

Operation of EMEP 'supersites' in the United Kingdom

Annual Report for 2006

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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 2006, the first 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 2006.

The first 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 June and December 2006, 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 sharp contrast between maritime and continental air masses during a 5-day period in mid-October 2006.

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

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1. Overview

This project covers the installation and 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_{2.5}) and up to 10 micrometre (PM₁₀). 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).

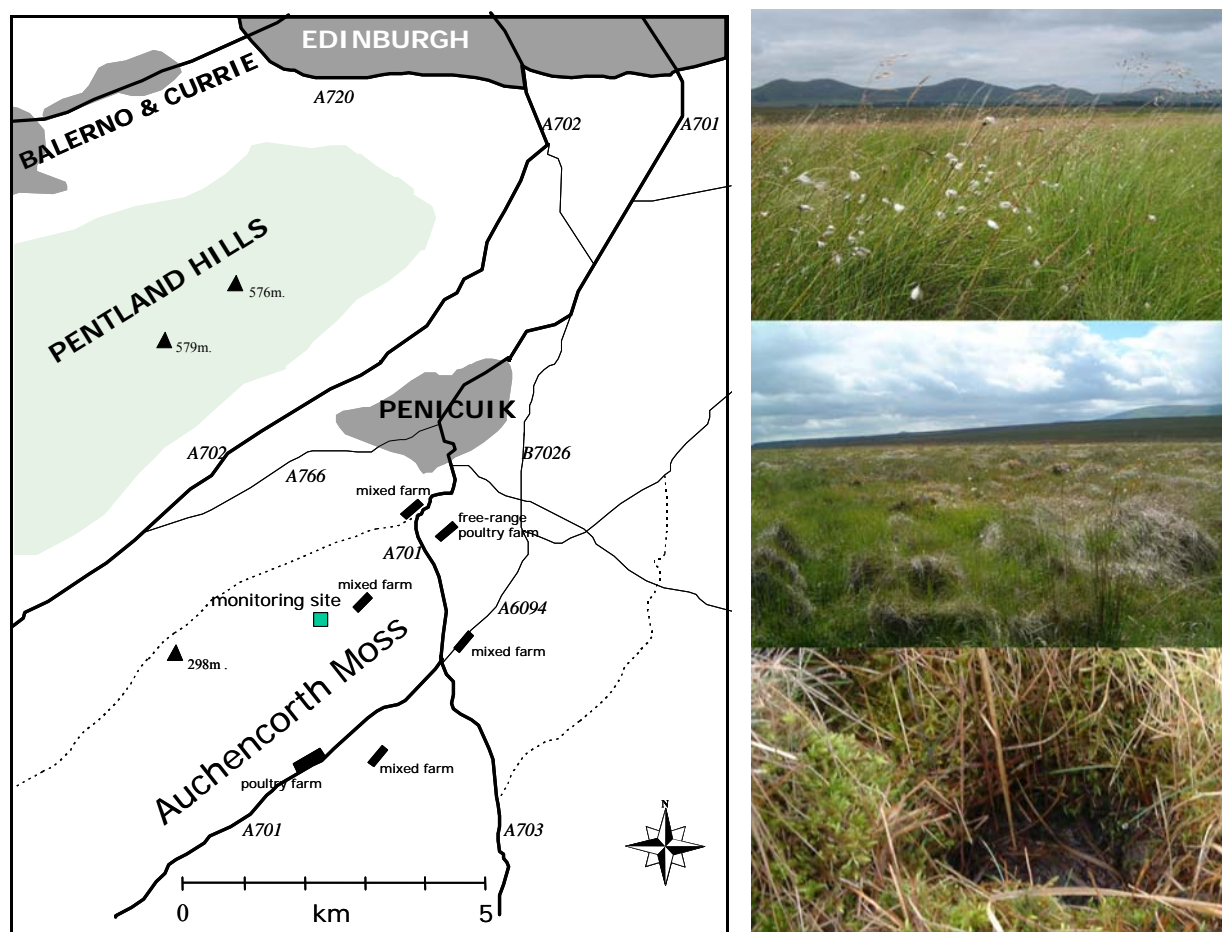
The Norwegian Institute for Air Research (NILU) arranged an EMEP Task Force on Measurements and Modelling (TFMM) workshop on the implementation of the EMEP monitoring strategy (EB.AIR/GE.1/2004/5) in Oslo on 22-24 November 2004 (see also <http://www.nilu.no/projects/ccc/reports/cccr9-2003.pdf>). The 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.

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) 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. 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 is 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 are listed below. Some were already in operation, and some started from June 2006. A summary overview is given in Table 1, which also shows the measurements that were currently 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 2006

Measurement	EMEP Level	Status (Funding)
<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
Trace gas and particle concentrations at PM_{2.5} and PM₁₀ (hourly)	II	This contract – MARGA
<i>Daily particle mass (PM_{2.5} and PM₁₀)</i>	I	Defra - AURN
Black carbon PM_{2.5} (30 min)	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 PM₁₀ (weekly)</i>	II	
<i>Mercury in precipitation (weekly)</i>	II	
<i>Speciated mercury in air (hourly)</i>	II	
Trace gas (O ₃ , NO _x , SO ₂) 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 installation and setup

The installation of several new, large items of monitoring equipment required the installation and servicing (electricity supply) of a second ‘Portakabin’. Provision of air conditioning was a requirement for the operation of the increased numbers of instruments during summer. The second cabin, equipped with electricity and air conditioning, was installed on the site by mid-May 2006, ready to accommodate the requirements (with the existing facility) of the full range of measurements listed in Table 1 above.

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.

A new wet-only collector was installed for the sampling of precipitation on a daily basis. The collector had already been purchased on behalf of Defra by Netcen. Daily samples 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.

2.5.2 Trace gas and aerosol concentrations

The existing integrated monthly concentration measurements of NH_3 , SO_2 , HNO_3 , HCl gases and NH_4^+ , SO_4^{2-} , NO_3^- , Cl^- , Na^+ , Mg^{2+} , 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 existing integrated monthly flux measurements of NH_3 , SO_2 , HNO_3 , HCl gases and NH_4^+ , SO_4^{2-} , NO_3^- , Cl^- , Na^+ , Mg^{2+} , 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 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.

2.5.4 *Trace gases*

Existing measurements of vertical gradients of O₃, NO_x and SO₂ 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 SO₂ measurements were part of the Acid Deposition Processes contract held by CEH (RMP2258).

To provide continuous monitoring at a fixed height, new monitors were installed and operated as follows:

Ozone – a continuous UV-photometric instrument was installed and operated by Bureau Veritas as part of the AURN (1/3/191). Data are recorded as hourly averages, but more frequent recording is possible during ‘intensive’ periods.

Volatile Organic Compounds (VOC) – an automated sampler/gas chromatograph was purchased by Netcen on behalf of Defra and was installed and operated at Auchencorth as part of the UK Hydrocarbons Monitoring Network (RMP1883). Data are recorded hourly.

Carbonyls (aldehydes and ketones) – automated samplers were constructed 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 problems with contamination which were not resolved during 2006.

2.5.5 *Heavy metals*

The existing 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 PM₁₀ 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.

3. Operation of instruments under this contract

Summaries of the start dates and data capture during 2006 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.

There was an intermittent fault with the humidity sensor during this period, and a fault with the tipping-bucket rainfall sensor and barometric pressure sensor. %data capture was low for these sensors (see Table 2) but gaps have been filled from instruments nearby. Wind speed and direction data are missing from most of June, some of July and October, because of instrument faults.

3.2 *Trace gas and aerosol concentrations (MARGA)*

A new automated continuous-flow denuder and steam-jet aerosol sampler (MARGA) was purchased by CEH on behalf of Defra. This 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 PM₁₀ and PM_{2.5} aerosols. Internal standards of Li⁺ (cations) and Br⁻ (anions) are used for calibration checks.

Initially, data capture was poor because of teething problems with both hardware and software, but data capture gradually improved through the year.

3.3 *Particulate carbon (Aethalometer)*

A new monitor for the continuous measurement of black carbon in air (aethalometer) was purchased by Netcen on behalf of Defra and was installed. 30-minute average data are recorded. The data for 2006 represent PM_{3.3} rather than PM_{2.5} 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_{2.5} because at this site, remote from particle sources, the long-range transported aerosols are likely to be in the size range of < 1 micrometre.

3.4 *Trace gases (ANNOX)*

Nitrogen oxides: a high-sensitivity automated NO/NO₂ analyzer (ANNOX) had been purchased by Netcen on behalf of Defra. Installation was delayed because of the need to find space in the monitoring cabin. This chemiluminescent instrument uses UV photolysis to convert NO₂ to NO prior to analysis, as specified by the EMEP protocol. It is therefore specific for NO₂, and does not respond to other oxidised N species such as PAN and HNO₃, which are positive artefacts when using a thermal converter.

Table 2. Start dates and data capture for instrumentation operated and reporting under this contract, from 1 June 2006 onwards.

Instrument	Start date	% data capture for 2006
Wind speed and direction	1/6/06	76%
Air temperature	1/6/06	97%
Relative humidity	1/6/06	64%
Barometric pressure	1/6/06	10%
Precipitation (daily)	10/6/06	95%
MARGA PM ₁₀	1/6/06	43% (at least one ion > l.o.d)
MARGA PM _{2.5}	1/6/06	38% (at least one ion > l.o.d)
MARGA gases	1/6/06	40% (at least one gas > l.o.d)
Aethalometer	15/6/06	100%
VOCs	24/6/06 data from 14/9/06	39% (at least one VOC > l.o.d.)
Ozone (CEH)	1/6/06	98%
Sulphur dioxide	1/6/06	98%
Nitrogen oxides	1/6/06	98%
Daily PM ₁₀ and PM _{2.5}	1/6/06	0 (PM ₁₀) 93% (PM _{2.5})
Ozone (AURN)	1/11/06	94%
Hourly PM ₁₀ and PM _{2.5}	1/12/06	47%, 88%
Mercury: Hg ⁰ , RGM, part	1/6/06	84%, 73%, 73%

4. Data collation and QA/QC

The storage and transfer of data has evolved since the inauguration of the site. All 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:

Measurement	Data released within (period) after sampling
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
PM ₁₀ /PM _{2.5} concentrations	1 month

Aethalometer	2 weeks
VOCs	2 weeks
Ozone, NO/NO ₂	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 2006).

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. For the meteorological data with poor data capture, 'gap-filled' data from nearby sites have been used in calculating the statistics over the 7-month period. In all cases, the minimum concentrations recorded were 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). The database will become 'live' during 2009.

Table 3. Summary data for the period 1 June to 31 December 2006

Instrument	mean	median	min/max
Wind speed, m s ⁻¹ (30 min)	4.13	3.68	0.05/18.6
Air temperature, °C (30 min)	11.3	11.2	-5.5/28.5
Relative humidity, % (30 min)	88.6	92.0	39/100
Bar. pressure, kPa (30 min)	99.8	99.7	89.9/102.8
Precipitation (30 min)	0.072	0	0/8.2
Precipitation (daily wet-only)	7.1	1.4	0/66.0
Daily rain concentrations: H ⁺	13.1	6.3	0.5/110
(µequivalent L ⁻¹) NH ₄ ⁺	31.0	22.7	1/200
Na ⁺	48.9	18.0	0/370
K ⁺	2.9	2.1	0/20
Ca ²⁺	7.0	4.4	0/46
Mg ²⁺	9.3	4.1	0/68
Cl ⁻	51.2	19.3	2/401

Instrument		mean	median	min/max
SO ₄ ²⁻	NO ₃ ⁻	16.7	7.6	2/149
	SO ₄ ²⁻	20.3	14.1	2/168
	Non-sea	14.4	8.1	-2/165
		13.5	9.8	3/51
	Conductivity (µS cm)			
Daily rain deposition: (mequivalent NH ₄ ⁺ per rain day)	H ⁺	69	14	780
	m ⁻²	113	73	2160
		236	65	4640
	Na ⁺	11	6	86
	K ⁺	28	14	250
	Ca ²⁺	46	14	940
	Mg ²⁺	247	70	5000
	Cl ⁻	70	25	1670
	NO ₃ ⁻	93	43	1450
	SO ₄ ²⁻	64	23	1330
Rain wtd. concentrations: (µequivalent L ⁻¹)	Non-sea			
MARGA PM ₁₀ : (µg m ⁻³)	NH ₄ ⁺	0.96	0.40	6.7
	Na ⁺	0.49	0.31	4.2
	K ⁺	0.04	0.03	0.36
	Ca ²⁺	0.06	0.03	0.99
	Mg ²⁺	0.04	0.03	0.50
	Cl ⁻	0.79	0.49	7.4
	NO ₃ ⁻	1.92	1.42	12.6
	SO ₄ ²⁻	1.63	0.89	16.0
MARGA PM _{2.5} : (µg m ⁻³)	NH ₄ ⁺	0.92	0.33	6.9
	Na ⁺	0.28	0.15	1.4
	K ⁺	0.05	0.04	0.55
	Ca ²⁺	0.07	0.03	0.73
	Mg ²⁺	0.04	0.03	0.22
	Cl ⁻	0.48	0.41	3.5
	NO ₃ ⁻	1.33	0.78	1.1
	SO ₄ ²⁻	1.44	0.73	15.9
MARGA gases: (µg m ⁻³)	NH ₃	1.78	0.78	27
	HCl	0.50	0.43	8.5
	HNO ₃	0.09	0.03	2.1
	HNO ₂	0.14	0.02	2.2
	SO ₂	0.60	0.32	62

Instrument		mean	median	min/max
Aethalometer ($\mu\text{g C m}^{-3}$)		0.31	0.20	4.0
VOCs ($\mu\text{g m}^{-3}$)	1,3-butadiene	0.019	0.02	0.16
	1-butene	0.007	0	0.07
	cis-2-butene	0.003	0	0.07
	trans-2-butene	0.019	0.02	0.05
	ethane	0.36	0.36	1.06
	ethene	0.051	0.04	0.66
	ethyne	0.024	0.03	0.10
	isoprene	0.047	0.03	0.91
	propane	0.263	0.26	0.75
	propene	0.033	0.04	0.12
	n-butane	0.135	0.12	0.70
	iso-butane	0.074	0.07	0.41
	n-pentane	0.046	0.03	0.24
	iso-pentane	0.055	0.06	0.39
Ozone (CEH) (ppb)		22.6	21.8	98.6
Sulphur dioxide (ppb)		0.31	0.15	57.1
Nitrogen oxides: NO (ppb)		0.12	0	26.0
NO ₂ (ppb)		1.9	1.3	26.4
Mass PM _{2.5} ($\mu\text{g m}^{-3}$)		7.3	5	36
Ozone (AURN) ($\mu\text{g m}^{-3}$)		58	62	86
Mercury: Elemental (ng m^{-3})		1.14	1.07	0.6/5.7
Reactive gaseous (pg m^{-3})		0.16	0	37
Particulate (pg m^{-3})		0.69	0	13
Heavy metals in air (weekly) (ng m^{-3})				
	As	0.30	0.21	3.1
	Cd	0.078	0.039	0.92
	Cr	0.38	0.12	2.8
	Cu	1.00	0.32	17.6
	Ni	0.61	0.26	12.9
	Pb	3.4	1.9	53
	Se	0.45	0.31	6.5
	V	1.61	0.65	40
	Zn	6.0	3.0	109
(two weekly) Hg		1.47	1.45	0.9/1.9
Heavy metals in rain (weekly) (ng L^{-1})				
	As	0.13	0.11	0.43
	Cd	0.019	0.011	0.092
	Cr	0.14	0.10	0.50
	Cu	0.53	0.42	2.3
	Ni	1.03	0.31	30
	Pb	0.50	0.28	2.6
	Se	0.15	0.13	0.46
	V	0.32	0.23	0.92
	Zn	5.2	3.2	21
(monthly) Hg		3.3	2.5	1.4/6.1

7. Discussion

7.1 Influence of wind direction

The site at Auchencorth is dominated by winds from the south-west, as shown in Figure 2 for the period 1 June to 31 December 2006. However, the wind does blow from all compass directions, albeit for short periods, so that the 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.

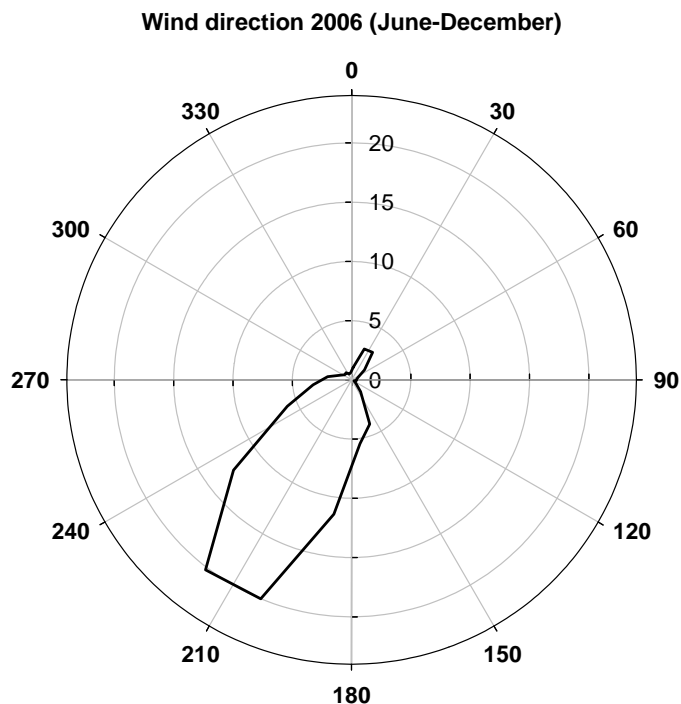


Figure 2: Distribution of wind direction frequency between June and December 2006, expressed as % time

Concentrations of sulphur dioxide (SO_2) were low (median 0.15 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 (O_3) concentrations is much less marked, with lowest concentrations to NNE and SE, reflecting higher NO_x concentrations from those directions. 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) reflect occasional peak concentrations when NO exceeded O₃ and so was not removed by reaction, usually at night.

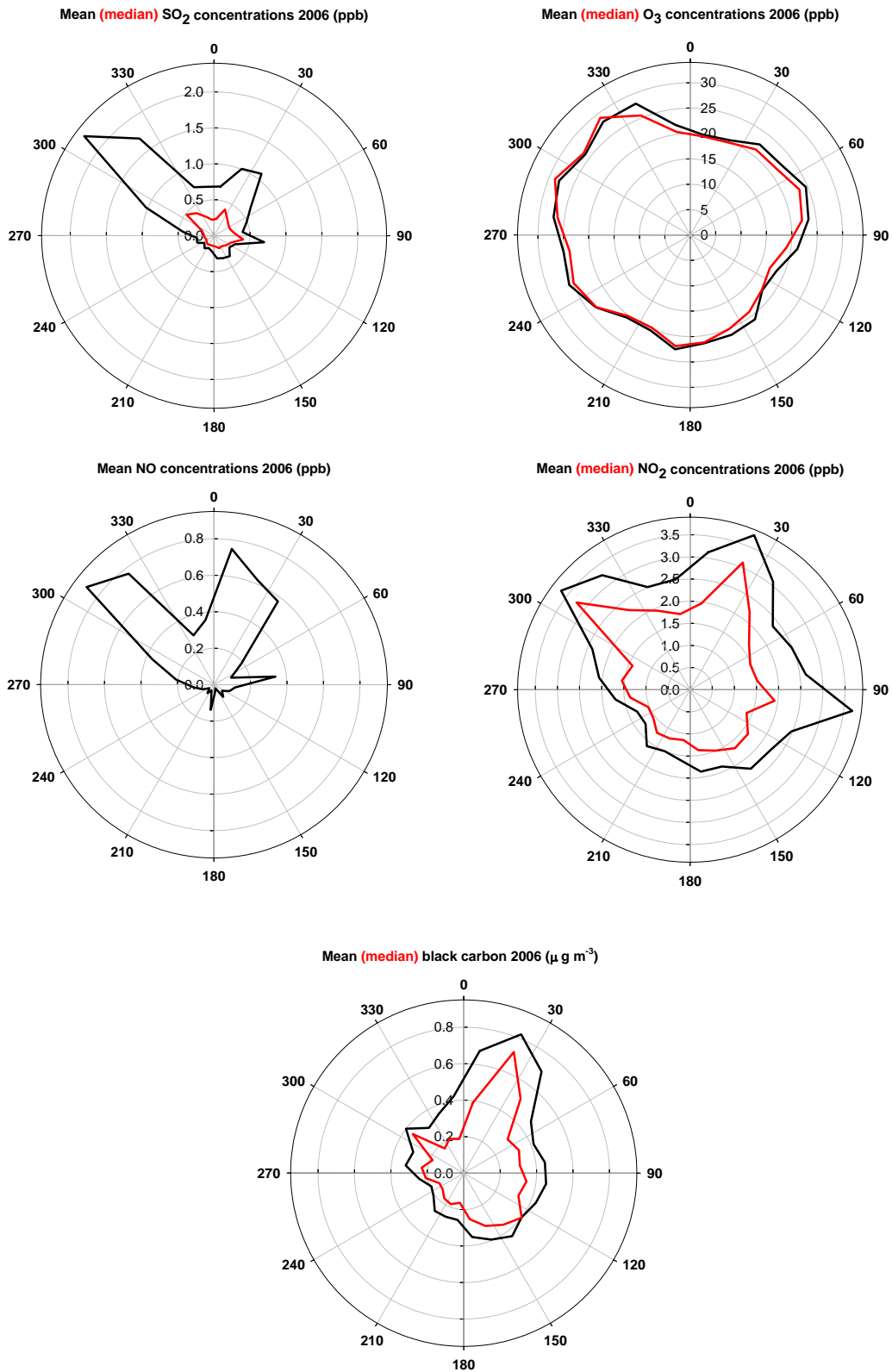


Figure 3: Directional dependence of air concentrations, from top left (a) sulphur dioxide, (b) ozone, (c) nitric oxide, (d) nitrogen dioxide, (e) black carbon.

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_2) the pattern (Figure 3d) is quite different from that for SO_2 , 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 SO_2 , however, there is no direction which has concentrations of NO_2 approaching zero. Black carbon concentrations, as measured by the aethalometer, show a similar spatial pattern to those for 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.

7.2 Diurnal cycles

Throughout the day, gas and particle concentrations vary systematically, as shown in Figure 4a-e, where 30-minute averages are presented over the whole period (June-December 2006).

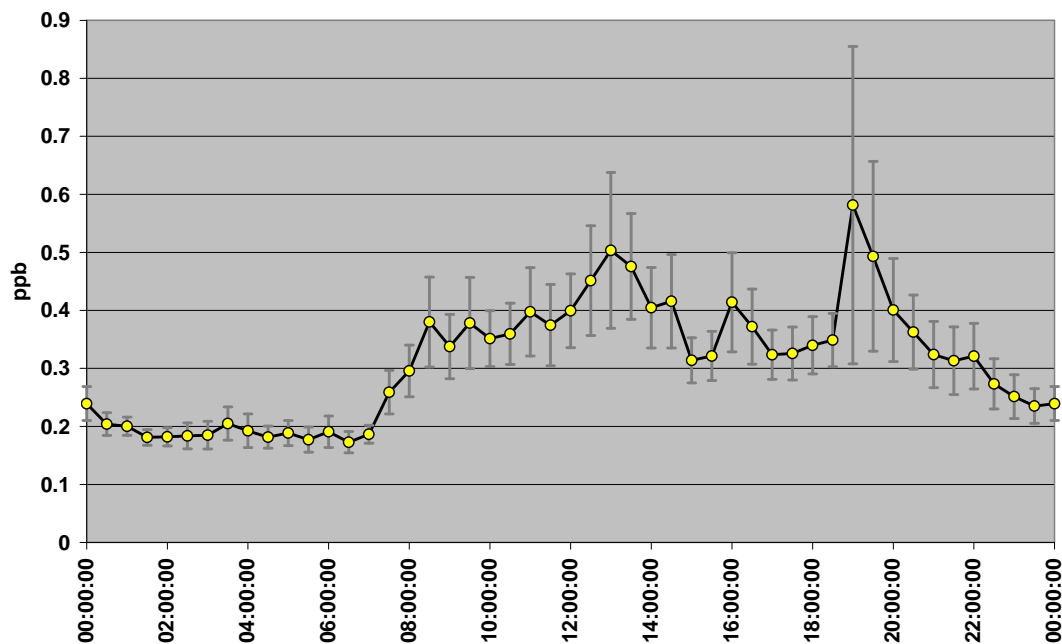


Figure 4a: Average diurnal variation of sulphur dioxide concentrations at Auchencorth, June-December 2006.

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_2 to give a small but consistent daytime peak in nitric oxide concentrations. The late evening data are very variable.

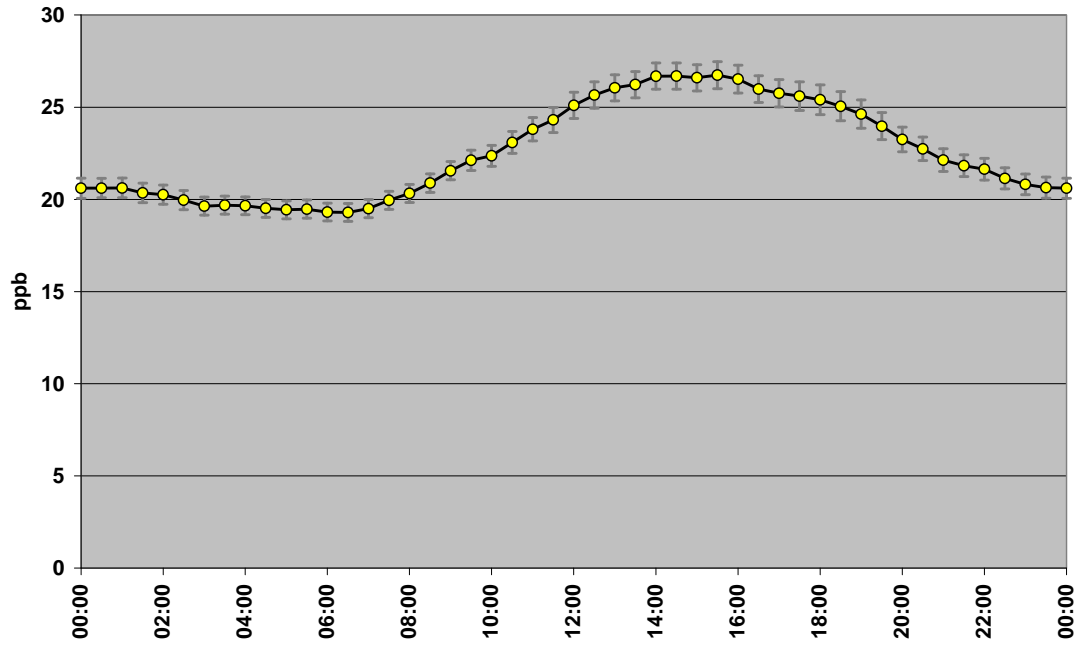


Figure 4b: Average diurnal variation of ozone concentrations at Auchencorth, June-December 2006.

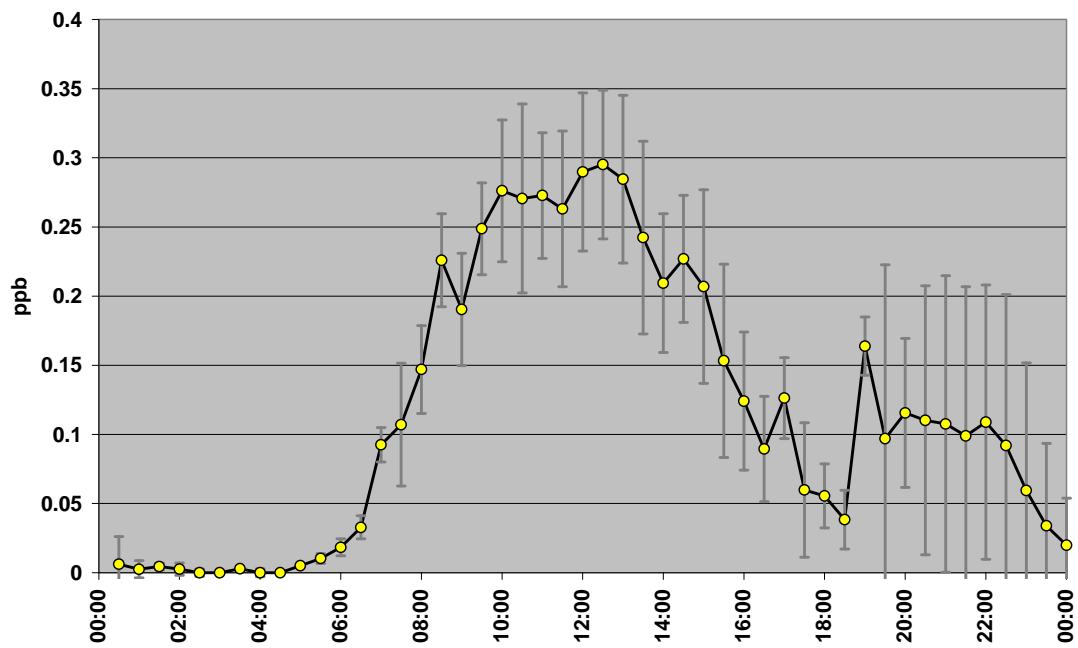


Figure 4c: Average diurnal variation of nitric oxide concentrations at Auchencorth, June-December 2006.

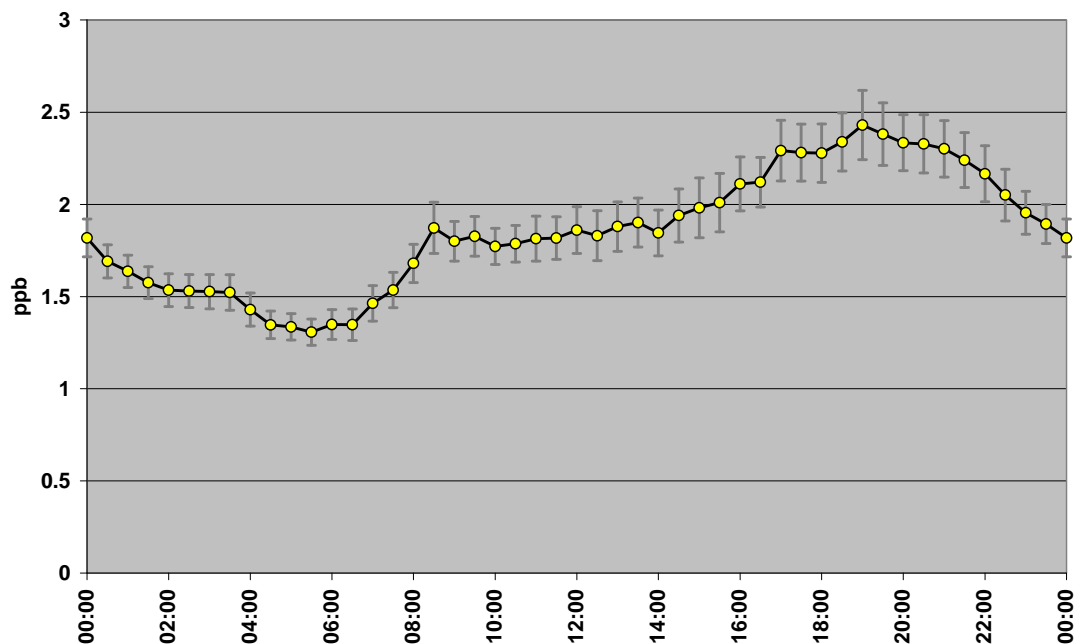


Figure 4d: Average diurnal variation of nitrogen dioxide concentrations at Auchencorth, June-December 2006.

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.

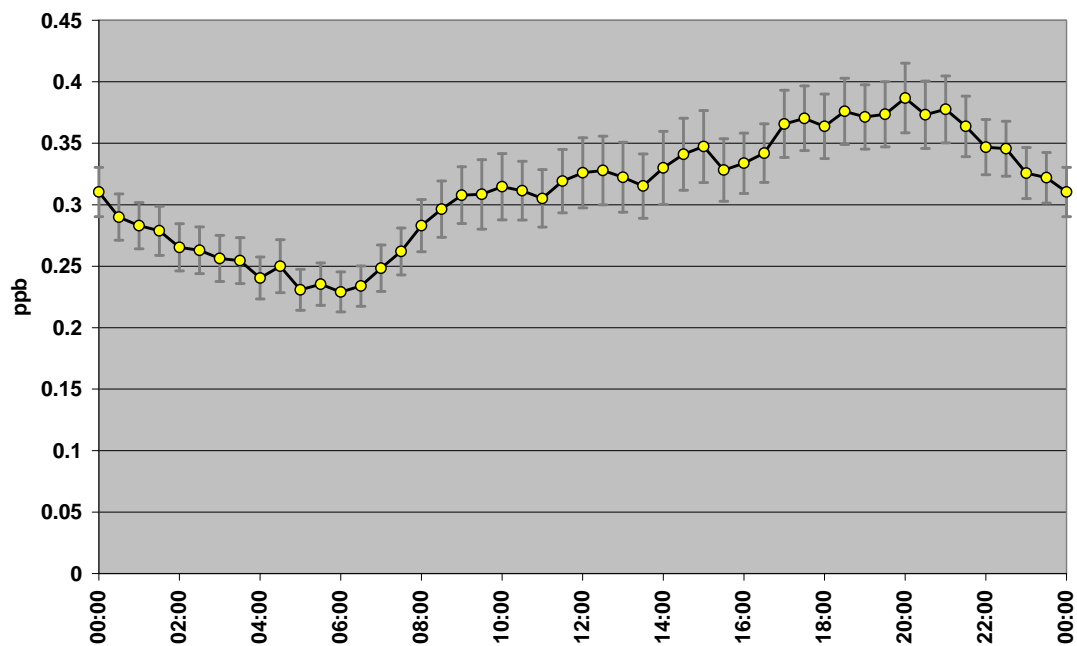


Figure 4e: Average diurnal variation of black carbon concentrations at Auchencorth, June-December 2006.

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 2006 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.

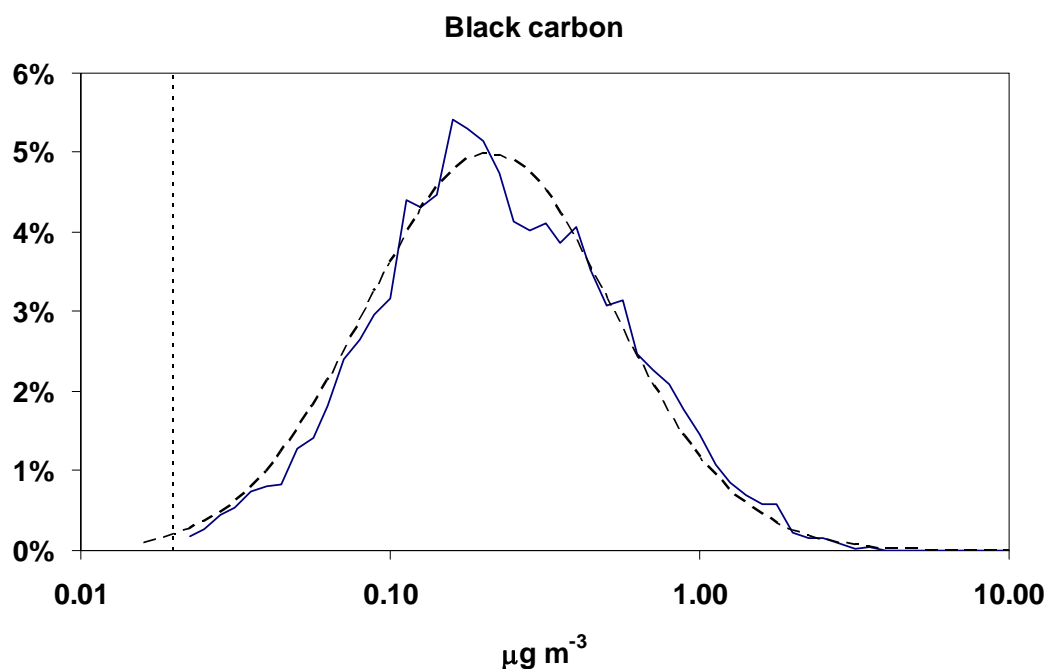


Figure 5a: Frequency distribution of 30-minute black carbon concentrations from June to December 2006. Note the log scale on the x-axis. The dotted line shows the lower limit of detection, and the dashed line shows the best-fit to a log-normal distribution (see Figure 5b).

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 discretisation at low concentrations reflects the resolution at which the data are reported ($0.01 \mu\text{g m}^{-3}$) and suggest that the effective limit of detection is at or below $0.01 \mu\text{g m}^{-3}$ because all the data appear to fall on the fitted line. The best-fit line from Figure 5b is shown on Figure 5a as the equivalent frequency distribution, as a dashed line.

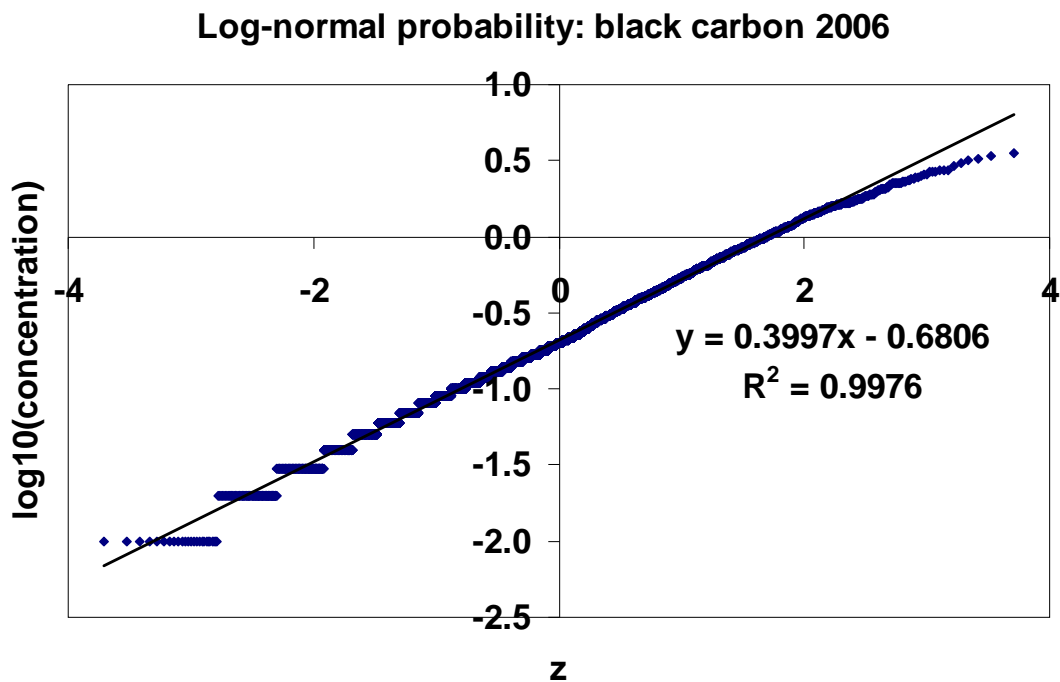


Figure 5b: Log-normal probability plot of black carbon concentrations between June and December 2006. The horizontal axis shows the standard normal variate (z), and the vertical axis the \log_{10} concentration of black carbon in $\mu\text{g m}^{-3}$. The geometric mean is given by the intercept after conversion from logarithms ($-0.6806 \Rightarrow 0.209 \mu\text{g m}^{-3}$), and the geometric standard deviation is given from the slope ($0.3997 \Rightarrow 2.51 \mu\text{g m}^{-3}$)

The frequency distributions and normal probability plots are shown below for some of the other gases and particles measured in 2006. Figure 6 shows the daily data for particulate matter (PM). Only $\text{PM}_{2.5}$ data are available for 2006. The smaller number of valid data points (198) 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.

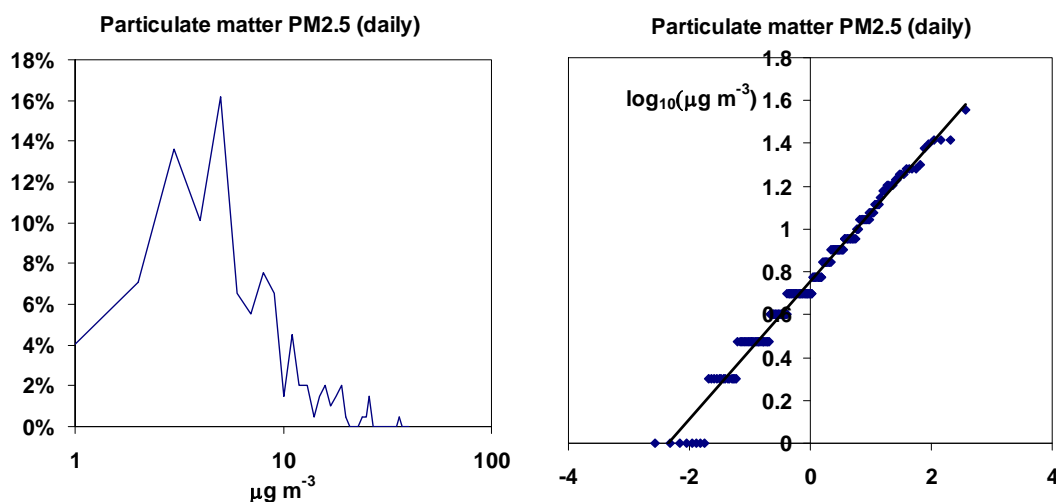


Figure 6: Frequency distribution and log-normal probability plot for daily $\text{PM}_{2.5}$, June-December 2006

Figure 7 shows data for sulphur dioxide. Although the data are fairly well described by a log-normal distribution, a large fraction of the data set falls below the instrumental detection limit, which may account for the deviation in linearity at low concentrations in the log-normal plot.

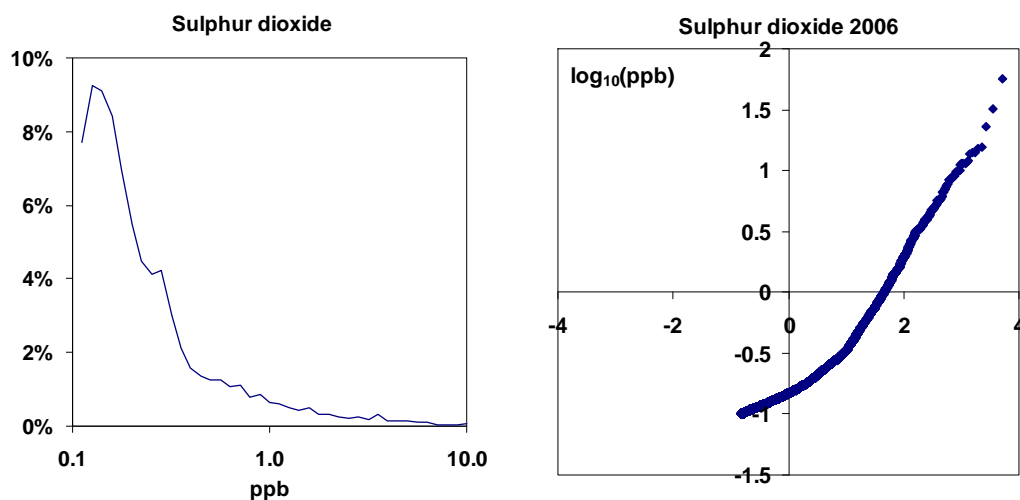


Figure 7: Frequency distribution and log-normal probability plot for sulphur dioxide, June-December 2006

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, but the few measurable data suggest a log-normal distribution (dashed line in the normal-probability plot).

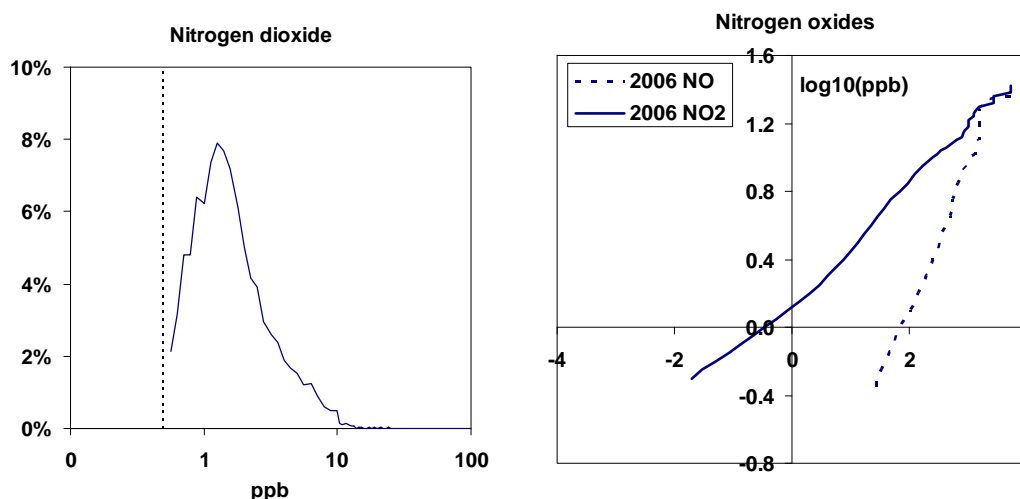


Figure 8: Frequency distribution and log-normal probability plot for nitrogen oxides, June-December 2006

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 40 ppb and higher than predicted from the overall distribution – these might be regarded as ozone ‘episodes’ (Figure 9.)

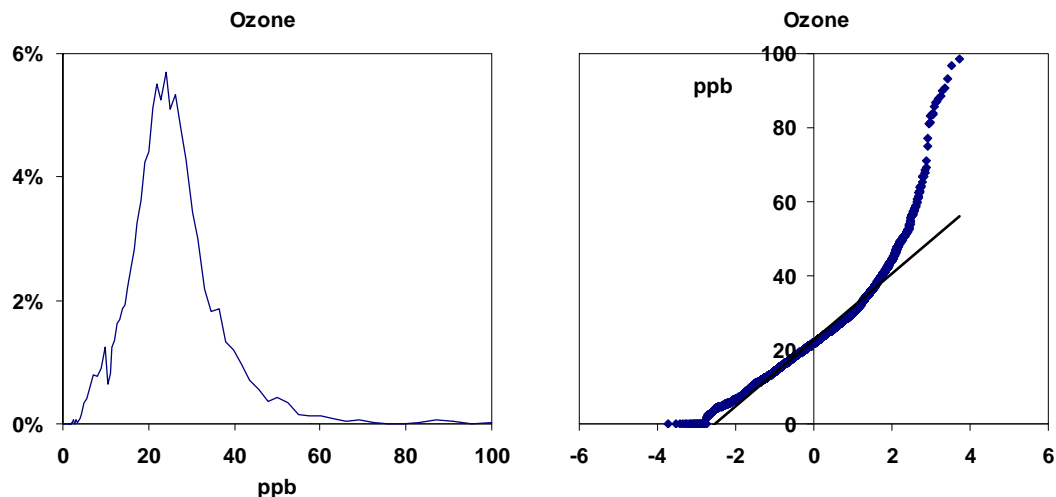


Figure 9: Frequency distribution and normal probability plot for ozone, June-December 2006

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).

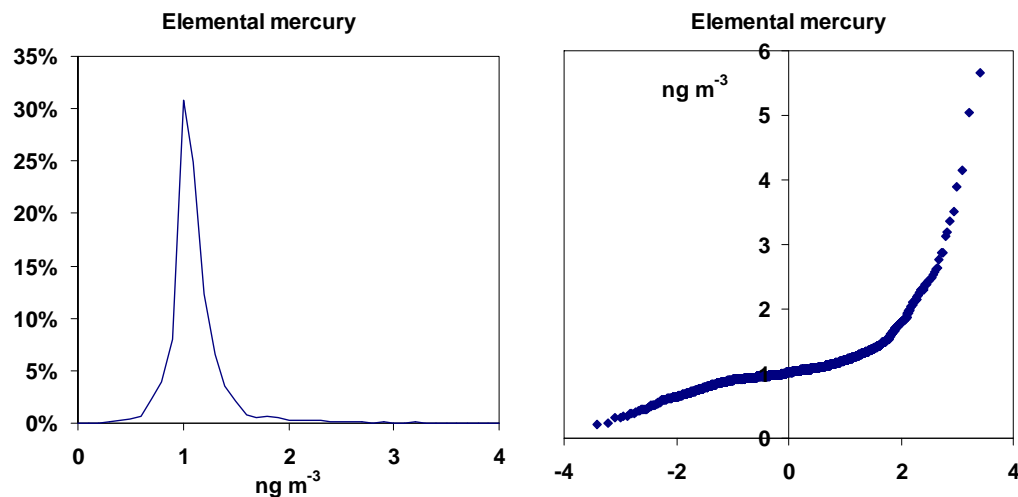


Figure 10: Frequency distribution and normal probability plot for elemental mercury, June-December 2006

8. Case studies

10-17 October 2006

This period illustrates the contrast between marine and continental air experienced at the site. At the start of the period (Figure 11a) the air arriving at the site had come from across the Atlantic Ocean, with relatively high wind speeds as shown by the distances between the 12-hour markers on the plots. As expected, concentrations of sea-salts in particulate matter (MARGA) are relatively high (Figure 12a), while concentrations of particles derived from pollutant gases (ammonium, nitrate, sulphate) are low (Figure 12b). Between midnight and noon on 14th October the trajectories move rapidly and now come from the south-east, originating over continental Europe, and keeping close to the surface (Figure 11b). The concentrations of sea-salts consequently decrease markedly, almost to zero (Figure 12a), while concentrations of pollutant-derived ions increase in the more polluted air (Figure 12b).

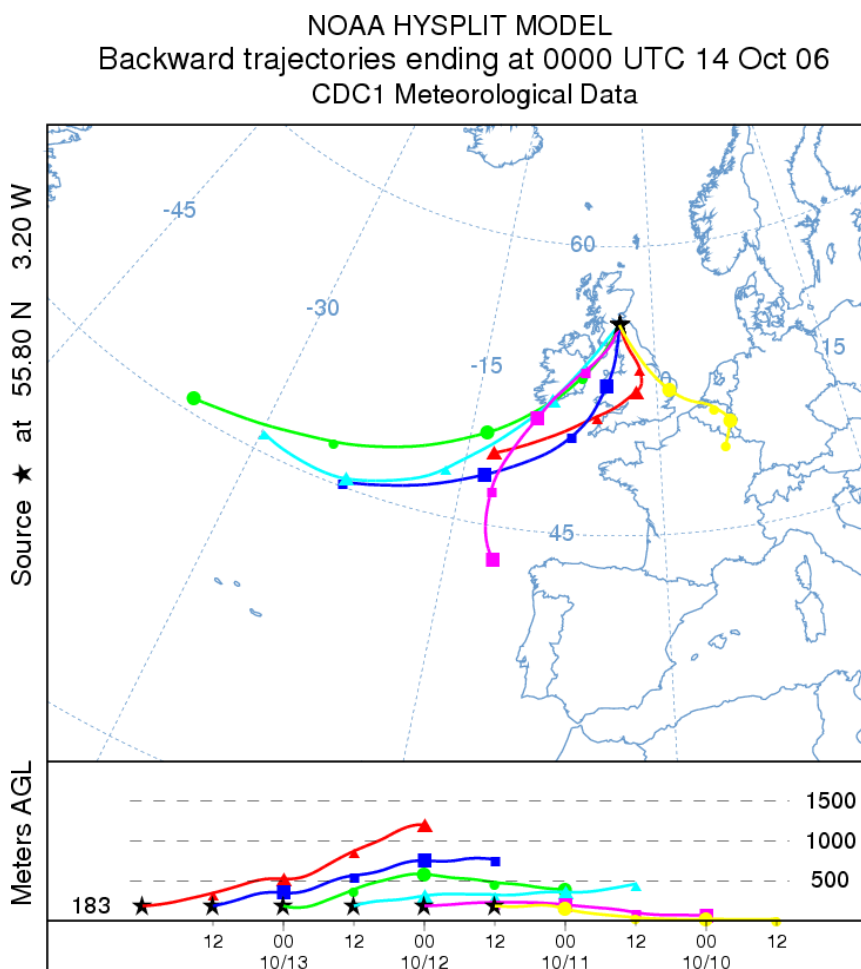


Figure 11a: HYSPLIT (www.ready.noaa.gov) trajectory maps for arrival times between 1200 on 11 October and 0000 on 14 October, showing the paths air parcels took during the 48h before arriving at the site. Symbols are shown every 12h. The lower figure shows the vertical path of the air parcels. Trajectories shown above start (yellow) with those arriving at 1200 on 11 October, and finish (red) with those arriving at midnight on 13 October, and are shown at 12h intervals. The later air parcels are shown as descending towards the site (lower panel), and more slowly moving.

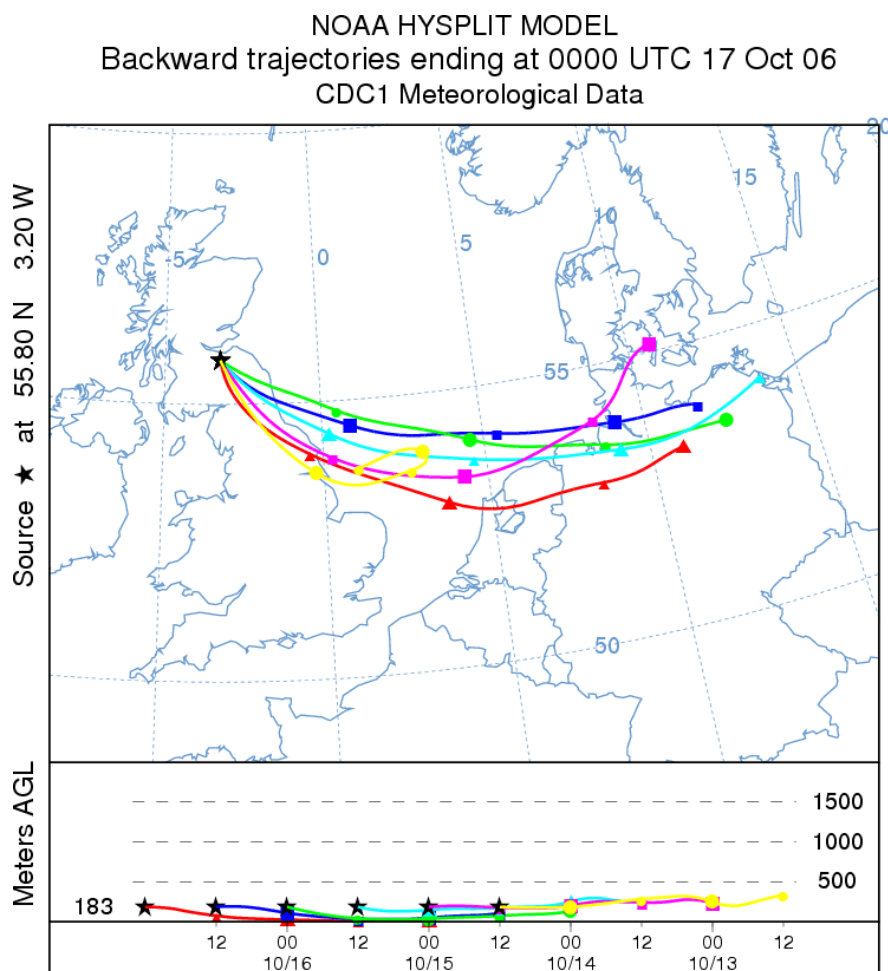


Figure 11b: HYSPLIT (www.ready.noaa.gov) trajectory maps for arrival times between 1200 on 14 October and 0000 on 17 October, showing the paths air parcels took during the 48h before arriving at the site. Symbols are shown every 12h. The lower figure shows the vertical path of the air parcels. Trajectories shown above start (yellow) with those arriving at 1200 on 14 October, and finish (red) with those arriving at midnight on 17 October, and are shown at 12h intervals. All the air parcels are shown as remaining close to the surface (lower panel).

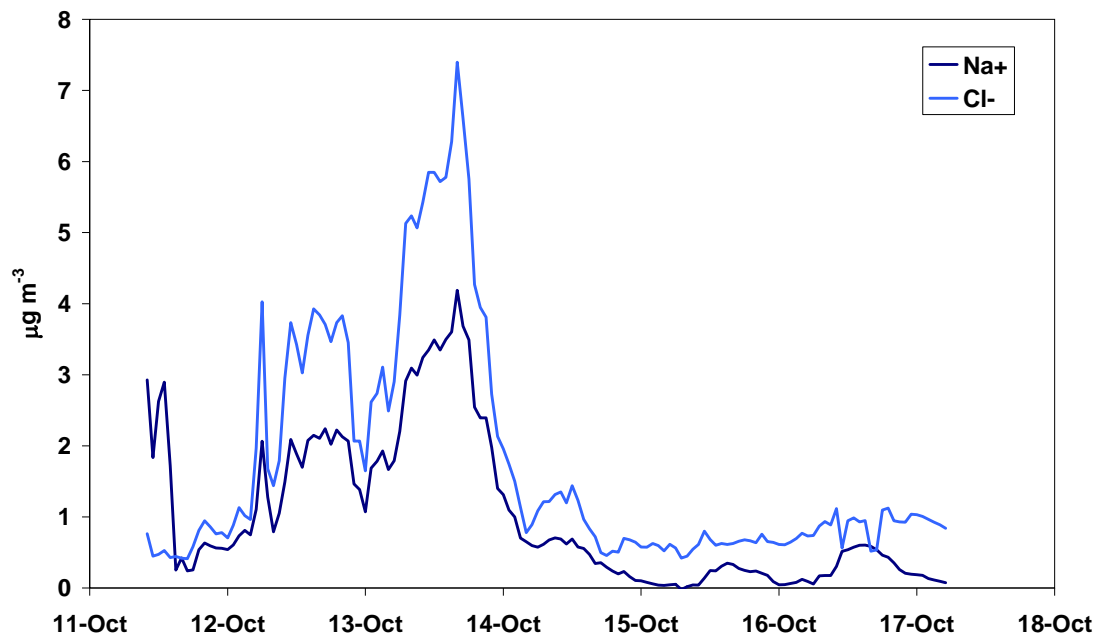


Figure 12a: Concentrations of sea-salts in particulate matter (PM₁₀) sampled by the MARGA between 11 and 17 October 2006

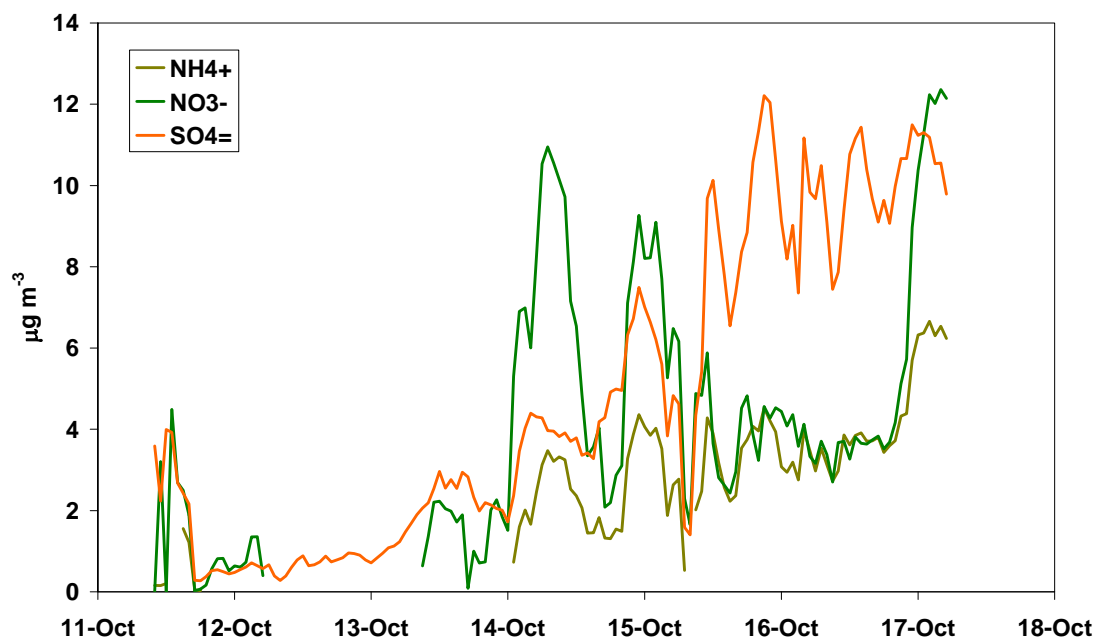


Figure 12b: Concentrations of pollutant-derived material in particulate matter (PM₁₀) sampled by the MARGA between 11 and 17 October 2006

APPENDIX – Data recorded during 2006

Meteorological data

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

MARGA data (PM₁₀, PM_{2.5} and gases)

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

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
- PM₁₀ and PM_{2.5} (hourly)
- PM₁₀ (volatile and non-volatile)
- PM_{2.5} (volatile and non-volatile)
- PM₁₀ and PM_{2.5} (daily)

Mercury data

- Elemental mercury (Hg⁰)
- Reactive gaseous and particulate mercury

CEH flux gases

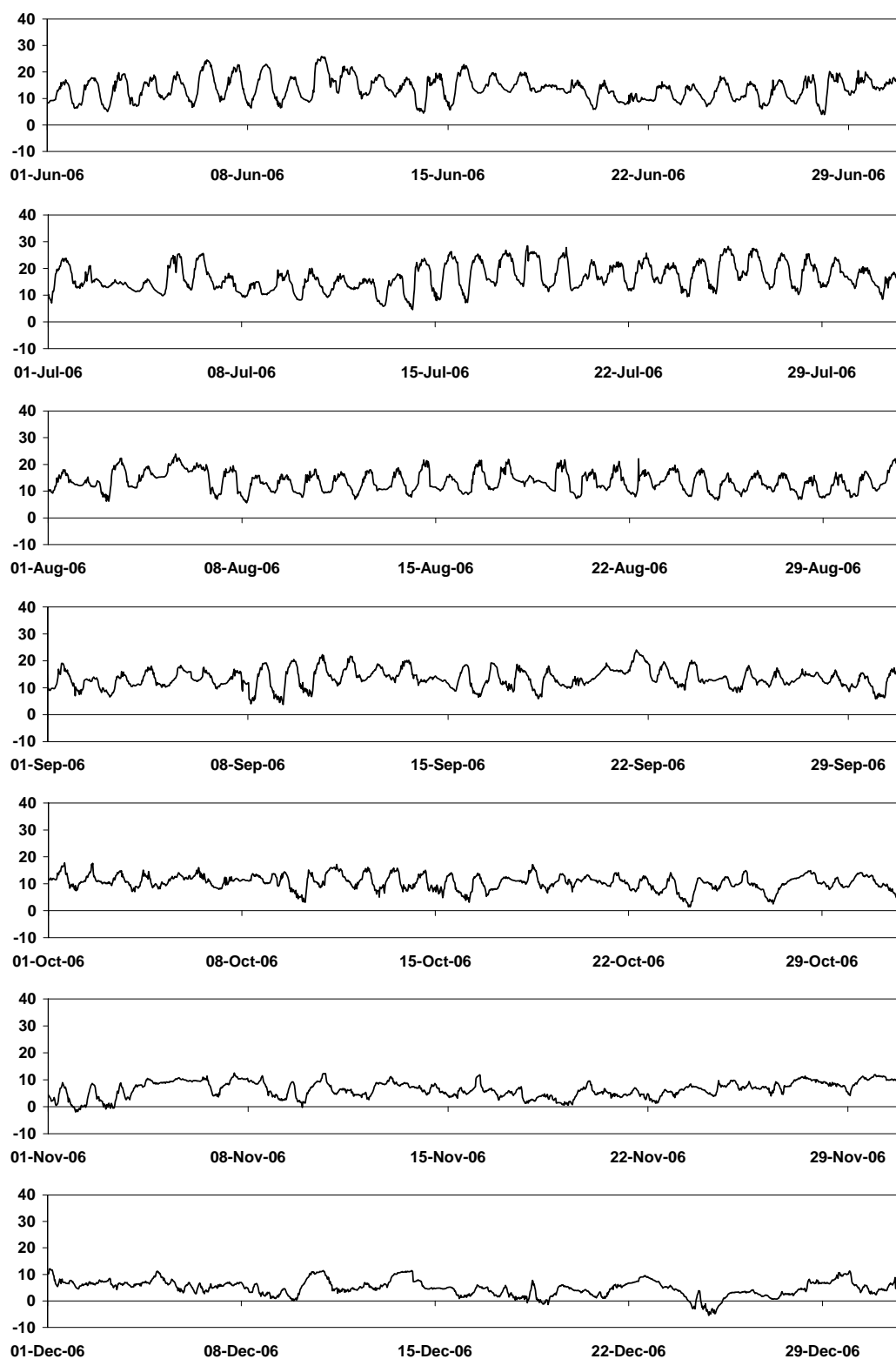
- Nitrogen oxides
- Ozone
- Sulphur dioxide

Black carbon

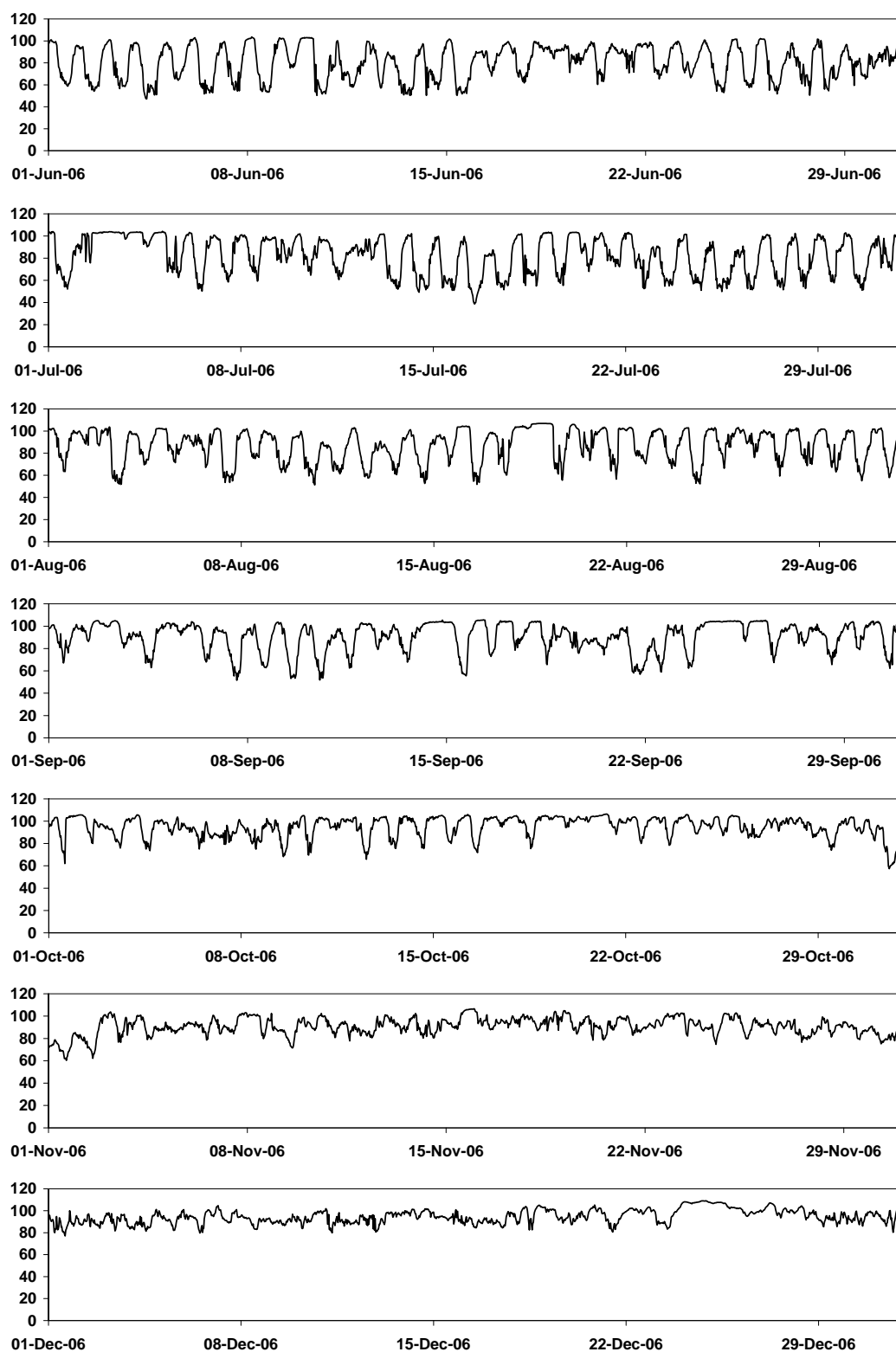
Wet-only precipitation

- Daily rainfall
- Concentrations of NH₄⁺, H⁺; Na⁺, Cl⁻; Mg²⁺, Ca²⁺; SO₄²⁻, NO₃⁻

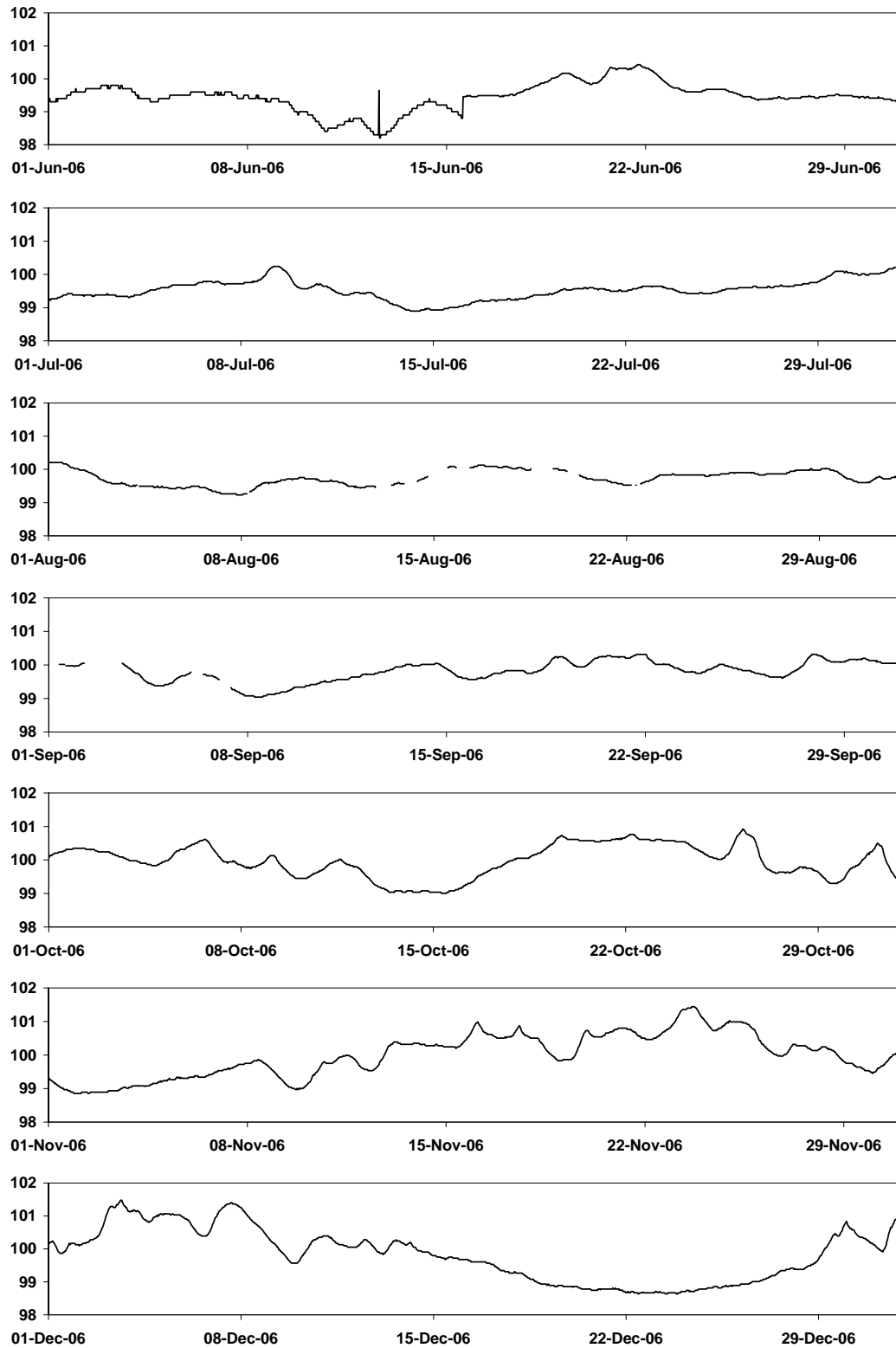
Air temperature °C



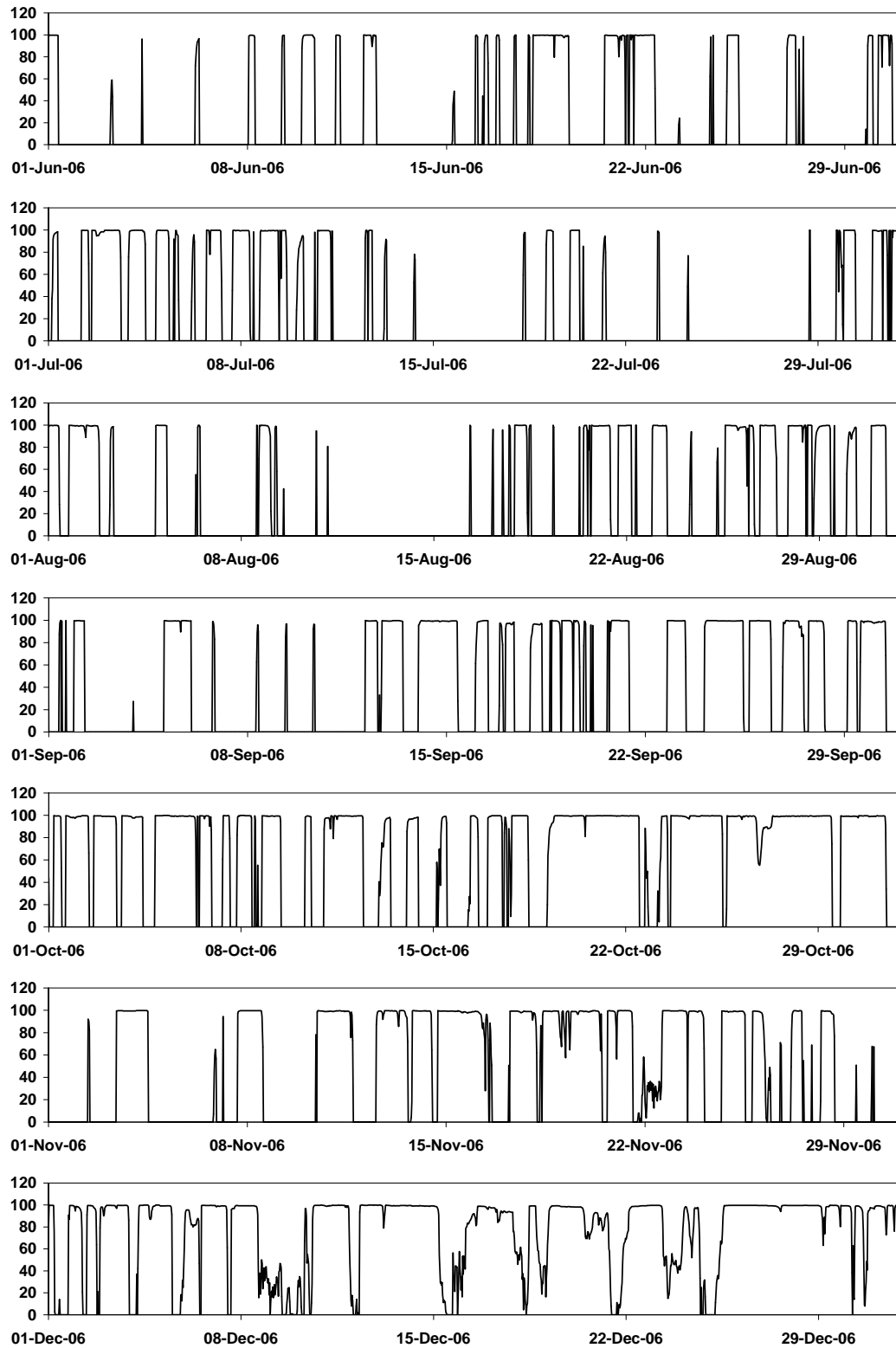
Relative humidity %



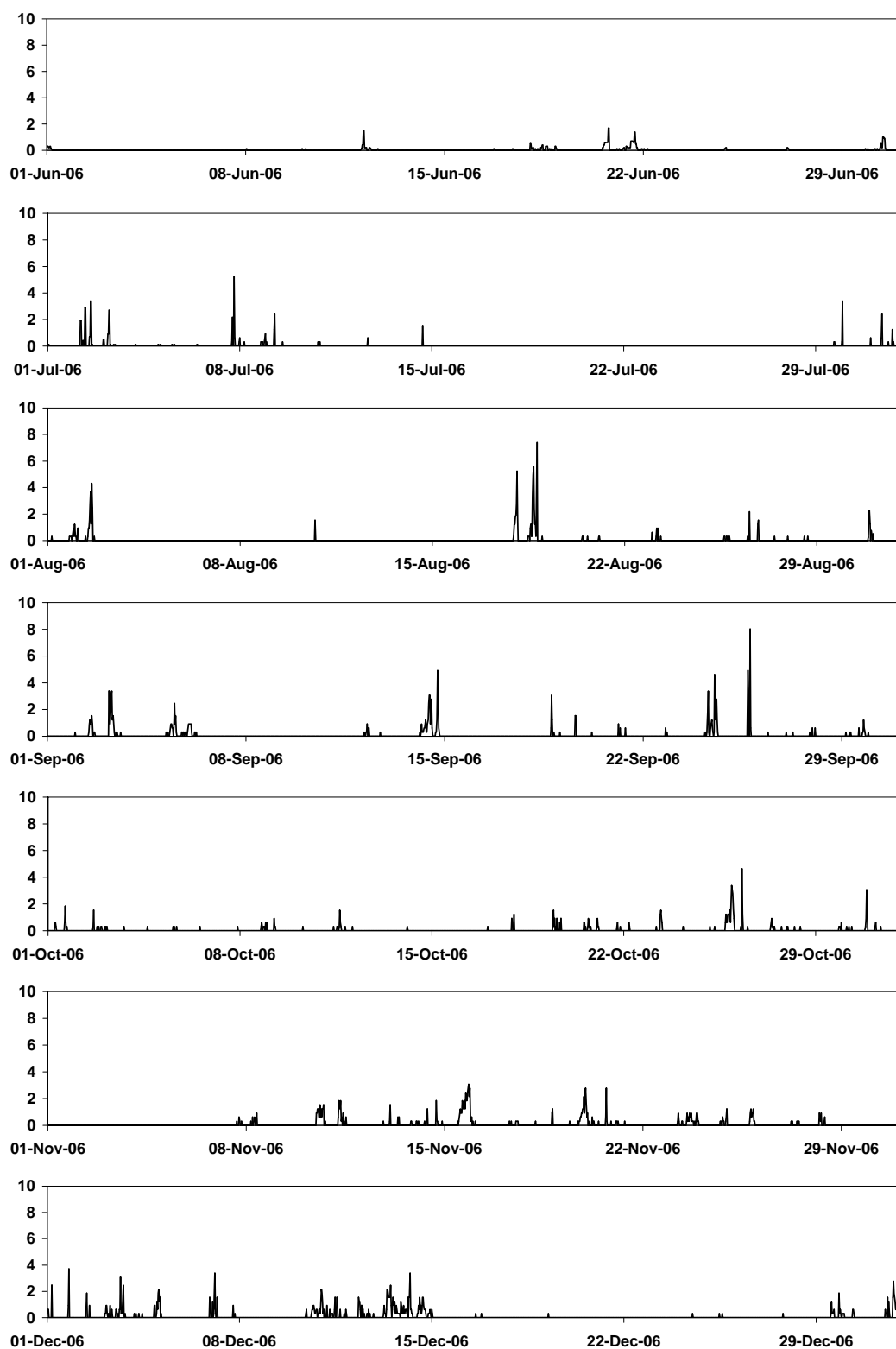
Atmospheric pressure mbar (Bush Estate)



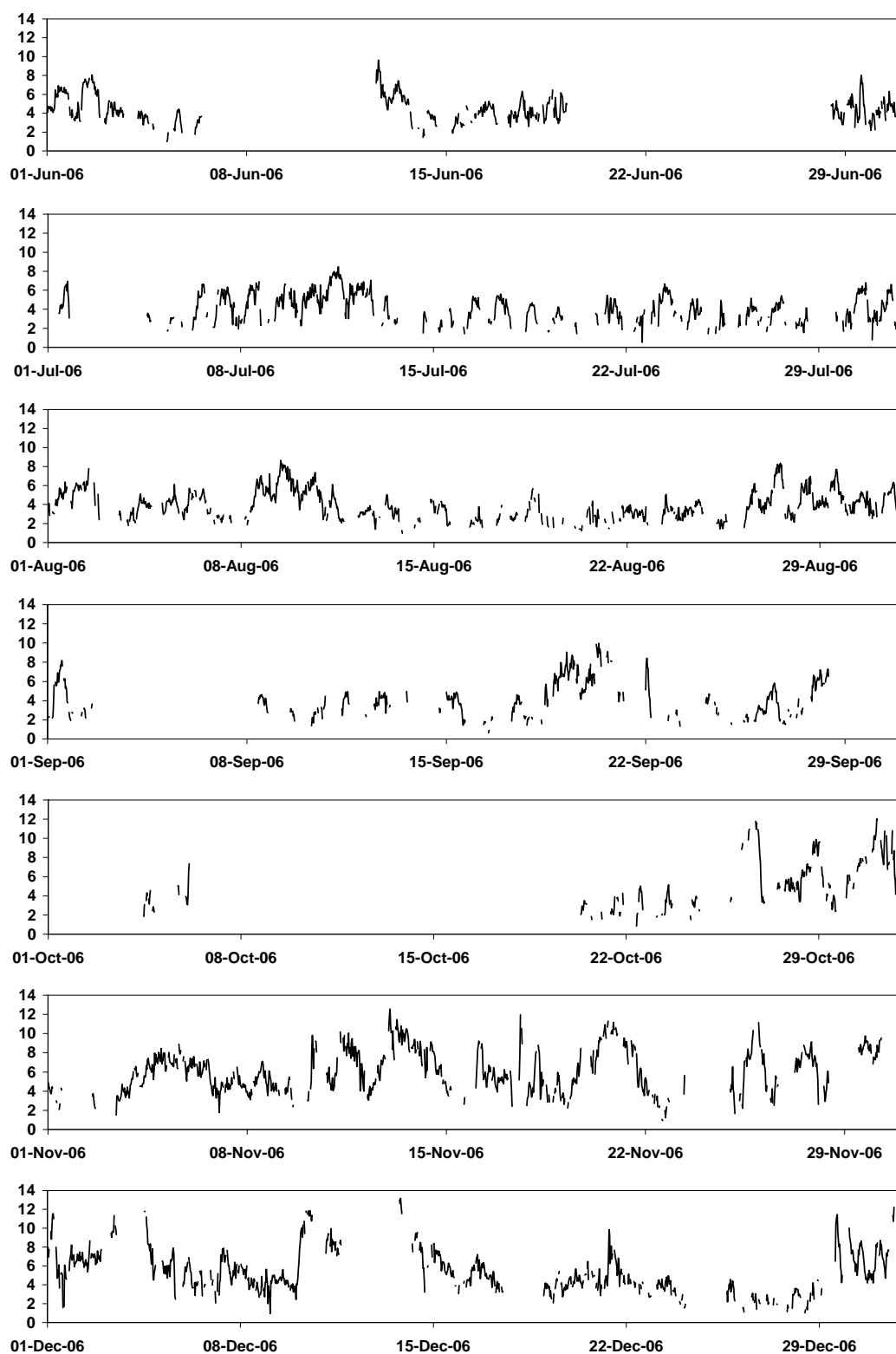
Surface wetness %



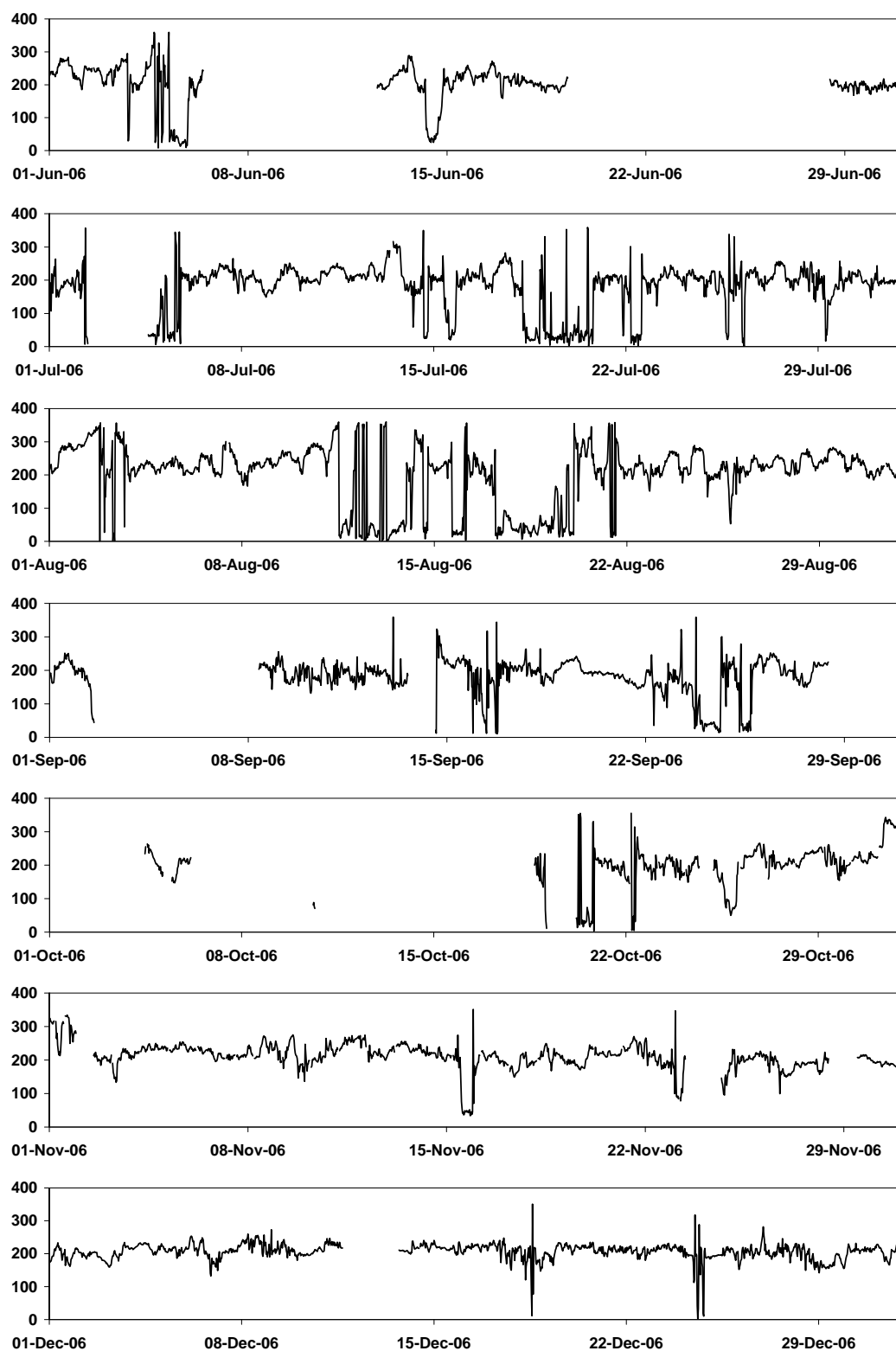
30-minute rainfall (mm)



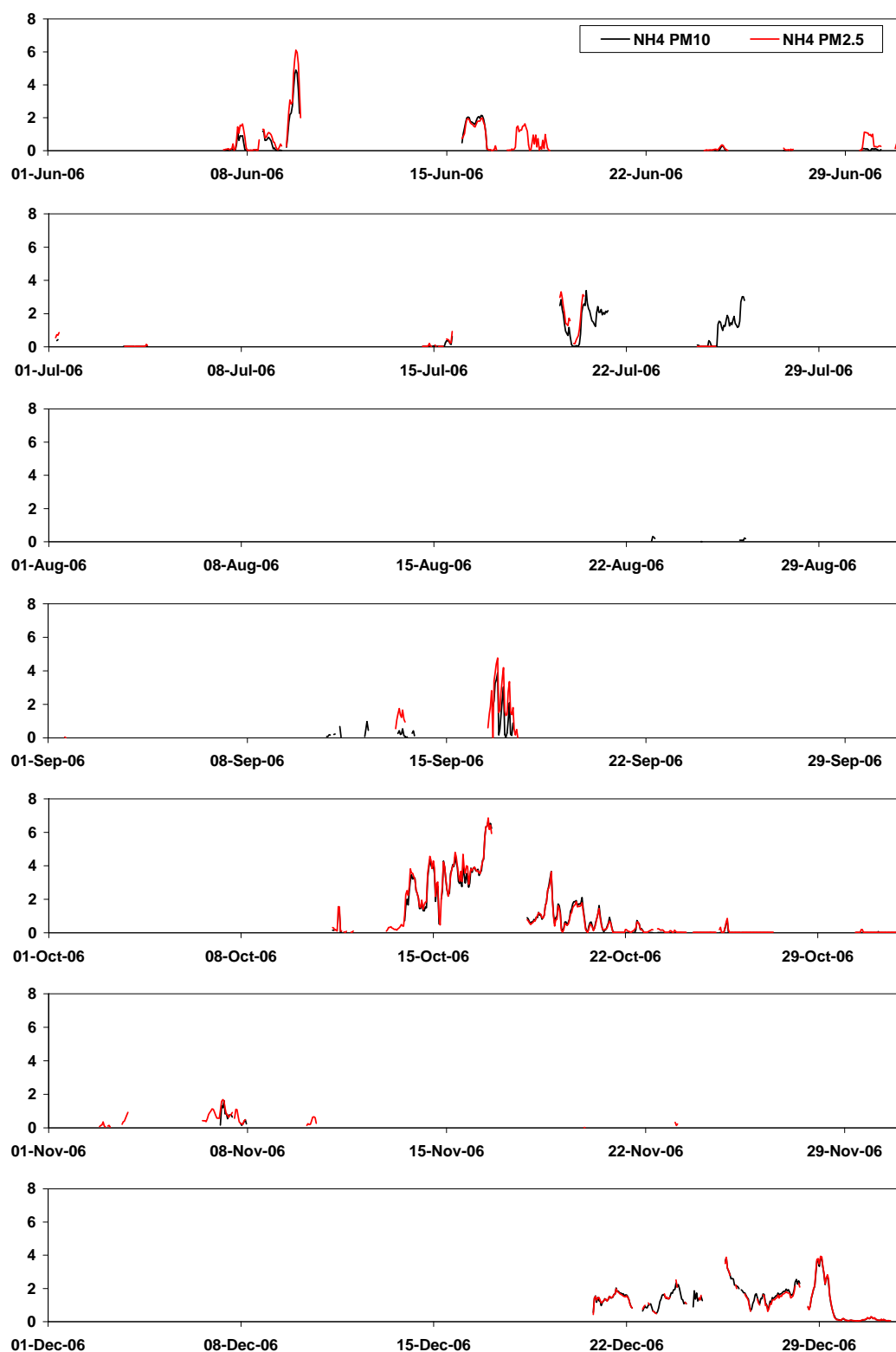
Wind speed (m s^{-1})



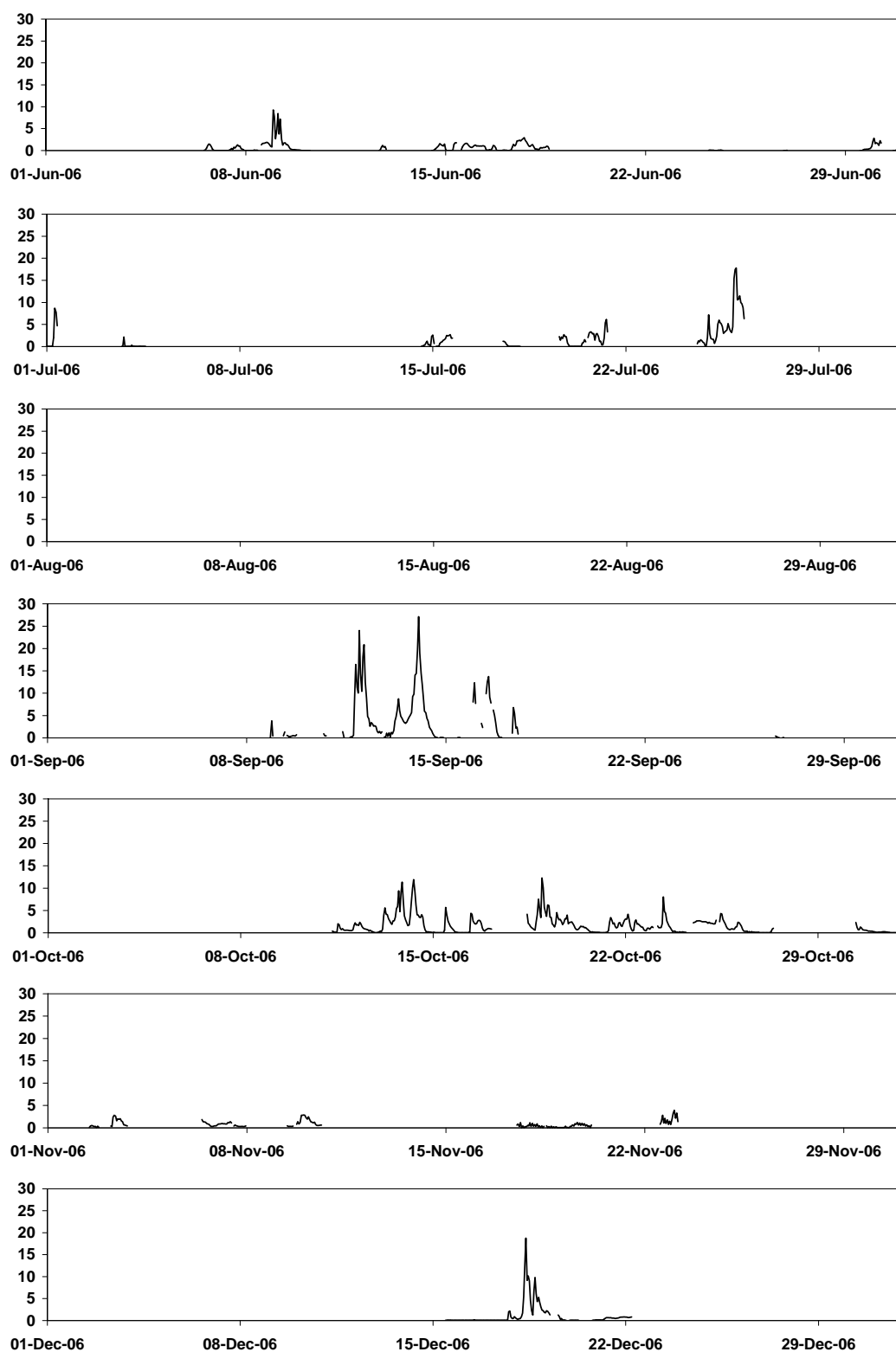
Wind direction (° from north)



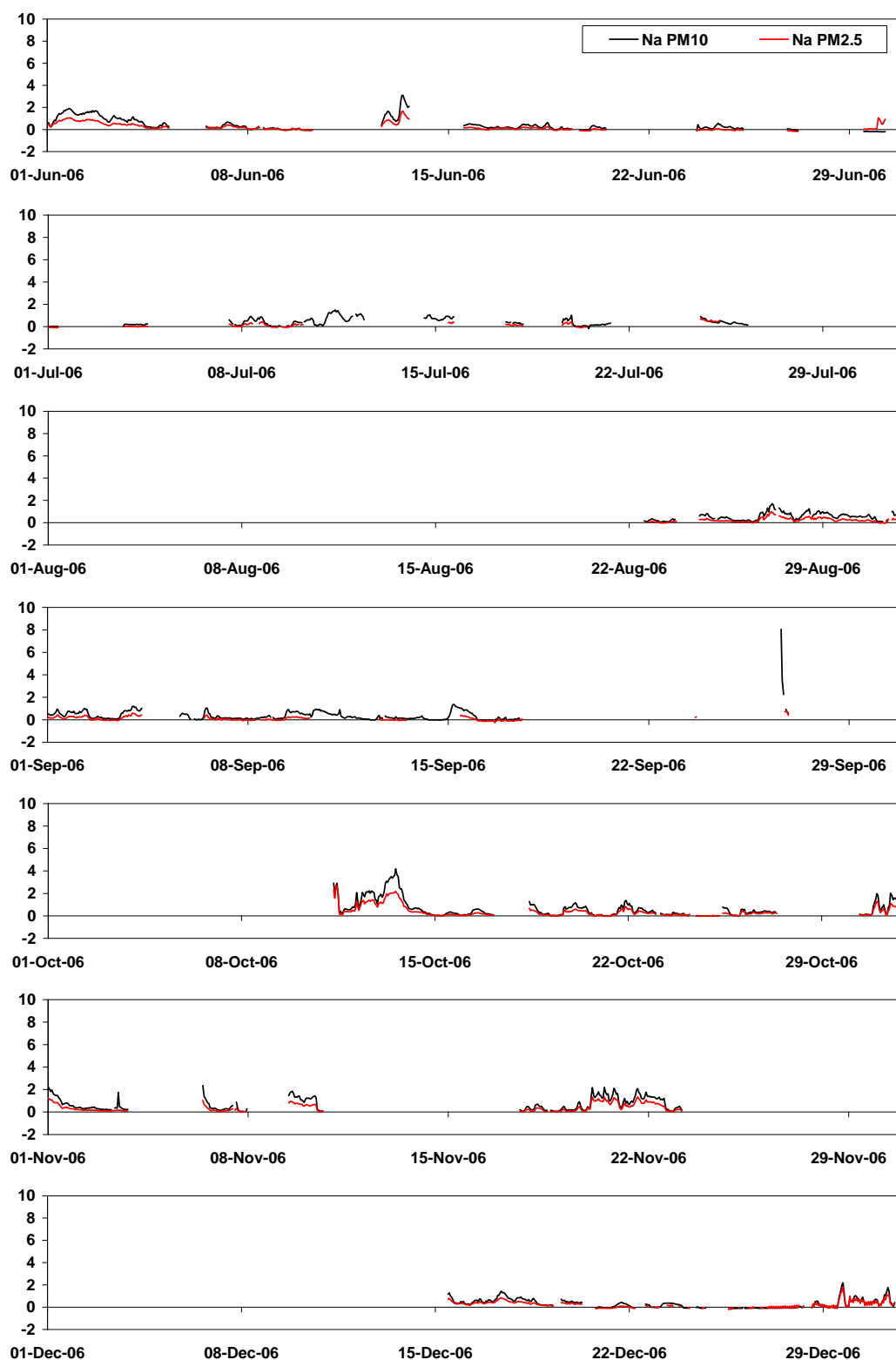
MARGA ammonium NH_4^+ $\mu\text{g m}^{-3}$



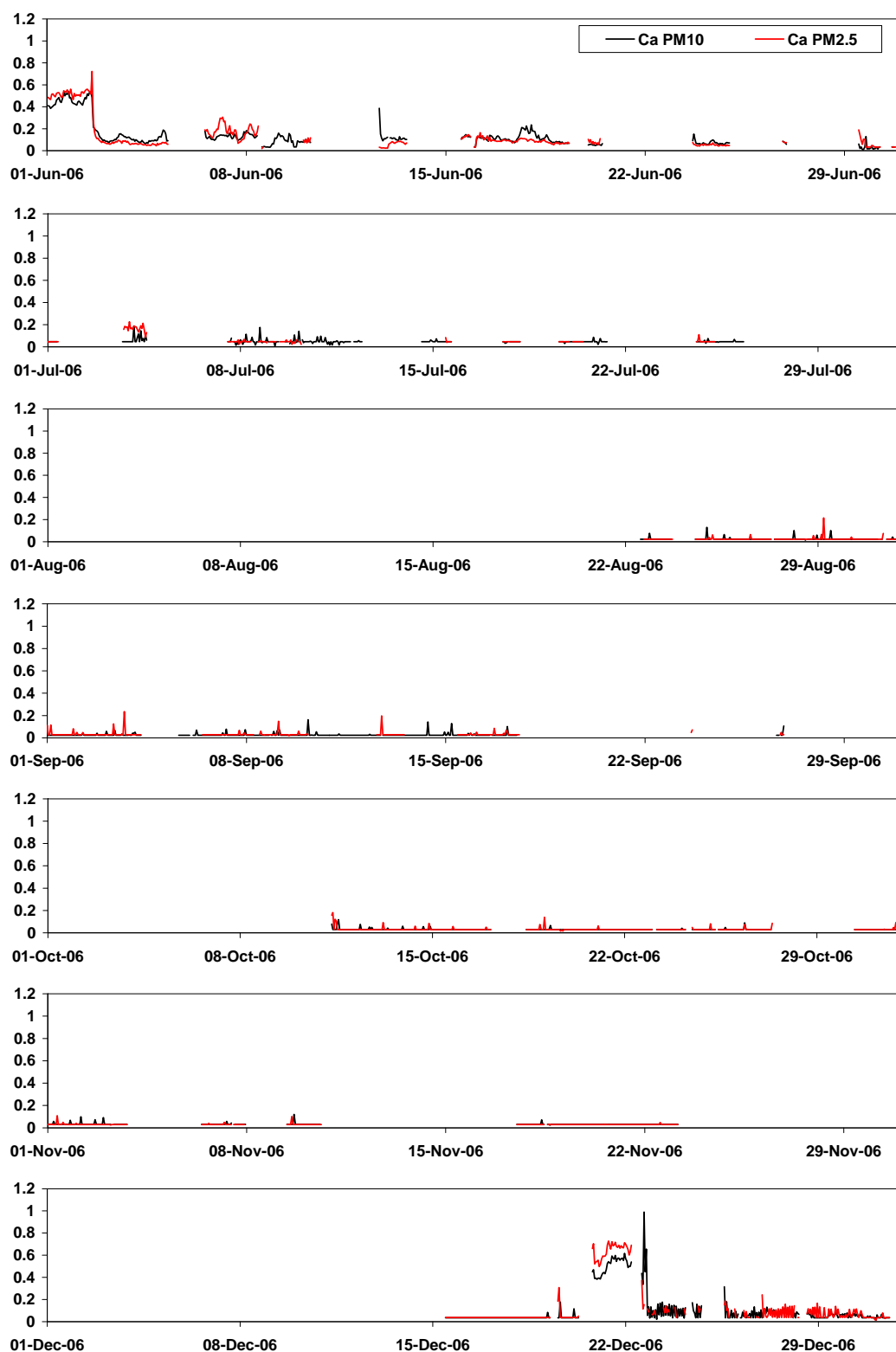
MARGA NH₃ µg m⁻³



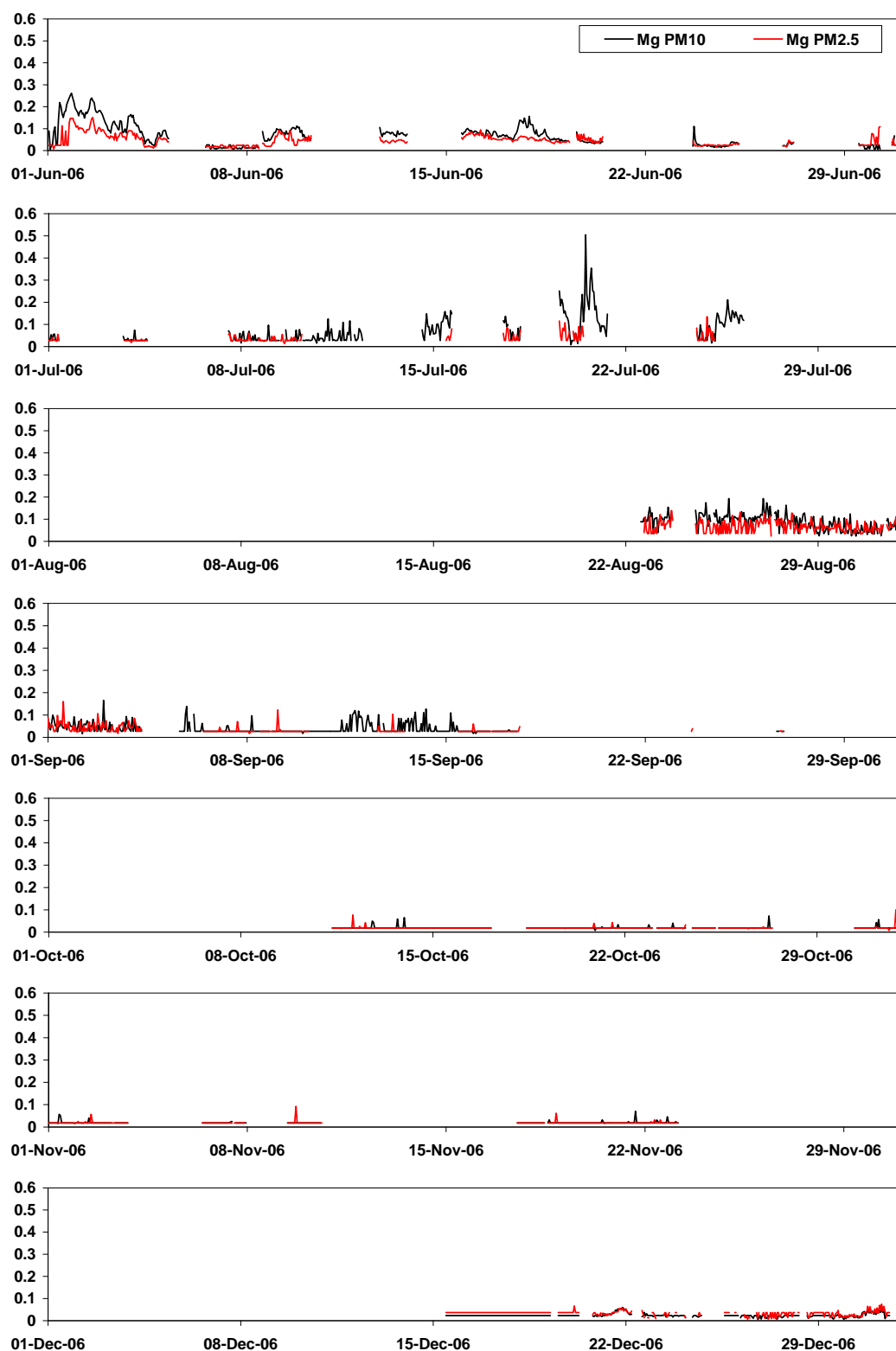
MARGA sodium Na^+ $\mu\text{g m}^{-3}$



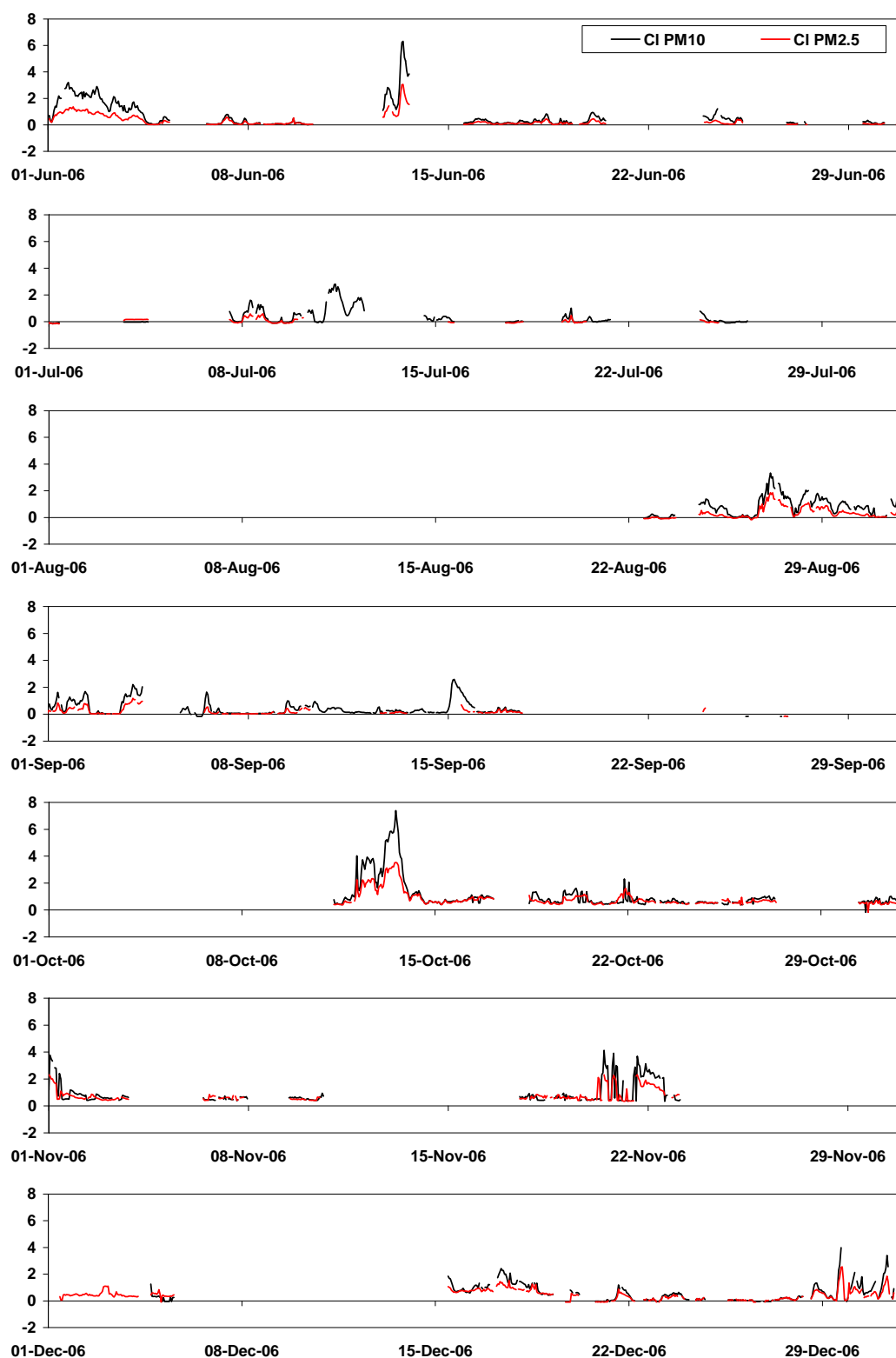
MARGA calcium Ca^{2+} $\mu\text{g m}^{-3}$



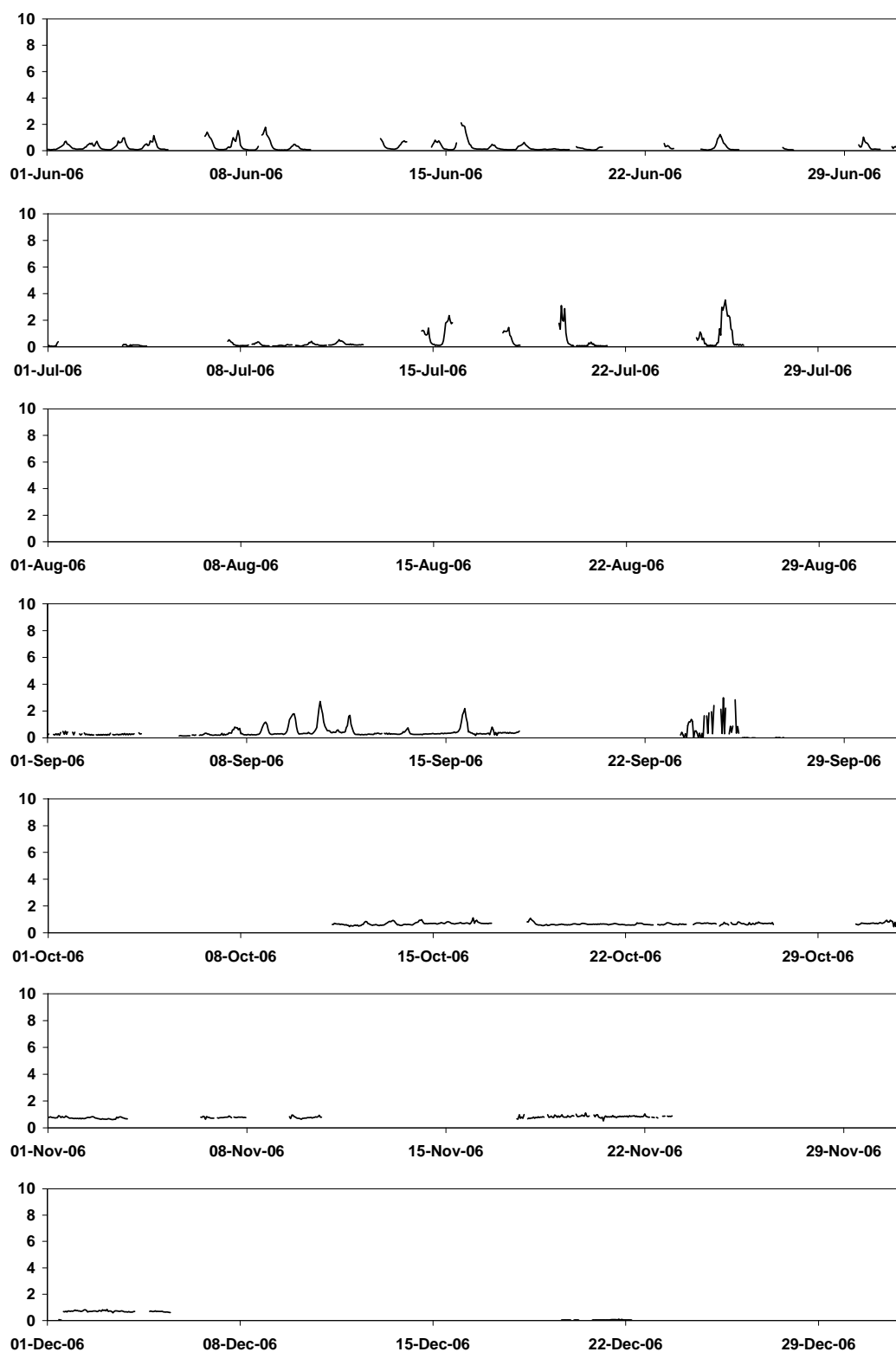
MARGA magnesium Mg^{2+} $\mu\text{g m}^{-3}$



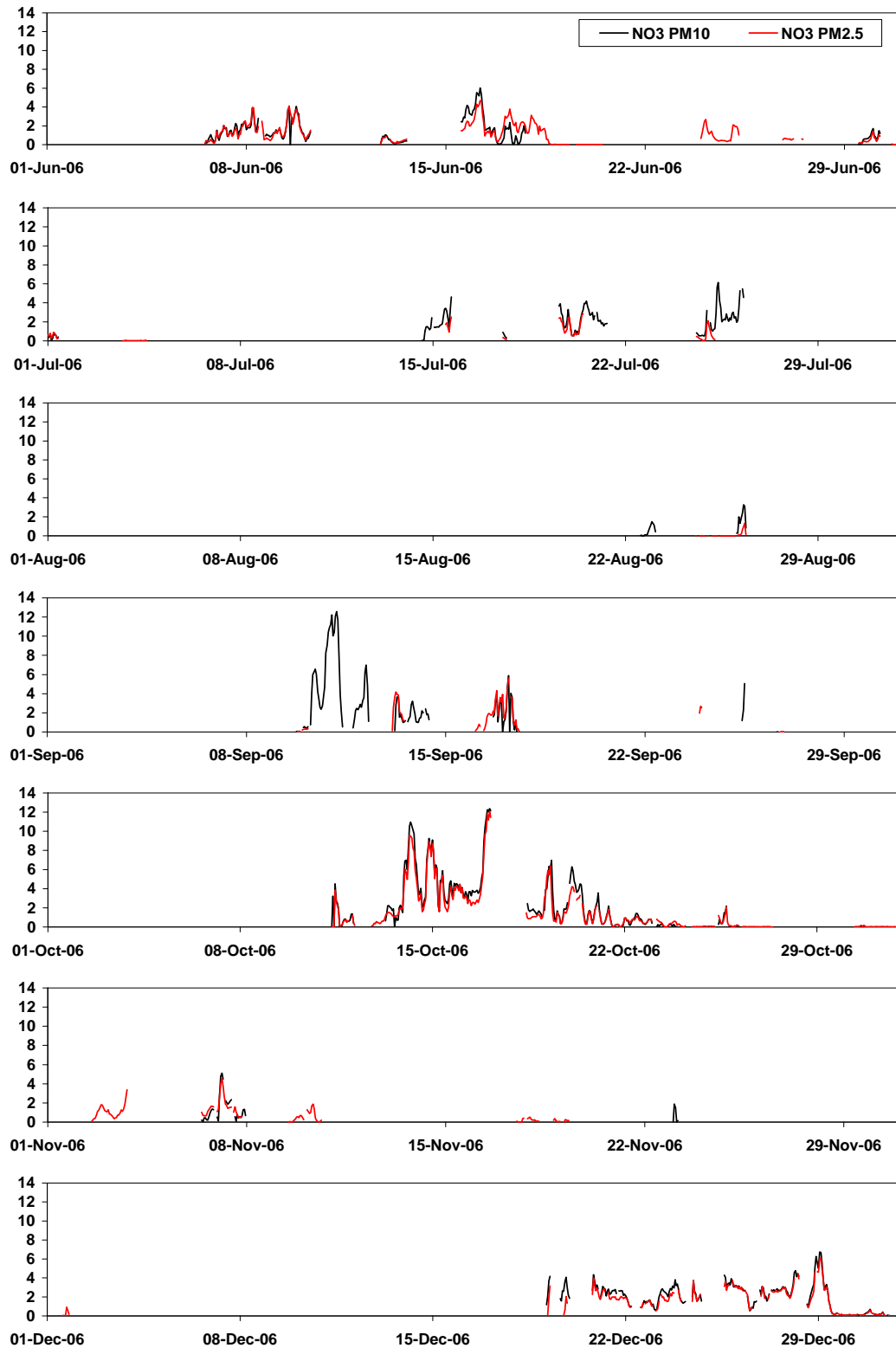
MARGA chloride $\text{Cl}^- \mu\text{g m}^{-3}$



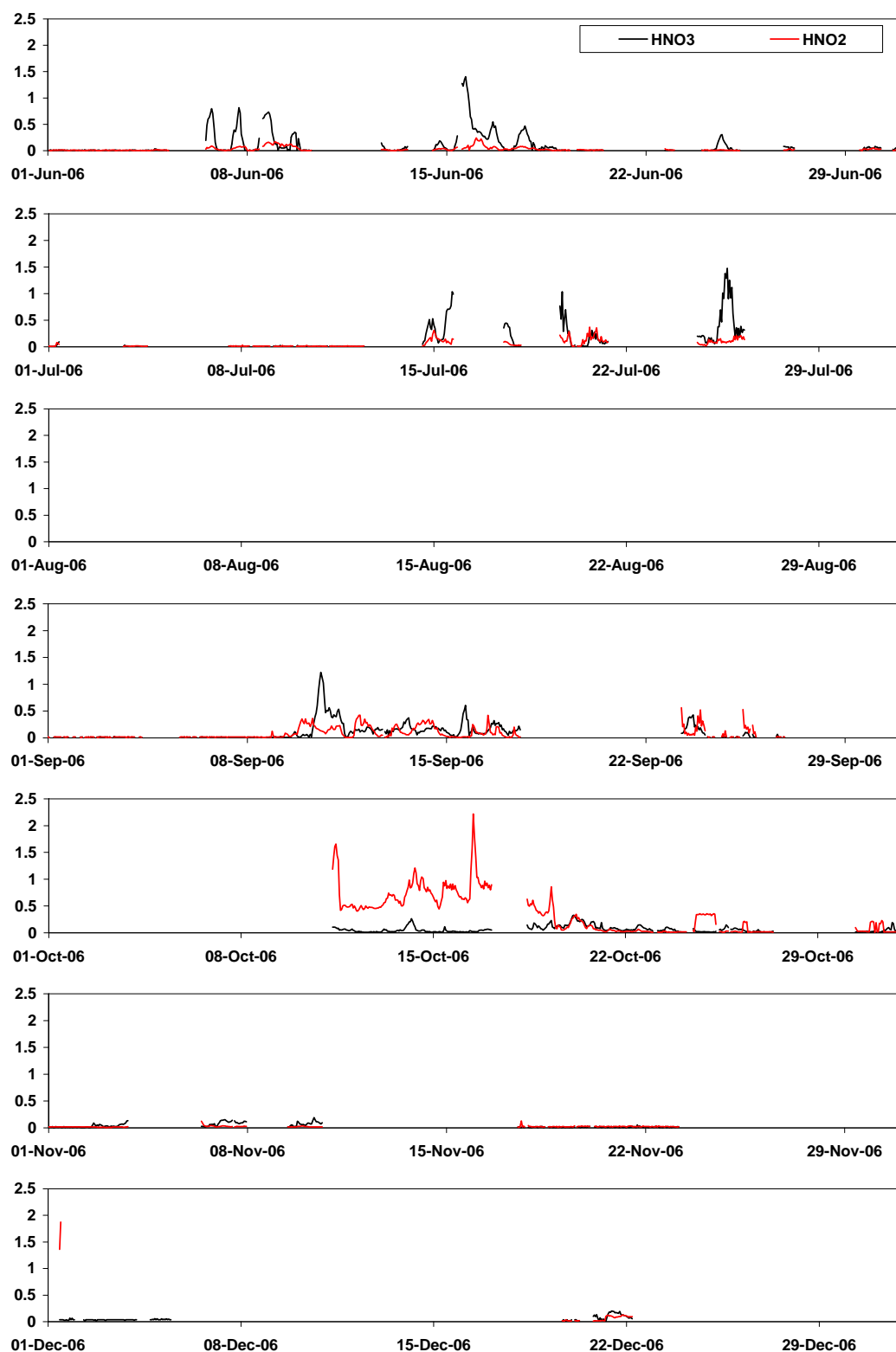
MARGA HCl $\mu\text{g m}^{-3}$



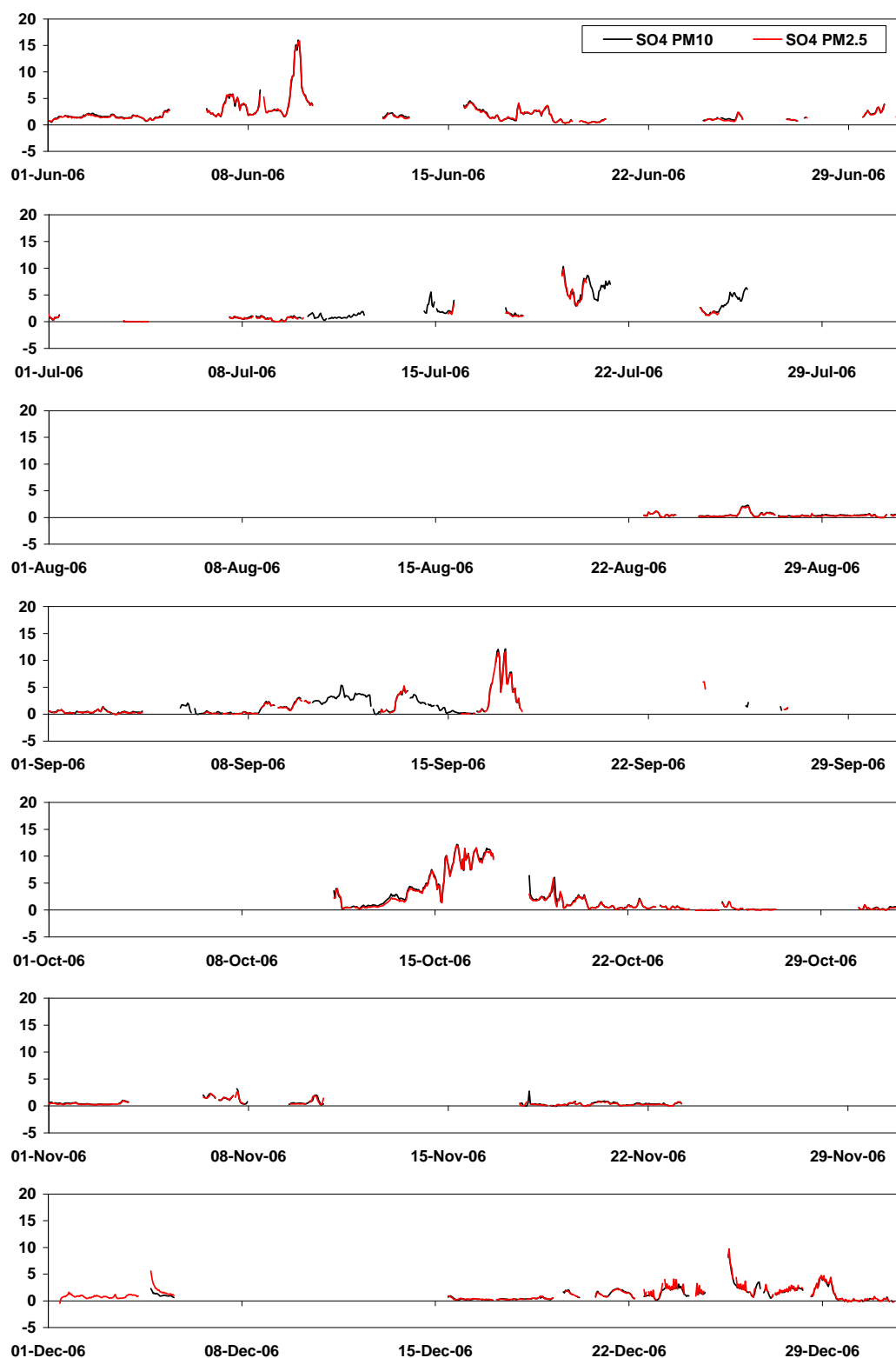
MARGA nitrate NO_3^- $\mu\text{g m}^{-3}$



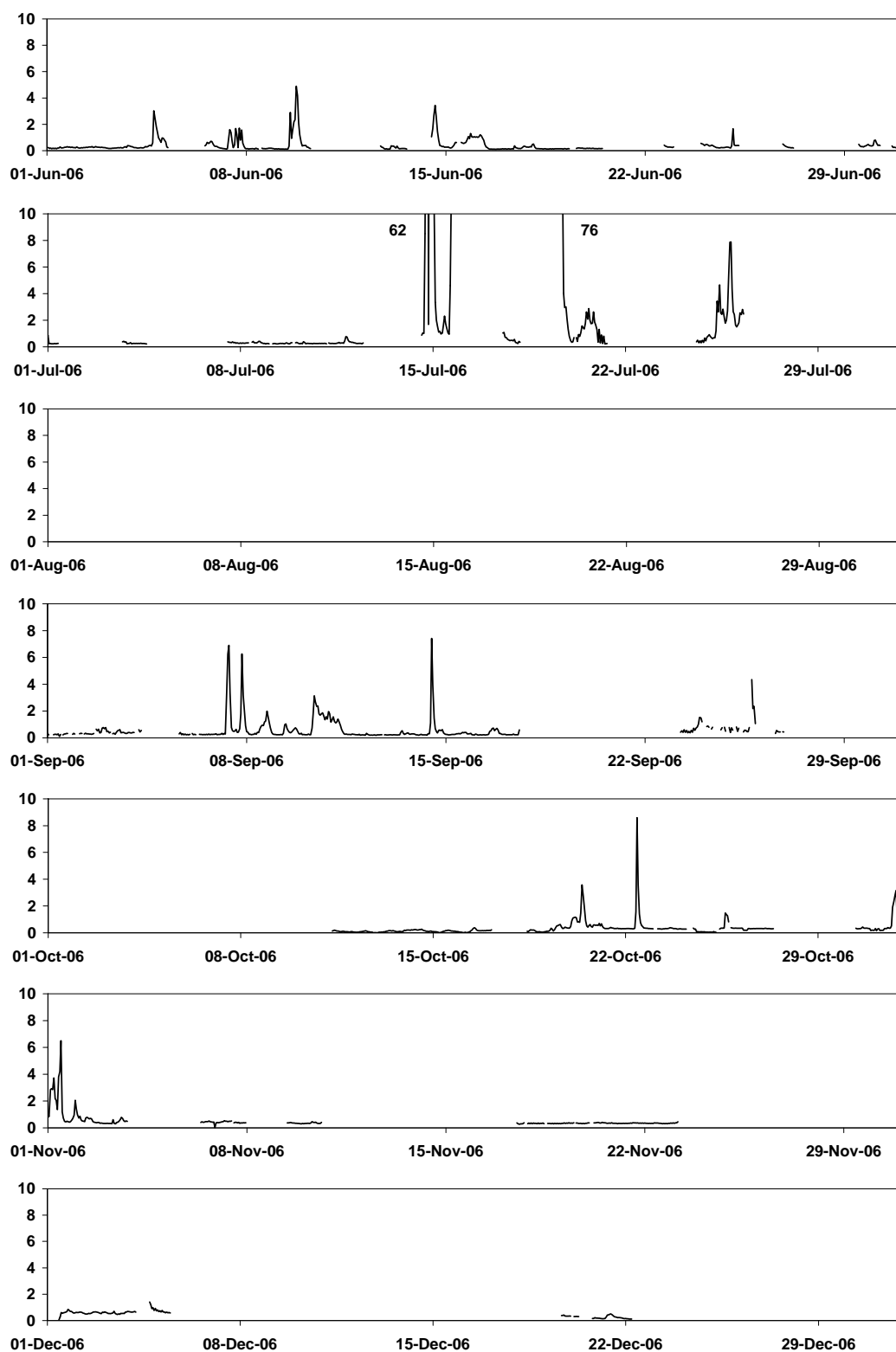
MARGA nitric and nitrous acid $\mu\text{g m}^{-3}$



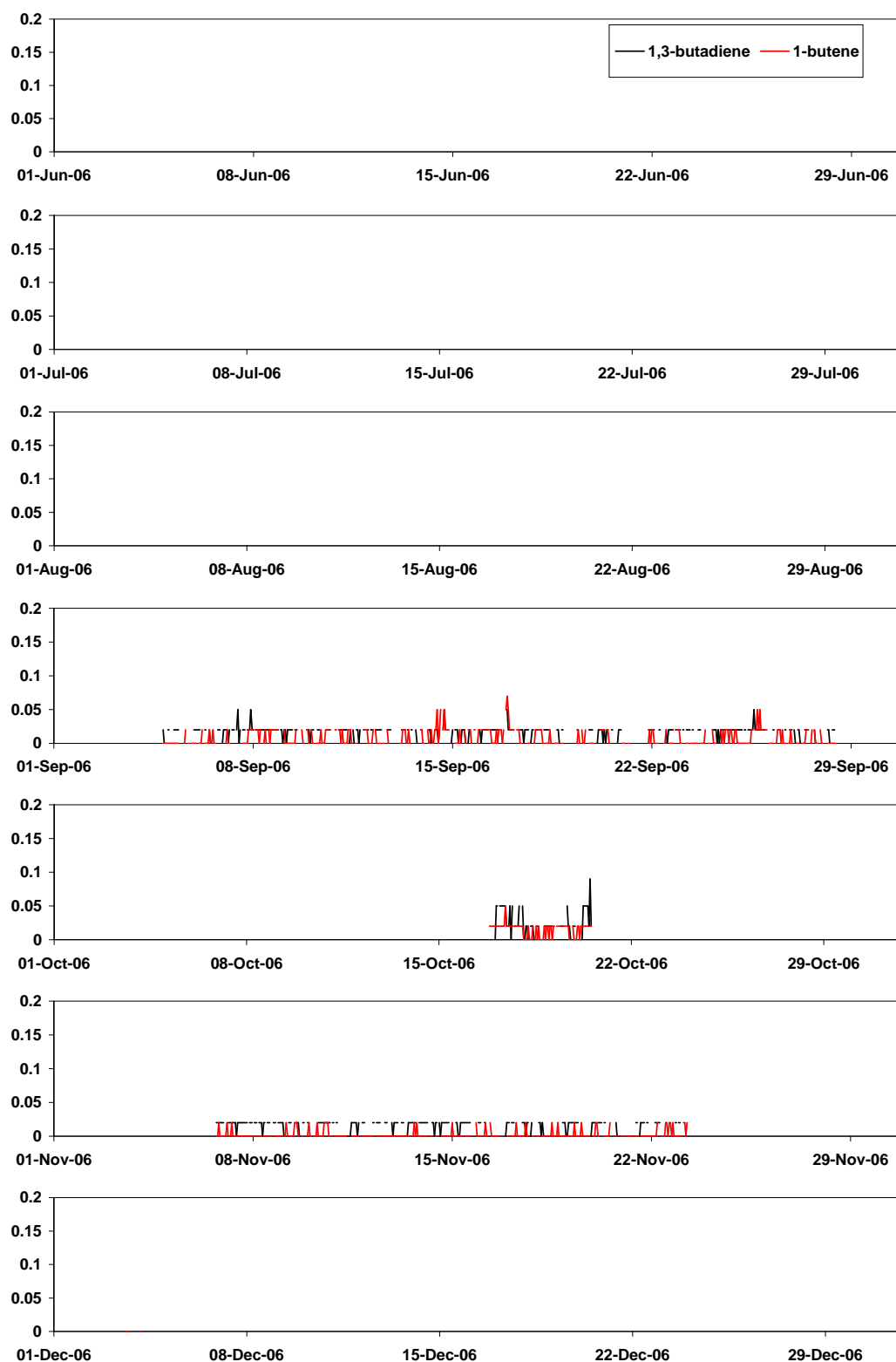
MARGA sulphate SO_4^{2-} $\mu\text{g m}^{-3}$



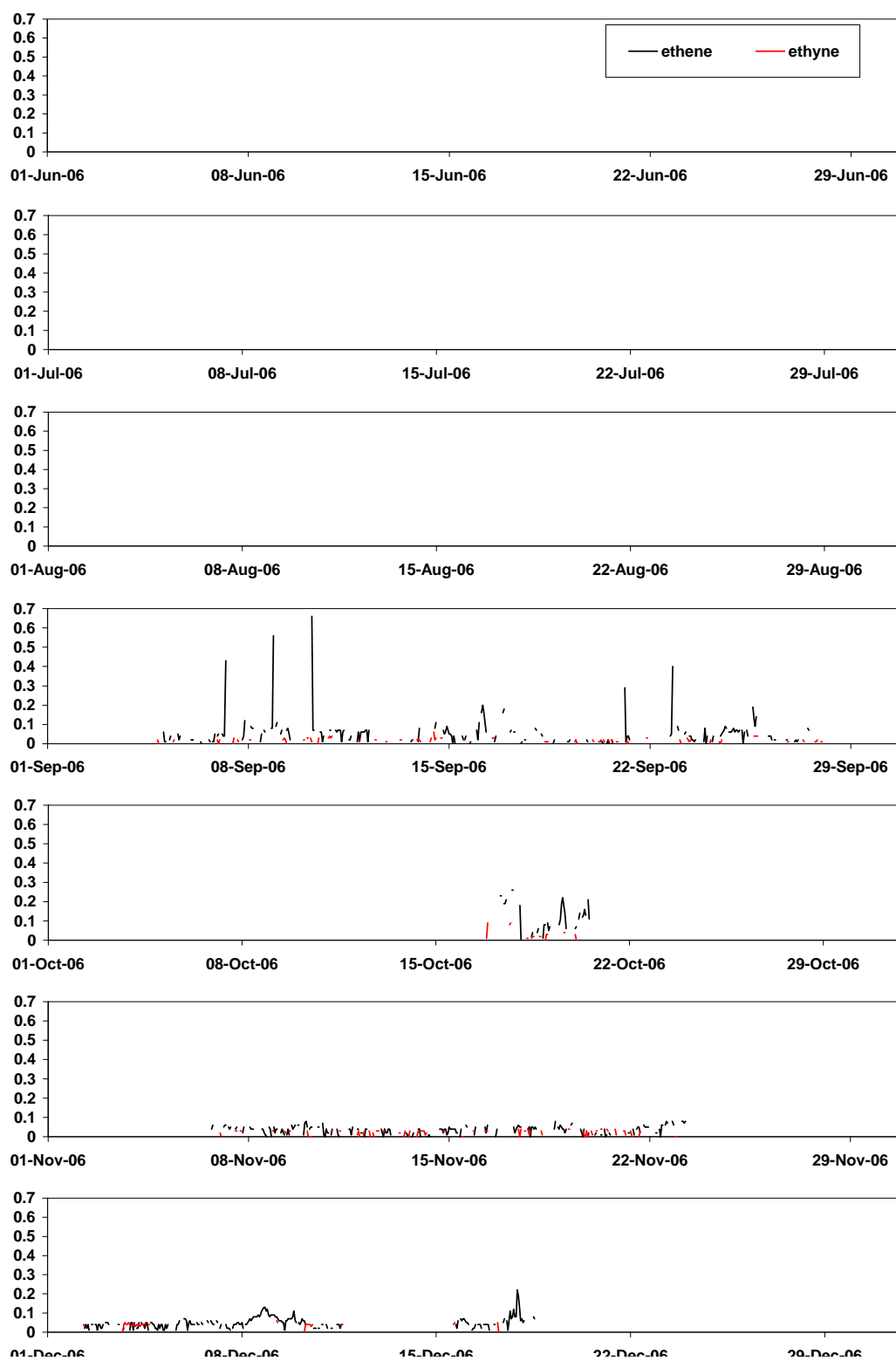
MARGA SO₂ µg m⁻³



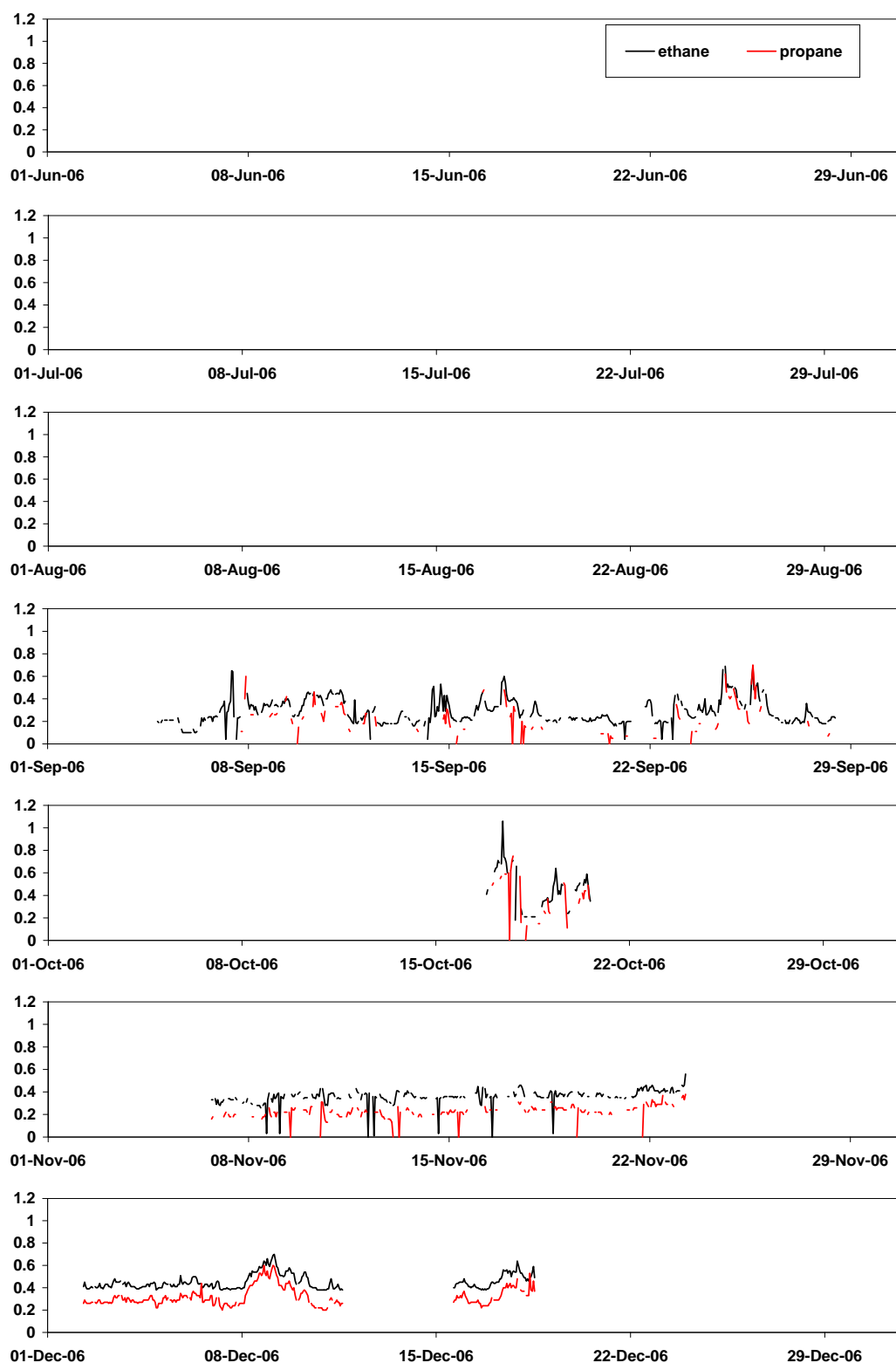
Hydrocarbons: 1,3-butadiene and 1-butene $\mu\text{g m}^{-3}$



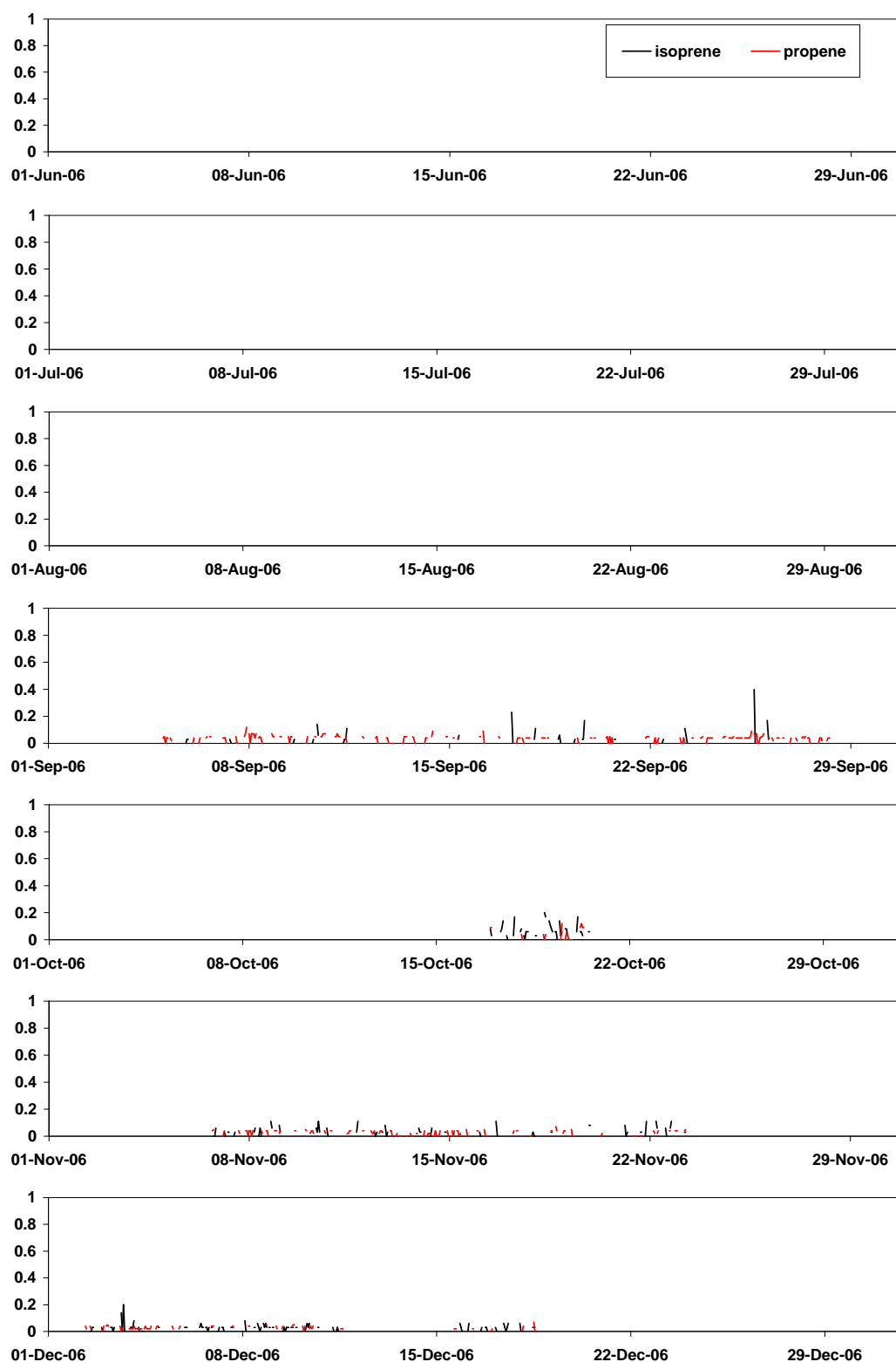
Hydrocarbons: ethene and ethyne $\mu\text{g m}^{-3}$



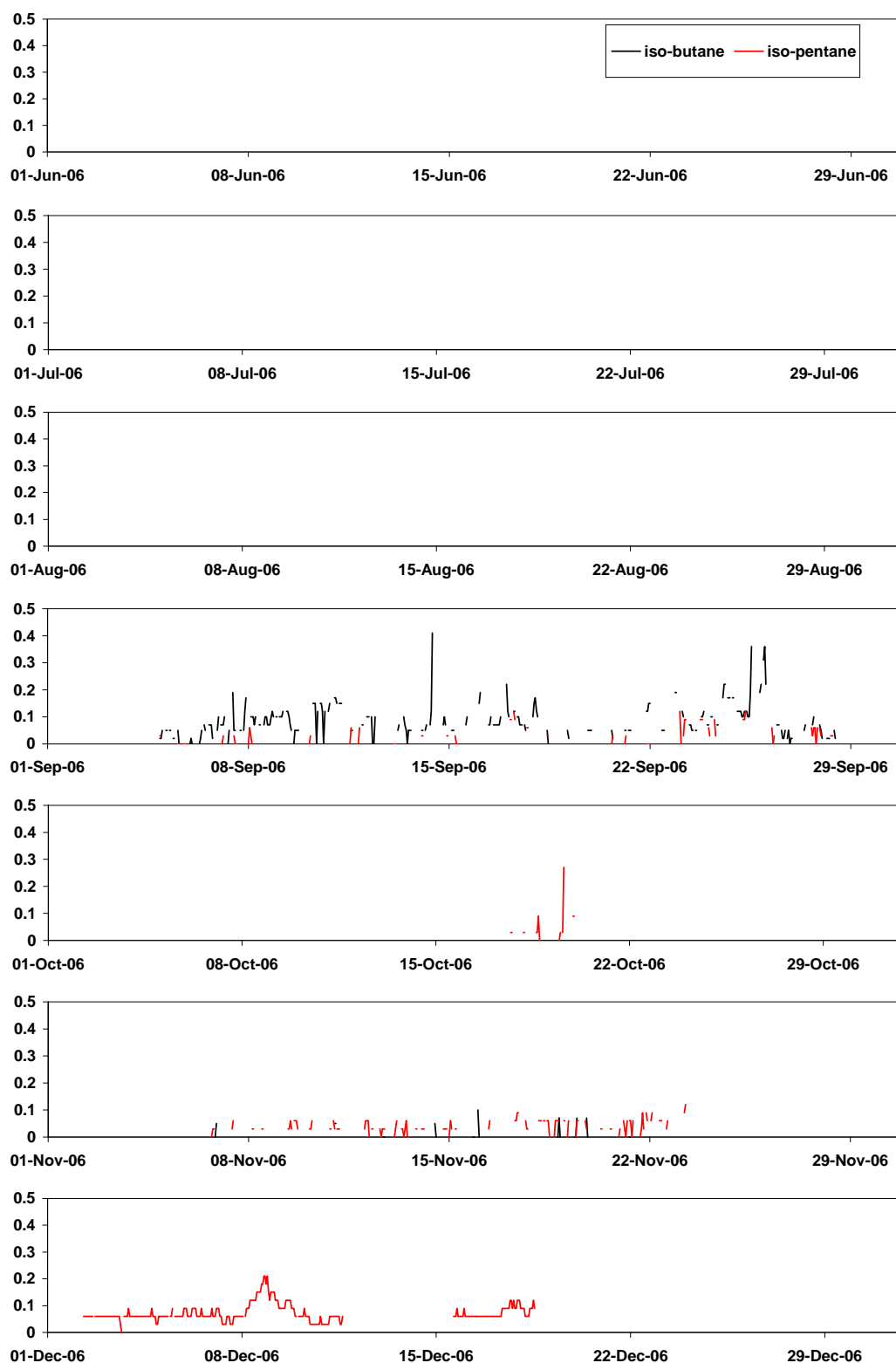
Hydrocarbons: ethane and propane $\mu\text{g m}^{-3}$



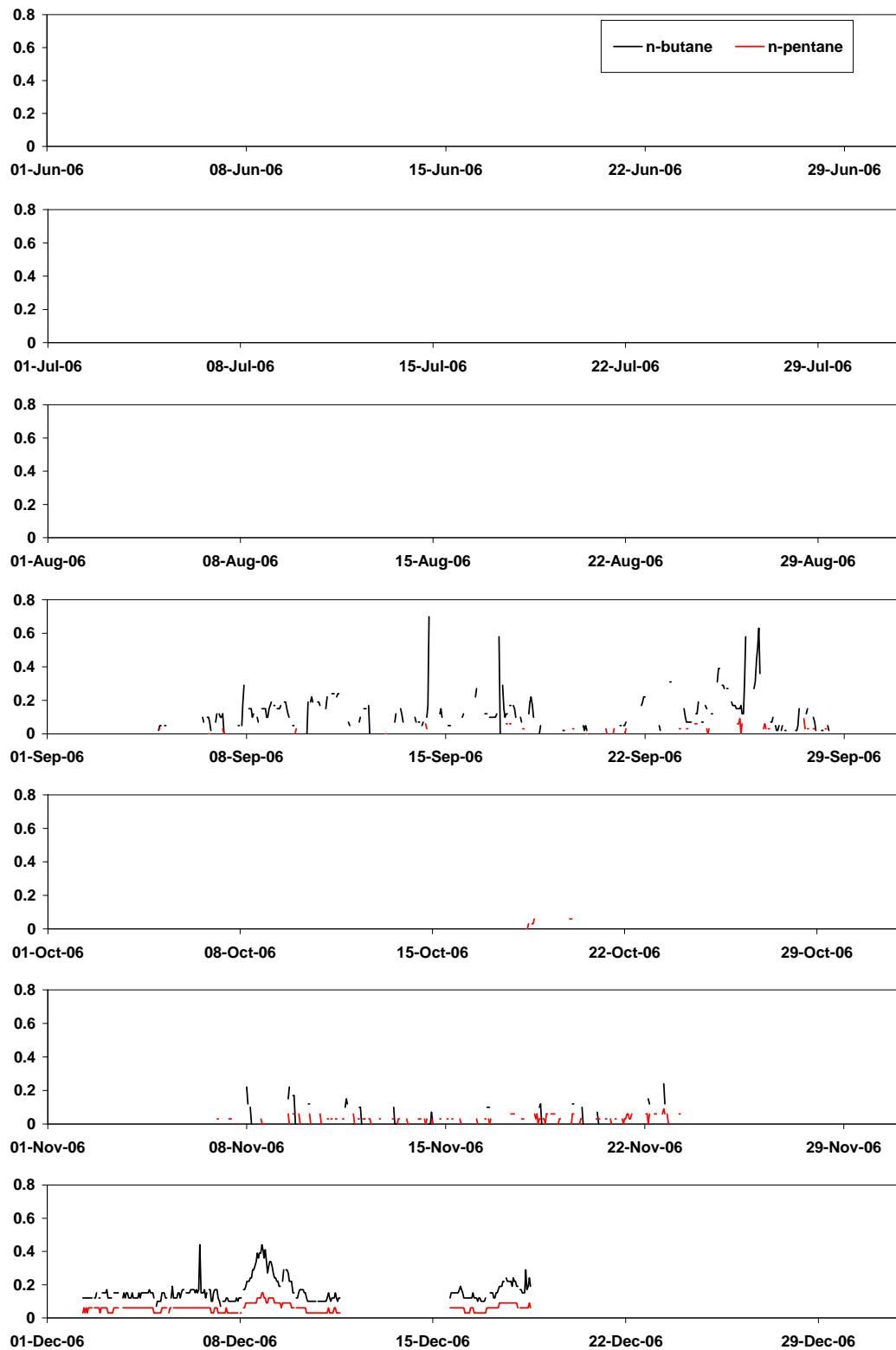
Hydrocarbons: isoprene and propene $\mu\text{g m}^{-3}$



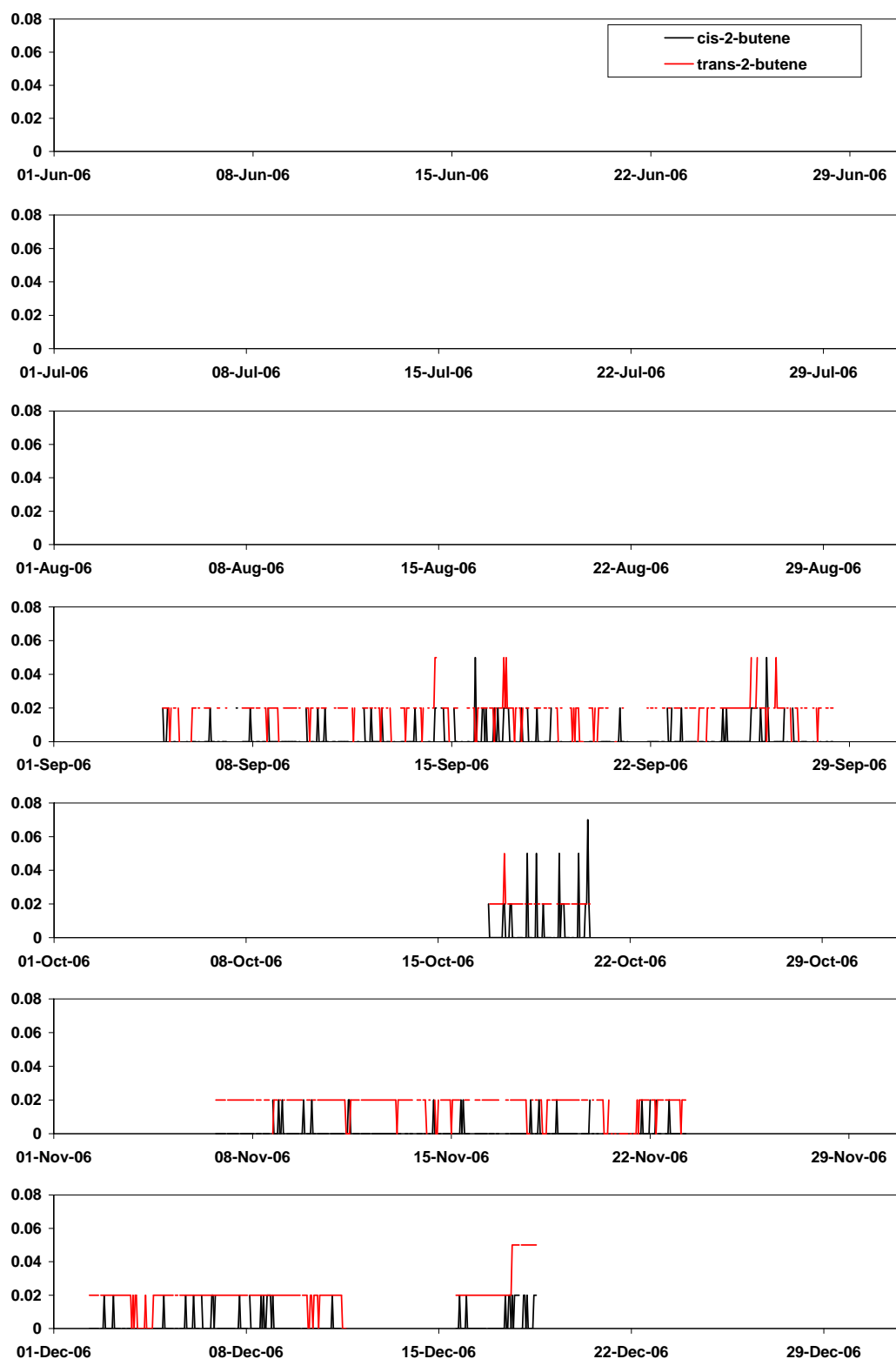
Hydrocarbons: iso-butane and iso-pentane $\mu\text{g m}^{-3}$



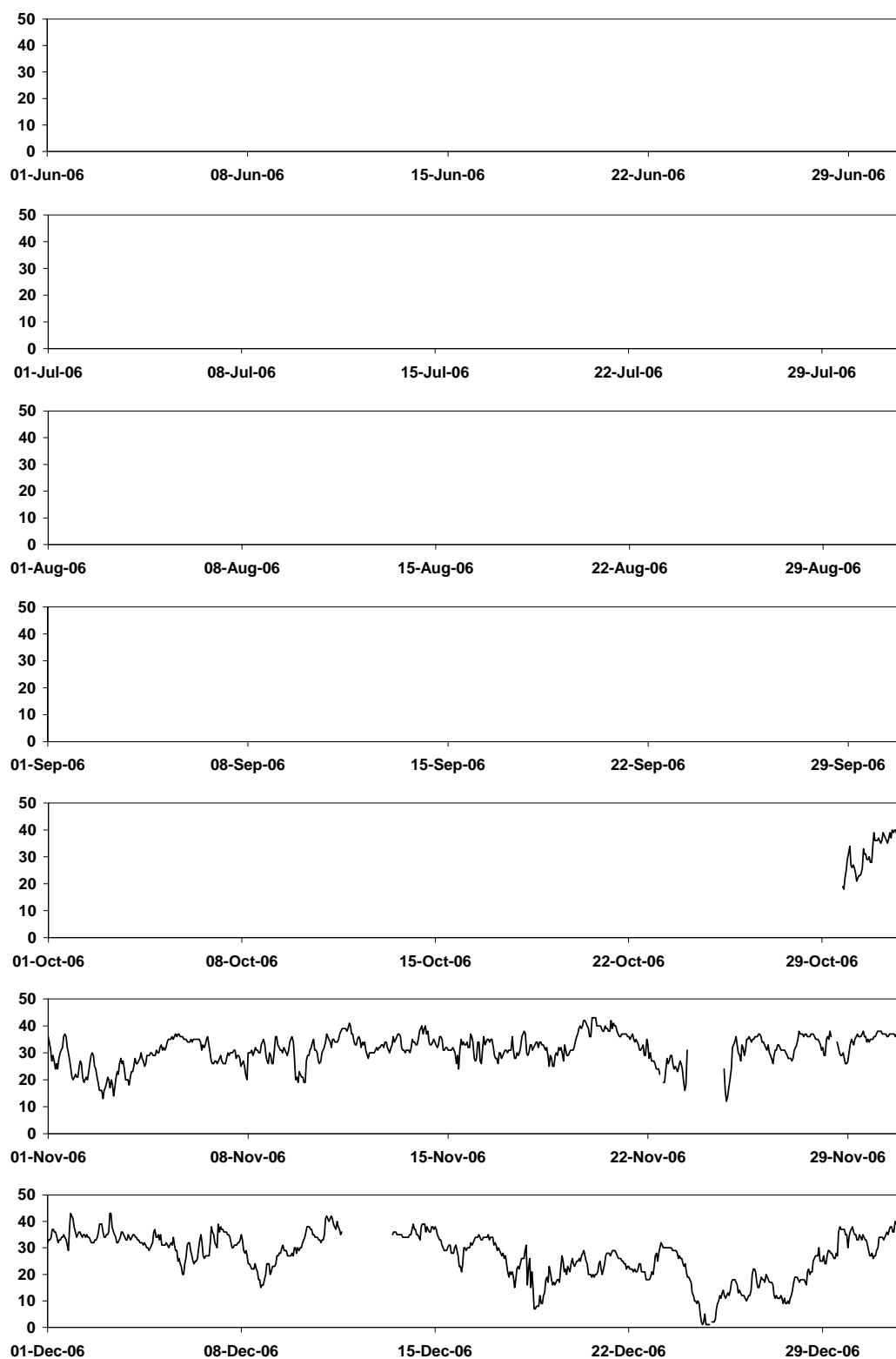
Hydrocarbons: n-butane and n-pentane $\mu\text{g m}^{-3}$



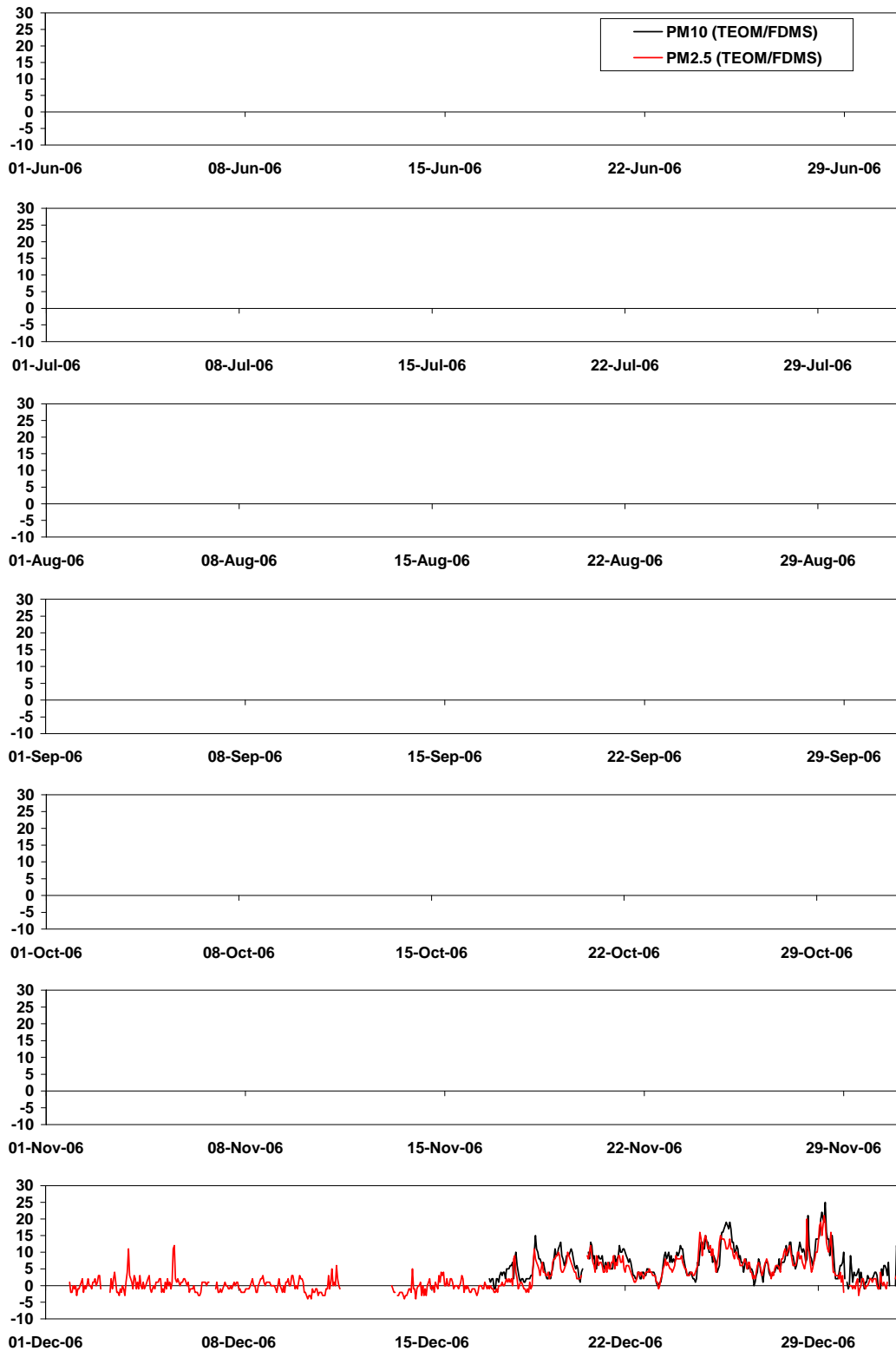
Hydrocarbons: 2-butenes $\mu\text{g m}^{-3}$



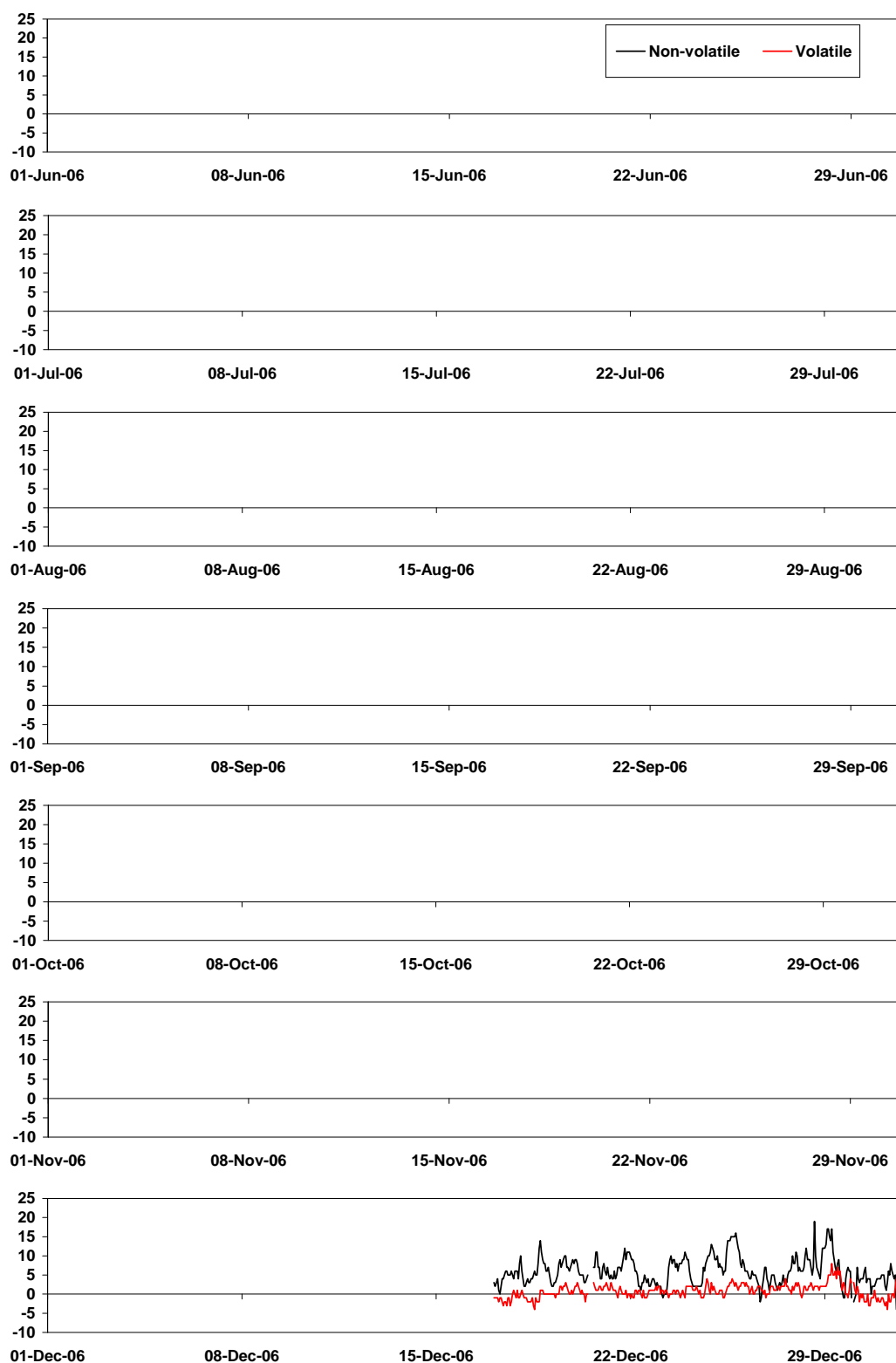
Ozone (AURN) ppb



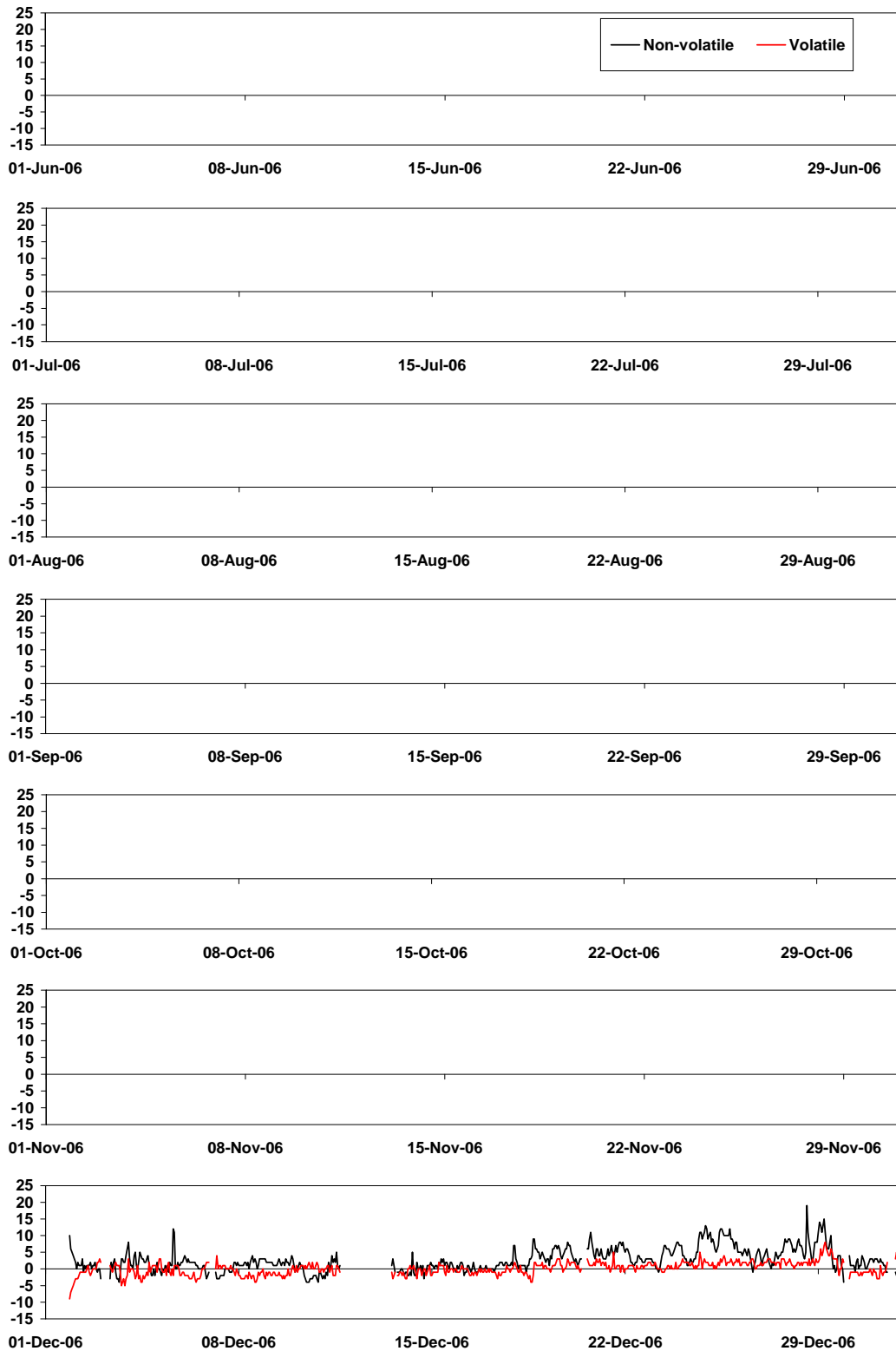
Particulate matter (TEOM/FDMS) $\mu\text{g m}^{-3}$



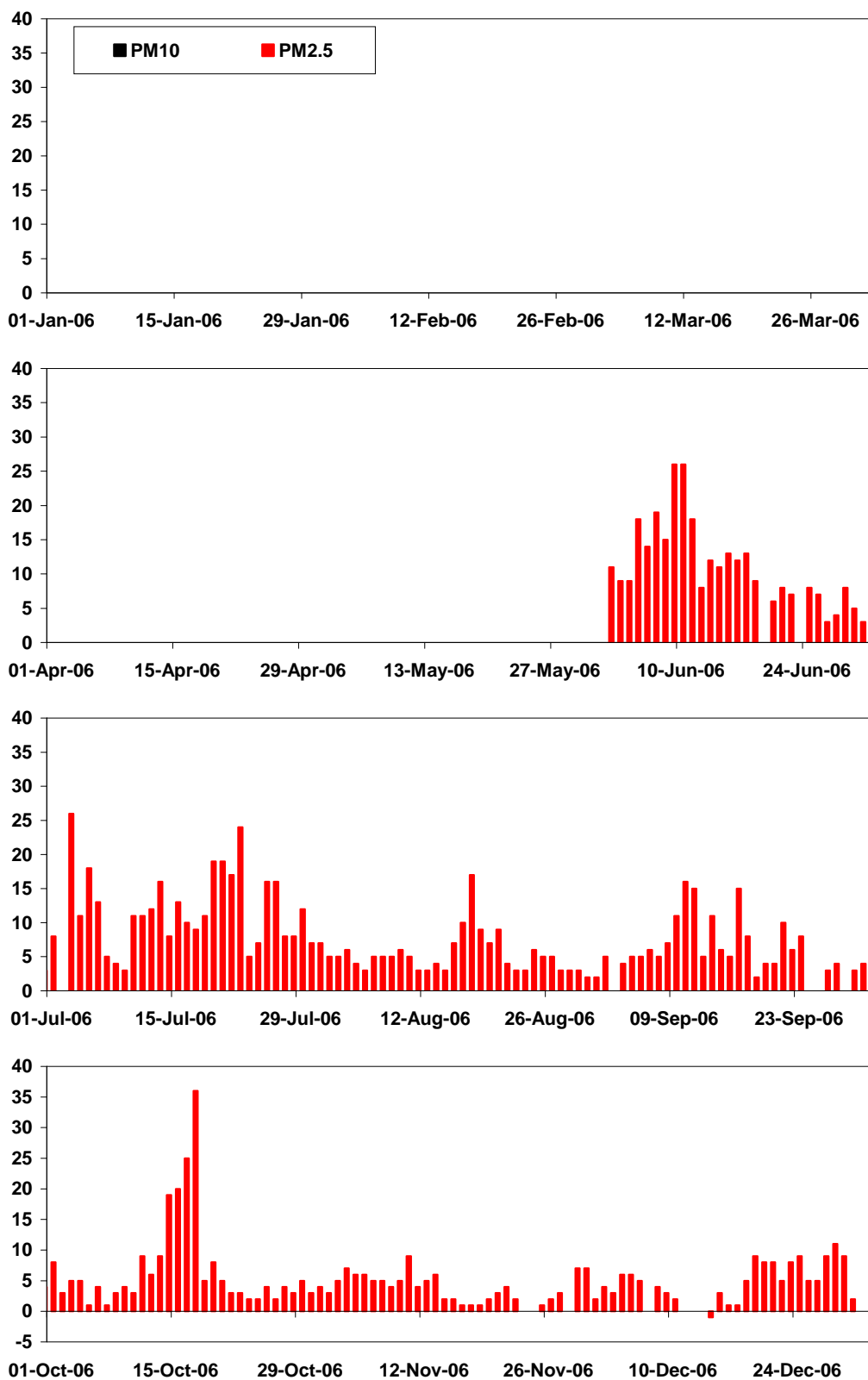
Particulate matter PM₁₀ (TEOM/FDMS) $\mu\text{g m}^{-3}$

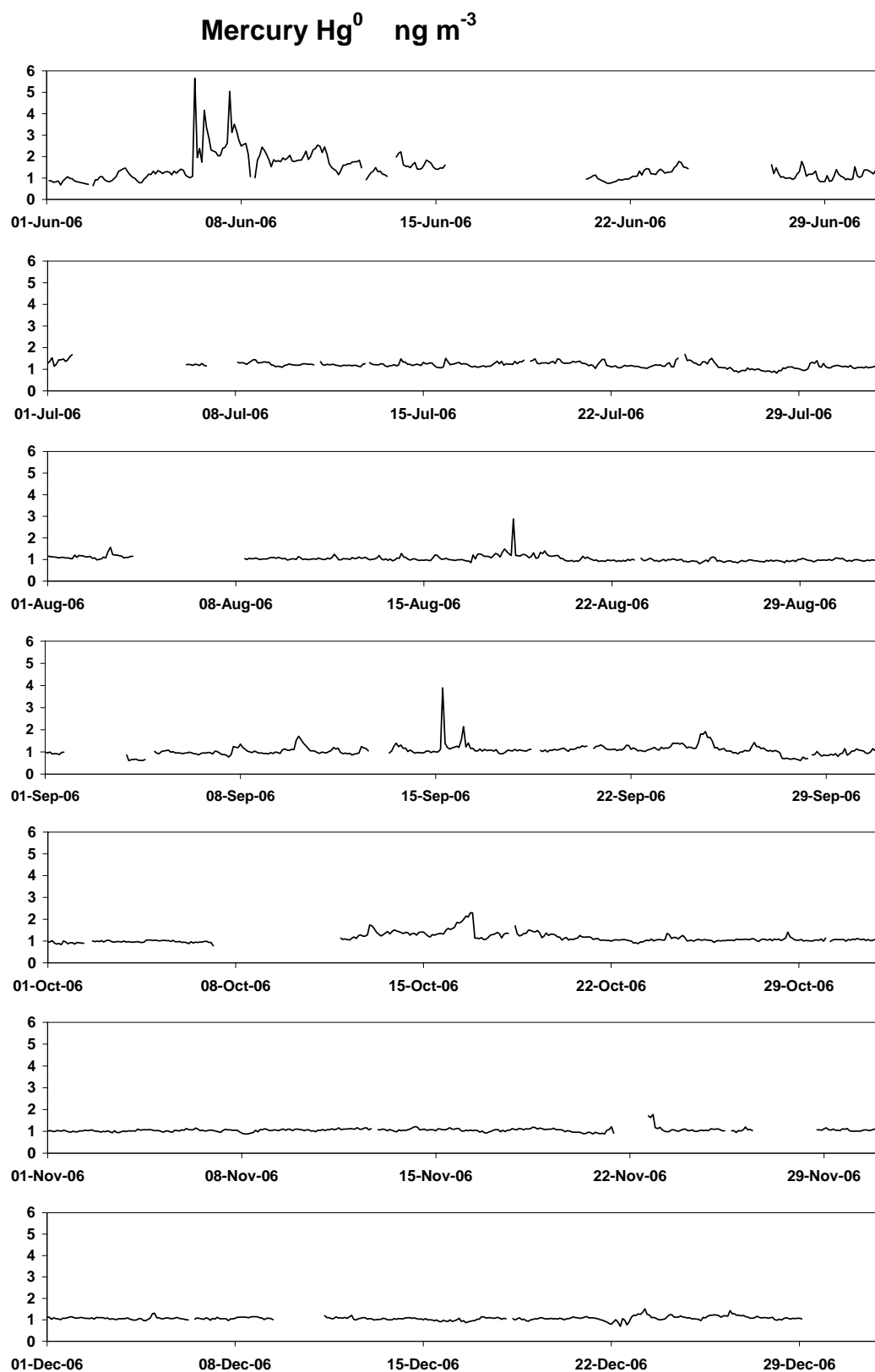


Particulate matter PM_{2.5} (TEOM/FDMS) $\mu\text{g m}^{-3}$

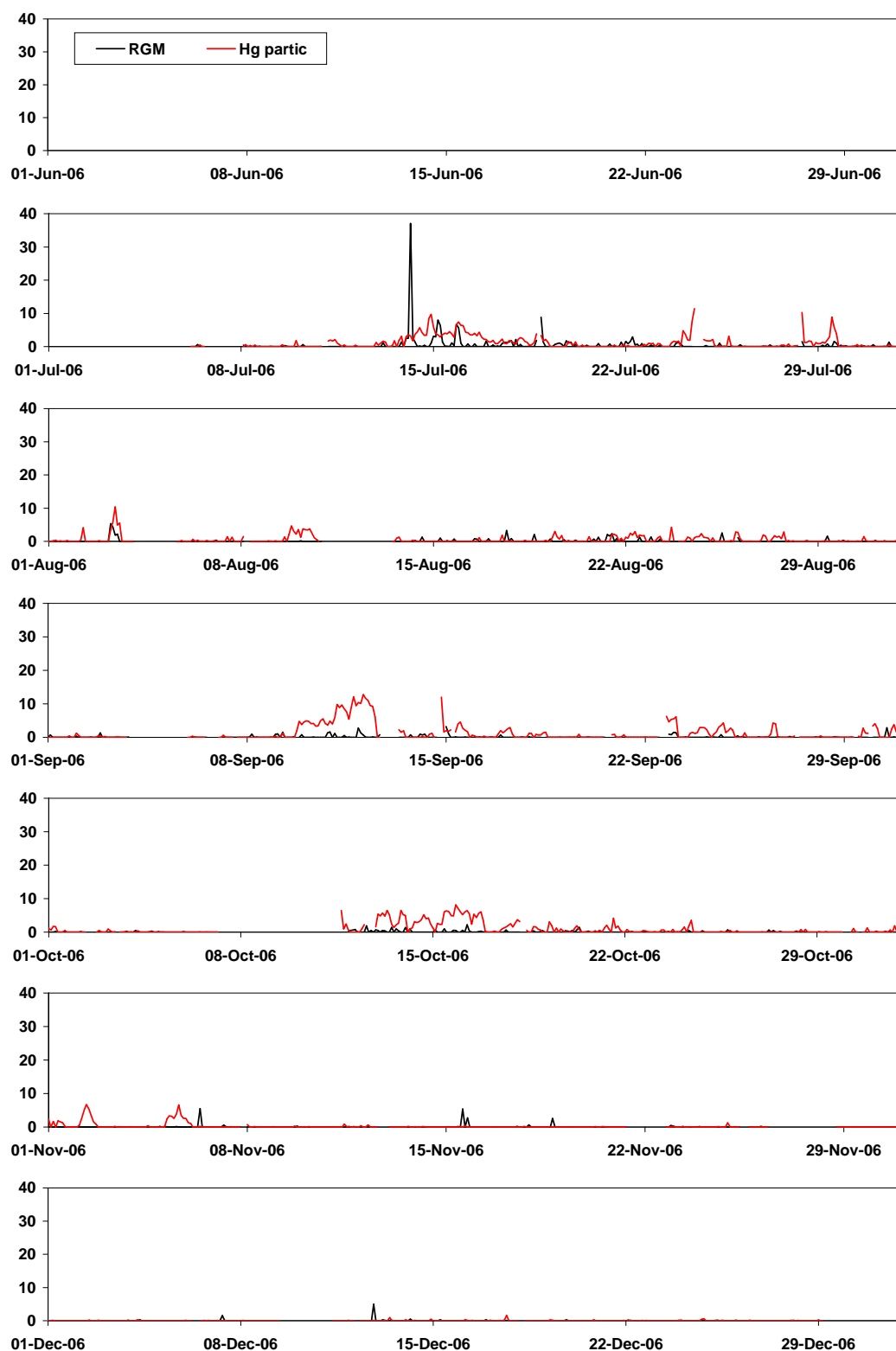


Particulate matter (daily) $\mu\text{g m}^{-3}$

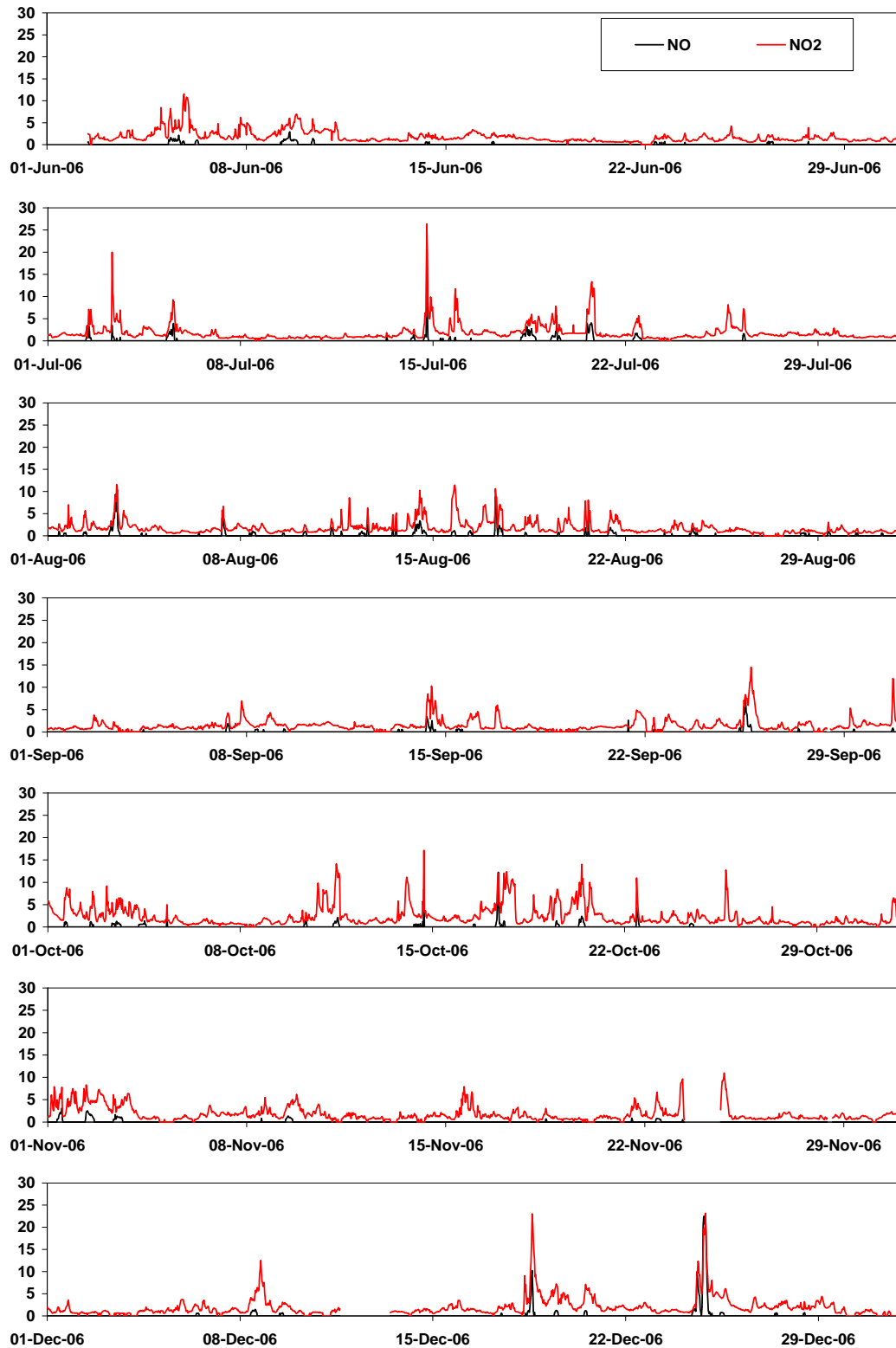




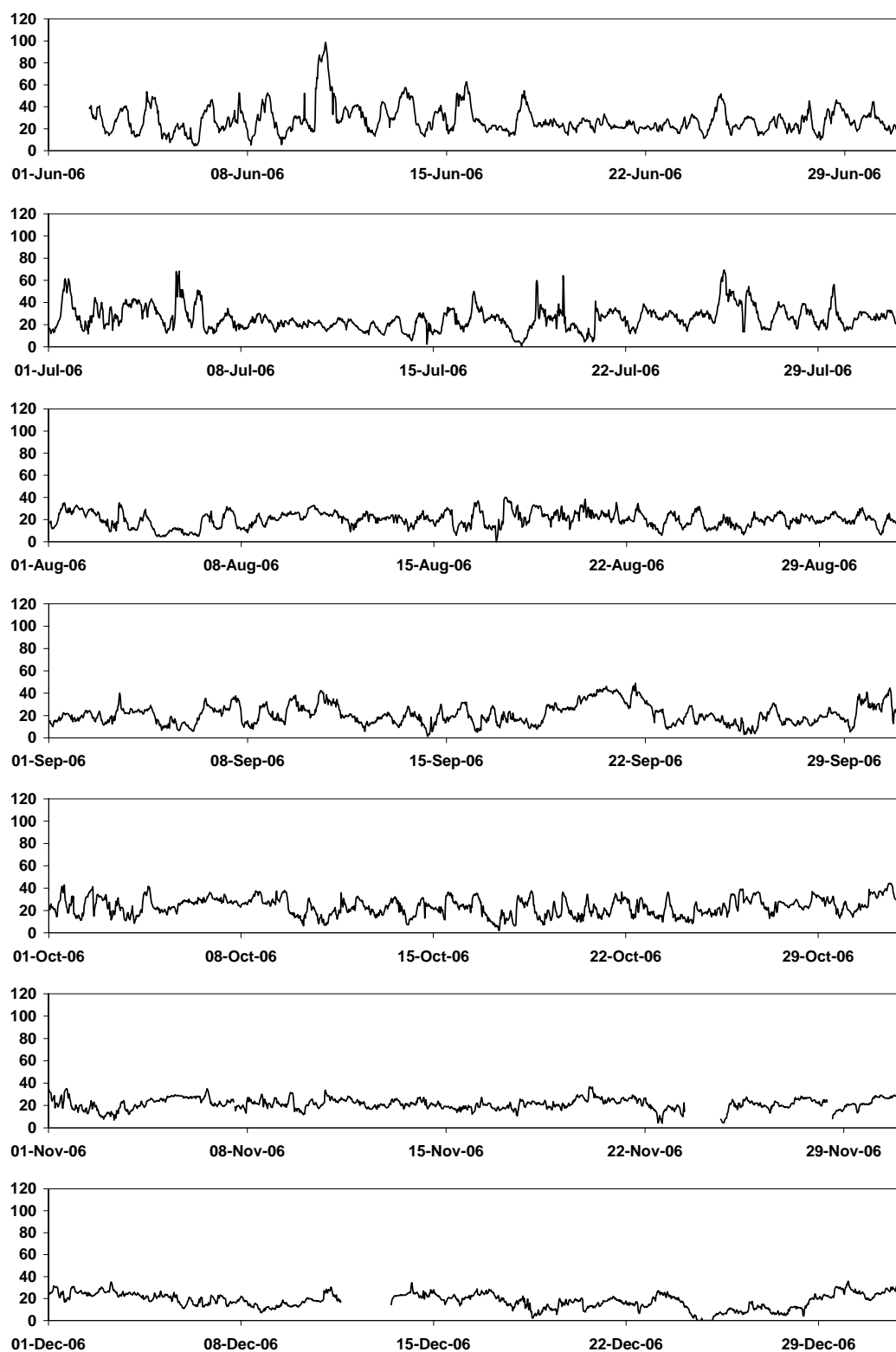
Mercury: reactive gaseous and particulate pg m^{-3}



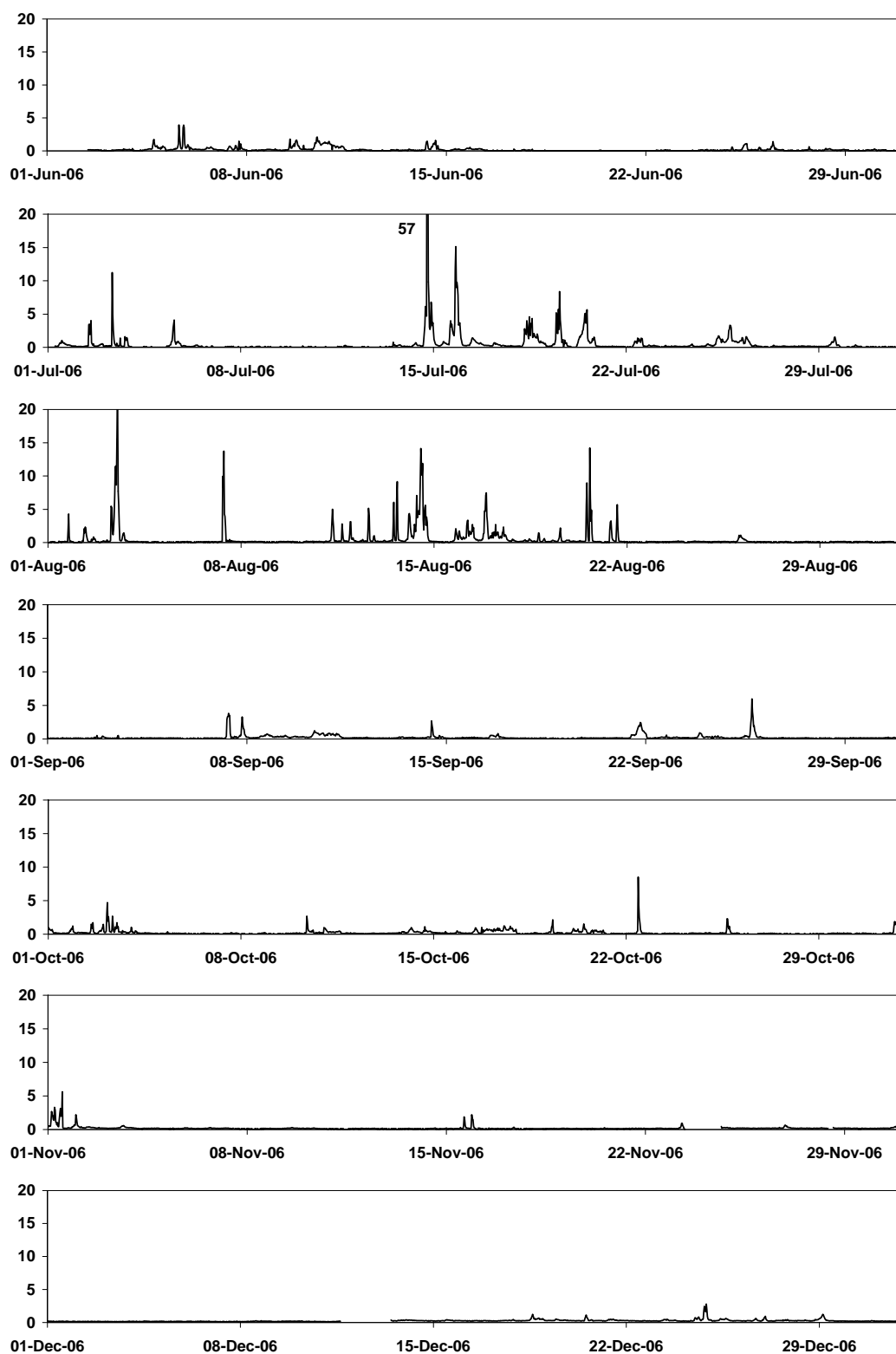
Nitrogen oxides (thermal converter) ppb



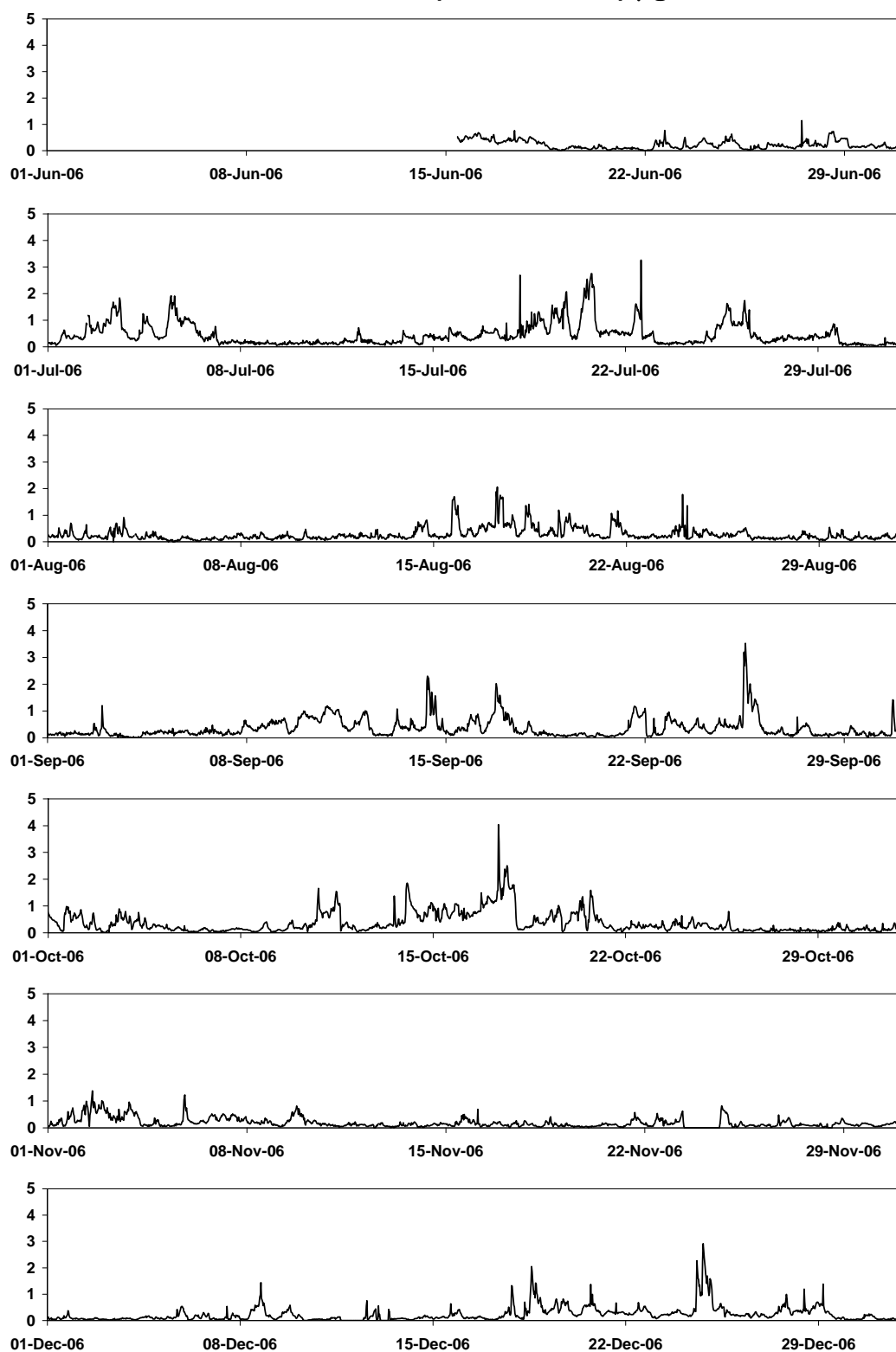
Ozone ppb



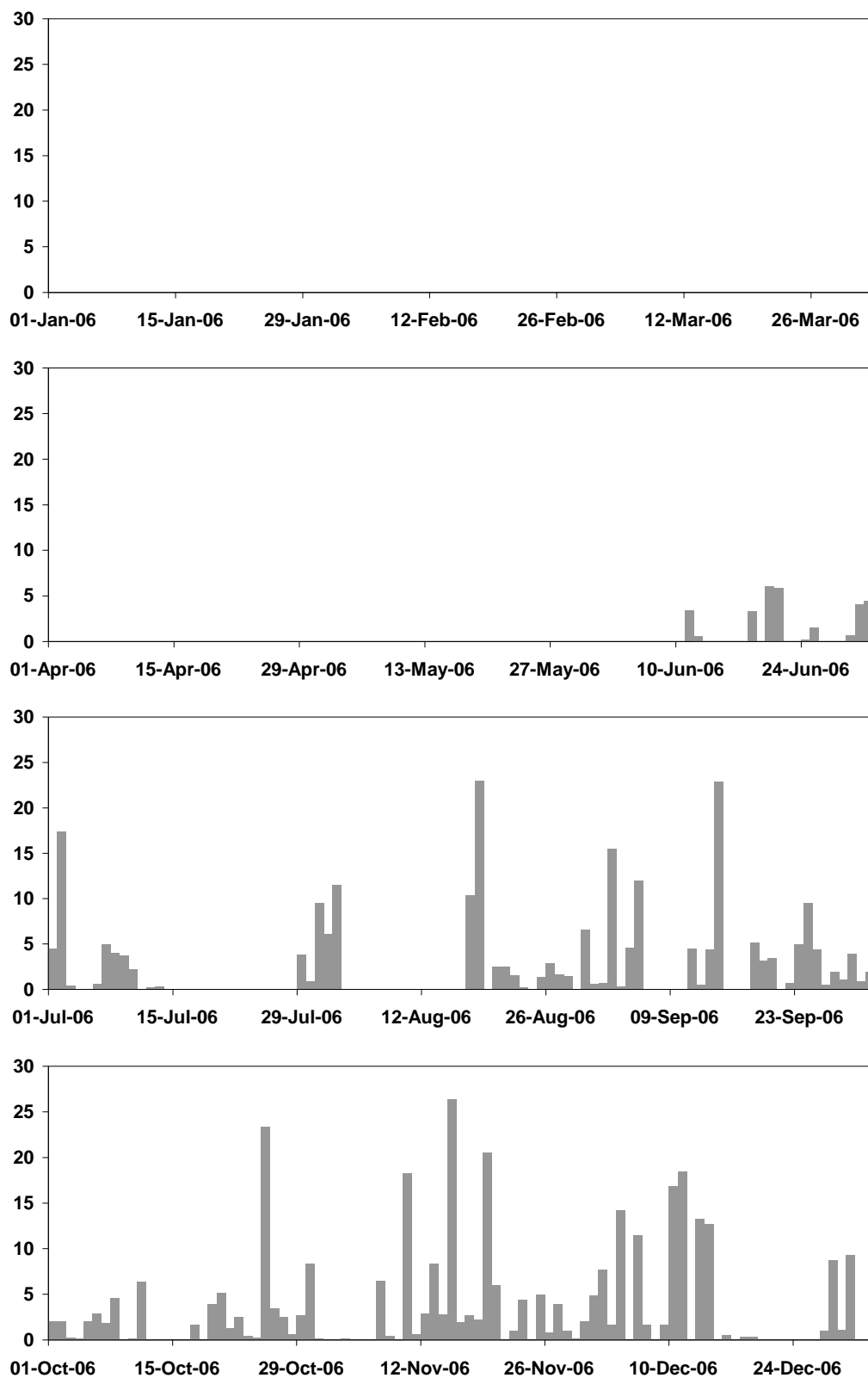
Sulphur dioxide ppb



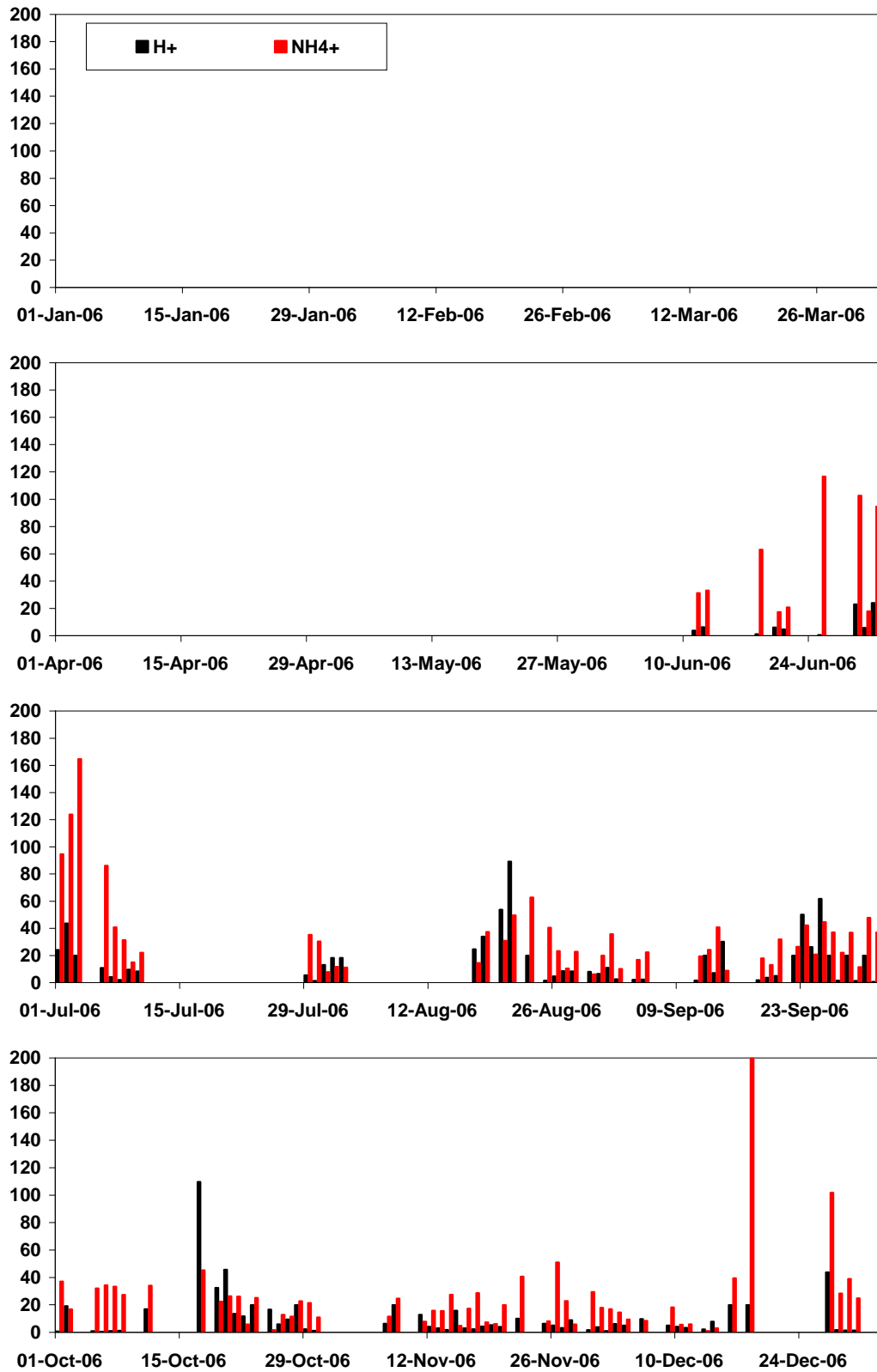
Black carbon (aethalometer) $\mu\text{g m}^{-3}$



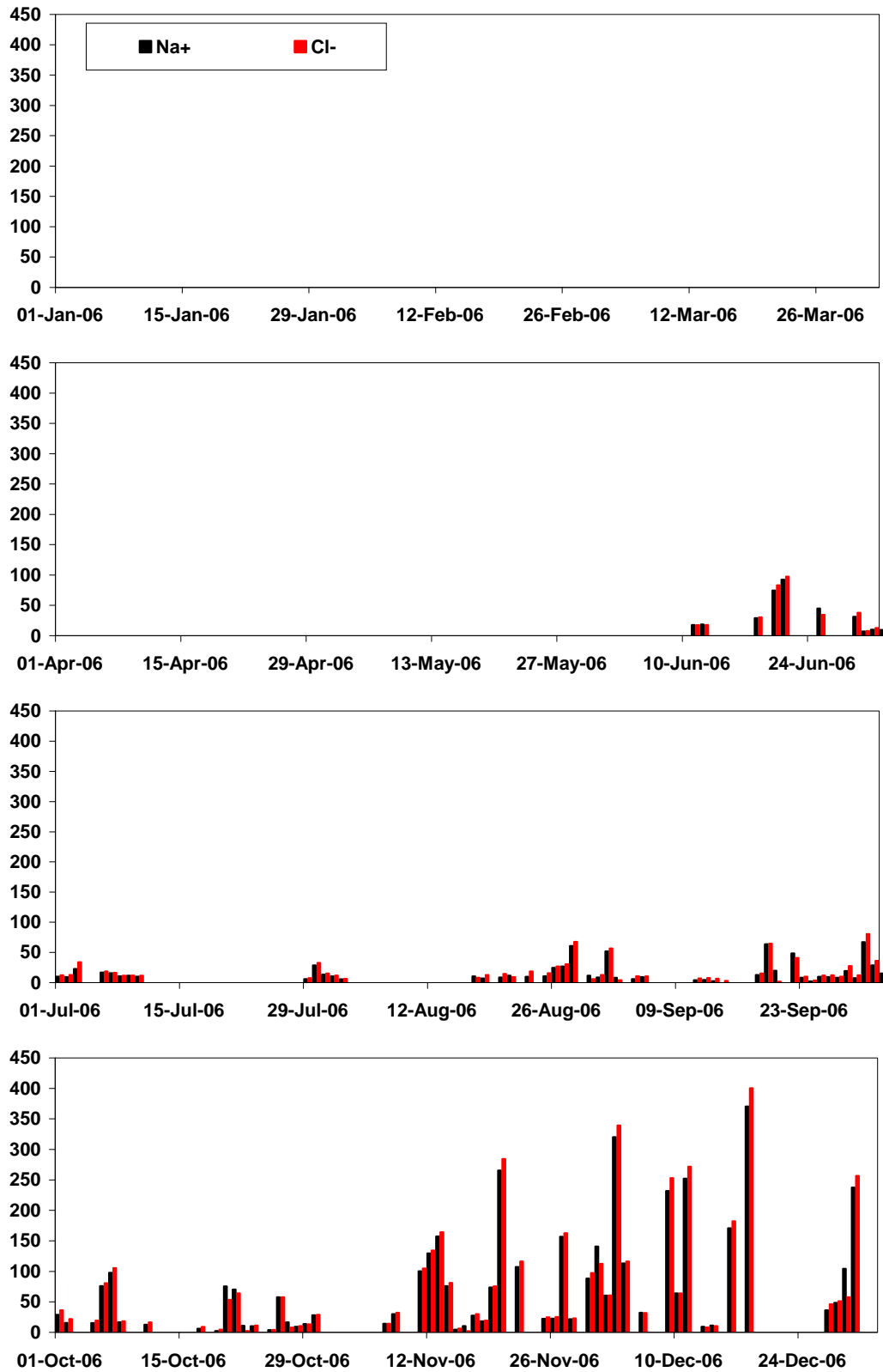
Daily rainfall (mm)



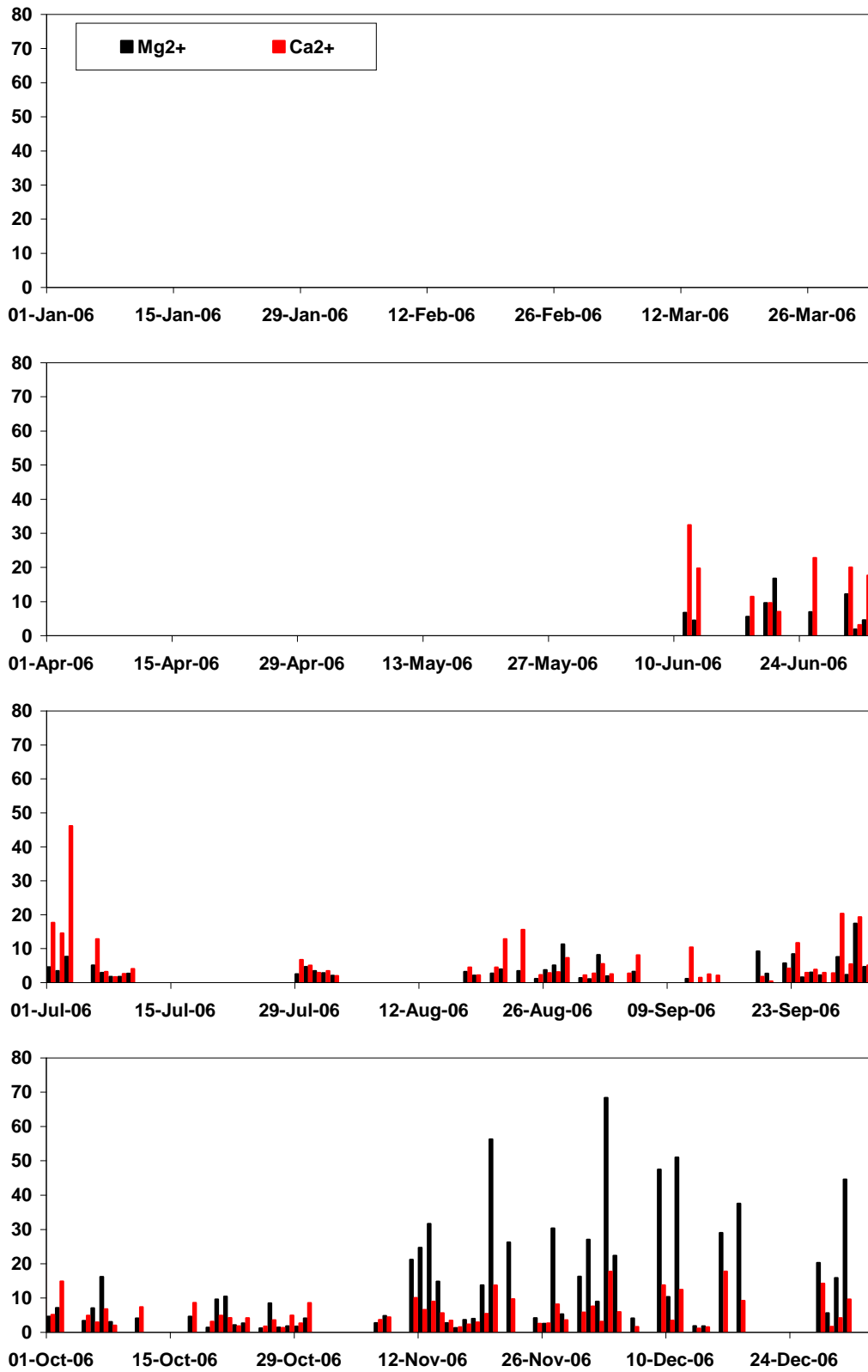
Wet-only concentrations (daily) H^+ and NH_4^+ $\mu\text{equiv L}^{-1}$



Wet-only concentrations (daily) Na^+ and Cl^- $\mu\text{equiv L}^{-1}$



Wet-only concentrations (daily) Mg^{2+} and Ca^{2+} $\mu\text{equiv L}^{-1}$



Wet-only concentrations (daily) SO_4^{2-} and NO_3^- $\mu\text{equiv L}^{-1}$

