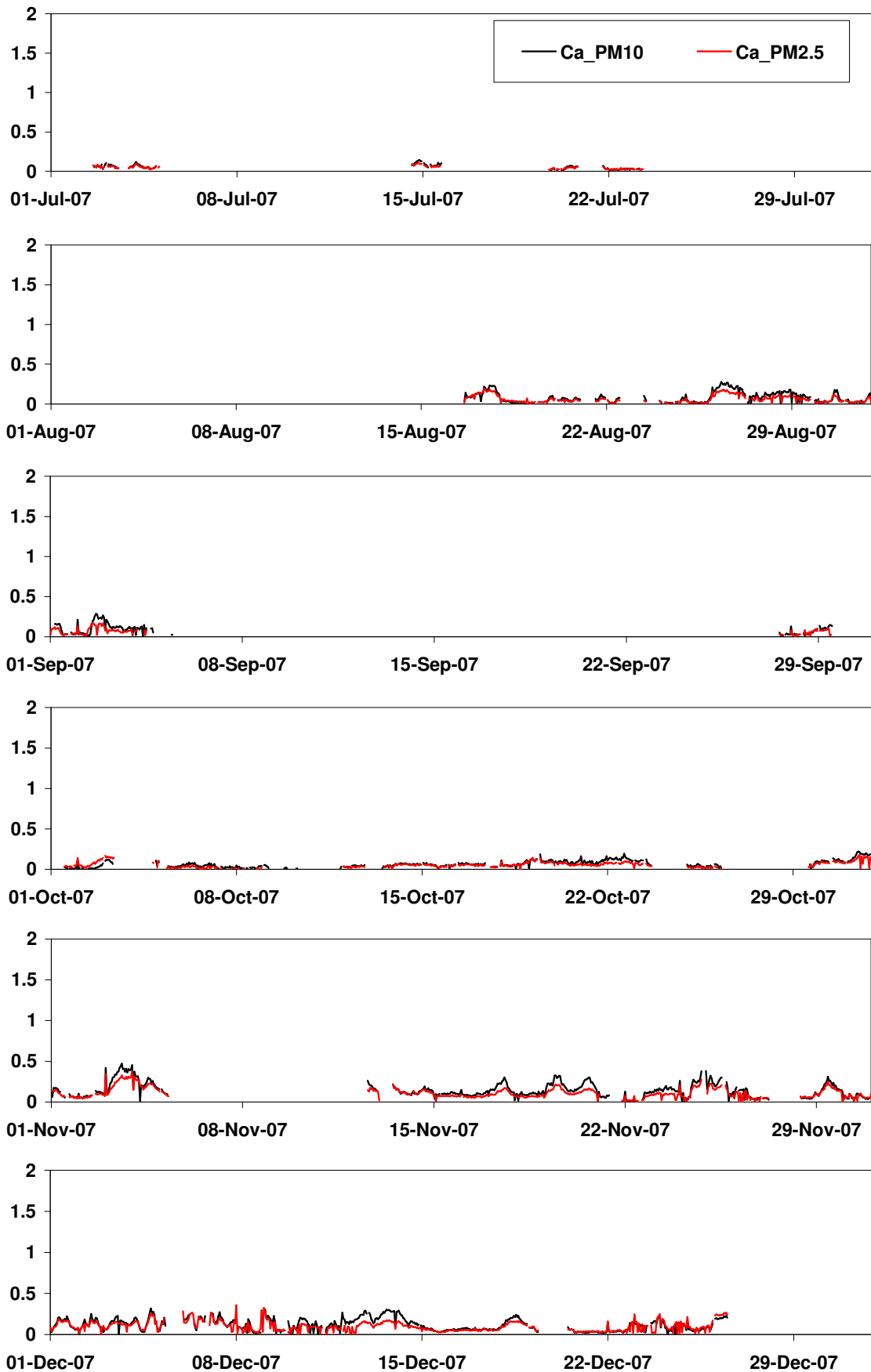
### PM10 sodium/PM2.5 sodium $\mu\text{g m}^{-3}$



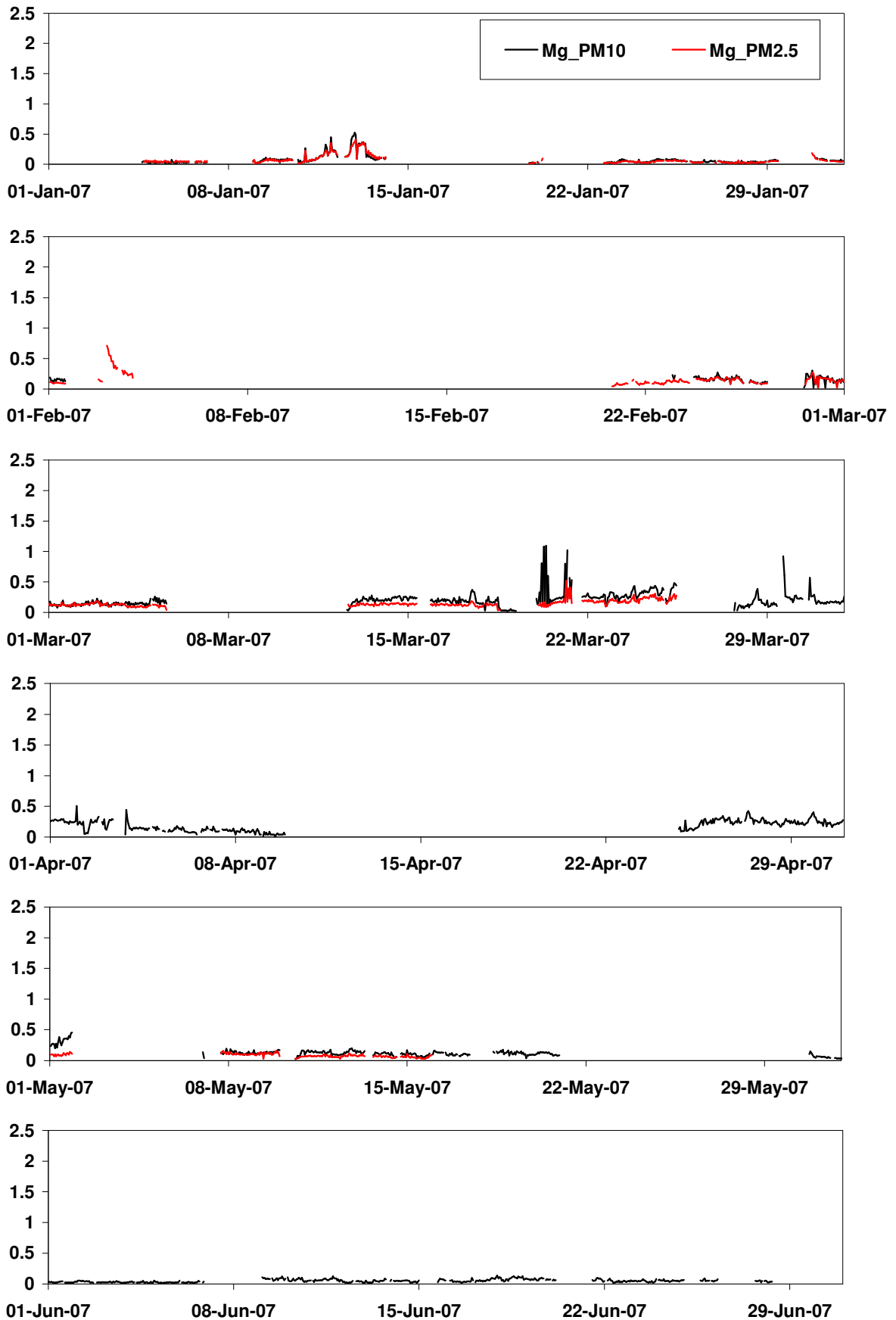
## PM10 calcium/PM2.5 calcium $\mu\text{g m}^{-3}$



### PM10 calcium/PM2.5 calcium $\mu\text{g m}^{-3}$

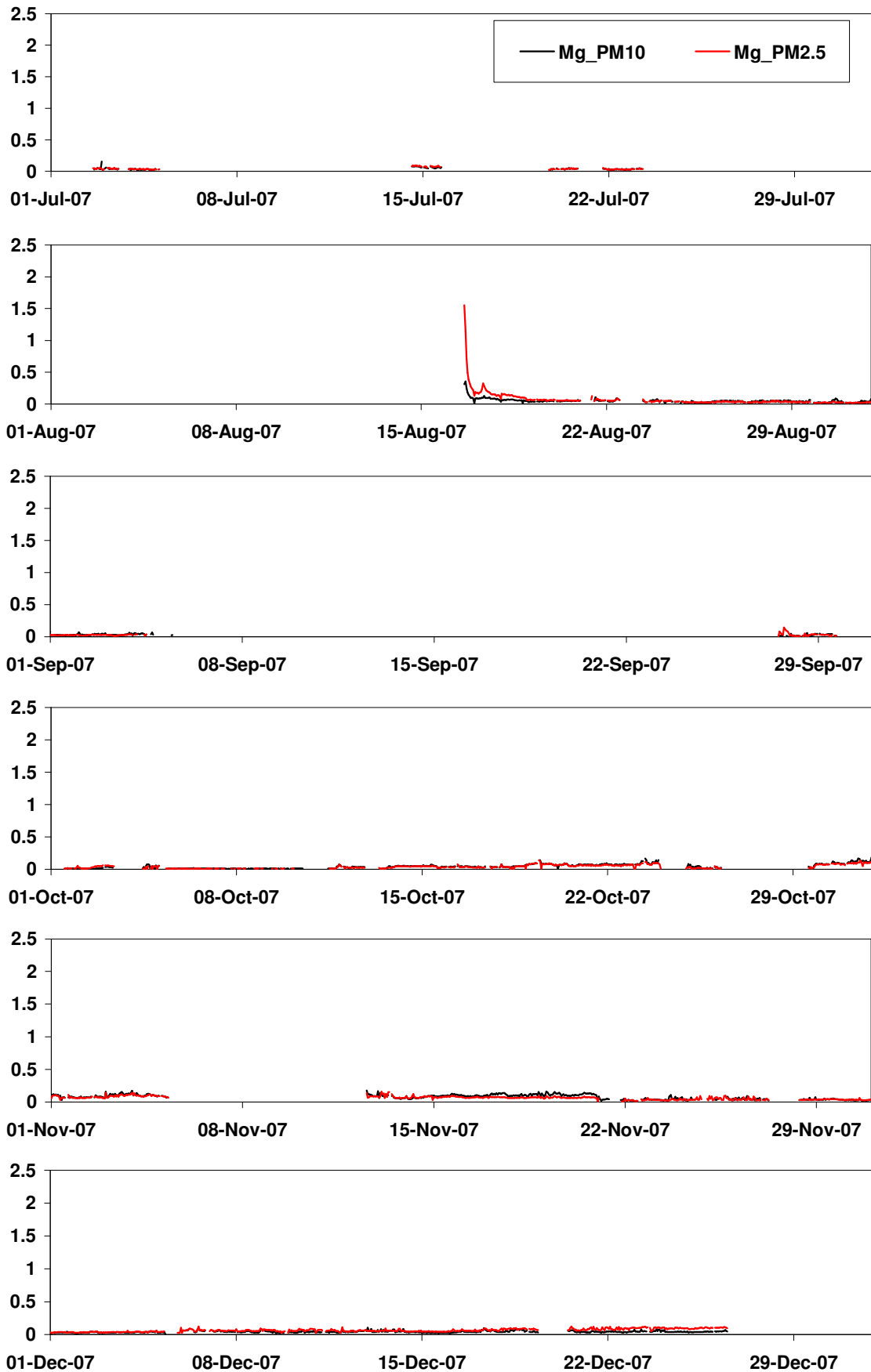


## PM10 magnesium/PM2.5 magnesium $\mu\text{g m}^{-3}$

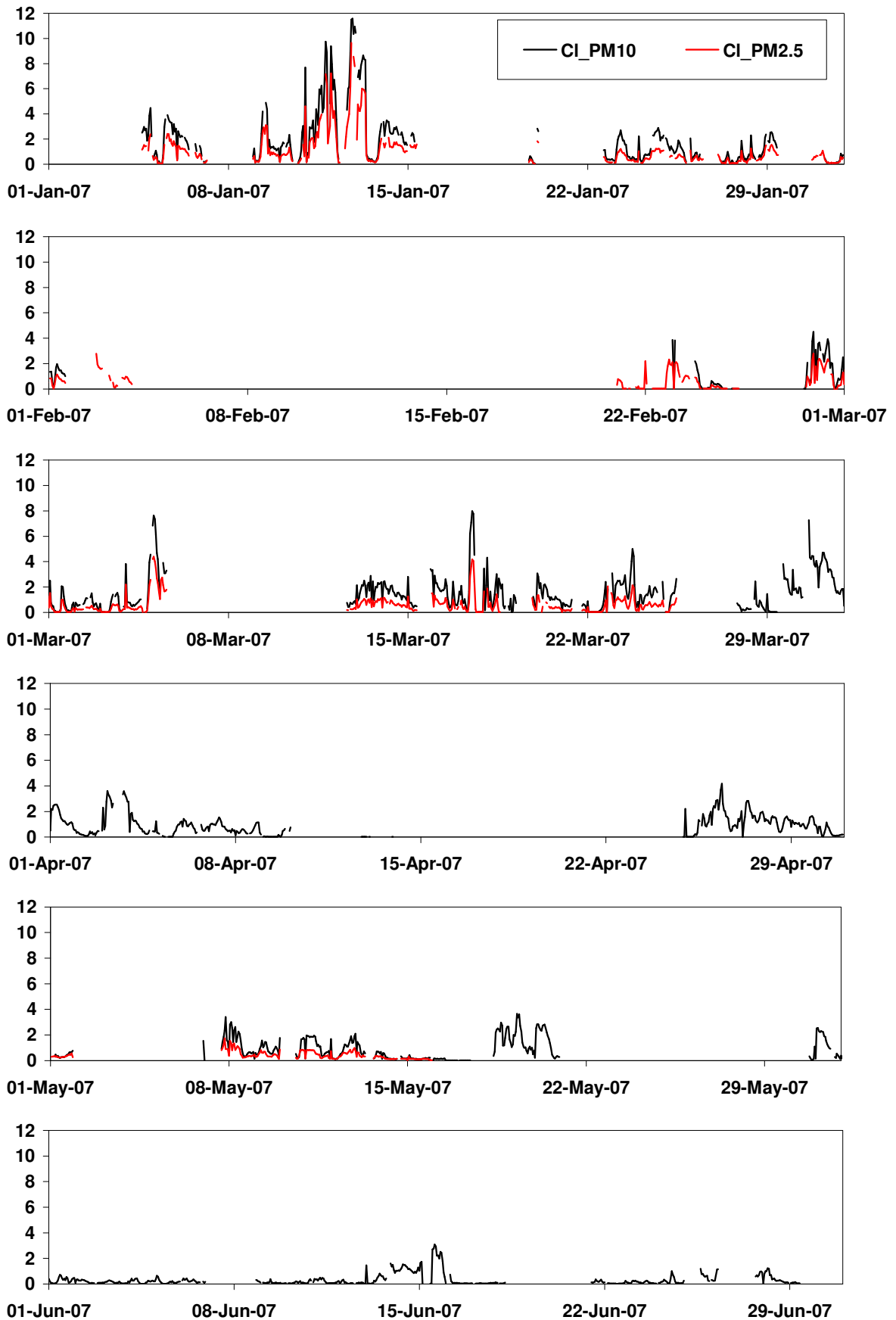




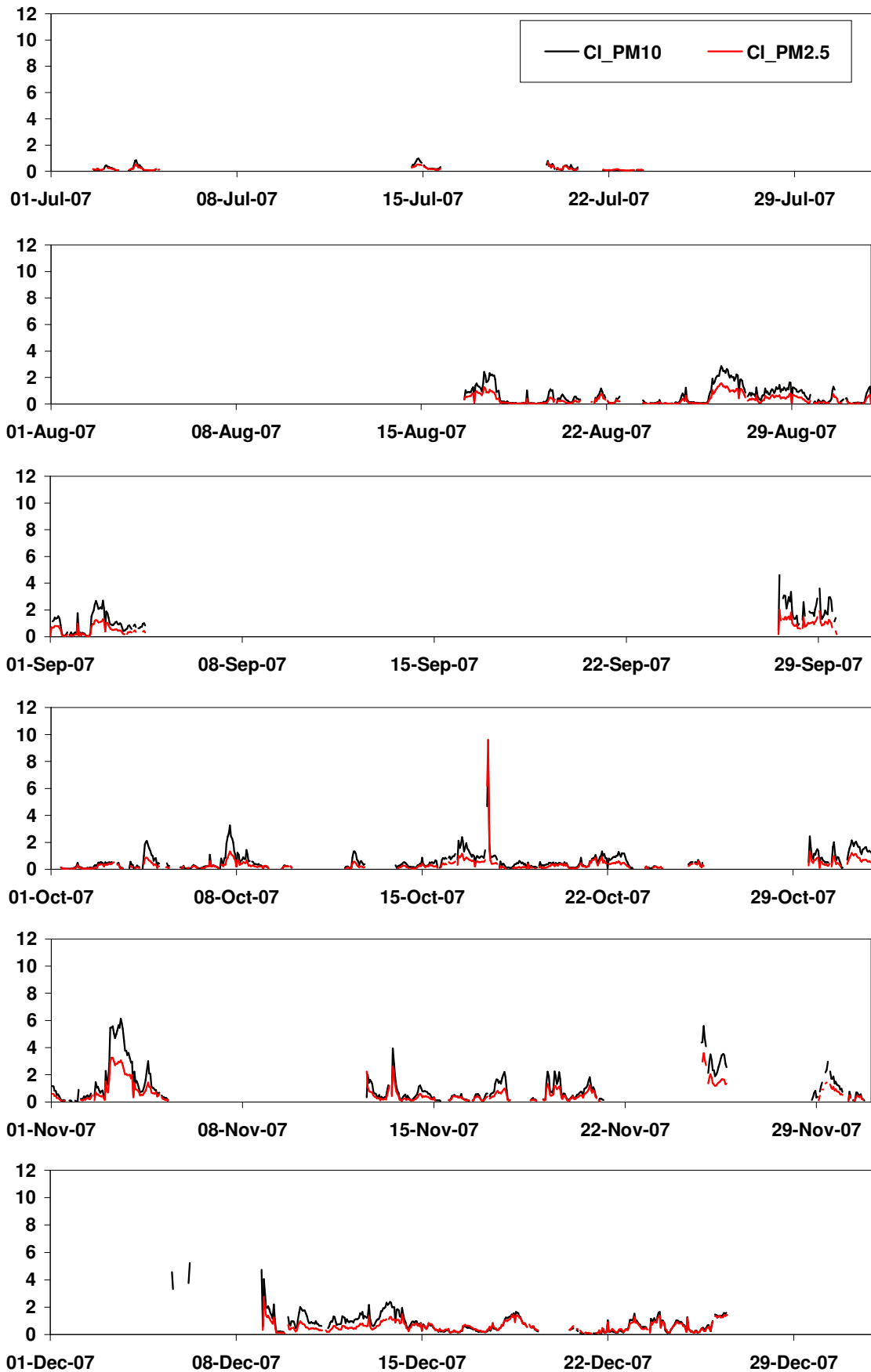
## PM10 magnesium/PM2.5 magnesium $\mu\text{g m}^{-3}$



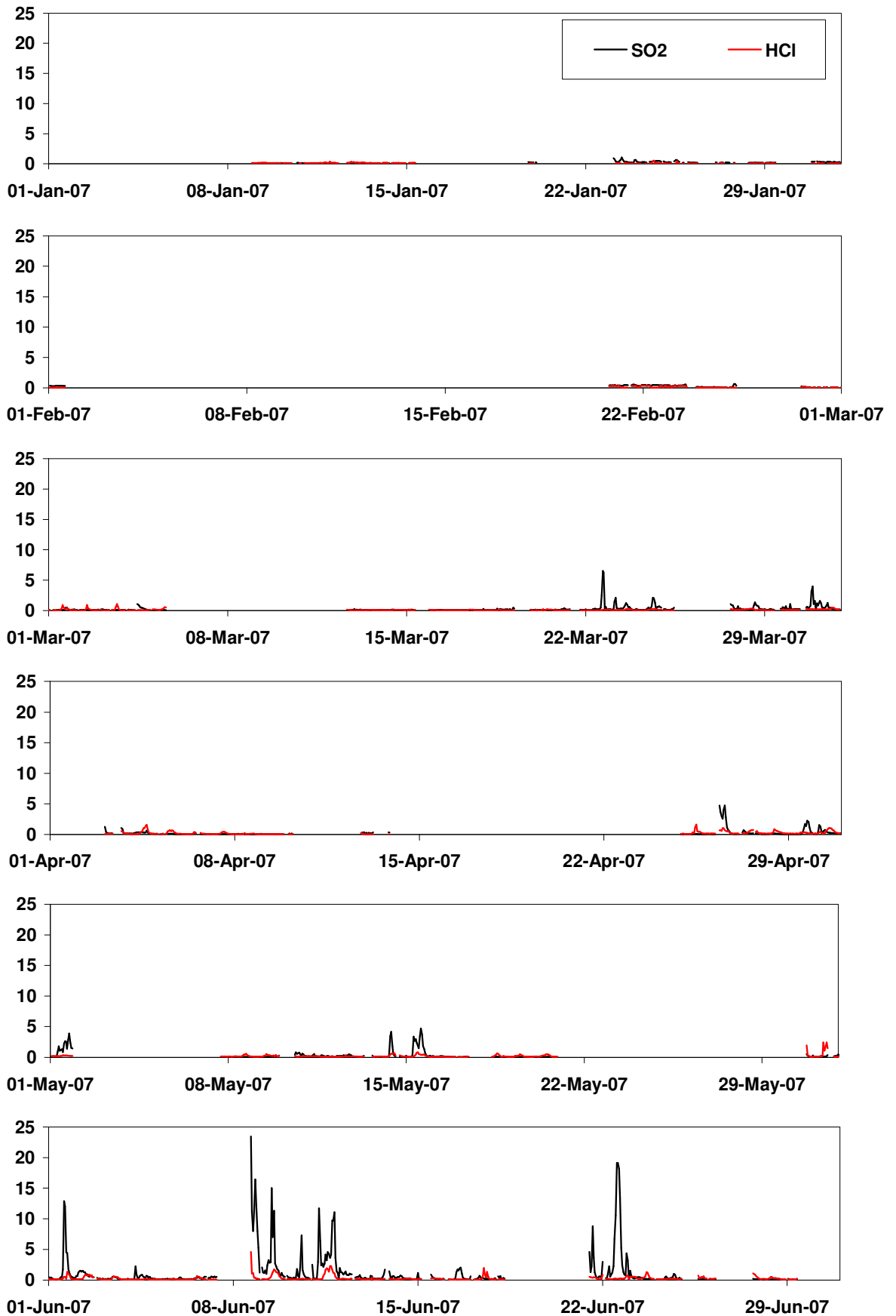
### PM10 chloride/PM2.5 chloride $\mu\text{g m}^{-3}$



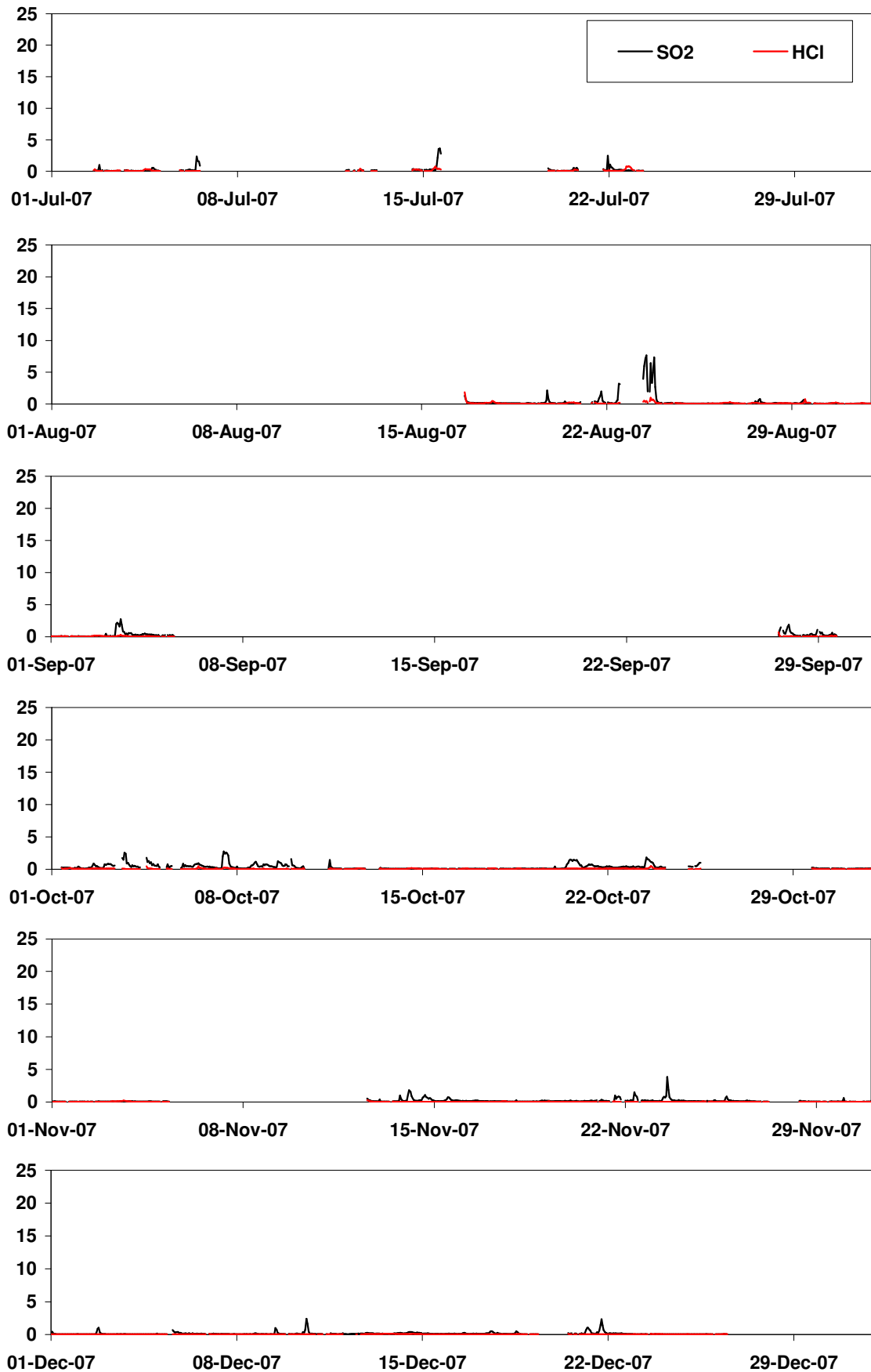
### PM10 chloride/PM2.5 chloride $\mu\text{g m}^{-3}$



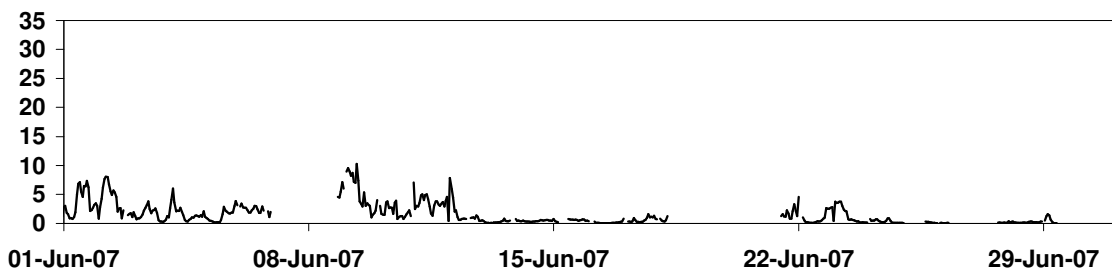
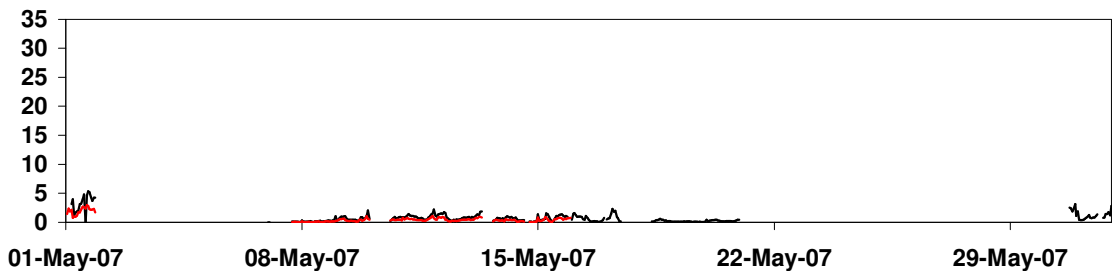
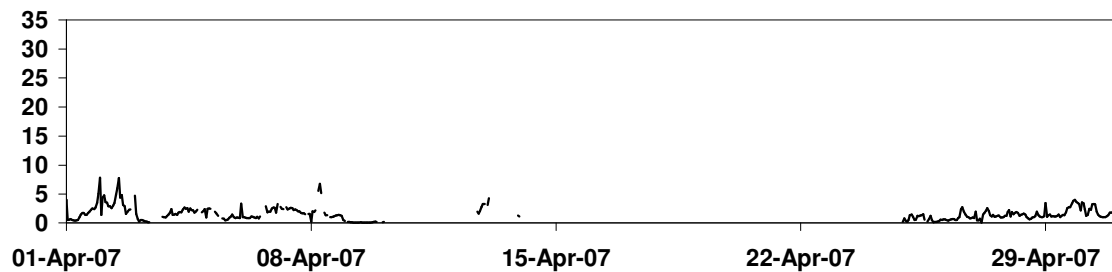
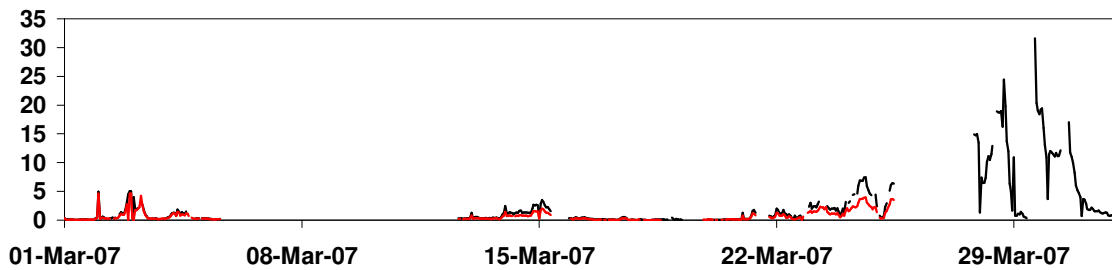
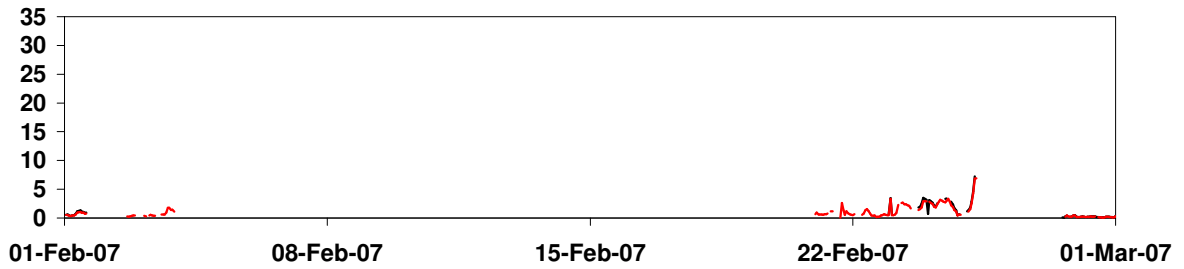
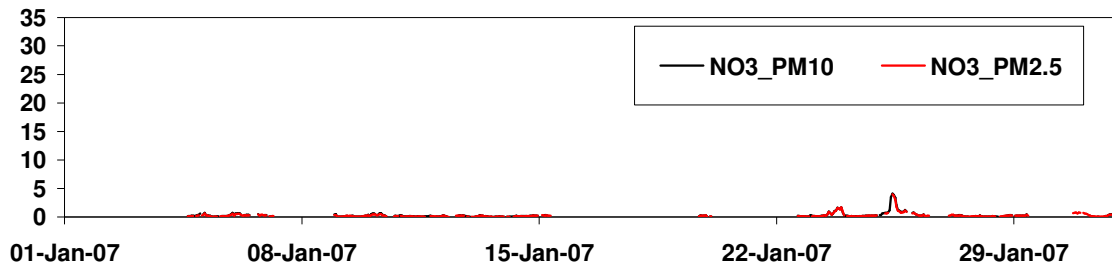
## sulphur dioxide/hydrogen chloride $\mu\text{g m}^{-3}$



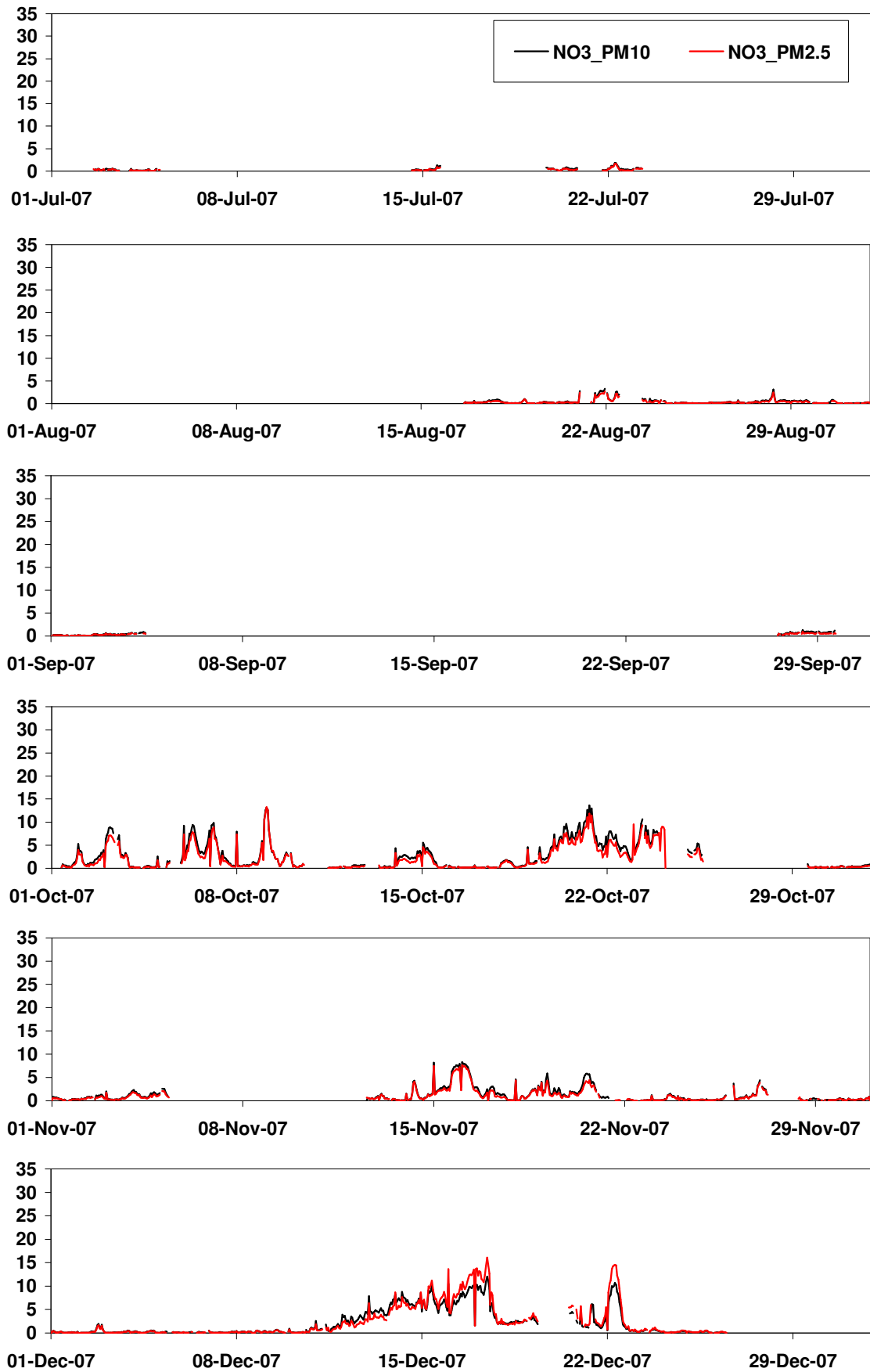
## sulphur dioxide/hydrogen chloride $\mu\text{g m}^{-3}$



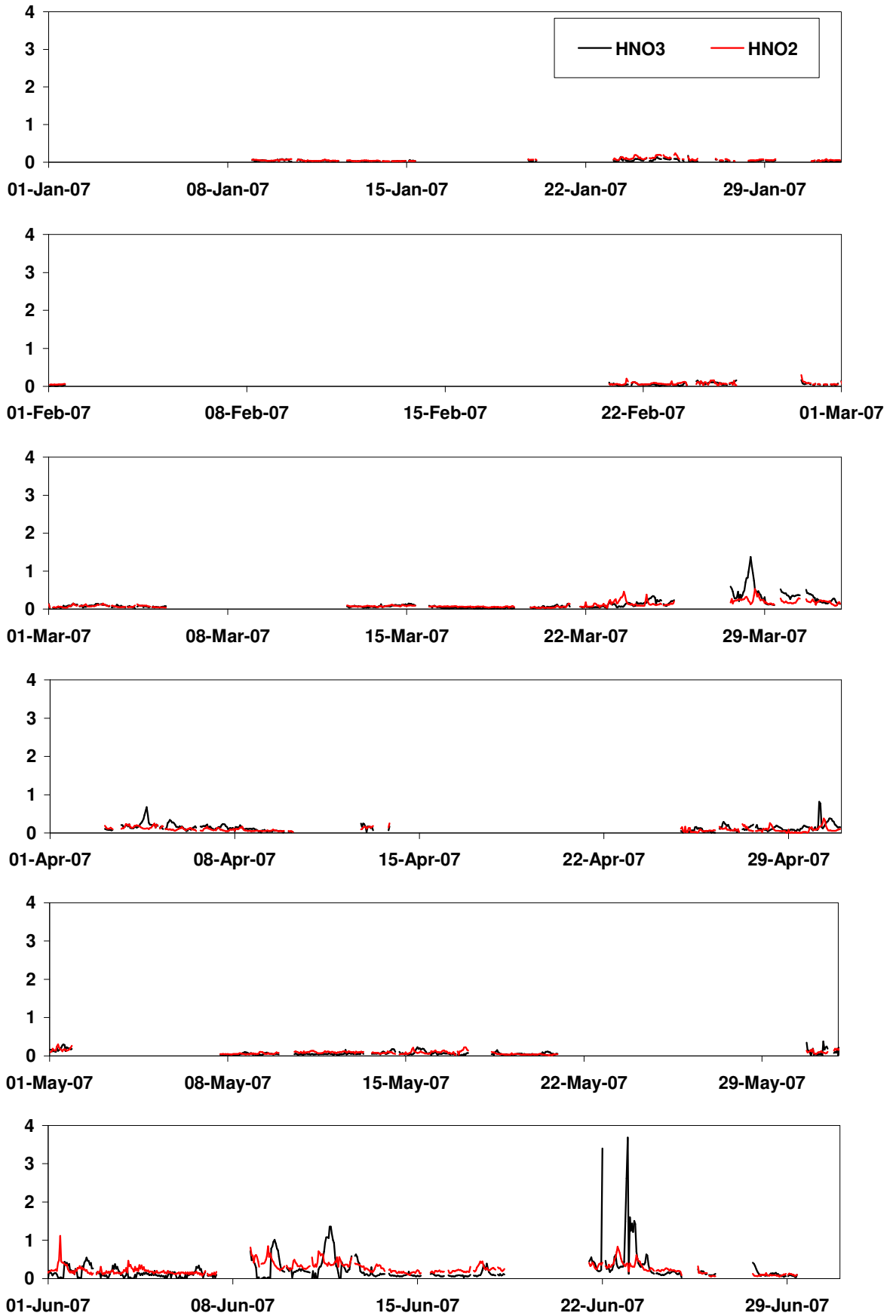
### PM10 nitrate/PM2.5 nitrate $\mu\text{g m}^{-3}$



### PM10 nitrate/PM2.5 nitrate $\mu\text{g m}^{-3}$

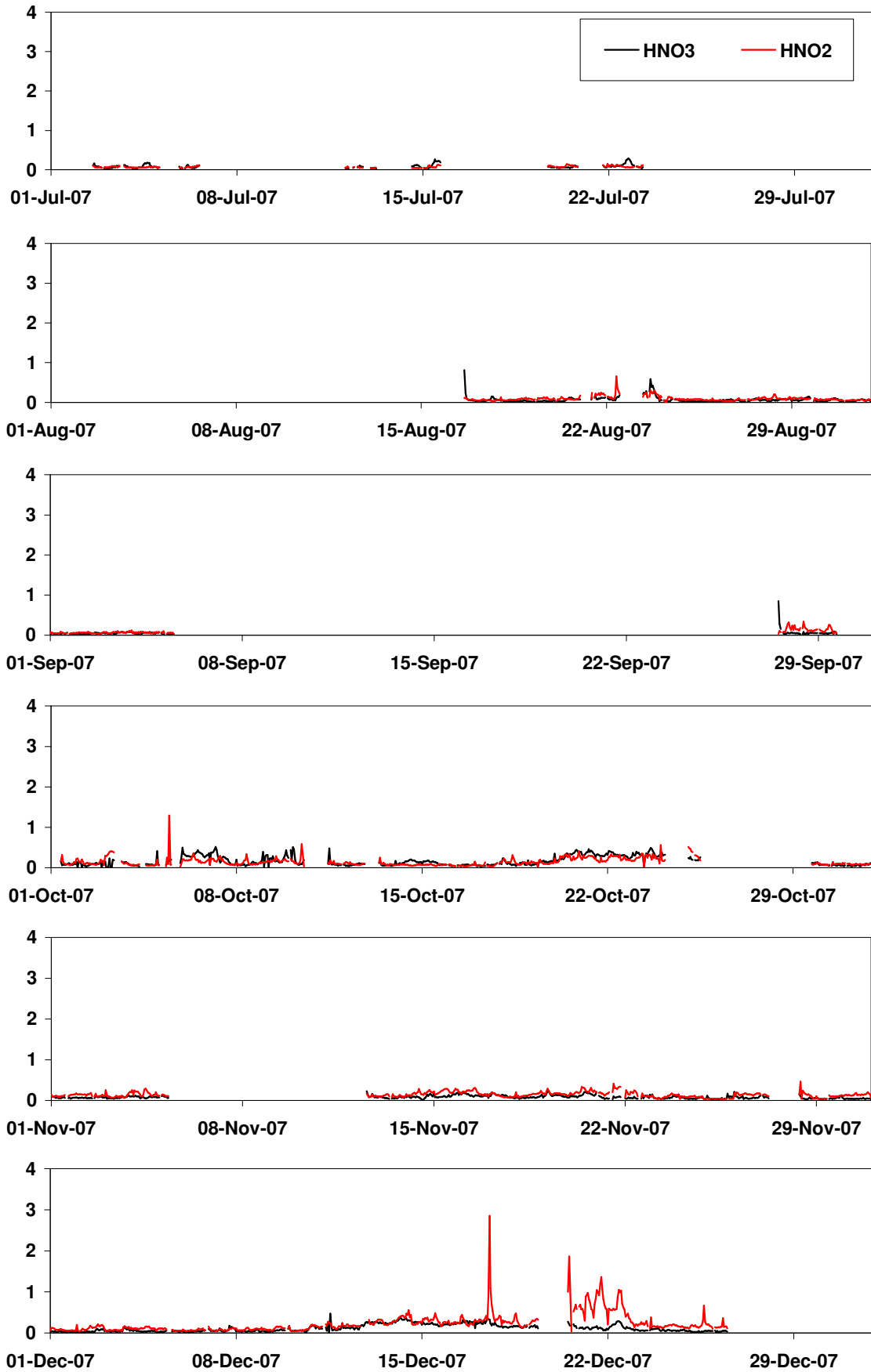


### nitric acid/nitrous acid $\mu\text{g m}^{-3}$

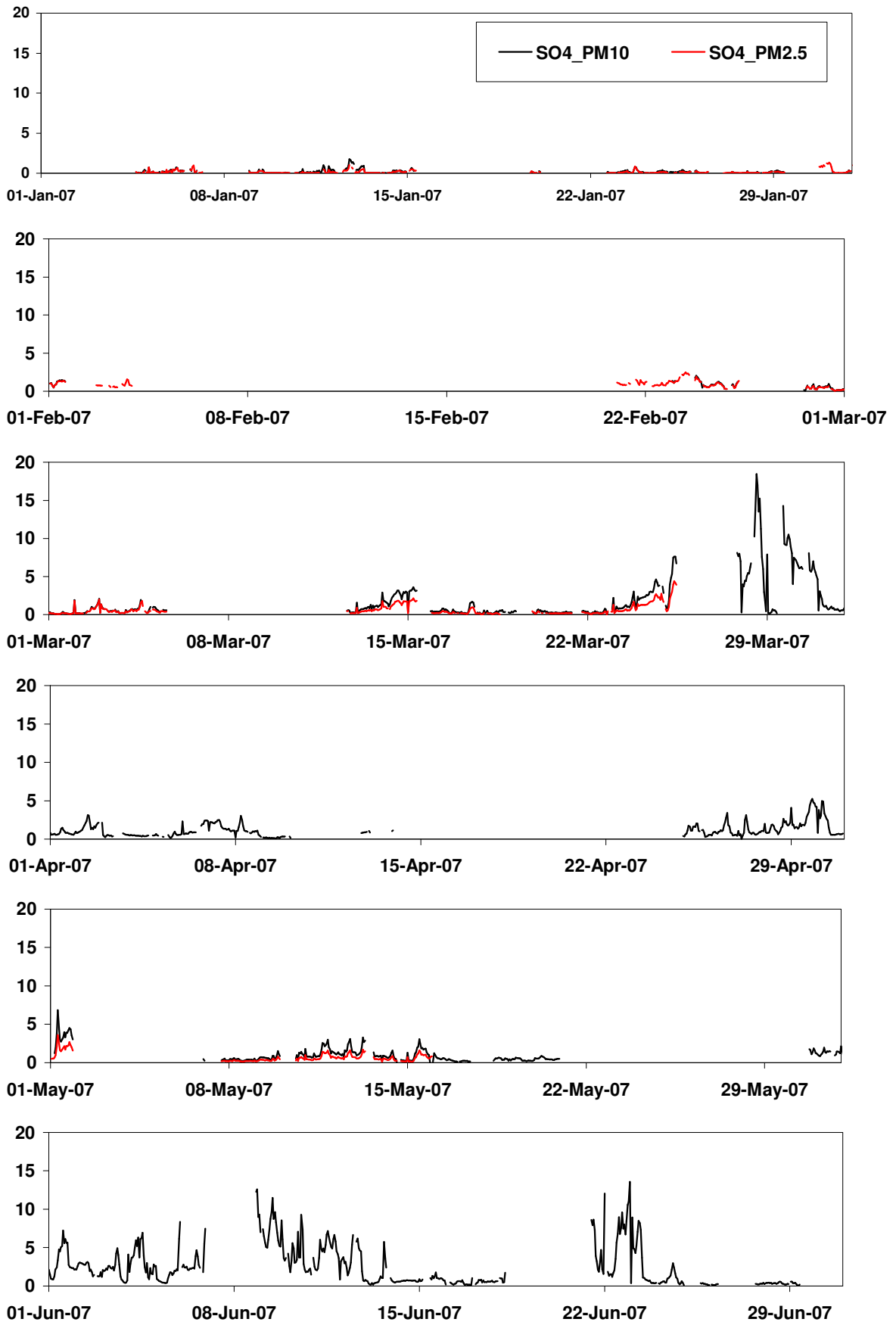




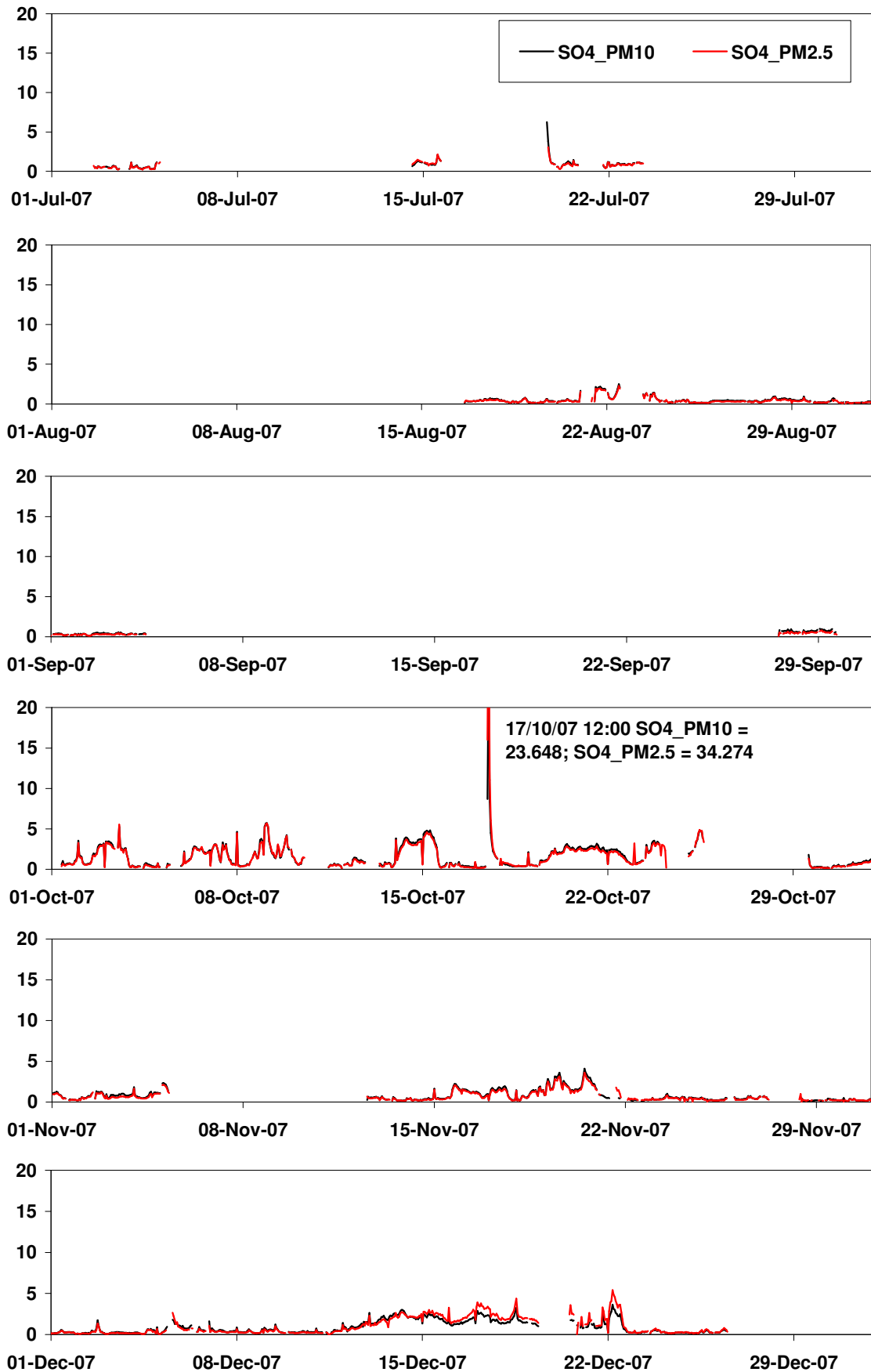
### nitric acid/nitrous acid $\mu\text{g m}^{-3}$



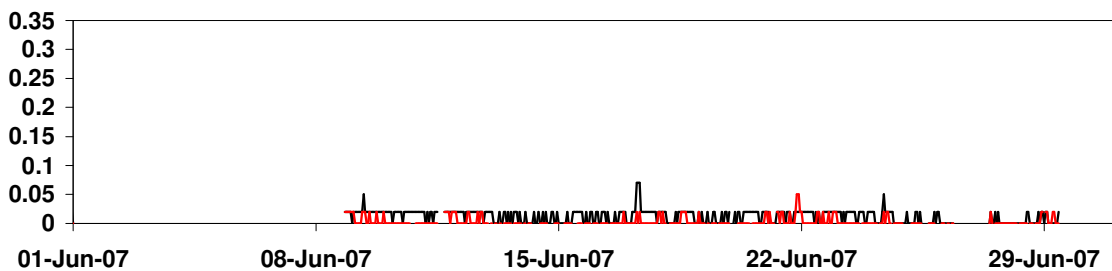
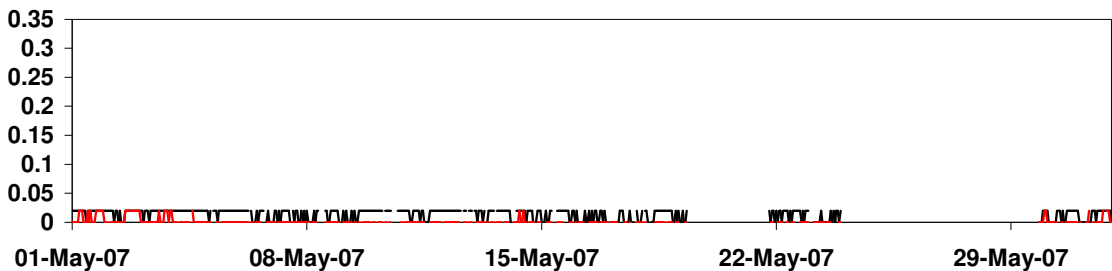
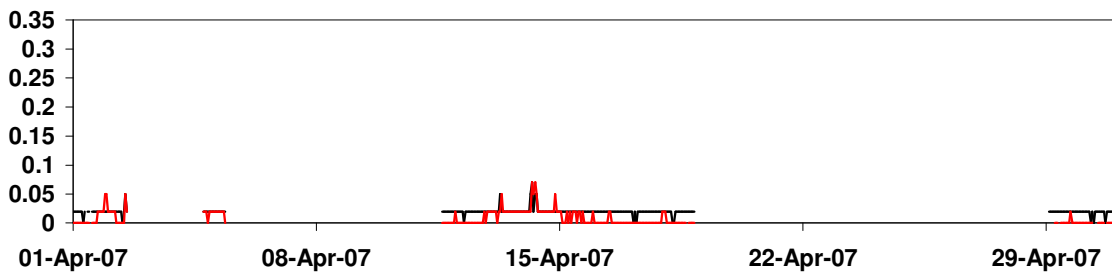
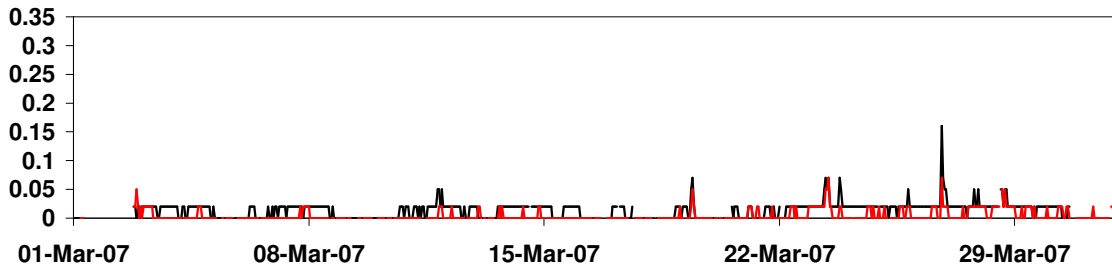
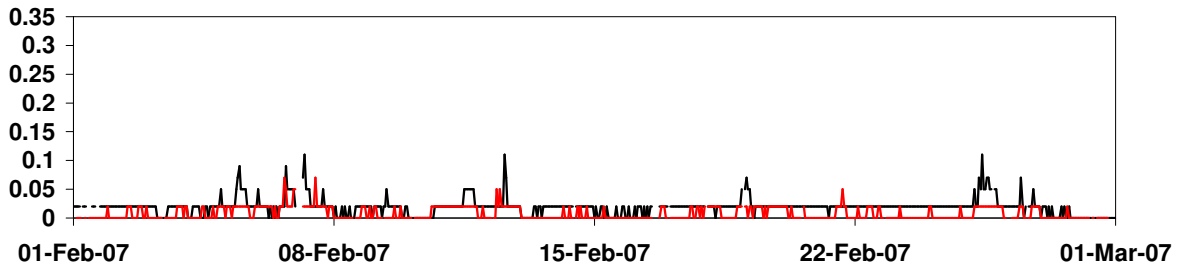
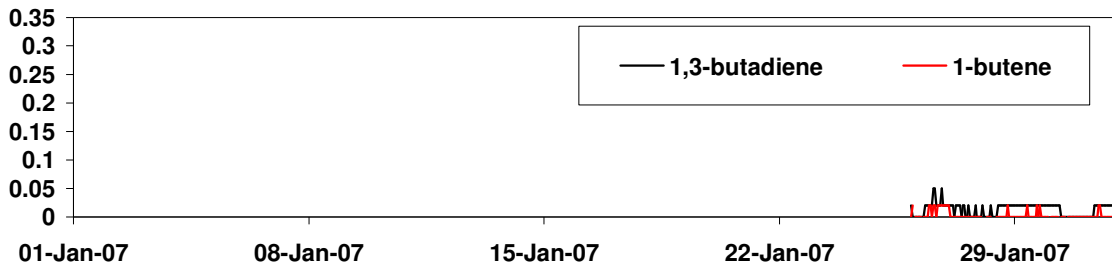
## PM10 sulphate/PM2.5 sulphate $\mu\text{g m}^{-3}$



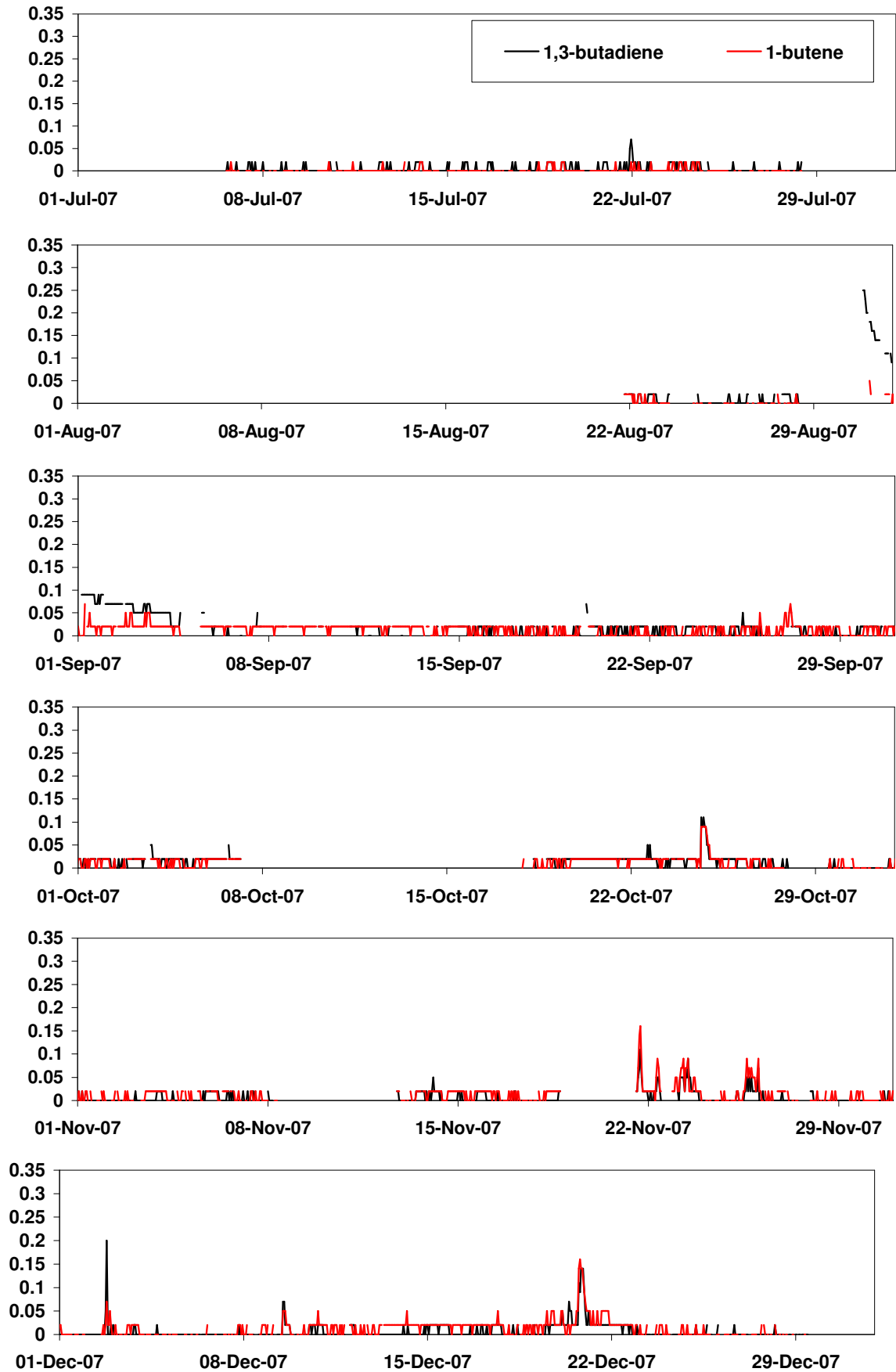
## PM10 sulphate/PM2.5 sulphate $\mu\text{g m}^{-3}$



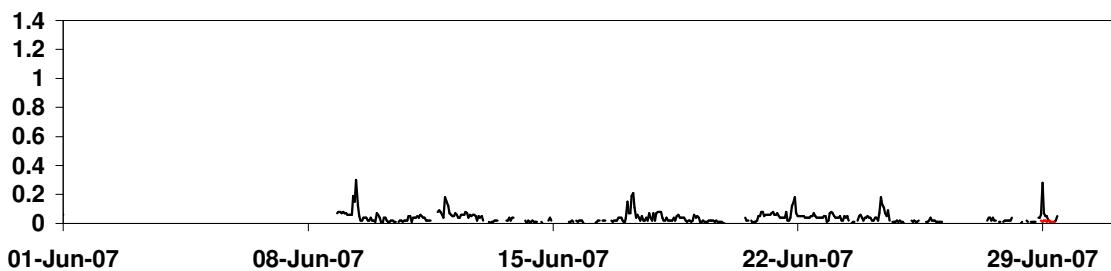
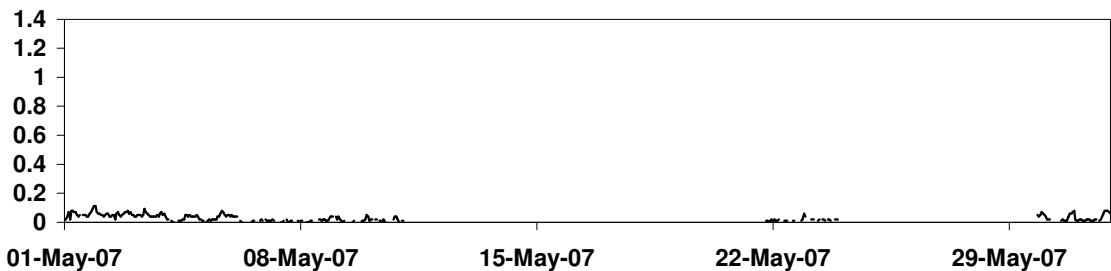
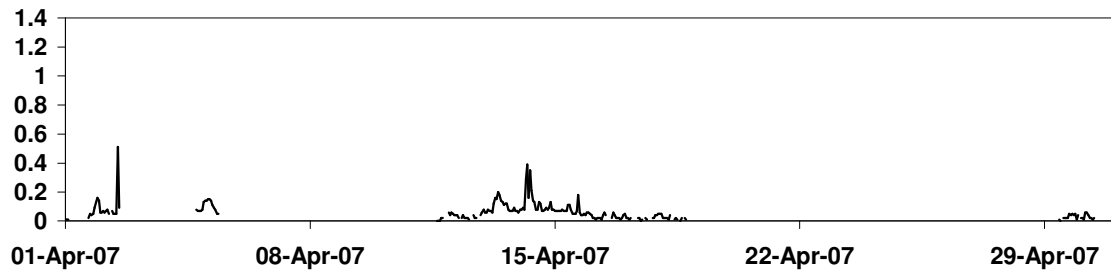
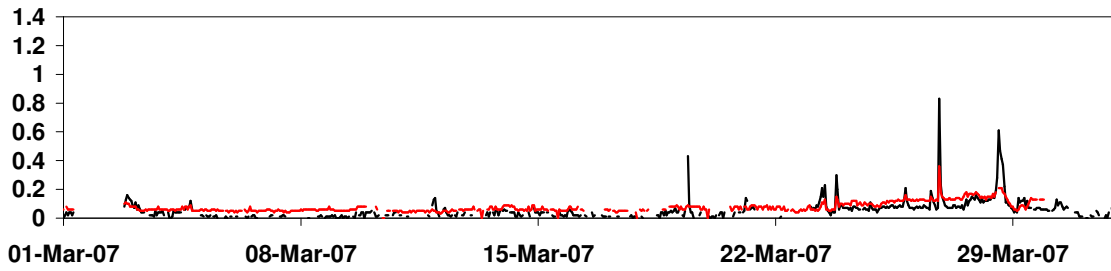
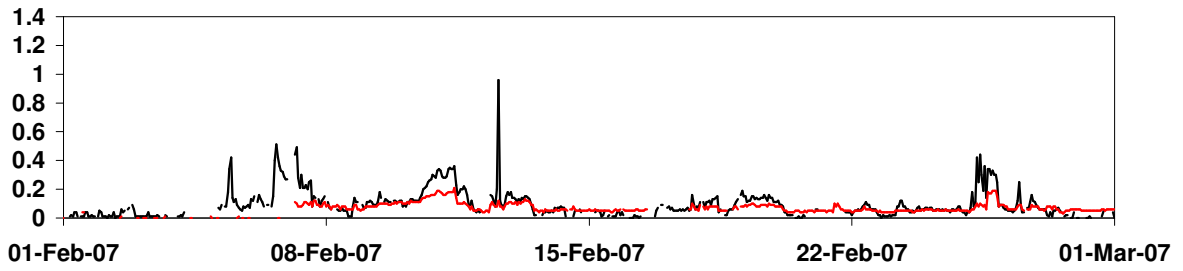
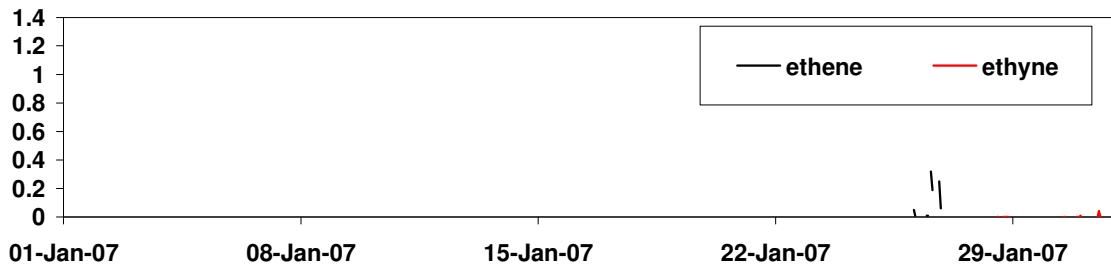
## 1,3-butadiene/1-butene $\mu\text{g m}^{-3}$



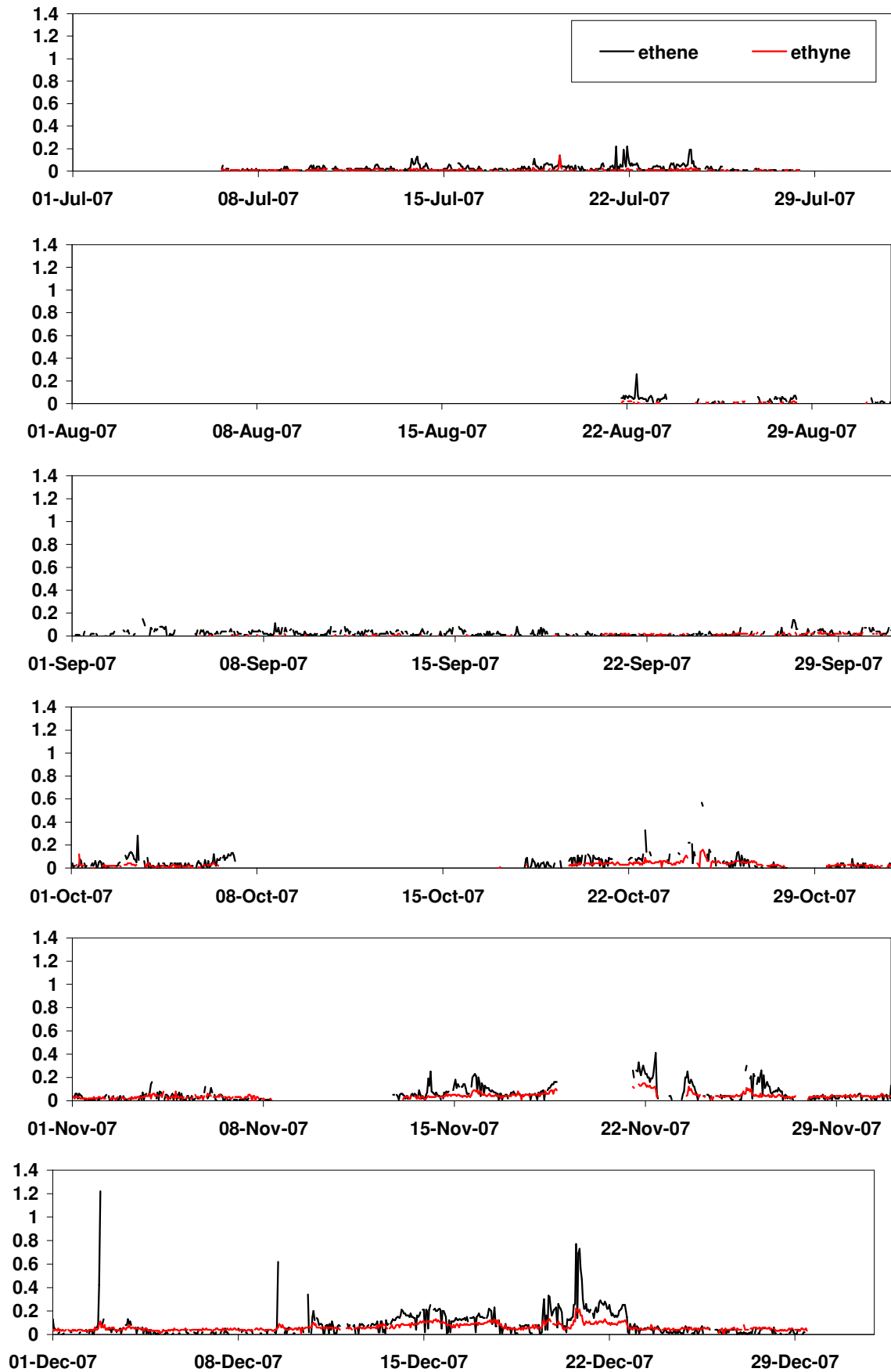
## 1,3-butadiene/1-butene $\mu\text{g m}^{-3}$



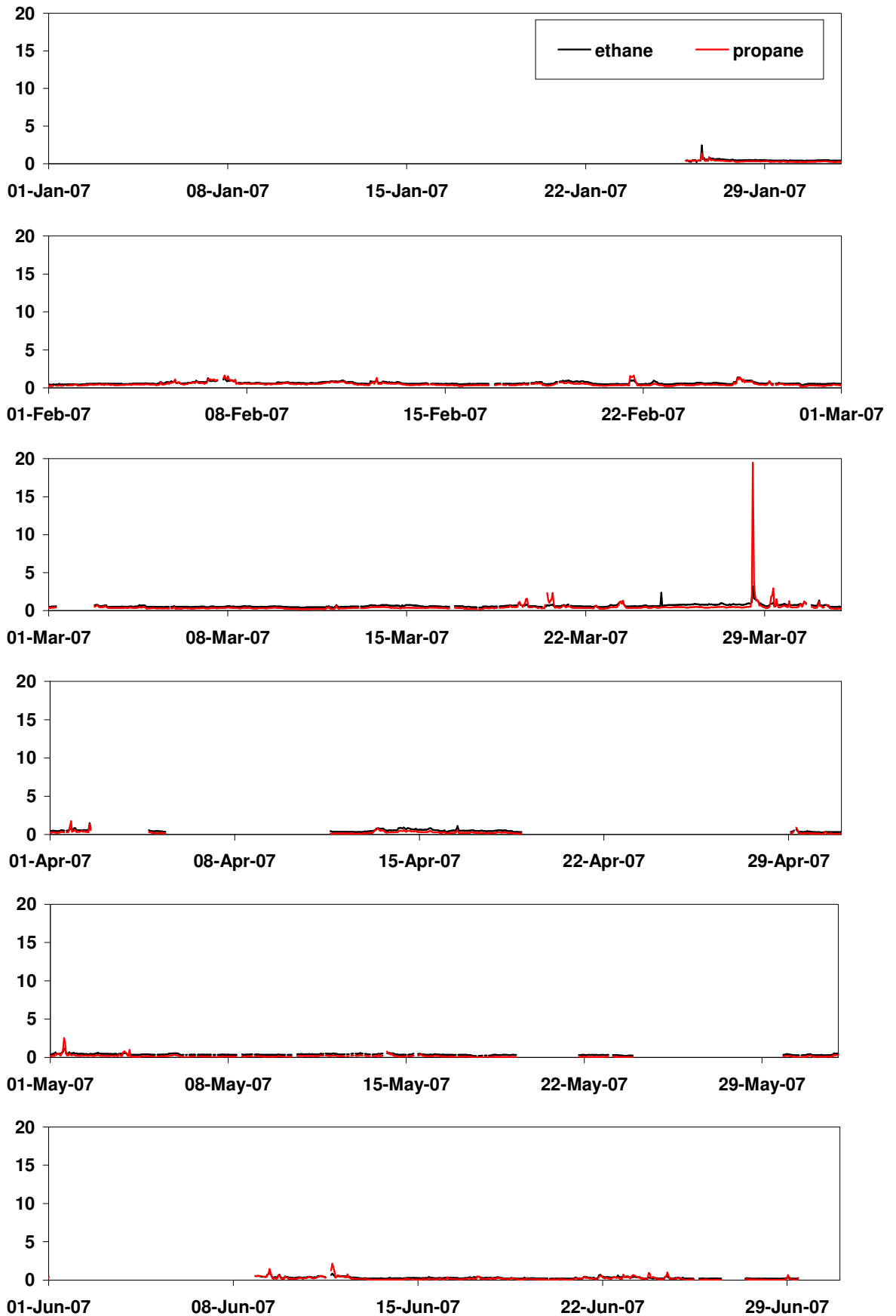
# ethene/ethyne $\mu\text{g m}^{-3}$



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

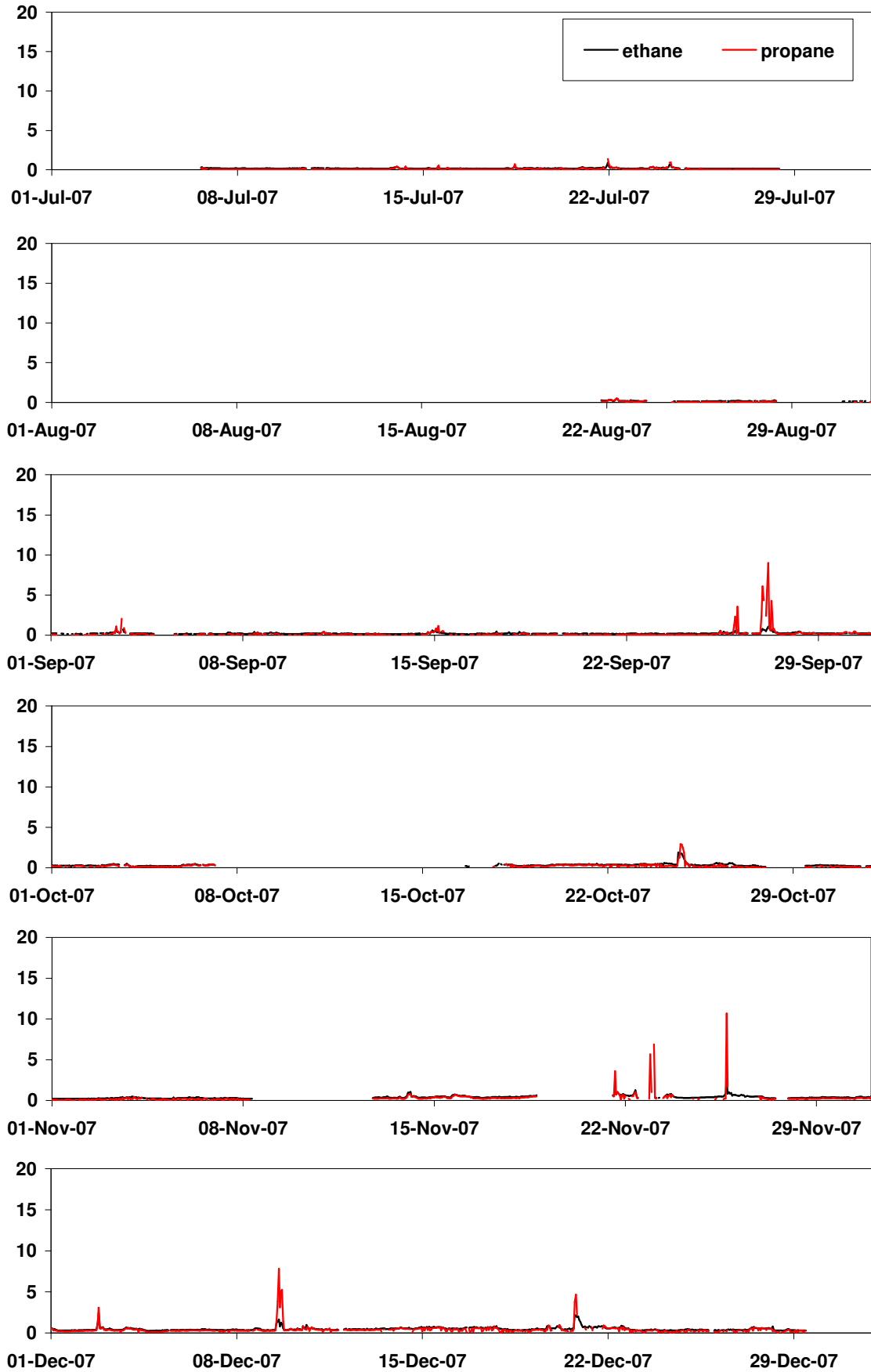


# ethane/propane $\mu\text{g m}^{-3}$

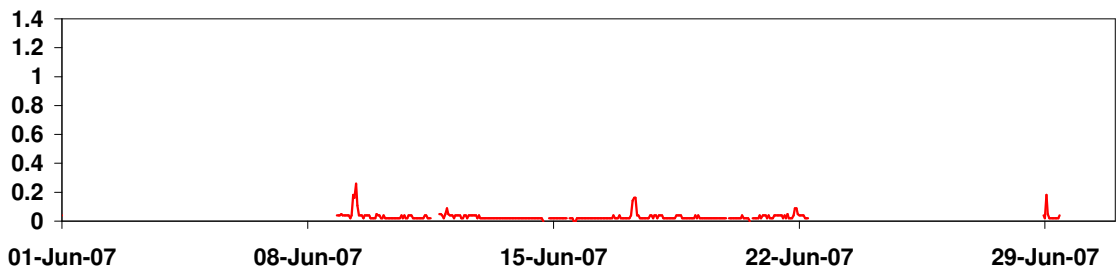
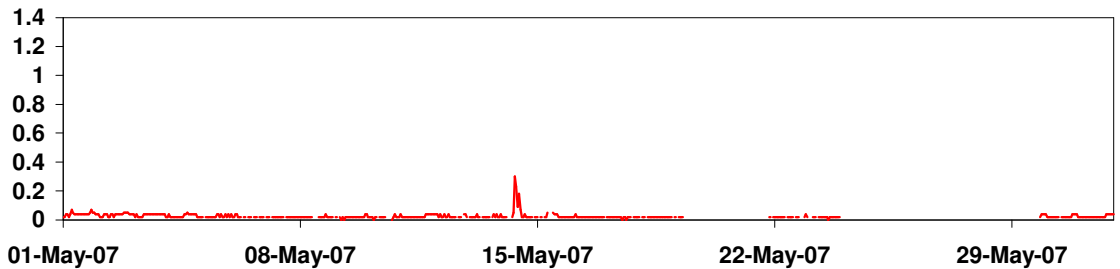
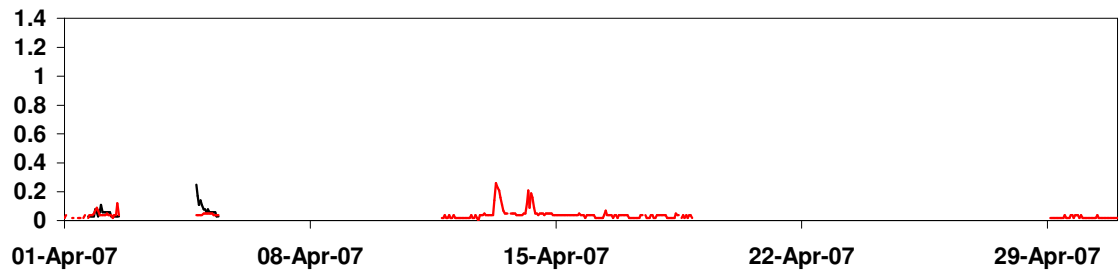
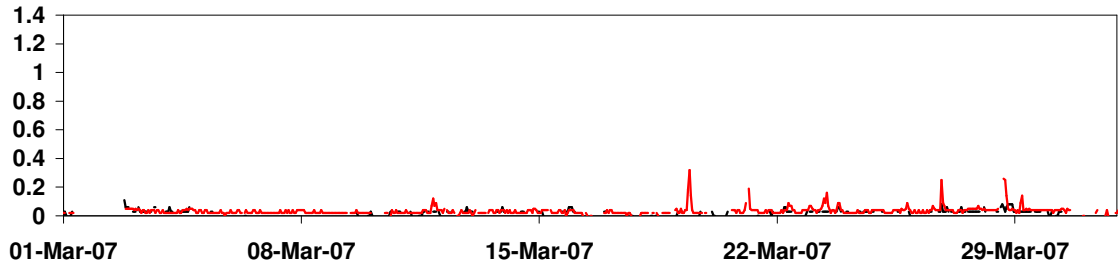
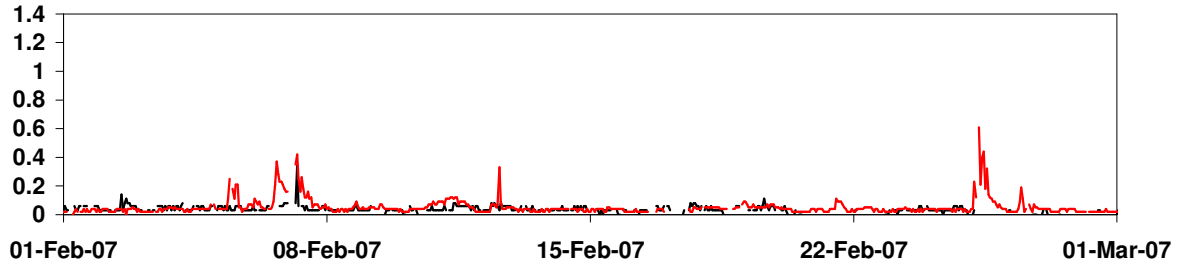
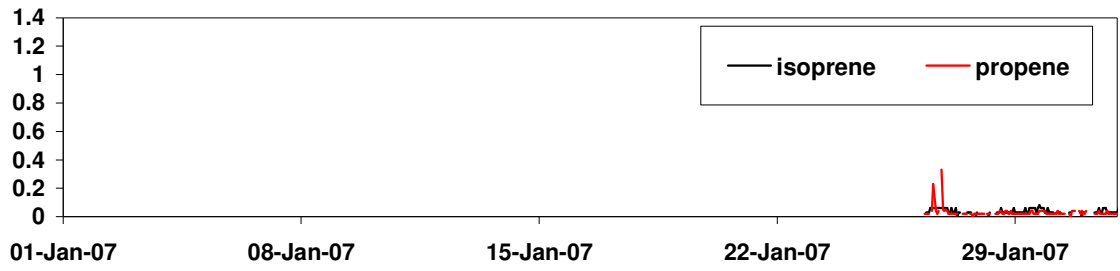




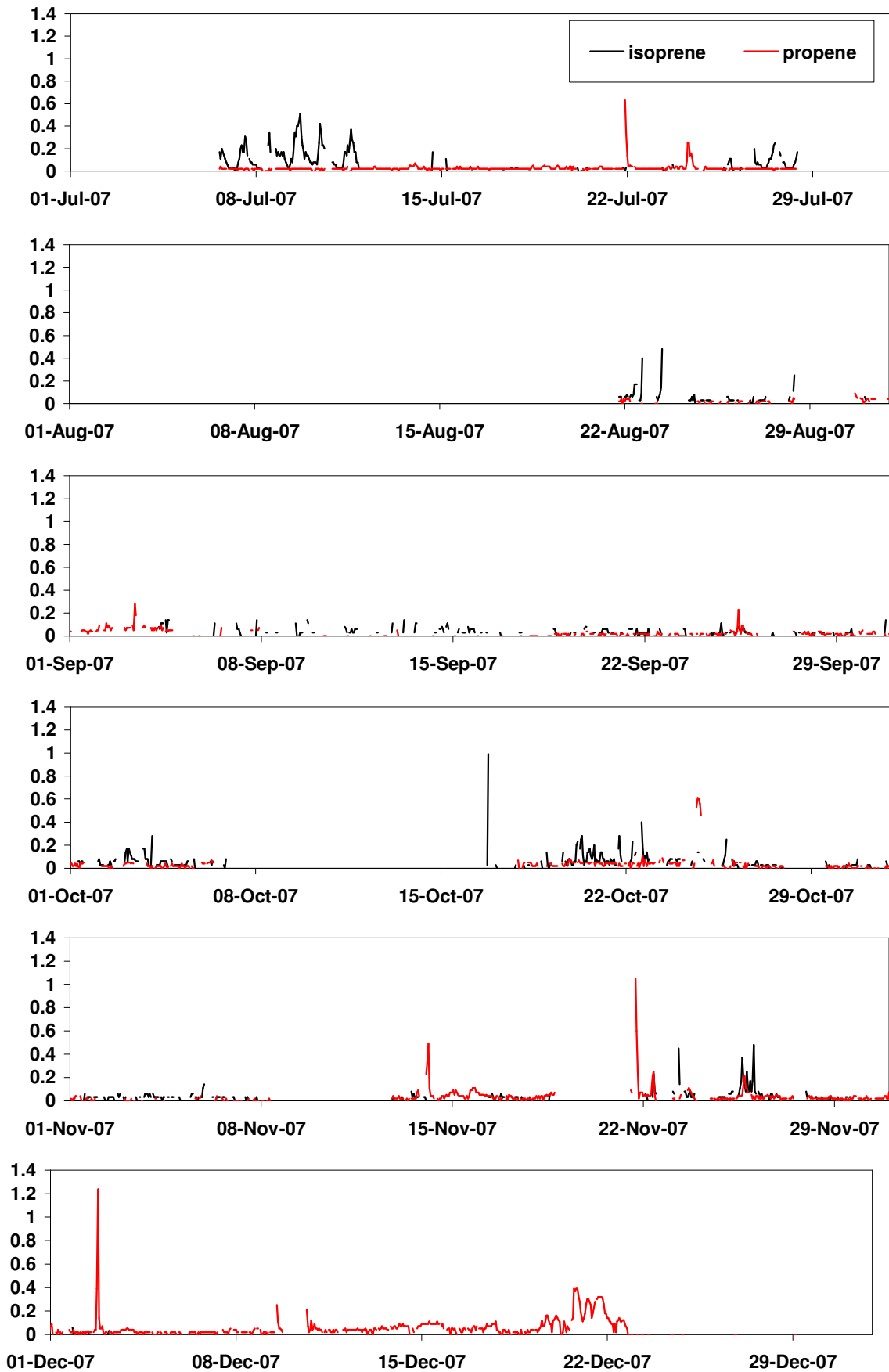
### ethane/propane $\mu\text{g m}^{-3}$



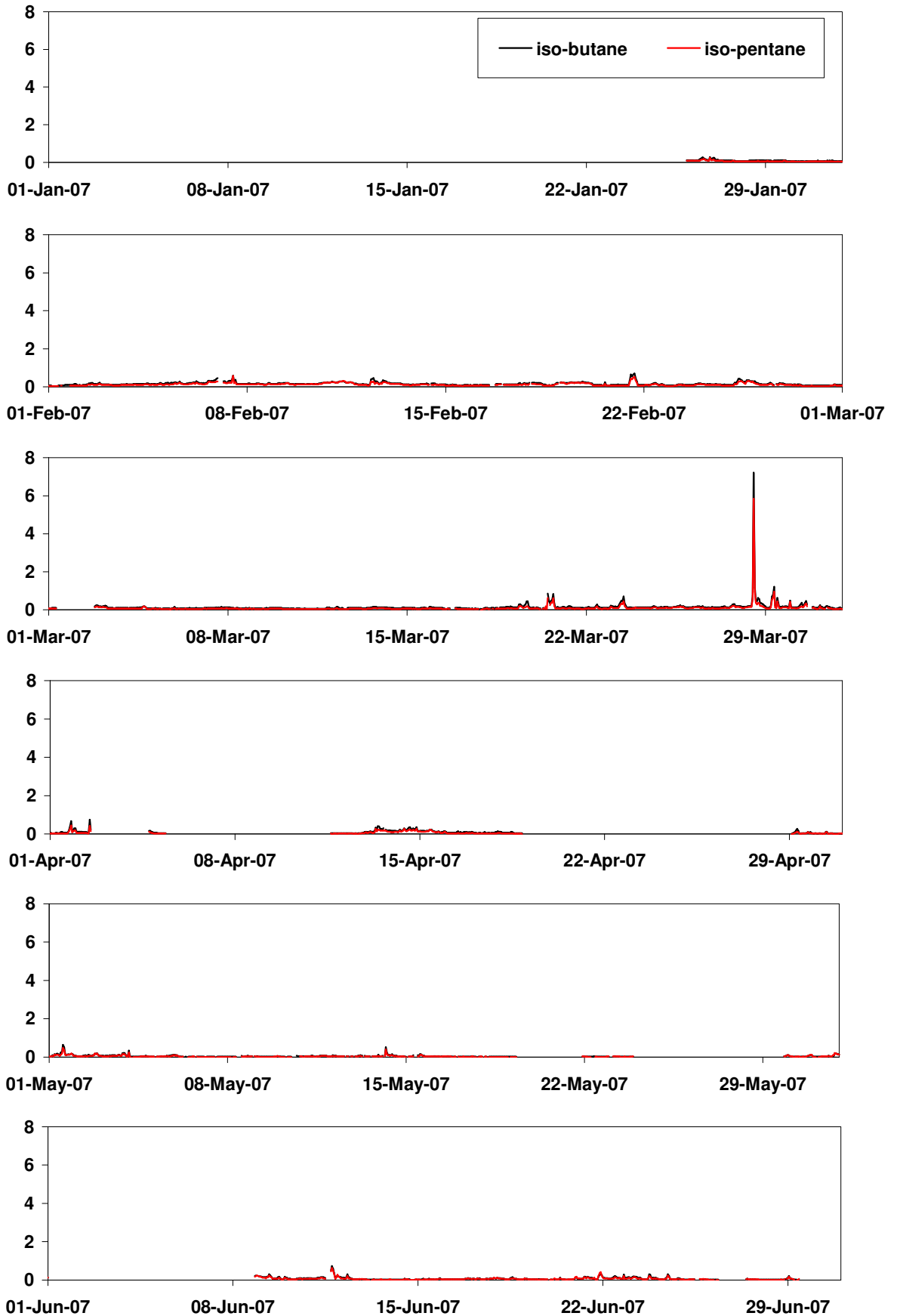
### isoprene/propene $\mu\text{g m}^{-3}$



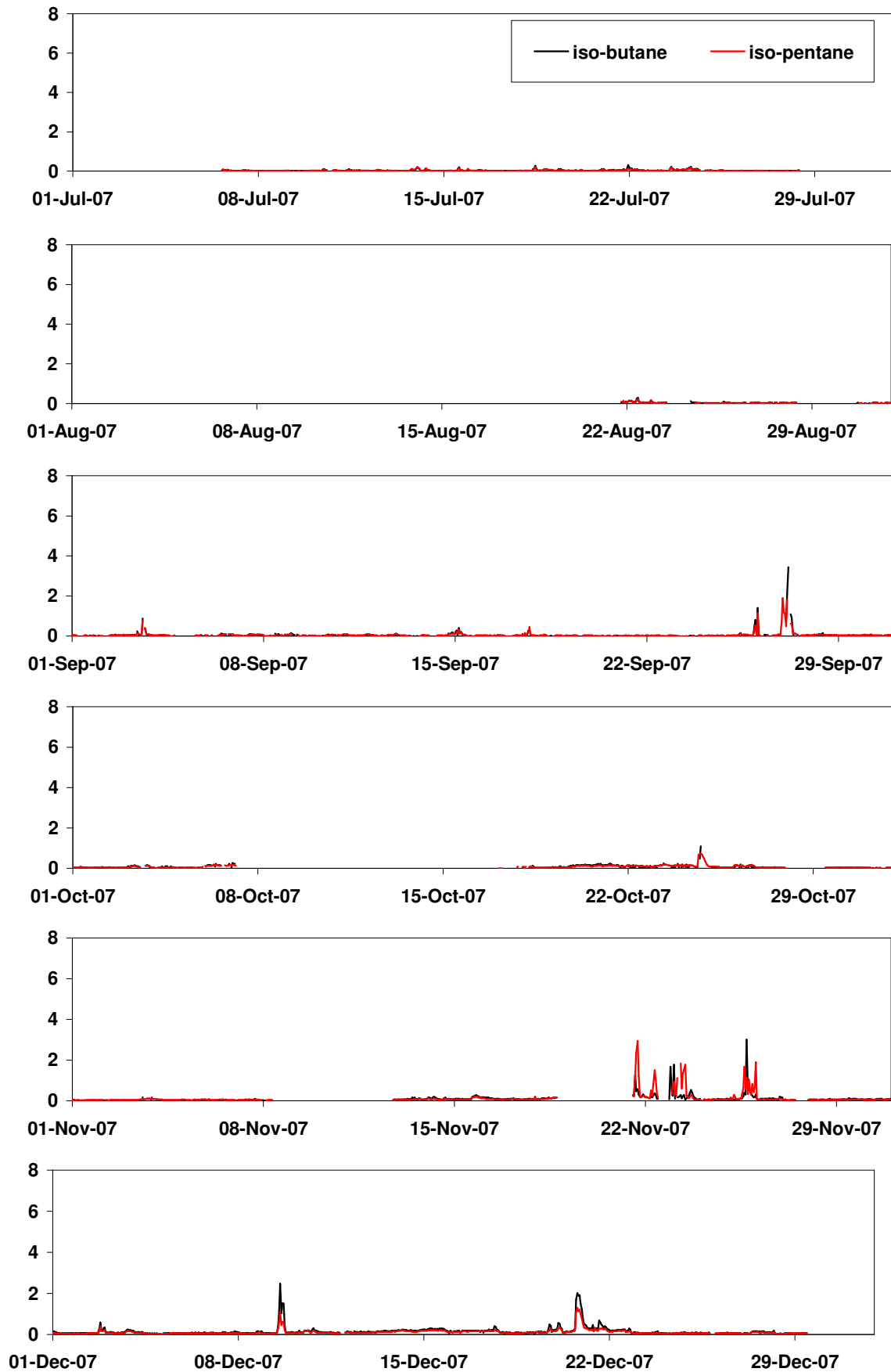
### isoprene/propene $\mu\text{g m}^{-3}$



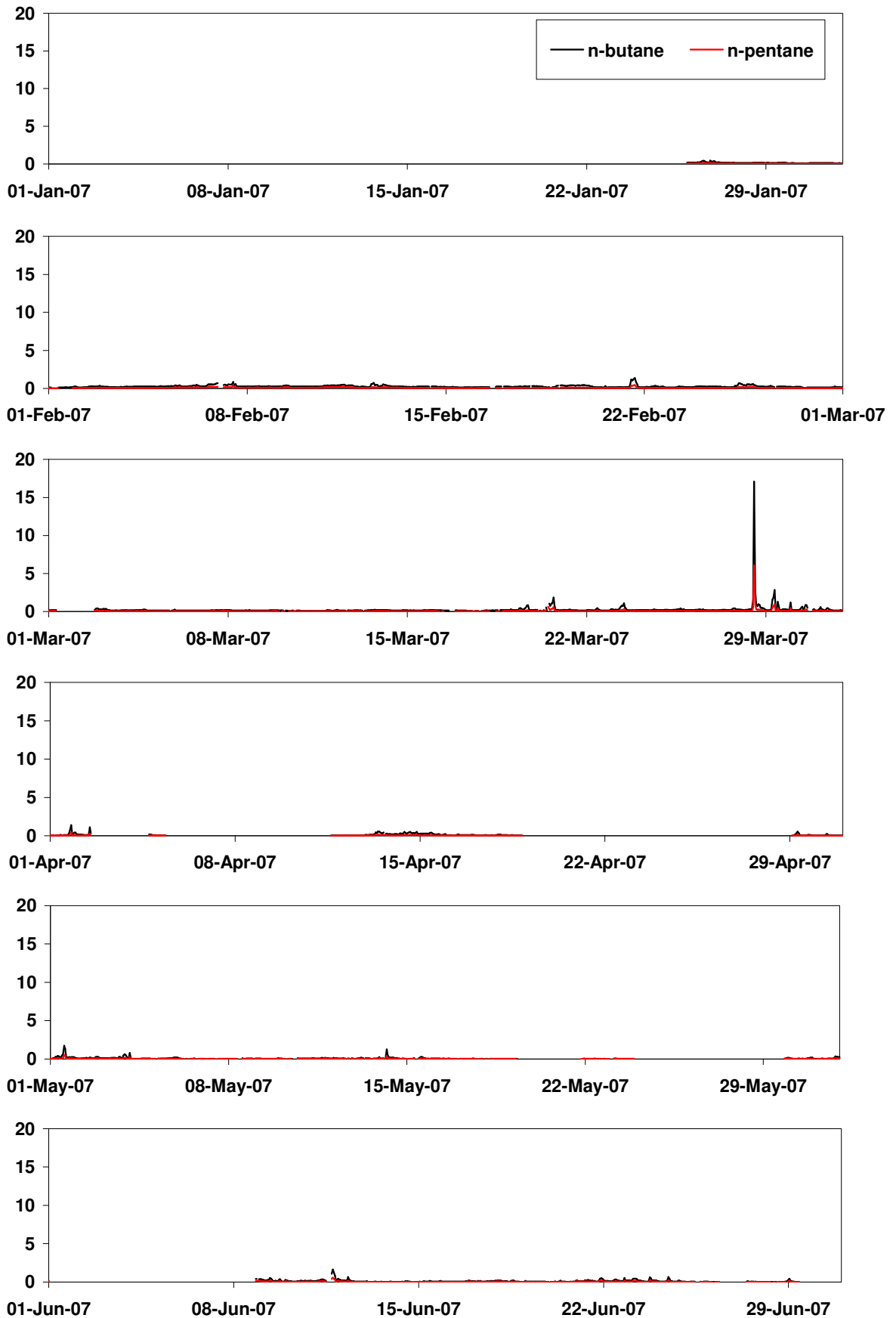
### iso-butane/iso-pentane $\mu\text{g m}^{-3}$



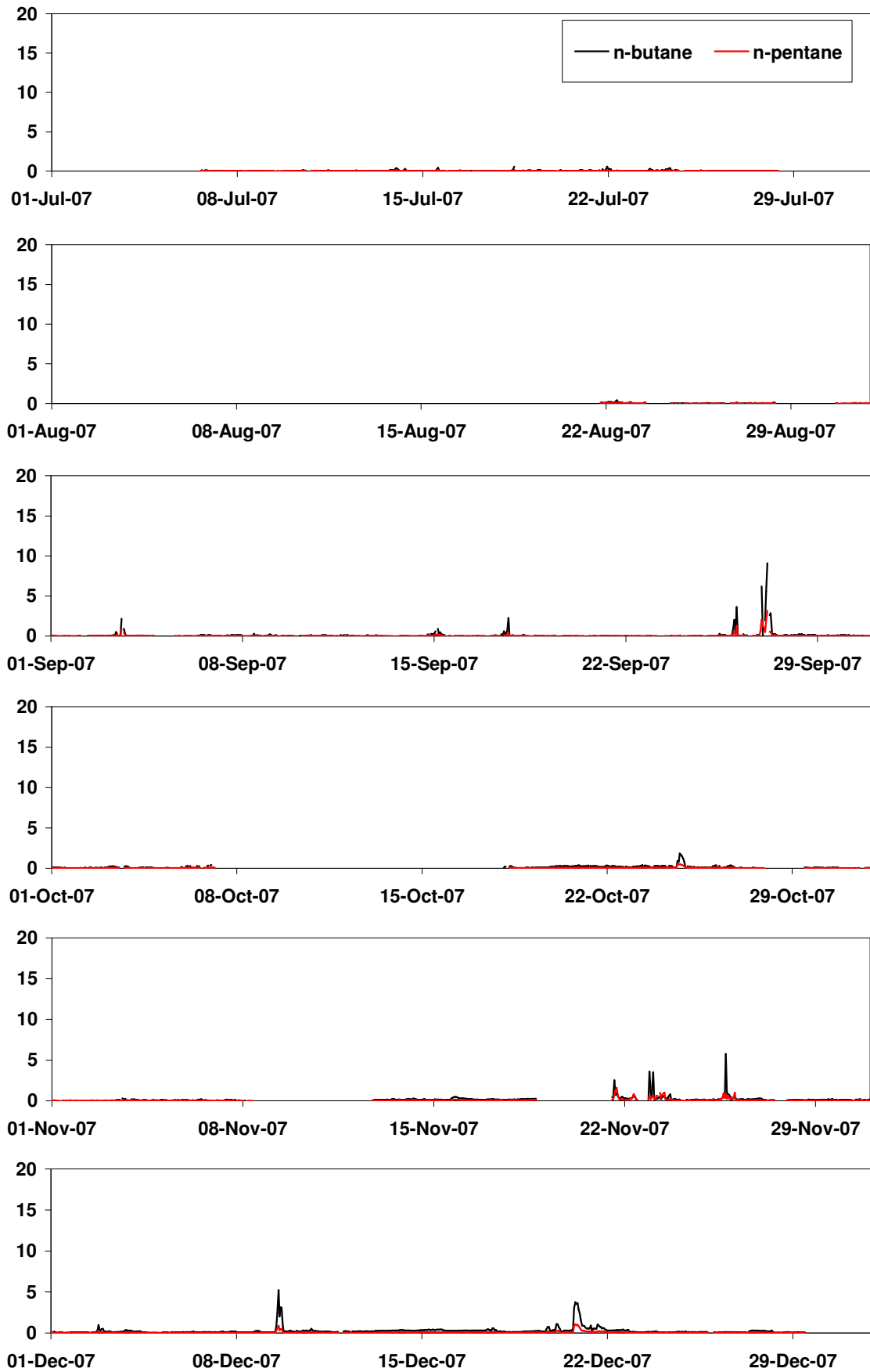
### iso-butane/iso-pentane $\mu\text{g m}^{-3}$



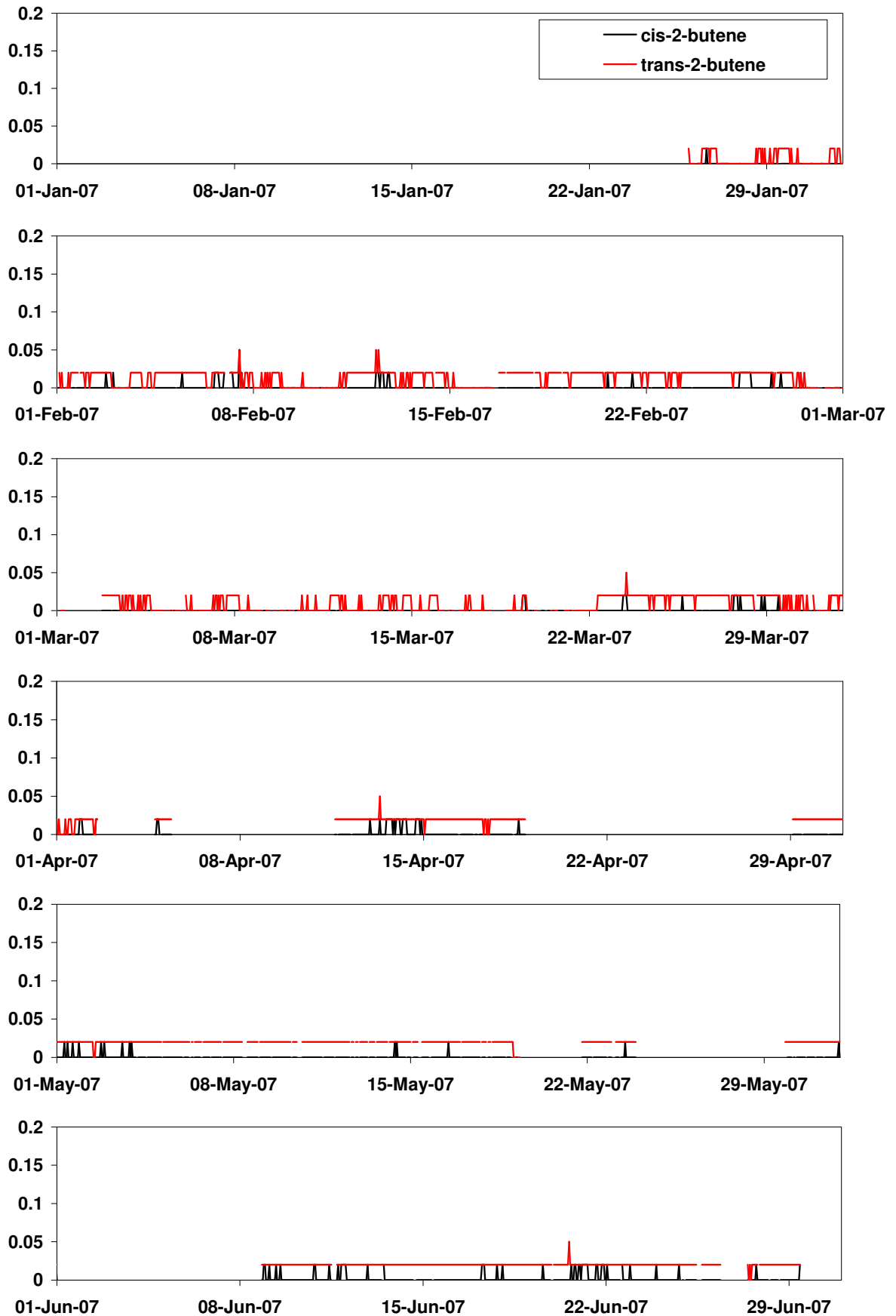
### n-butane/n-pentane $\mu\text{g m}^{-3}$



### n-butane/n-pentane $\mu\text{g m}^{-3}$

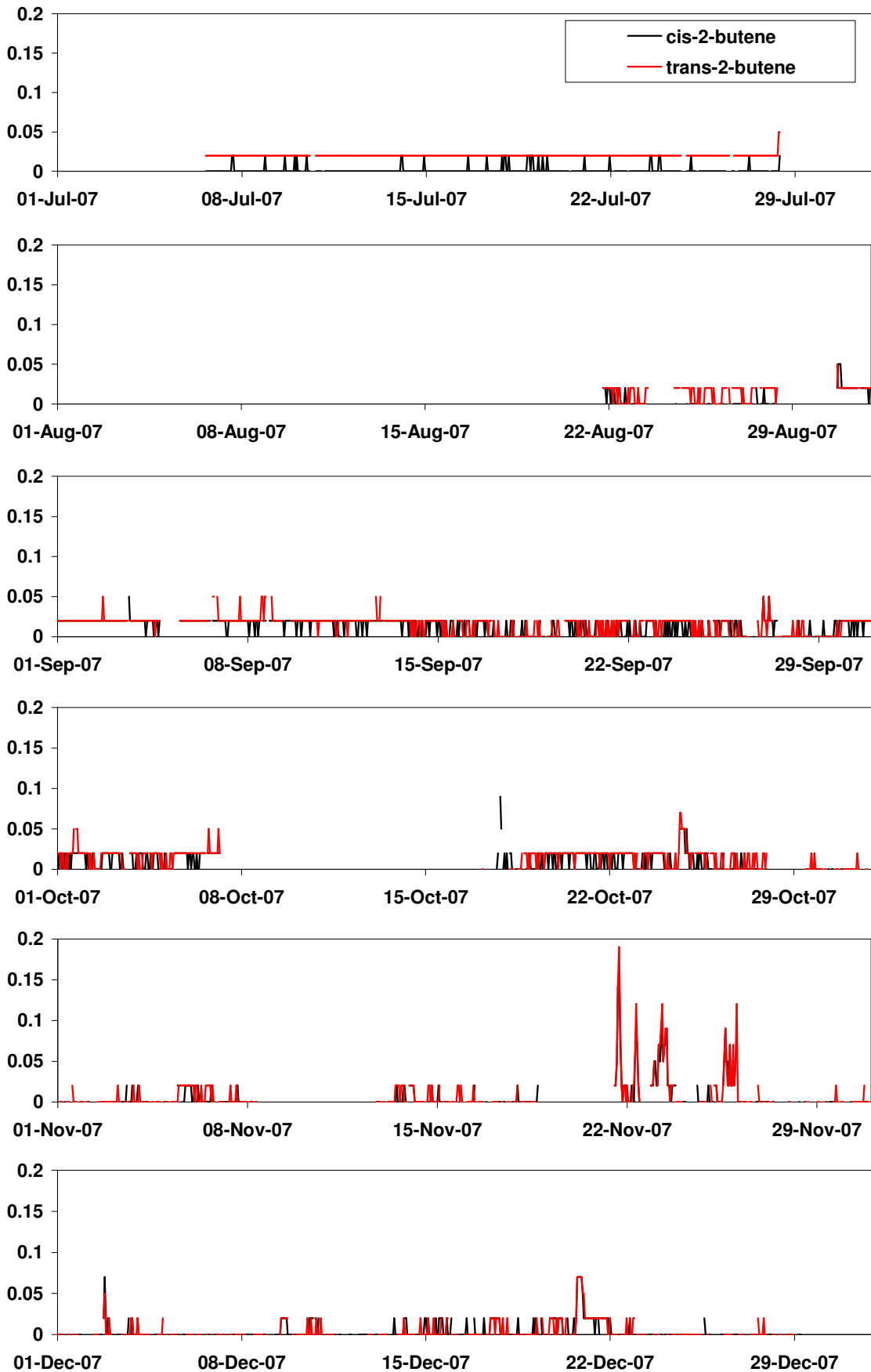


### cis-2-butene/trans-2-butene $\mu\text{g m}^{-3}$

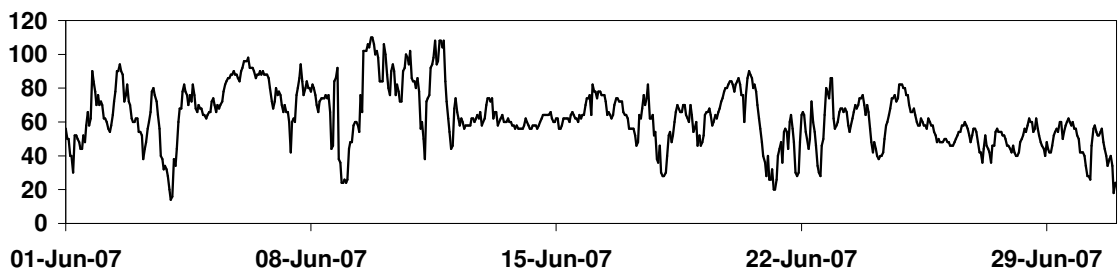
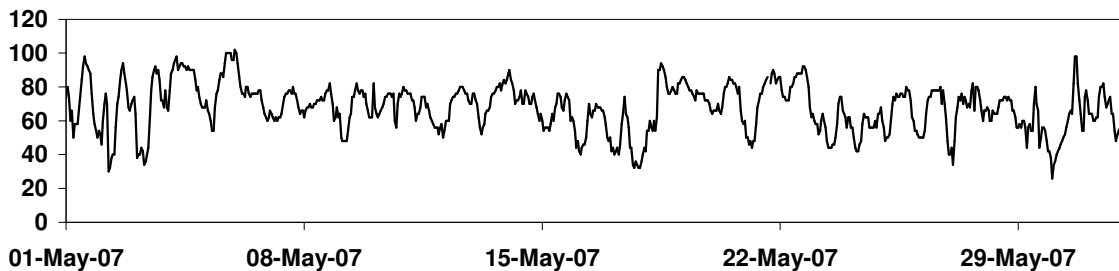
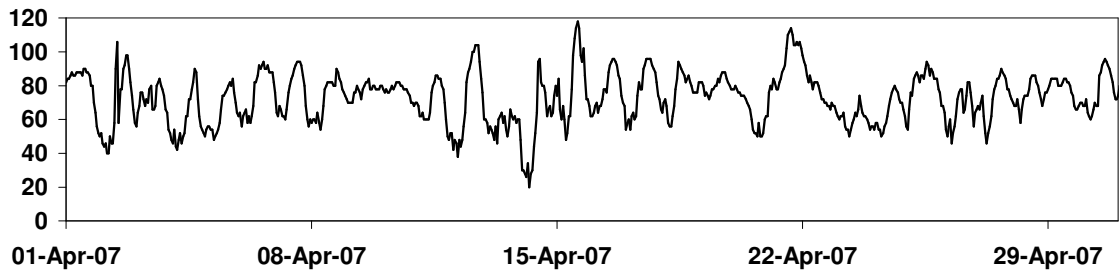
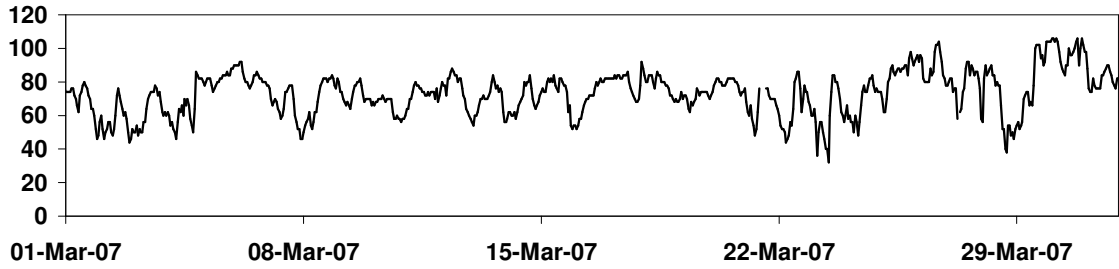
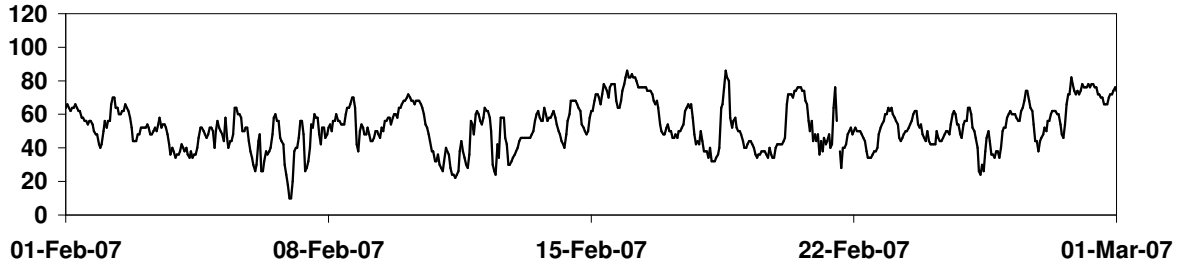
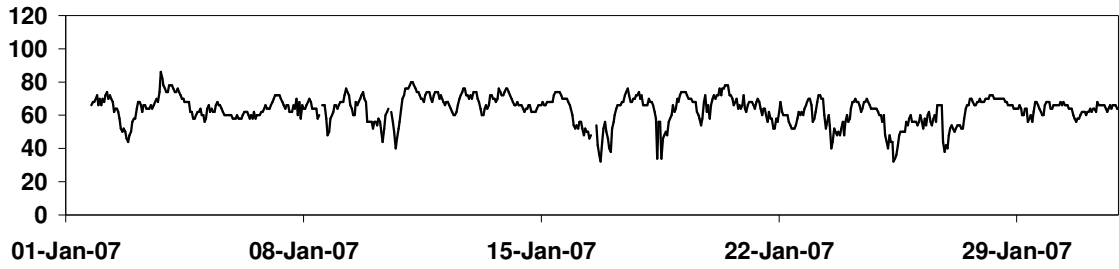




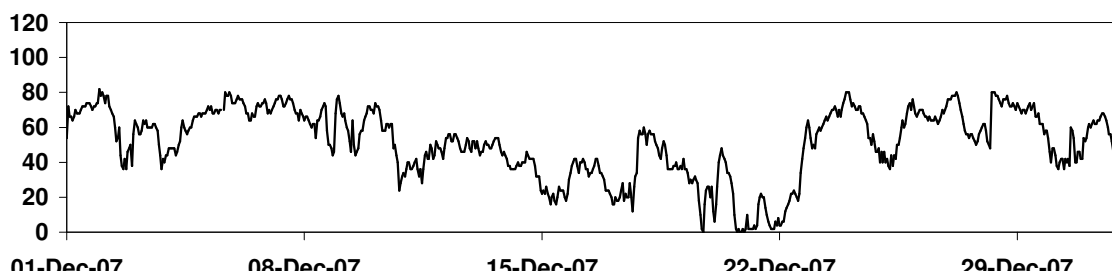
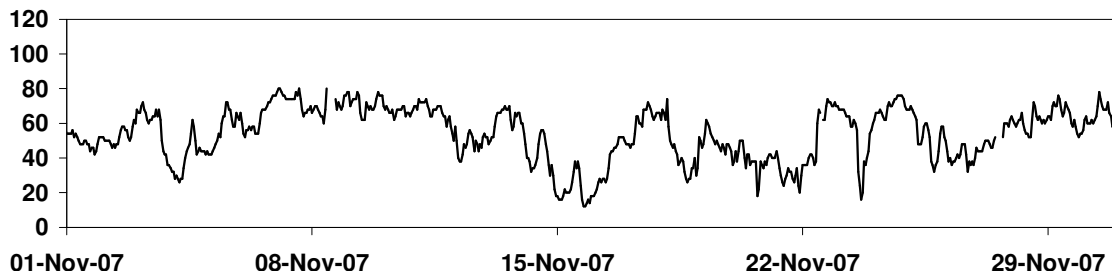
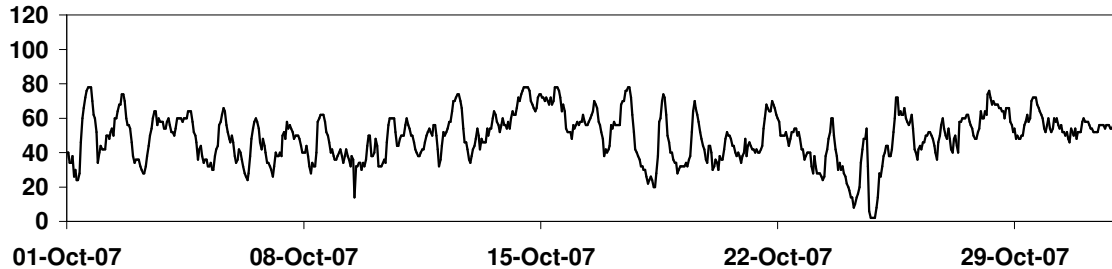
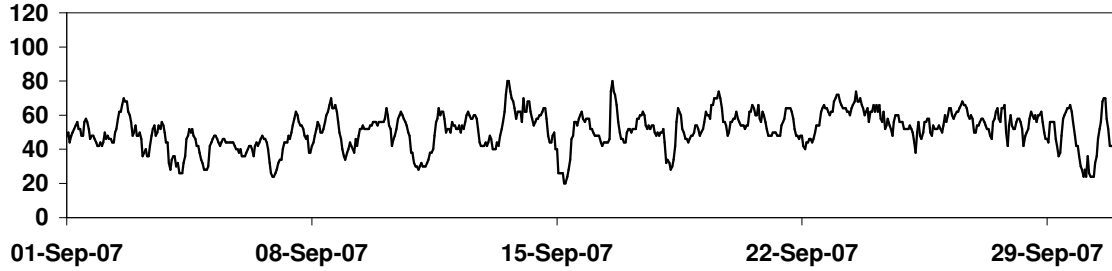
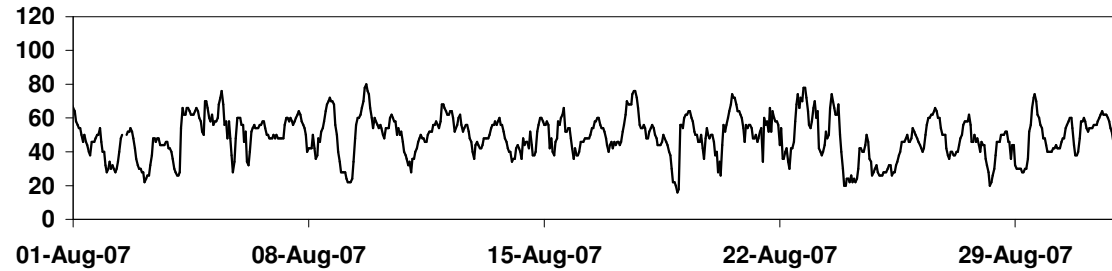
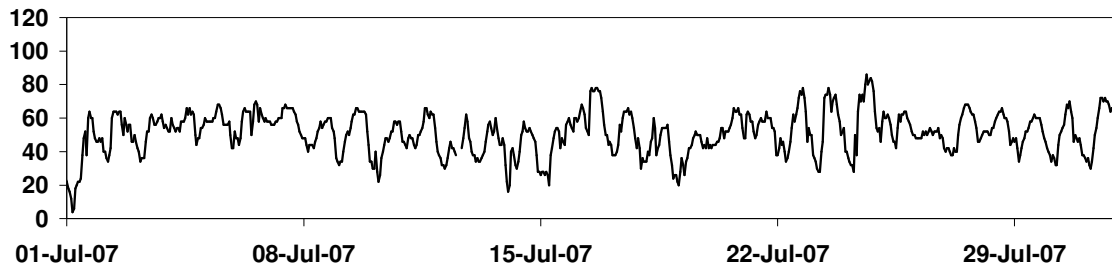
### cis-2-butene/trans-2-butene $\mu\text{g m}^{-3}$



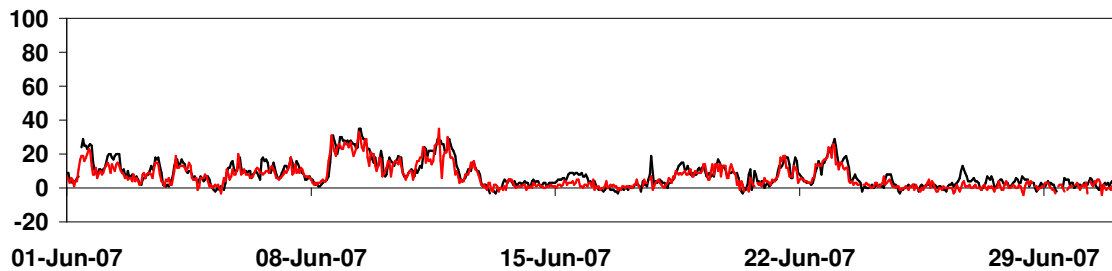
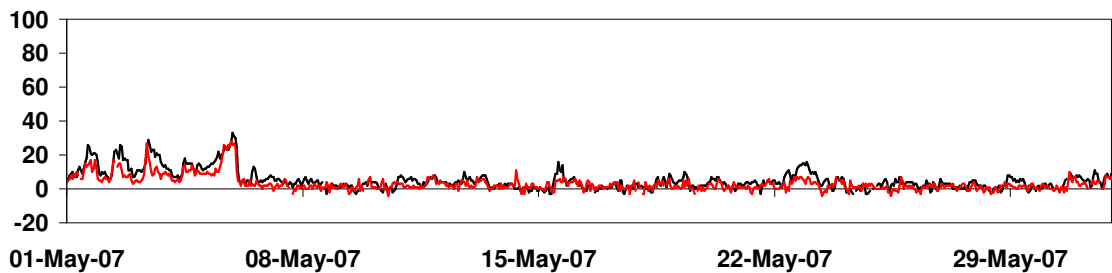
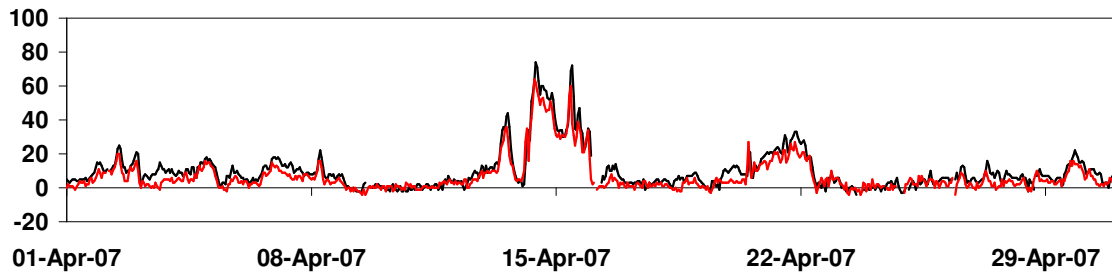
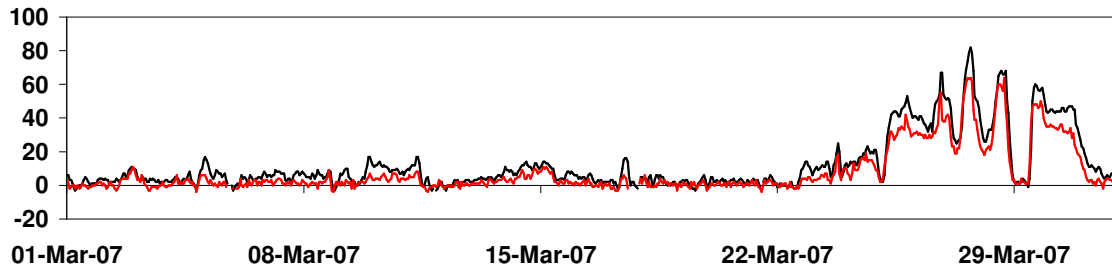
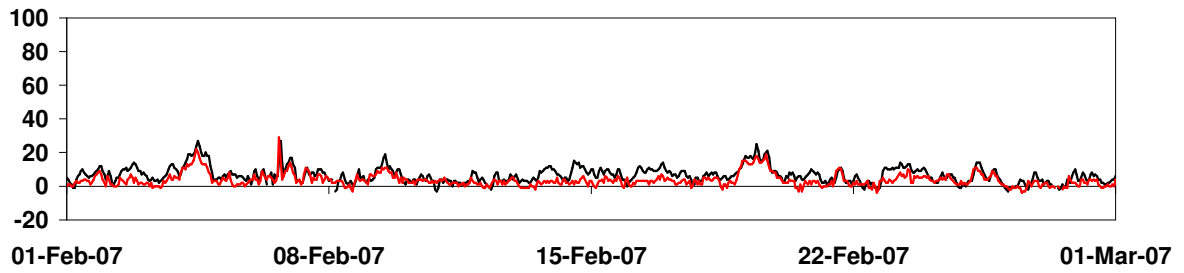
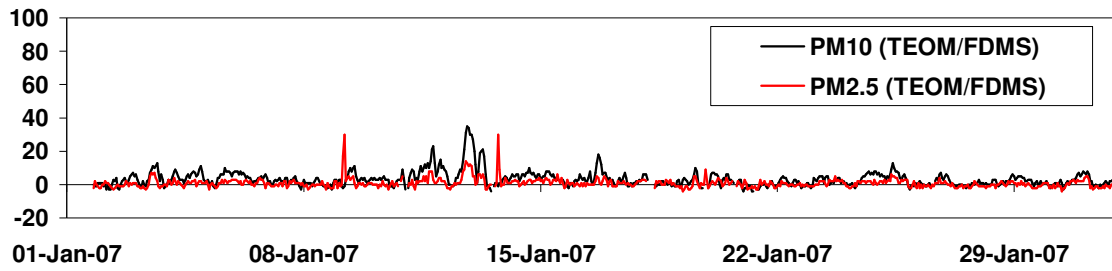
### Ozone (AURN) $\mu\text{g m}^{-3}$



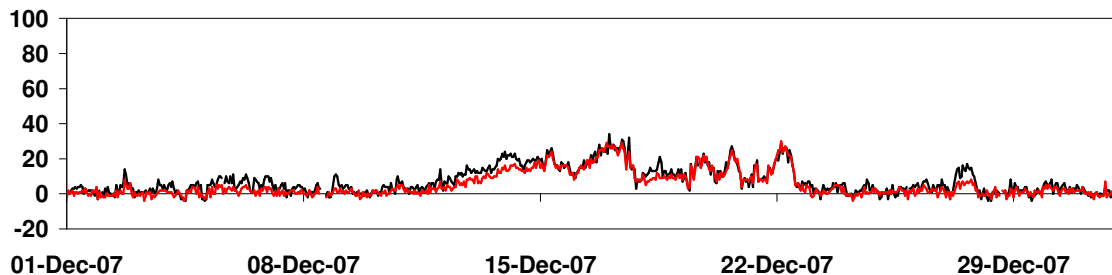
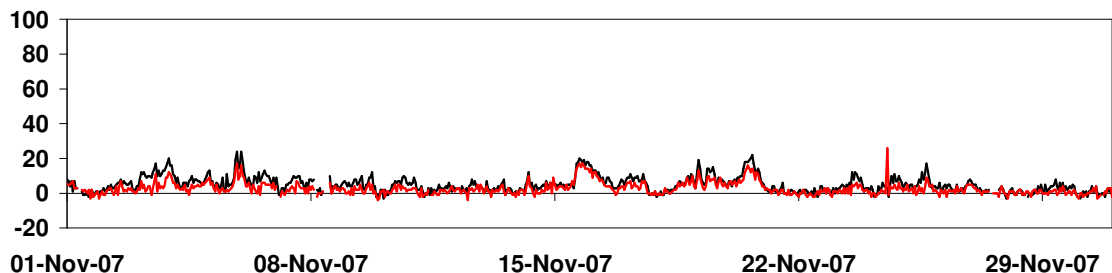
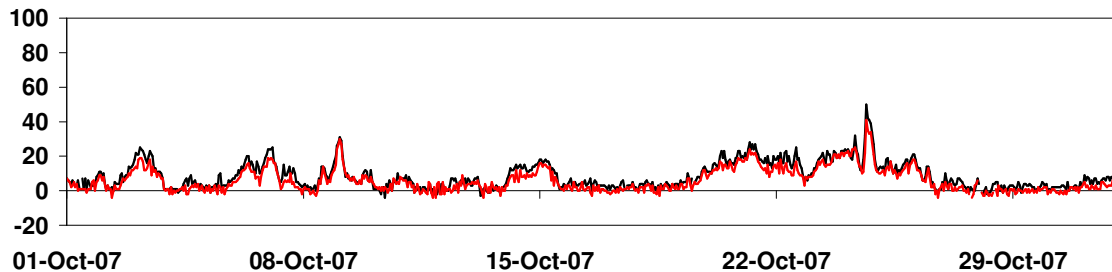
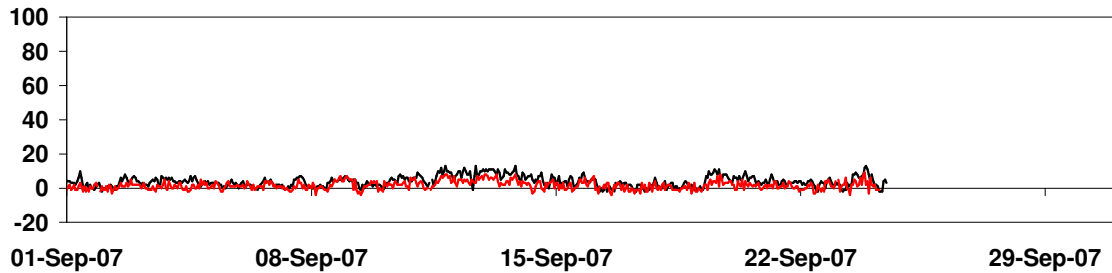
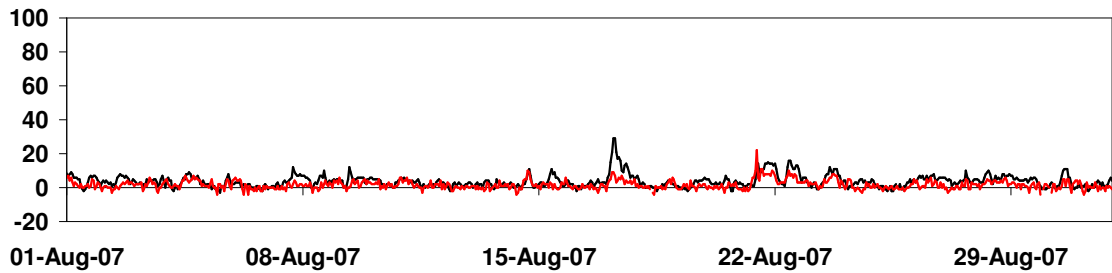
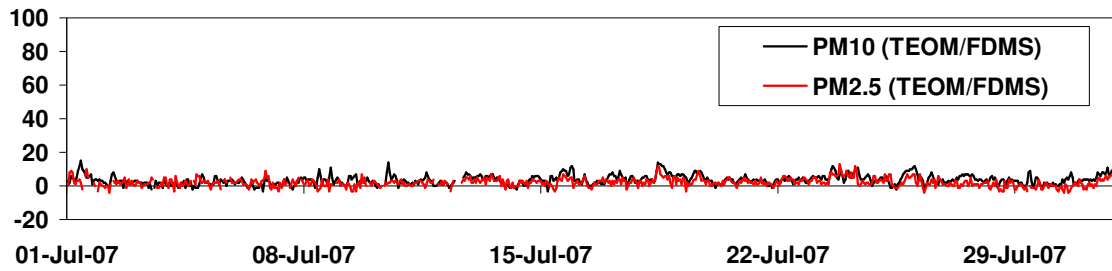
### Ozone (AURN) $\mu\text{g m}^{-3}$



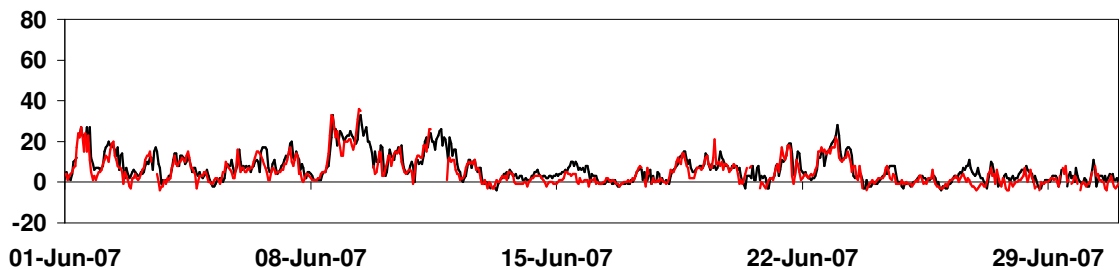
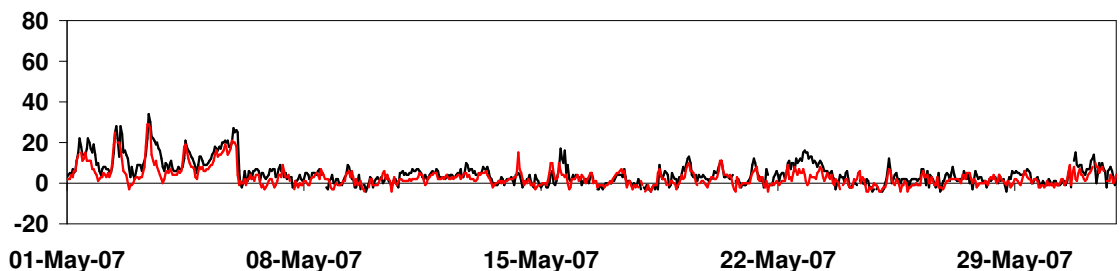
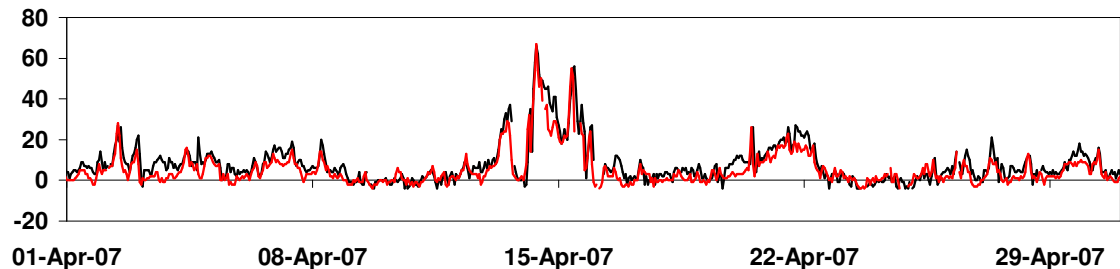
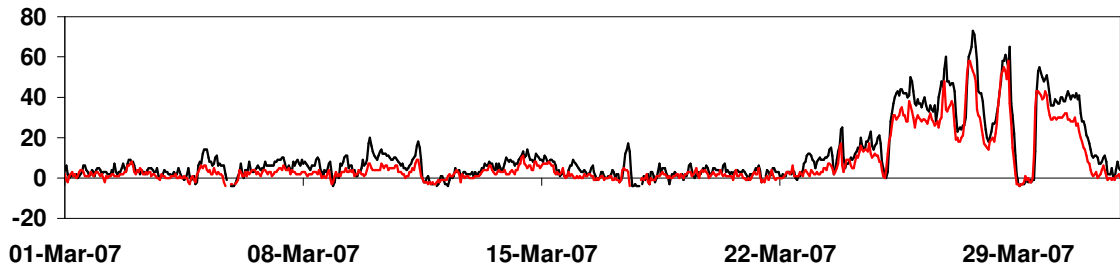
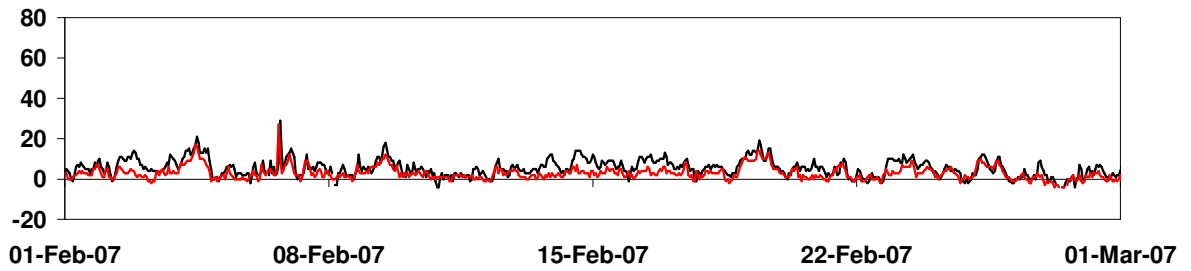
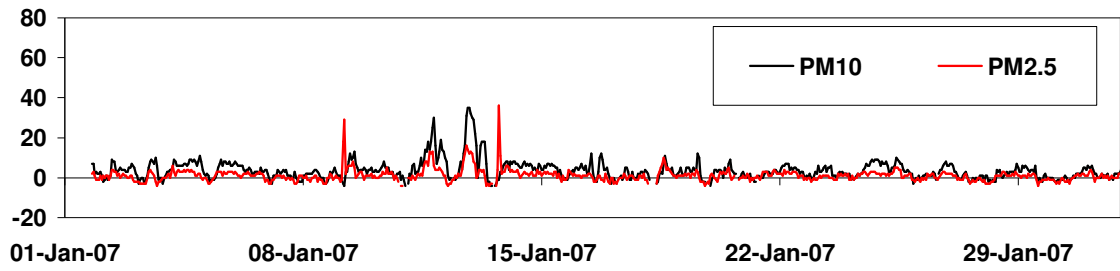
## Particulate matter (TEOM/FDMS) $\mu\text{g m}^{-3}$



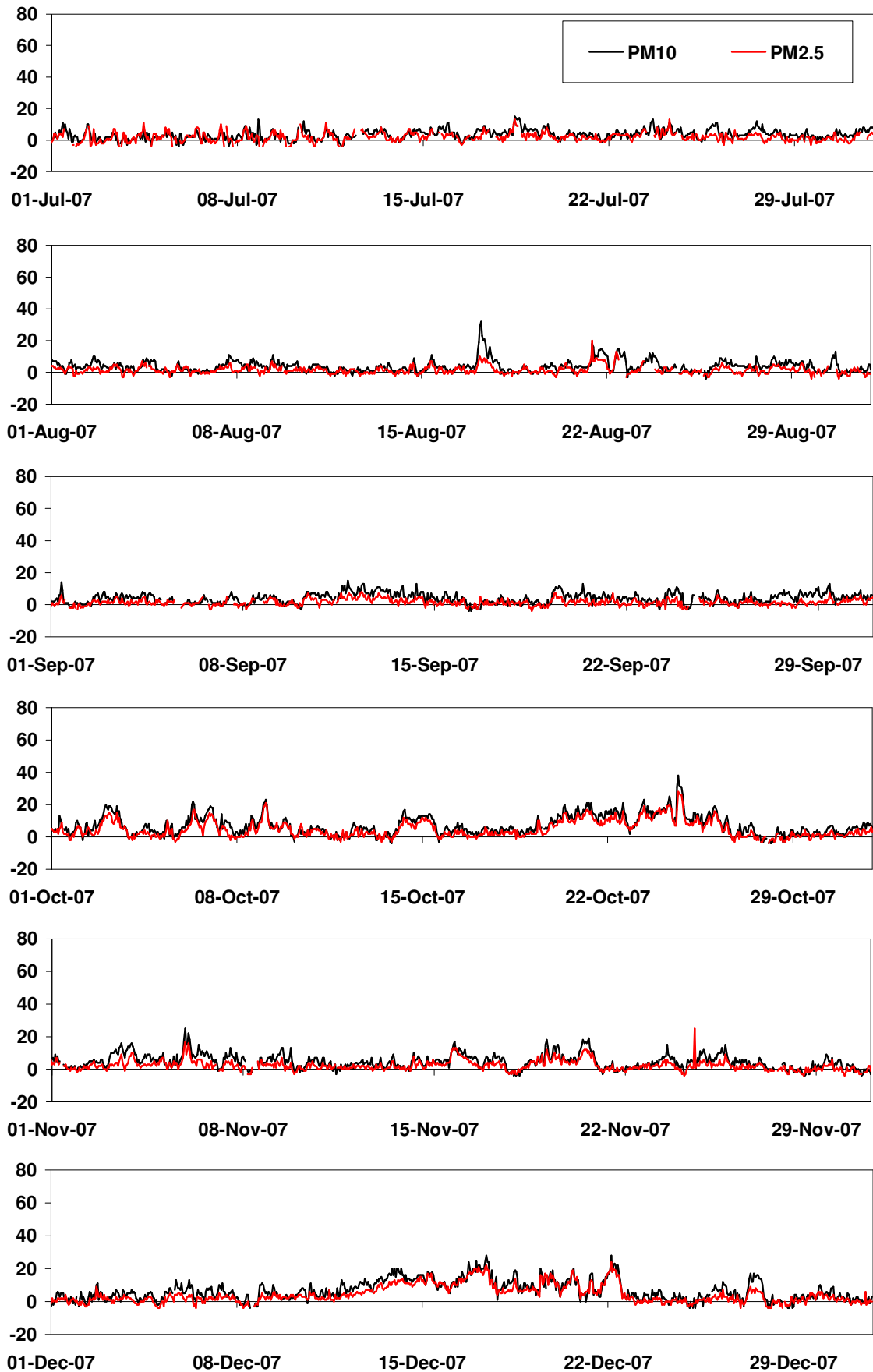
## Particulate matter (TEOM/FDMS) $\mu\text{g m}^{-3}$



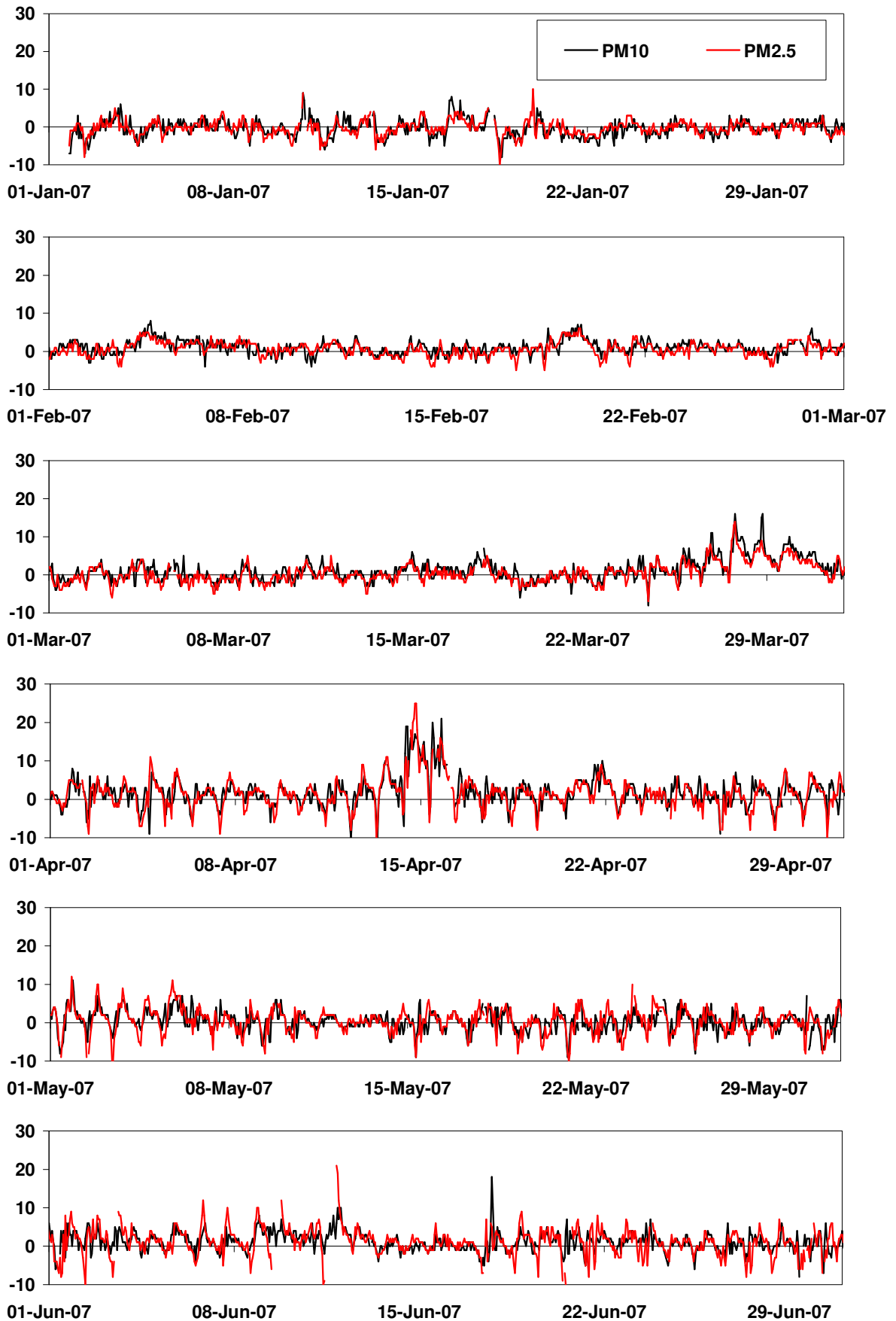
## Non-volatile particulate matter $\mu\text{g m}^{-3}$



## Non-volatile particulate matter $\mu\text{g m}^{-3}$

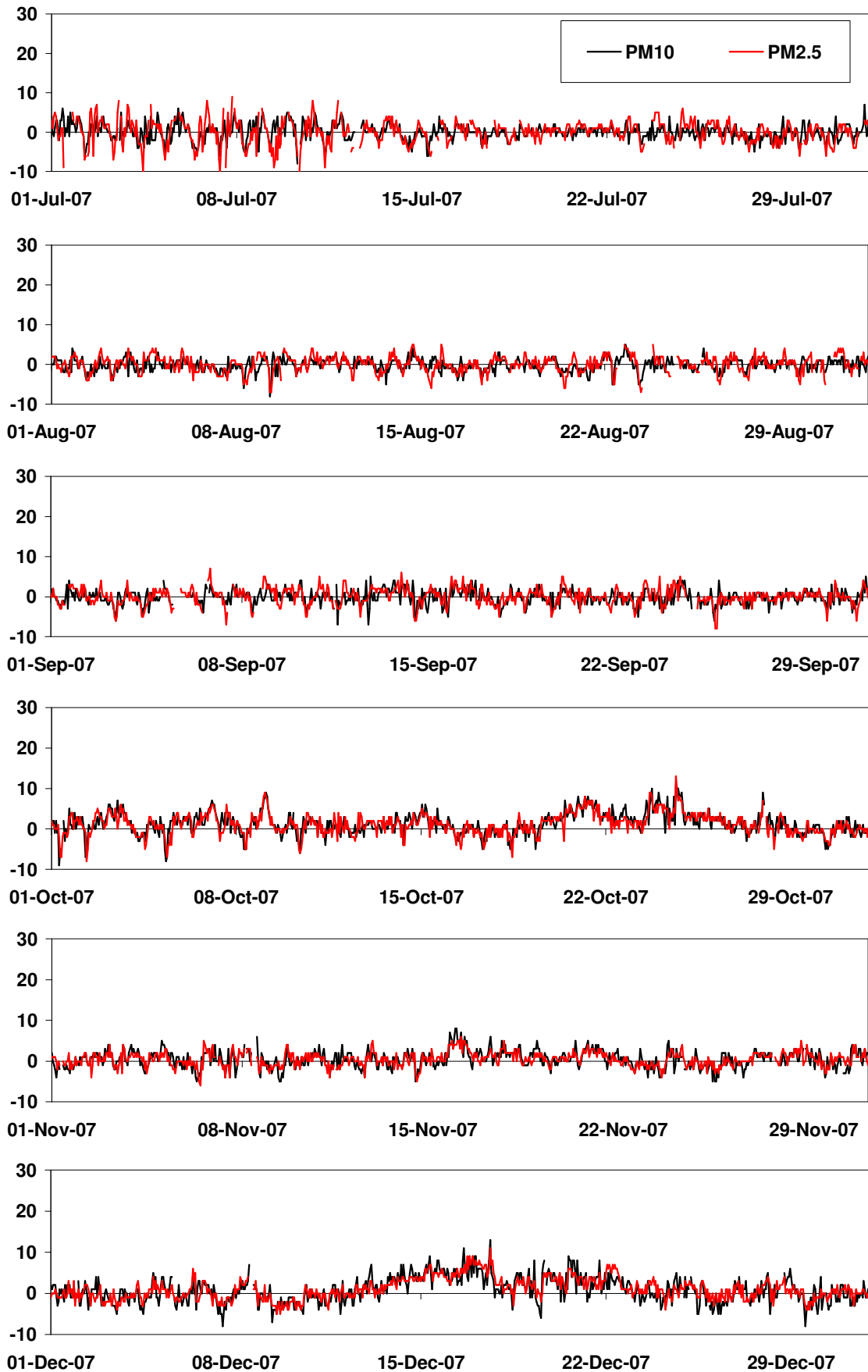


## Volatile particulate matter $\mu\text{g m}^{-3}$

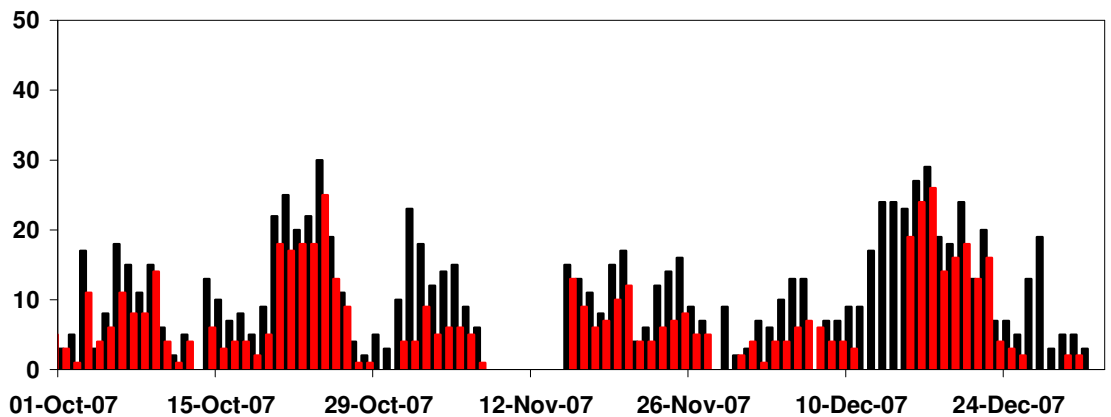
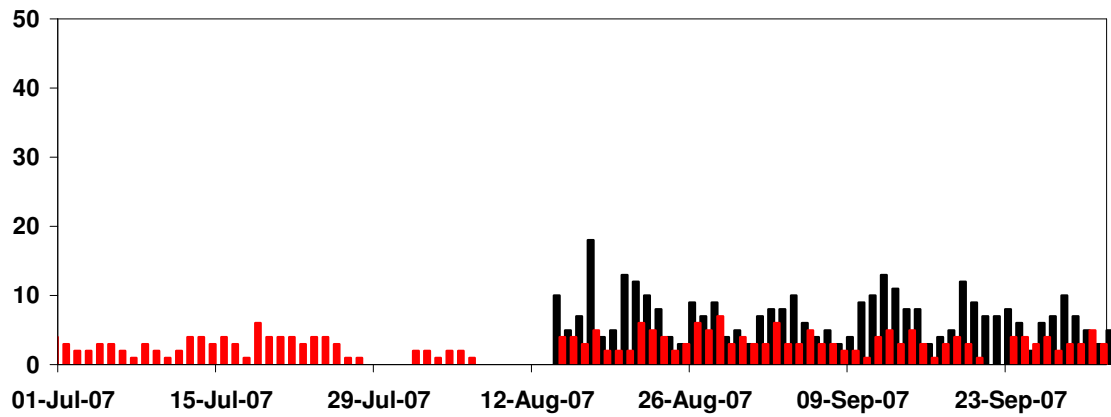
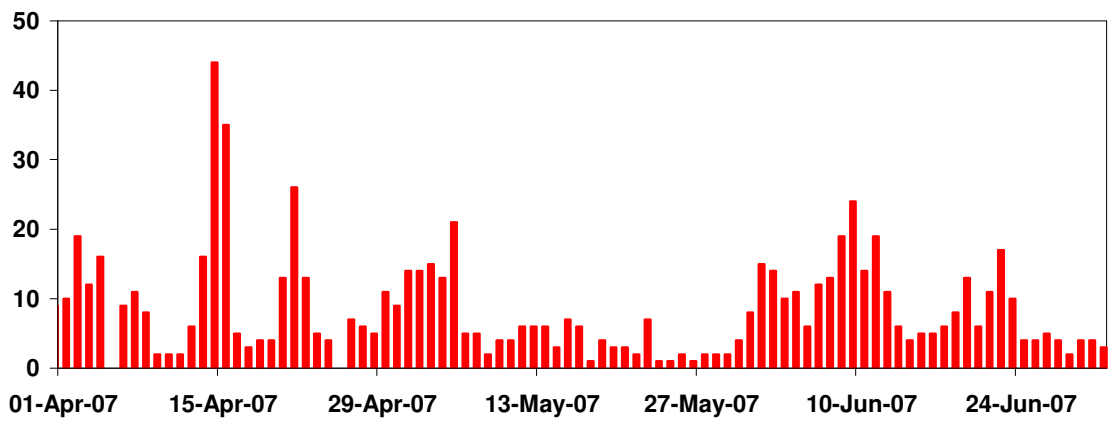
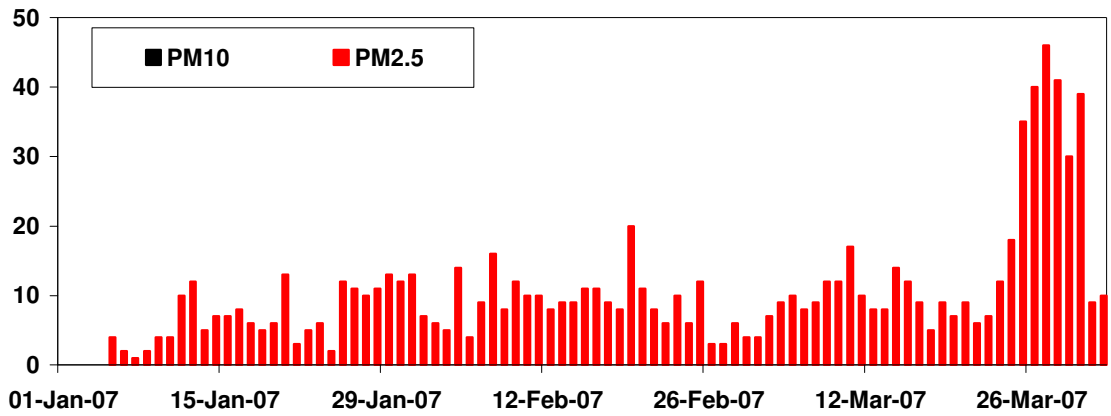




## Volatile particulate matter $\mu\text{g m}^{-3}$

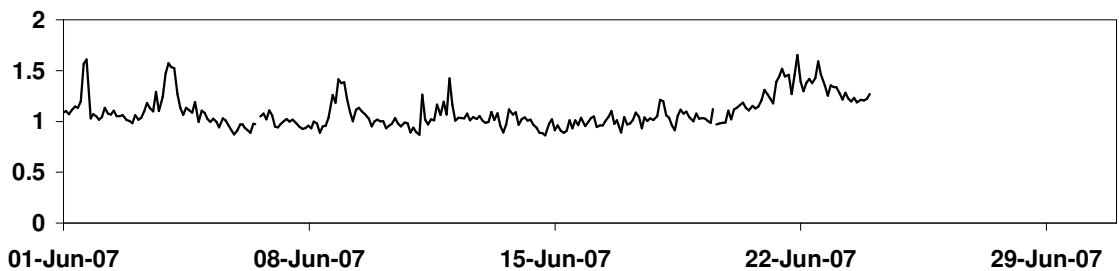
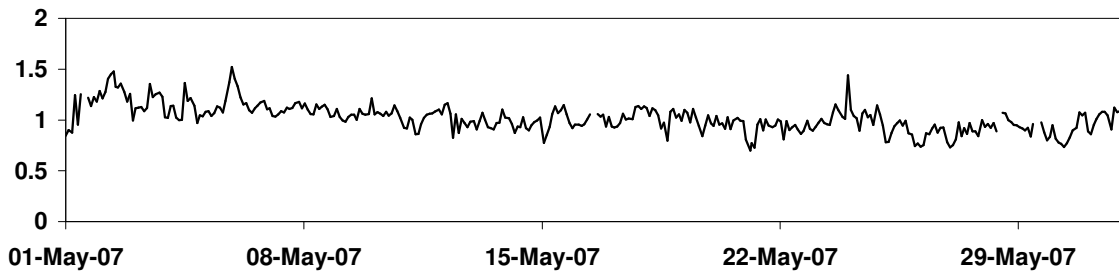
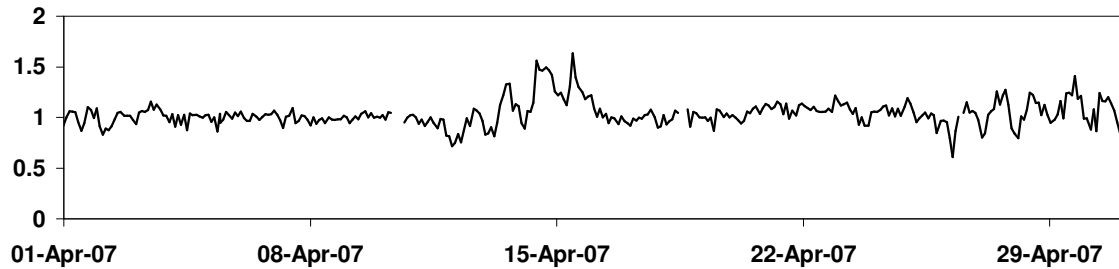
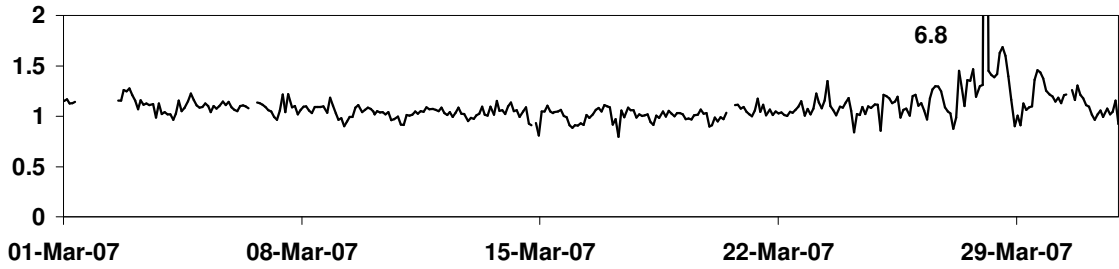
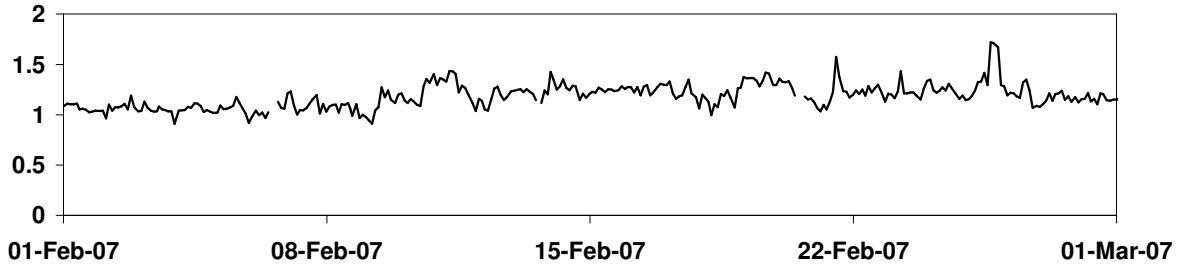
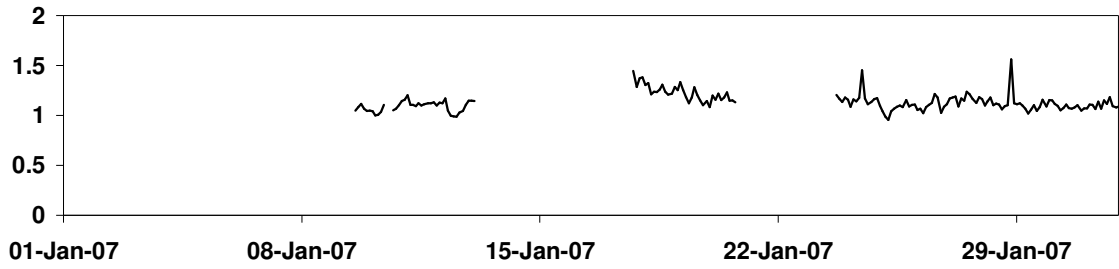


### Particulate matter concentrations, $\mu\text{g m}^{-3}$

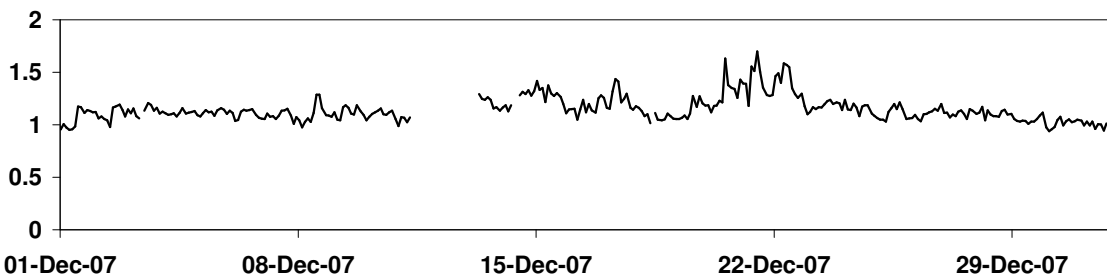
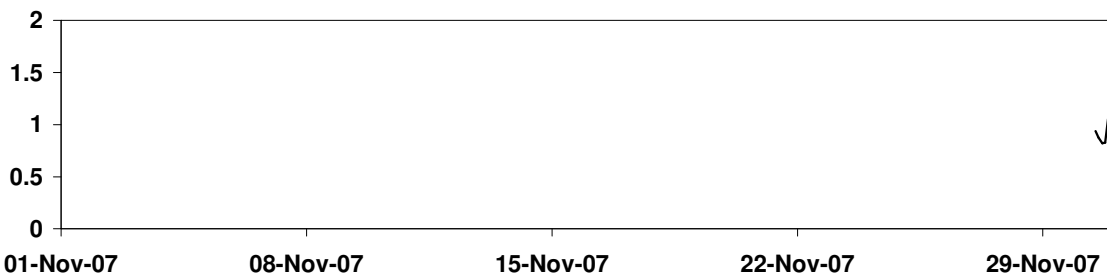
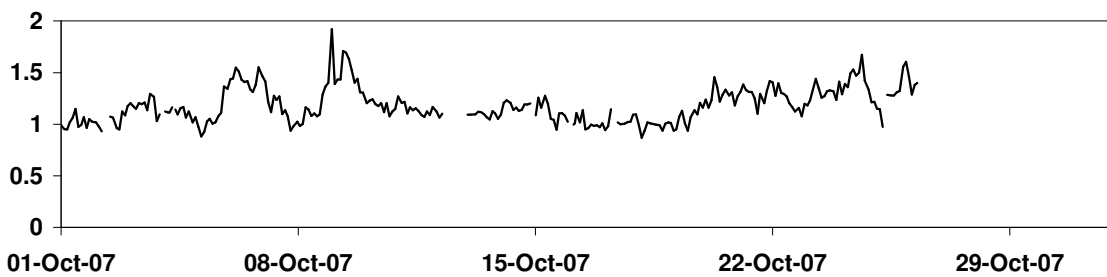
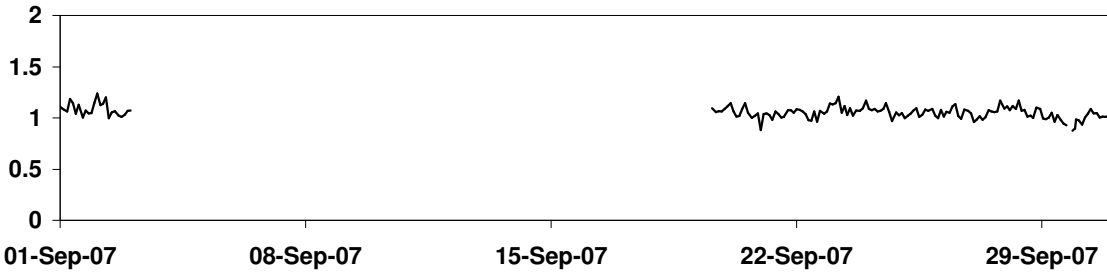
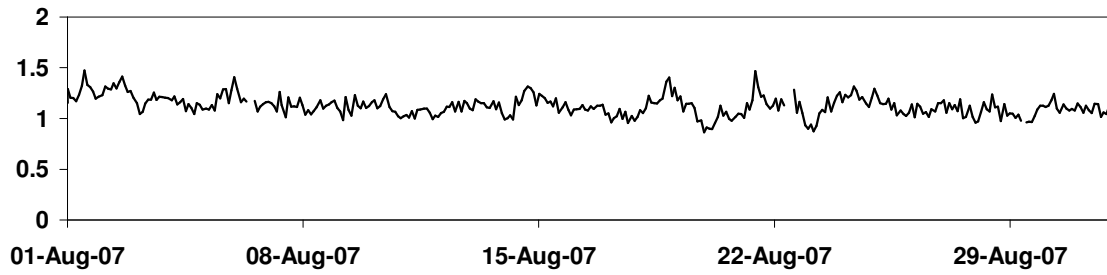
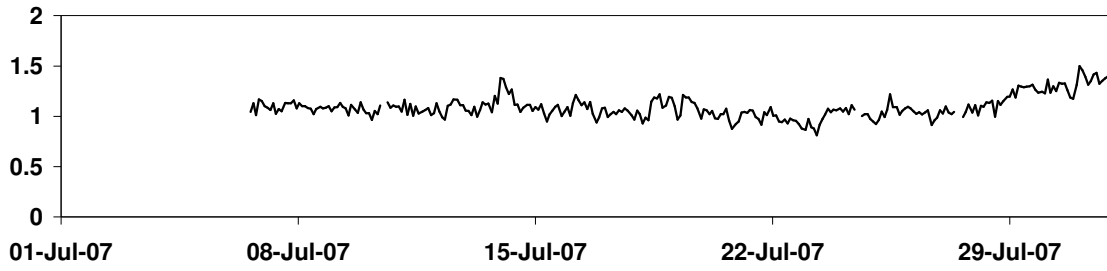




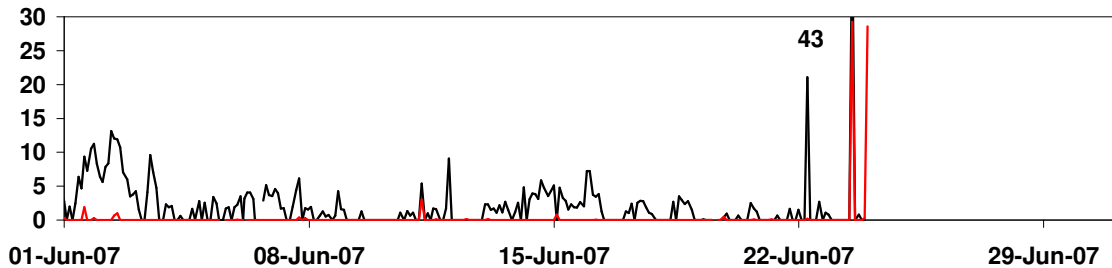
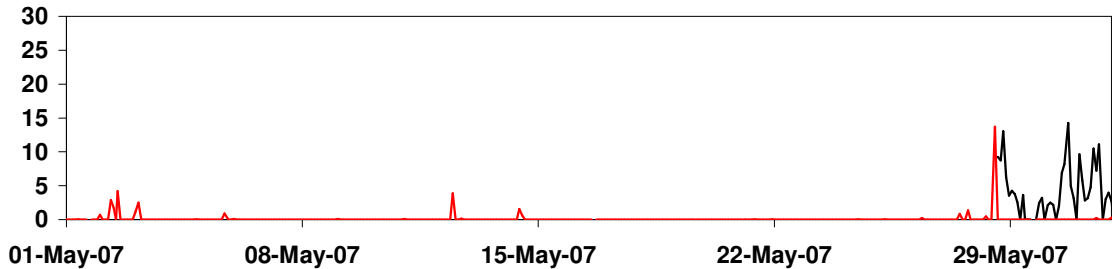
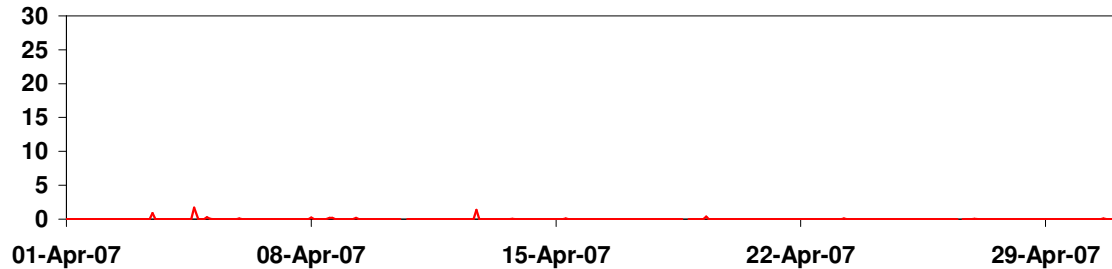
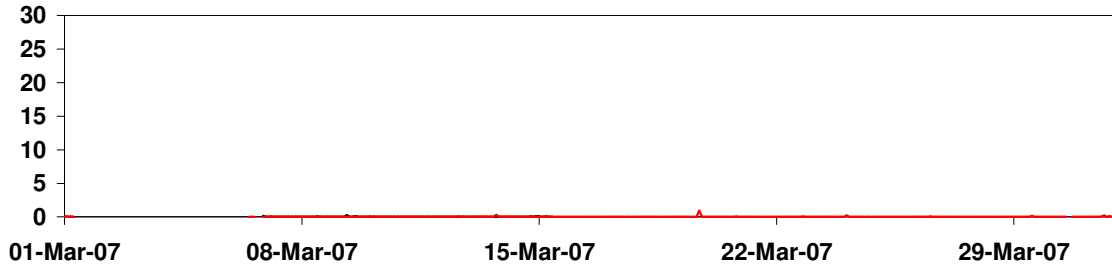
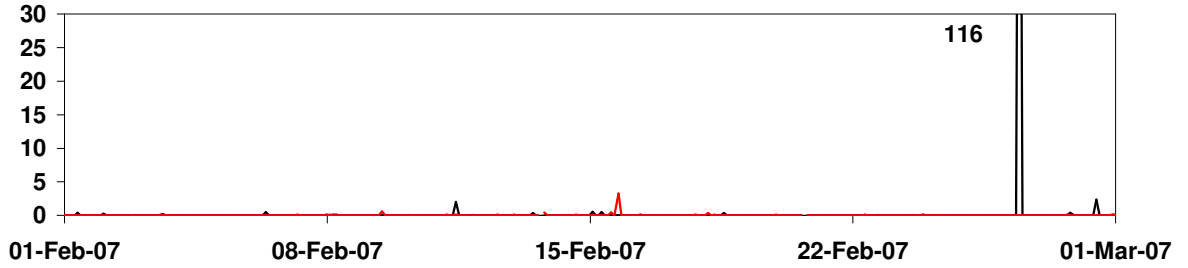
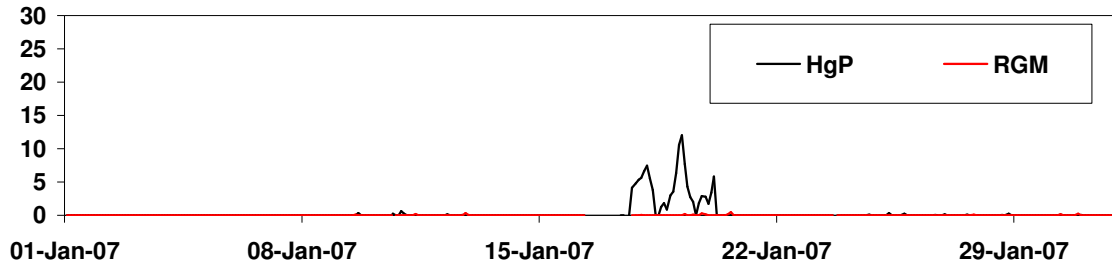
## Elemental mercury ( $\text{Hg}^0$ ) $\text{ng m}^{-3}$



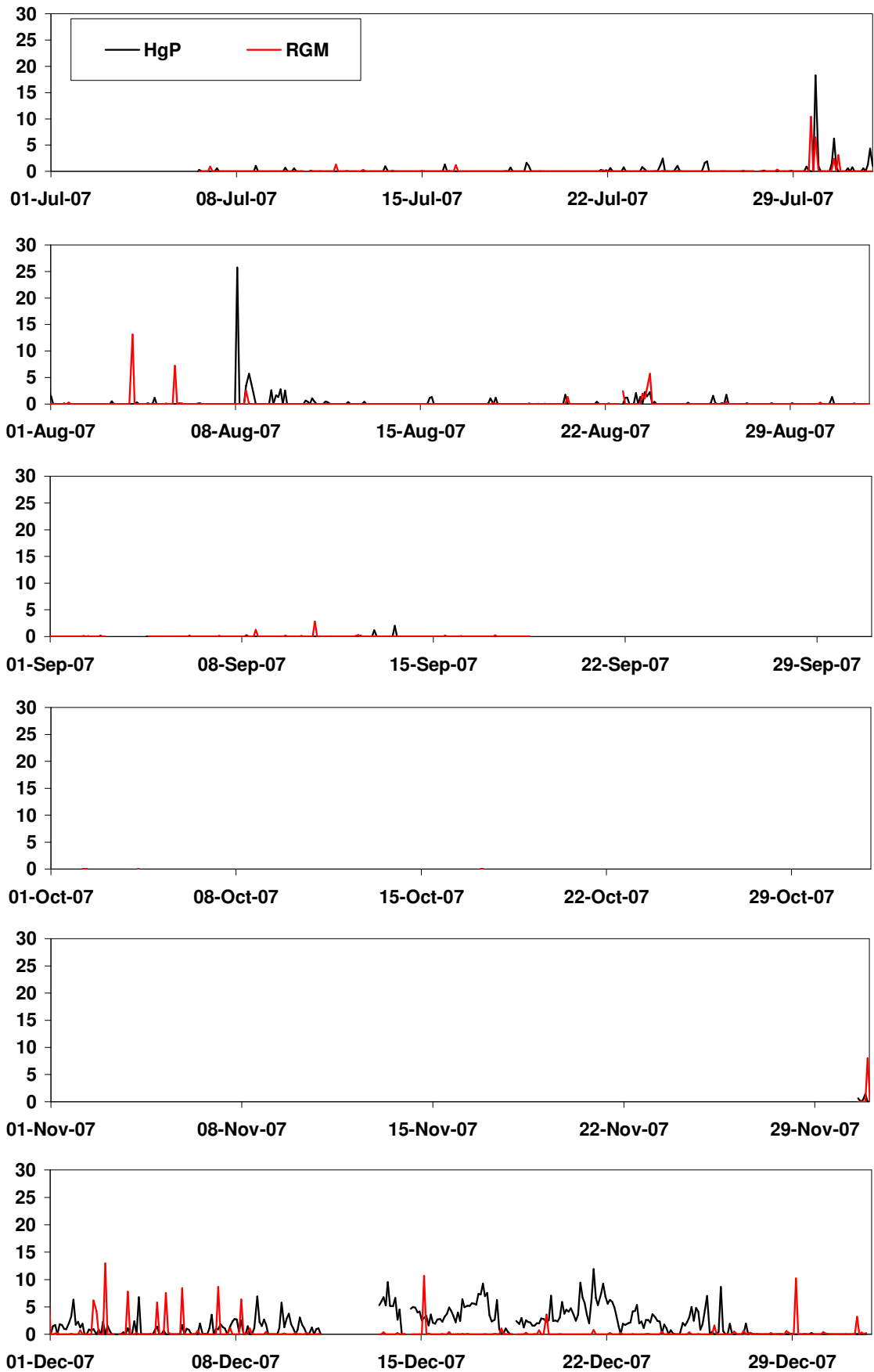
## Elemental mercury ( $\text{Hg}^0$ ) $\text{ng m}^{-3}$



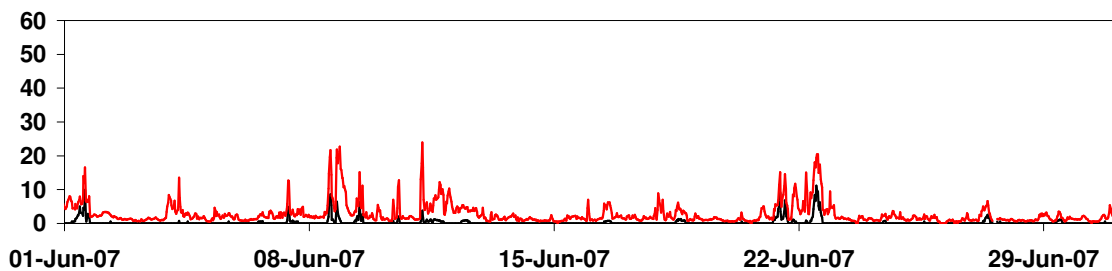
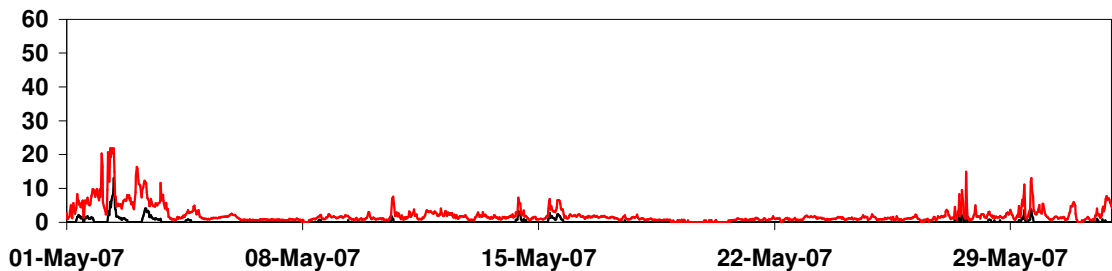
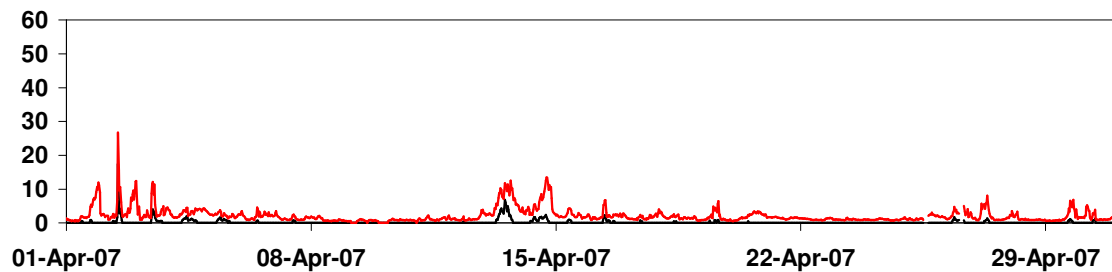
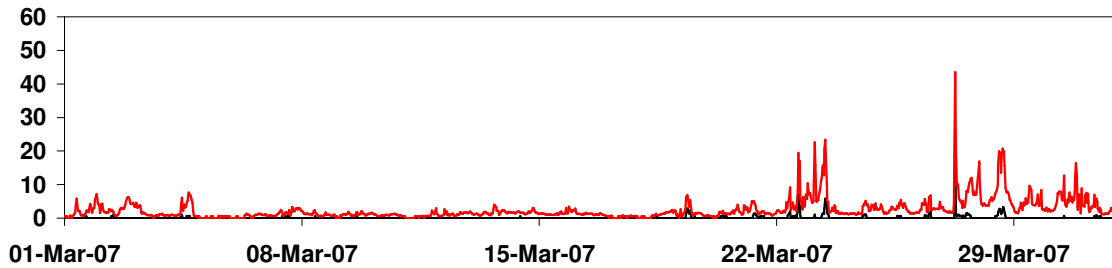
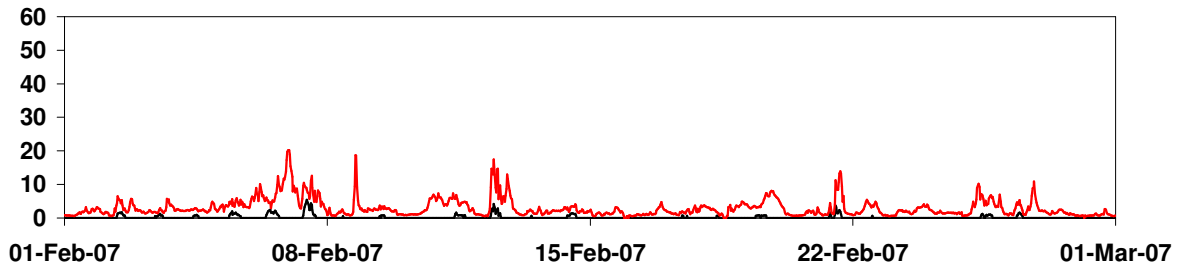
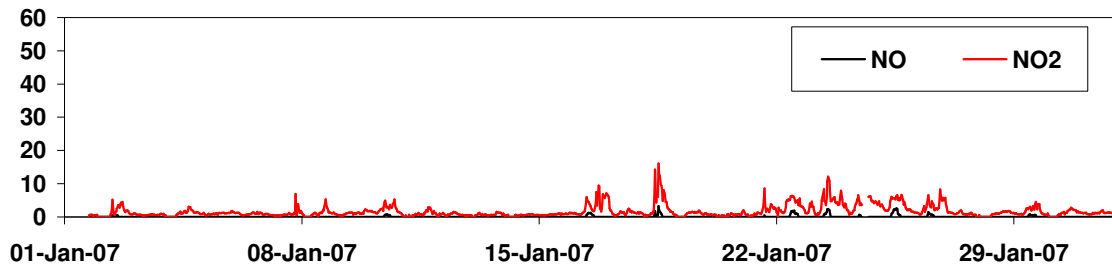
## Speciated mercury $\text{pg m}^{-3}$



## Speciated mercury $\text{pg m}^{-3}$

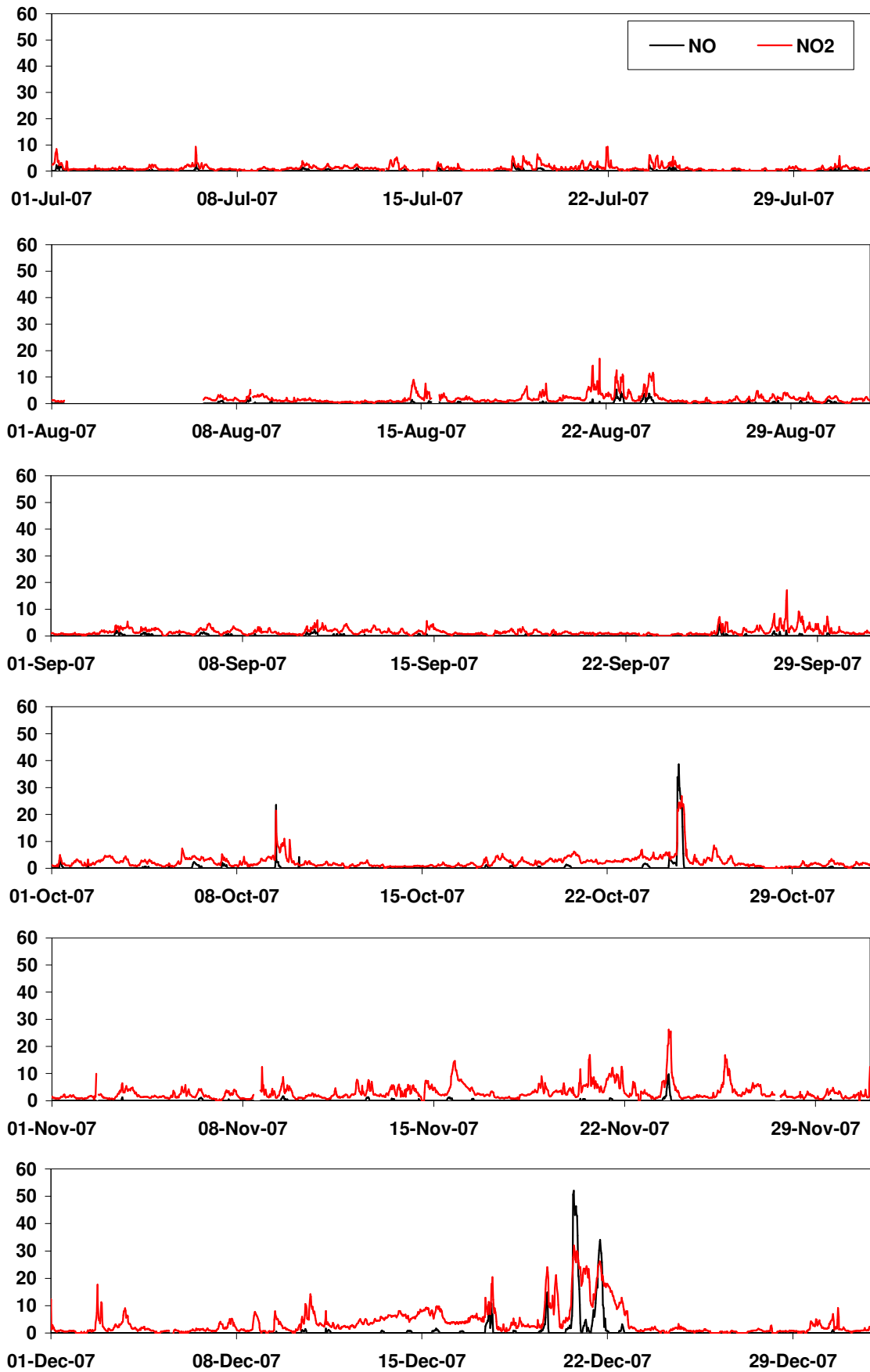


### nitric oxide/nitrogen dioxide ppb

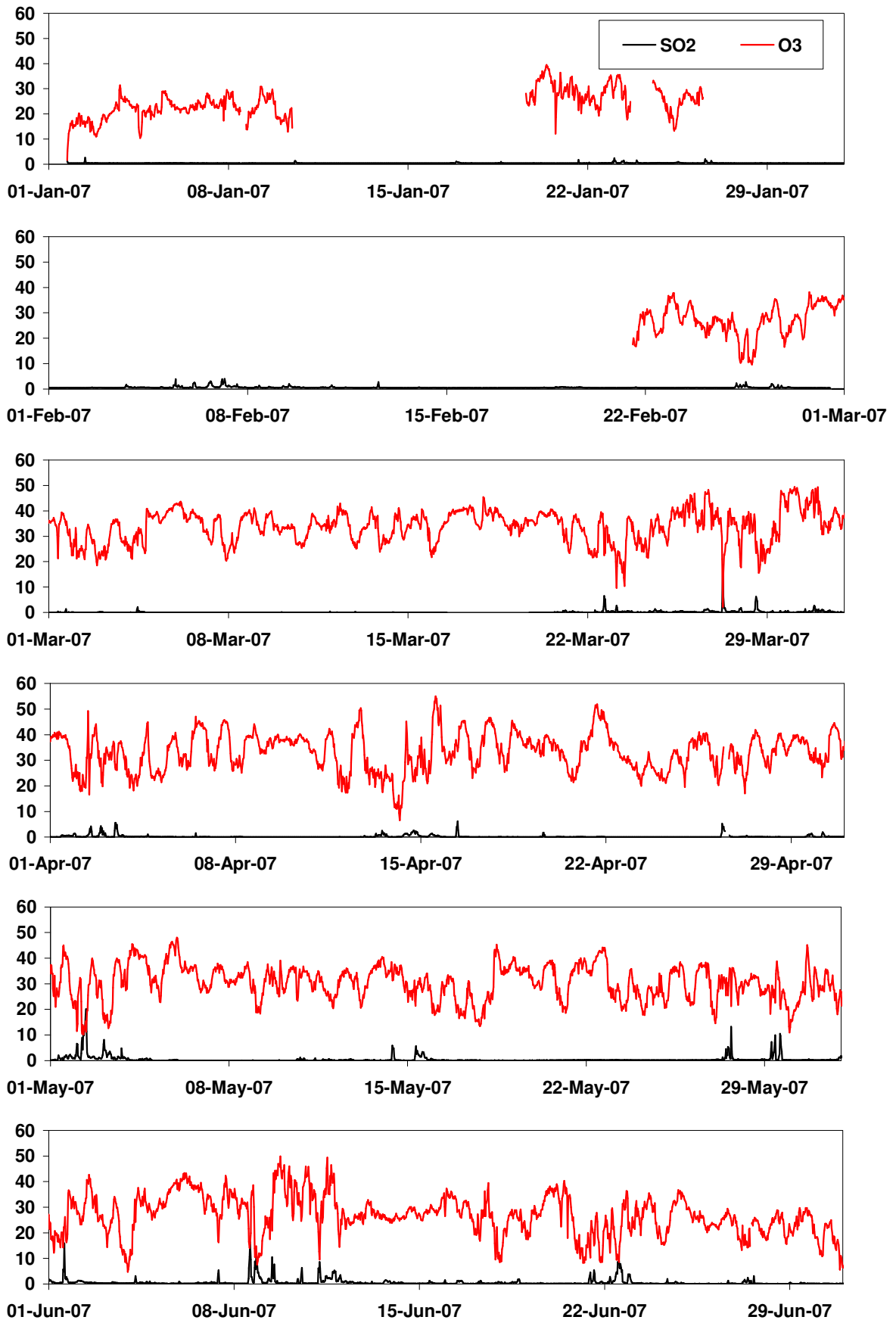




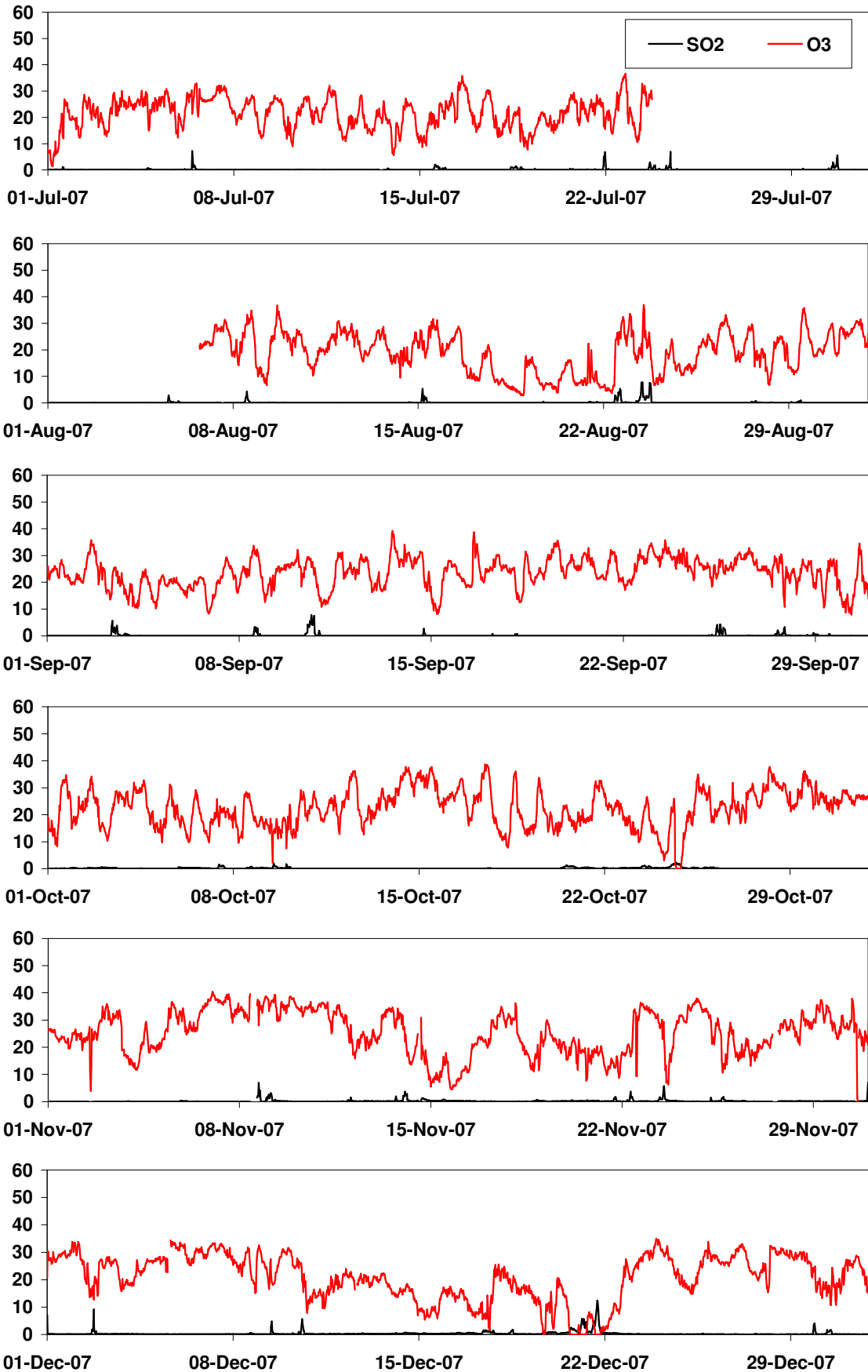
### nitric oxide/nitrogen dioxide ppb



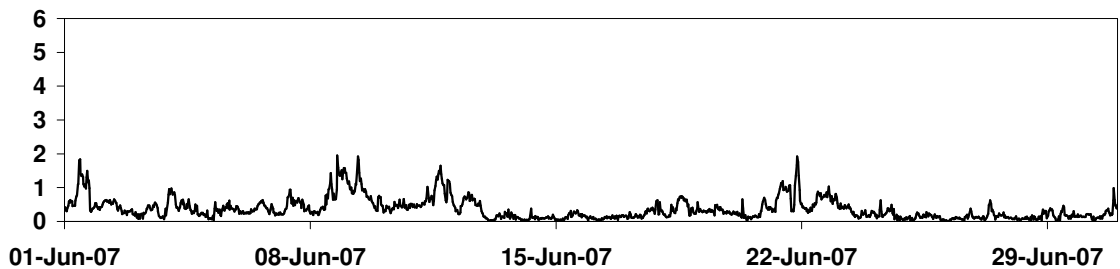
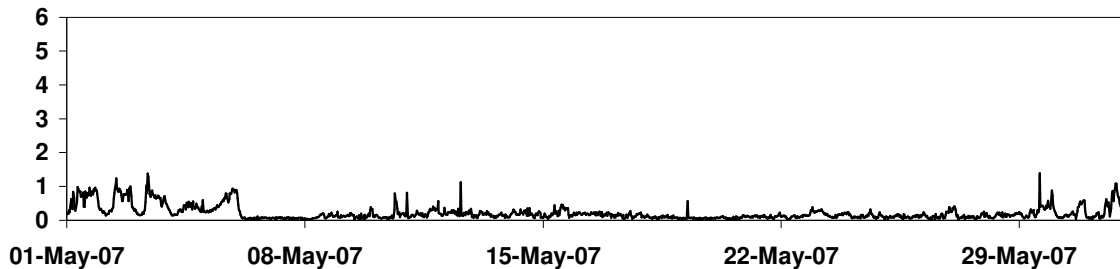
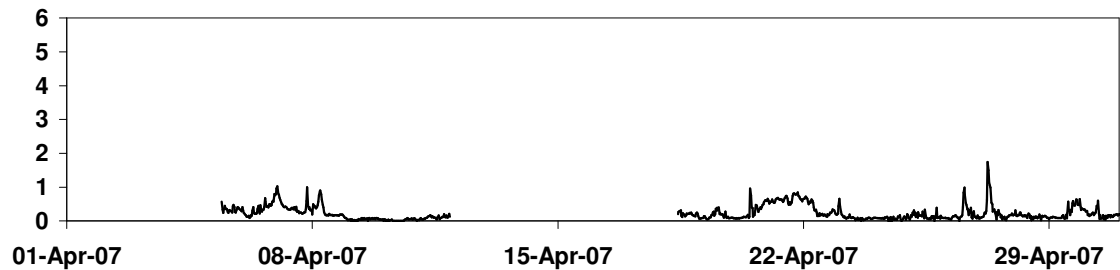
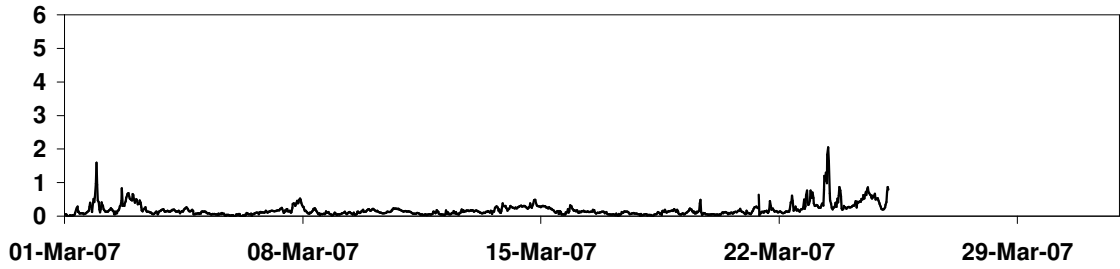
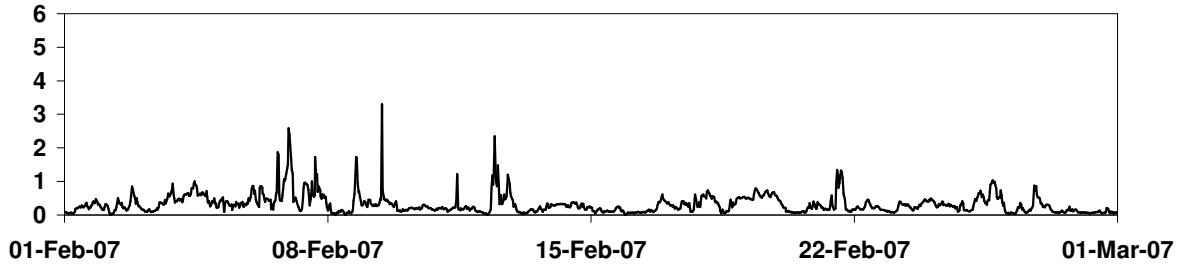
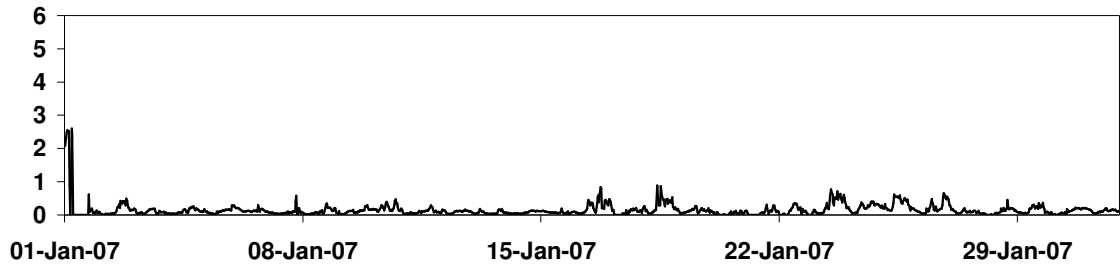
### sulphur dioxide/ozone ppb



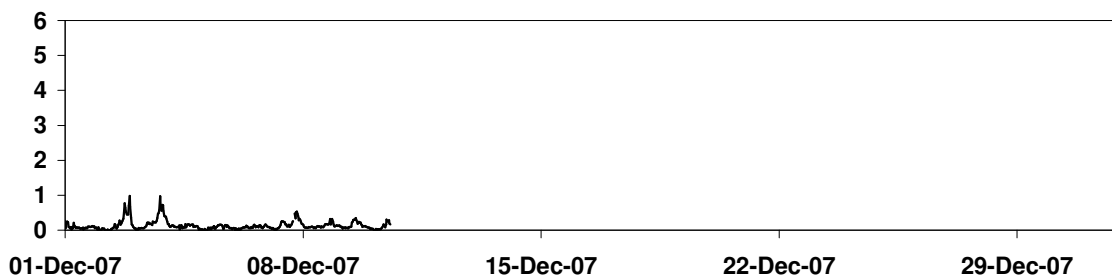
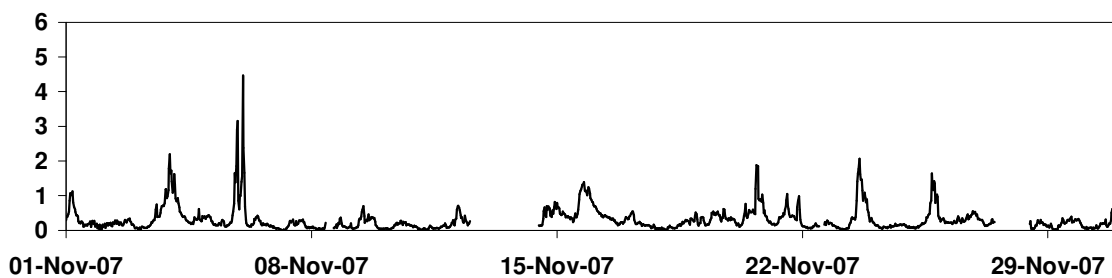
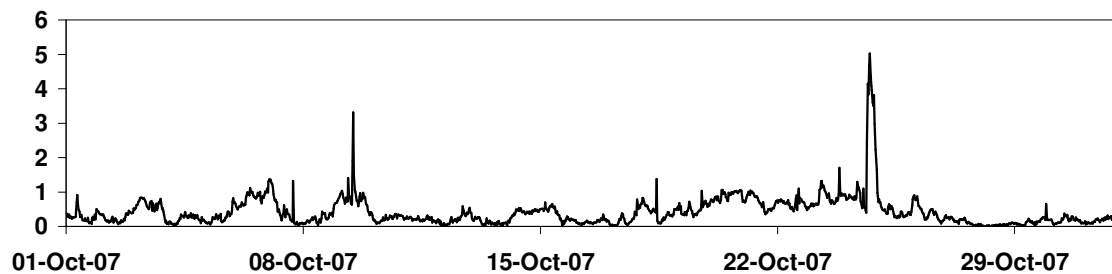
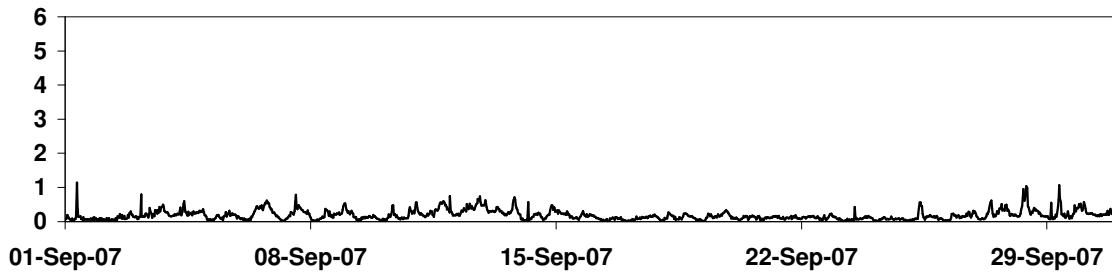
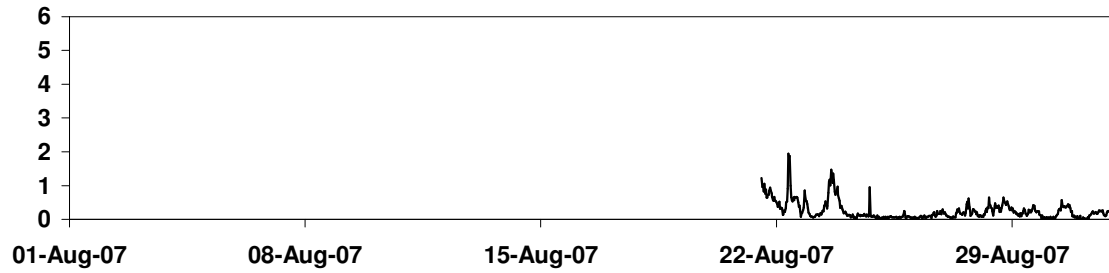
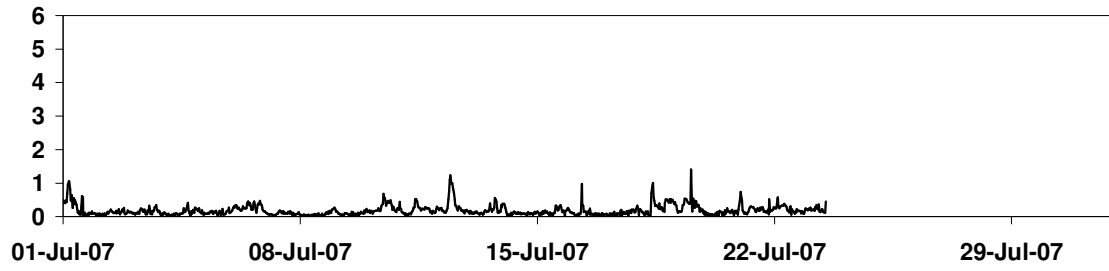
### sulphur dioxide/ozone ppb



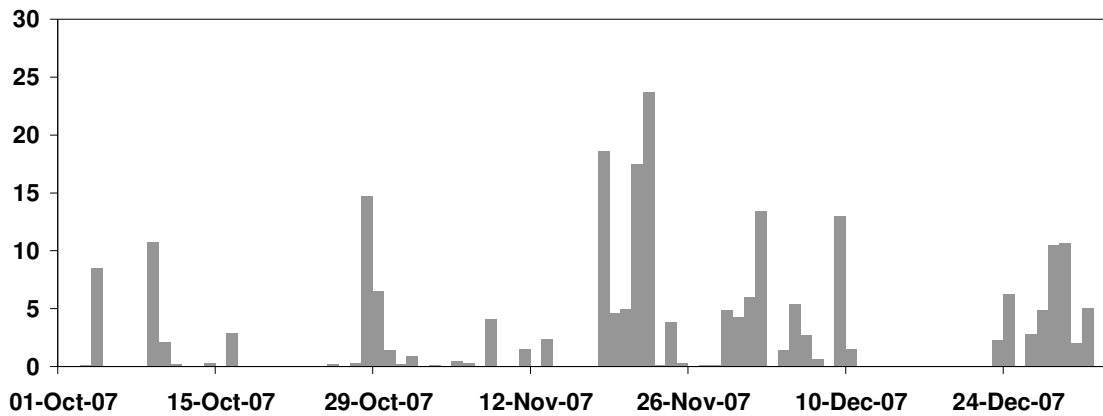
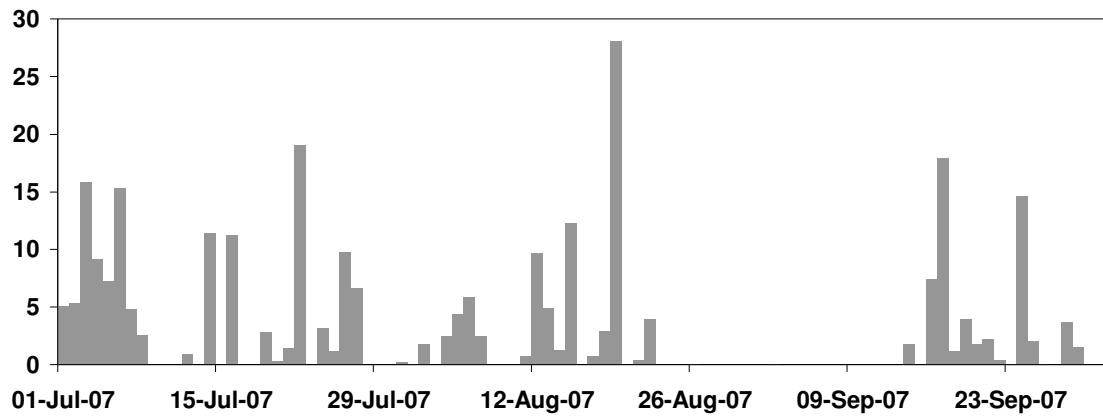
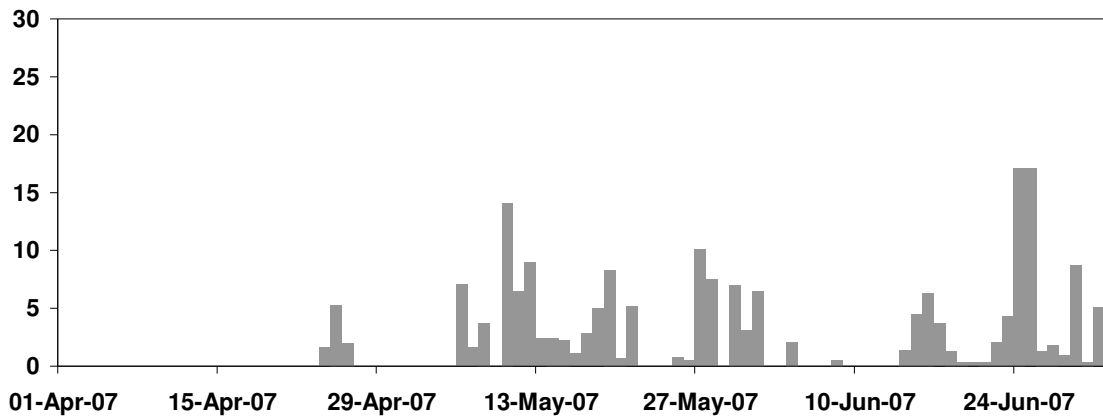
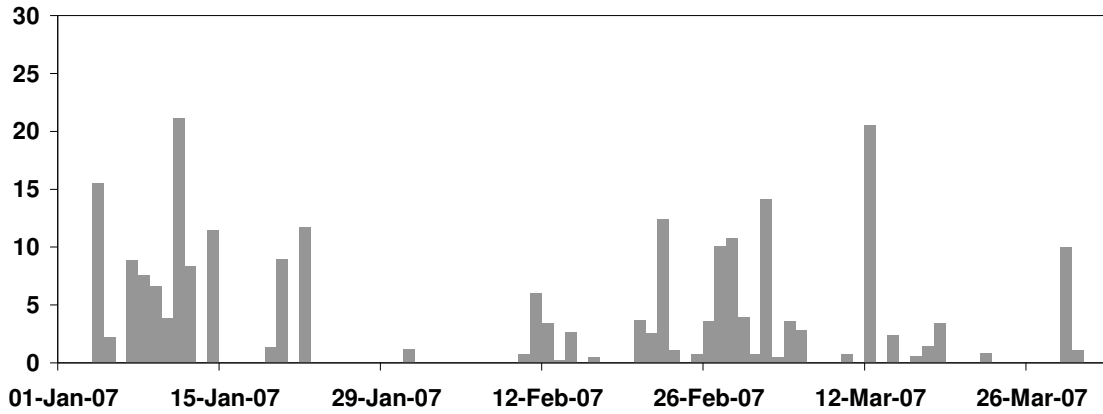
## Black carbon $\mu\text{g m}^{-3}$



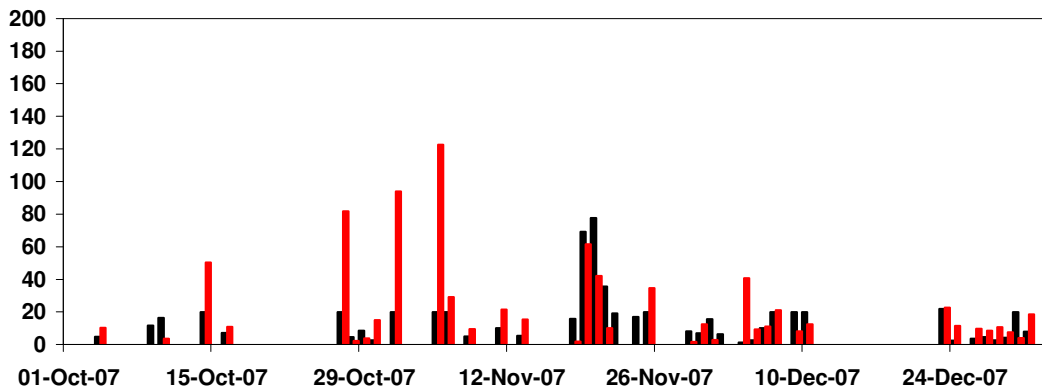
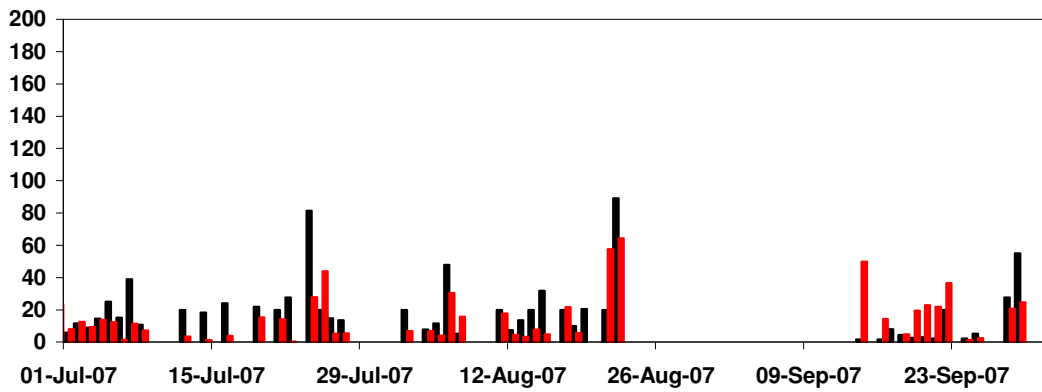
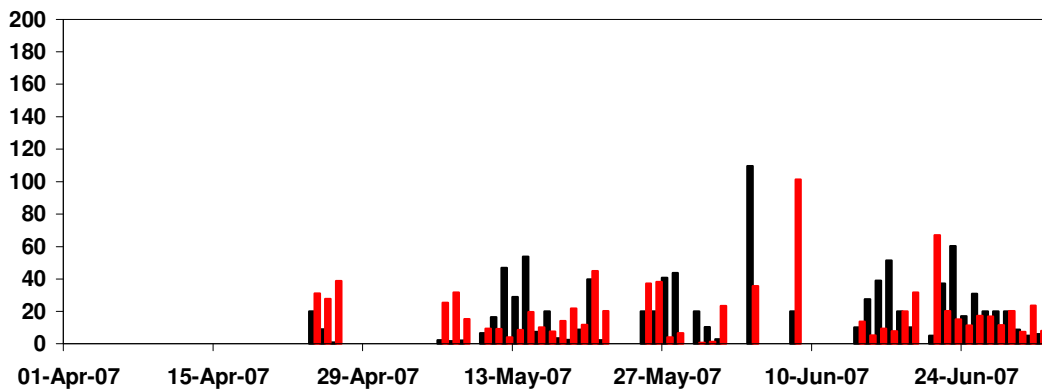
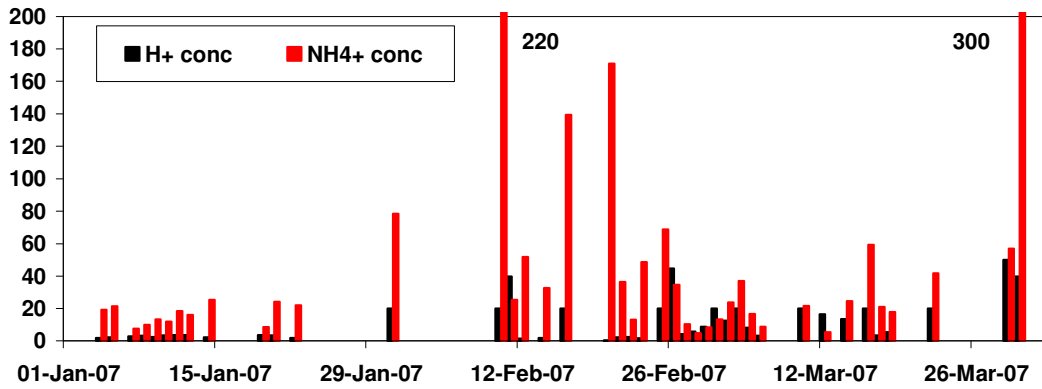
## Black carbon $\mu\text{g m}^{-3}$



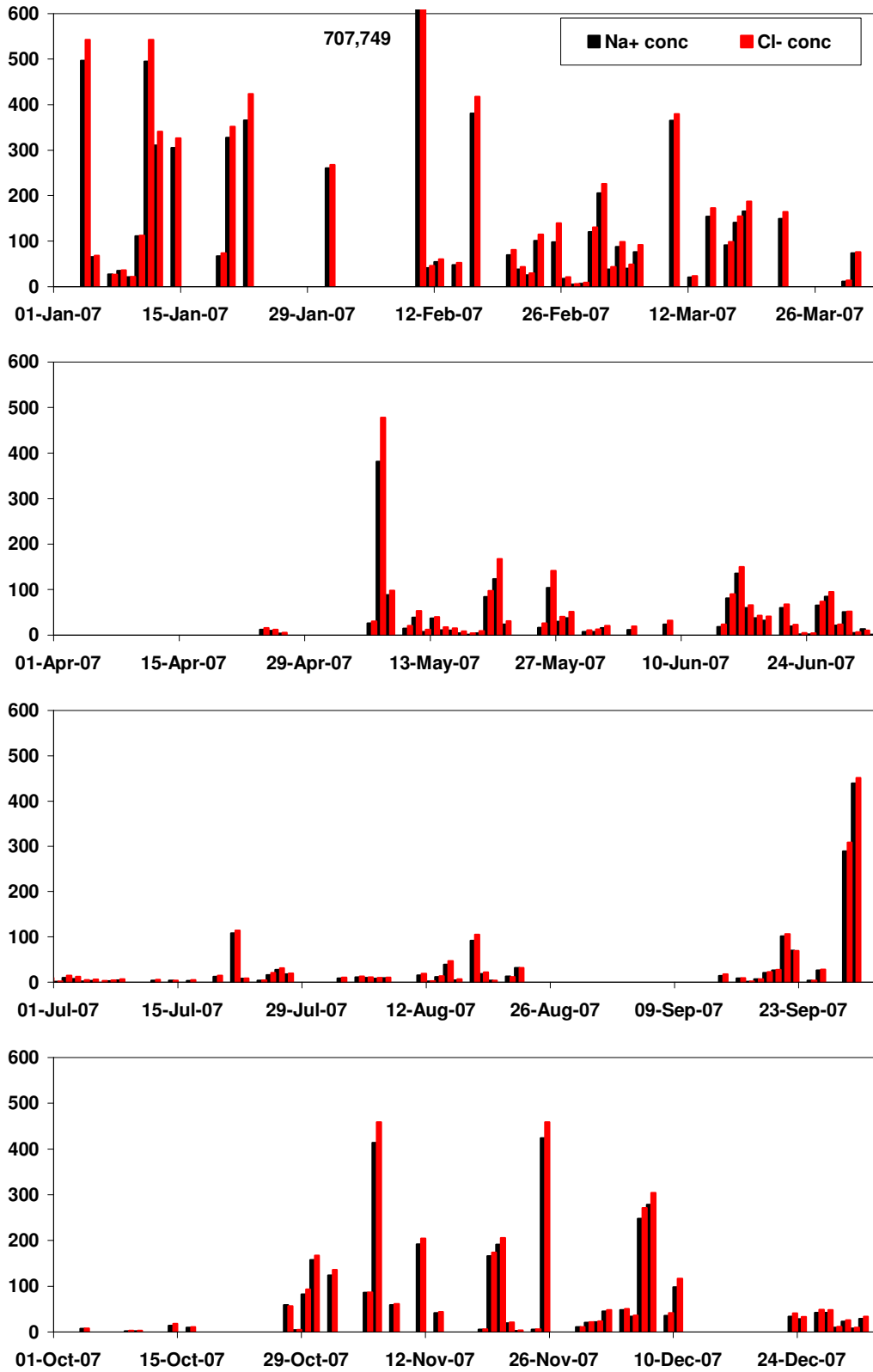
### Daily rainfall (mm)



Wet-only rain concentrations (daily)  $H^+$  and  $NH_4^+$   $\mu\text{equiv L}^{-1}$

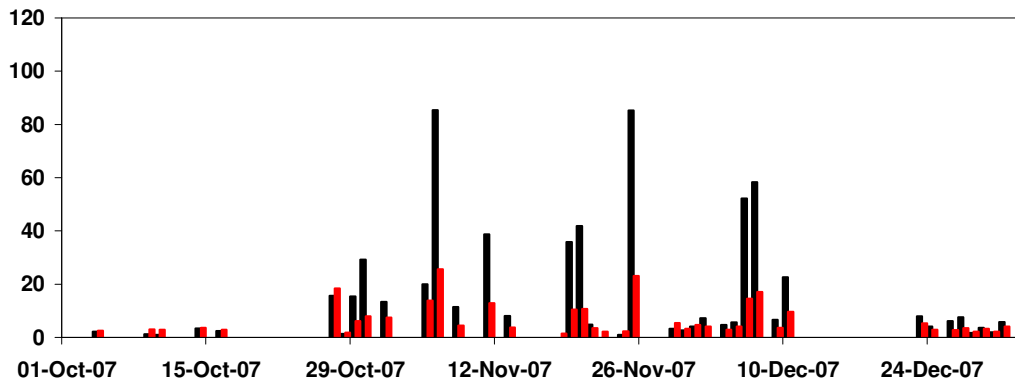
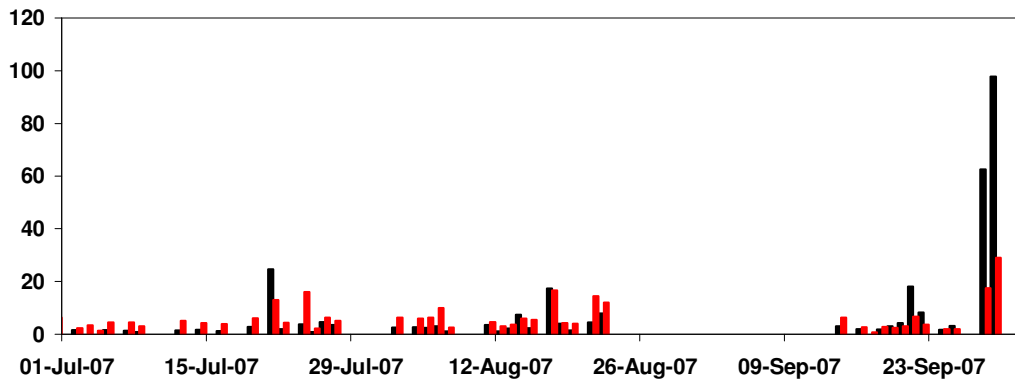
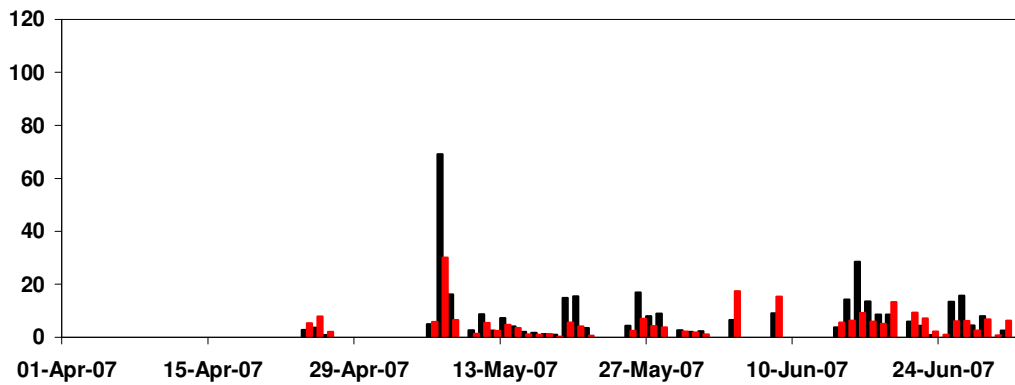
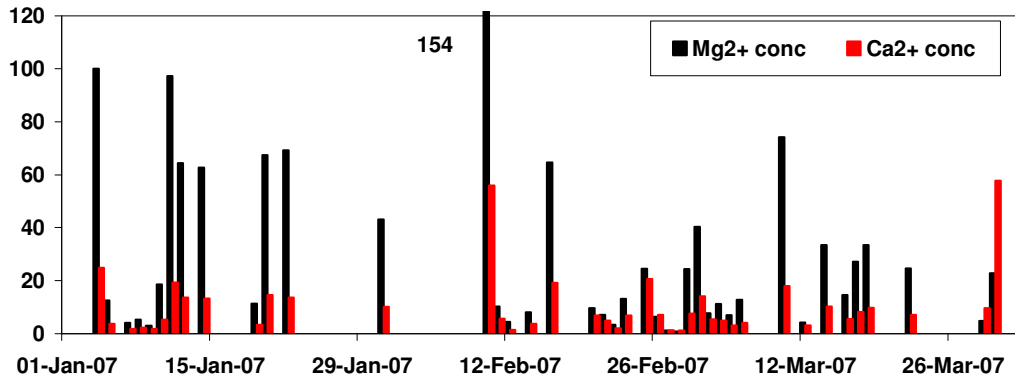


Wet-only rain concentrations (daily) Na<sup>+</sup> and Cl<sup>-</sup> µequiv L<sup>-1</sup>





Wet-only rain concentrations (daily) Mg<sup>2+</sup> and Ca<sup>2+</sup> µequiv L<sup>-1</sup>



Wet-only rain concentrations (daily)  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$   $\mu\text{equiv L}^{-1}$

