Measurement of VOCs in Marine Air at Cape Grim using PTR-MS

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Sarah Lawson , Ian Galbally, Erin Dunne, John Gras and Paul Krummel

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Outline

- Measuring VOCs using PTR-MS
  - Introduction to PTR-MS as a measurement technique
  - Review of suitability of PTR-MS for measuring VOCs in background air
  - How we use PTR-MS at Cape Grim
- Results from Cape Grim
  - VOC concentrations from two recent campaigns and comparison with other remote oceanic sites
  - Diurnal cycles of VOCs
  - VOCs from nearby biomass burning
- Plans for future work

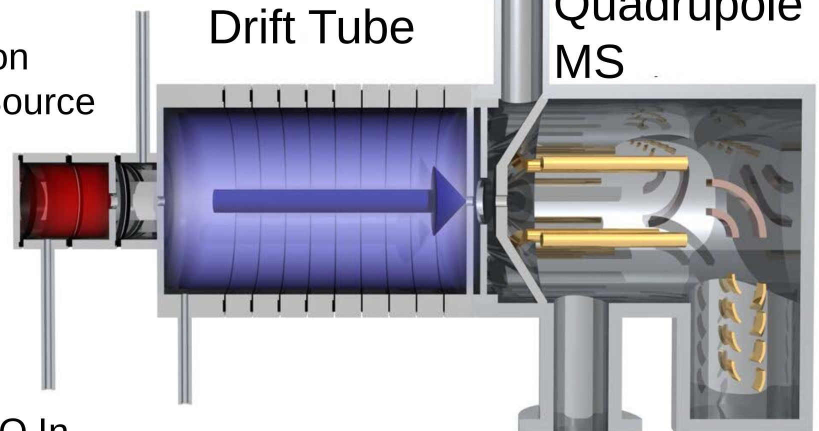
Why measure VOCs at Cape Grim?

- VOCs, NO_x and sunlight drive atmospheric chemistry
  - Essential for ozone production

- VOCs are precursors of Secondary Organic Aerosol (SOA) – marine sources
  - High proportion of aerosol in atmosphere is thought to be SOA – but formation mechanisms and properties poorly understood
  - SOA climatically active –uncertainty in radiative forcing attributed to aerosol is very high

Background on the PROTON TRANSFER REACTION MASS SPECTROMETER

- **Real time measurements, no Carrier gas, and no consequent dilution**
- **Ion Source > 98% H_3O^+, <2% O_2^+**
- **Primary reaction is:**
  $VOC + H_3O^+ \rightarrow VOCH^+ + H_2O$
- **detects compounds with proton affinities (PA) greater than H_2O**
- **Compounds detected include:**
  organics containing O, N and S, alkenes and aromatics
- **Cannot differentiate compounds with same MW**



Review of suitability of PTR-MS to measure VOCs

VOC	Protonated Mass	OK in background air?	Issues at this mass	Inter-comparison studies
methanol	33	Y	-	FTIR (Christian et al., 2004) (Karl et al., 2007)GCMS (de Gouw et al., 2003)
acetonitrile	42	Y	O_2^+ + propene but not significant when propene <100 ppt	GC-MS (de Gouw et al., 2003)
ethanol	47	Challenging	Formic acid Low sensitivity to ethanol due to fragmentation to H_3O^+ (Inomata Tanimoto, 2009b) Di methyl ether?	Saphir (Apel et al., 2008)
acetone	59	Y	Propanal contributes (~10%) possibly glyoxal	GC-MS (de Gouw et al., 2003) (Karl et al., 2007) Saphir (Apel et al., 2008)
di methyl sulphide (DMS)	63	Y	Hydrated acetaldehyde may contribute where [acetaldehyde] is >> [DMS]	GCMS (de Gouw Warneke, 2007)
isoprene	69	Y (providing no biomass burning)	Furan C_5H_8 hydrocarbons	GCMS(de Gouw et al., 2003) (Karl et al., 2007)
terpenes	81, 137	Y	-	GC-MS (de Gouw et al., 2003)
acetaldehyde	45	Y	Ethylene oxide?	GC-MS (de Gouw et al., 2003)

How we use PTR-MS at Cape Grim

- **Daily zeros and calibrations with gas standards**
- **Calibrated concentrations (5 minute) for a range of hydrocarbons and oxygenated VOCs**
- **Presented here is data from February 2006 and December 2007**
- **Data selected for 'clean air' conditions, CN10<3000 cm^{-3}, radon <200 SCM**

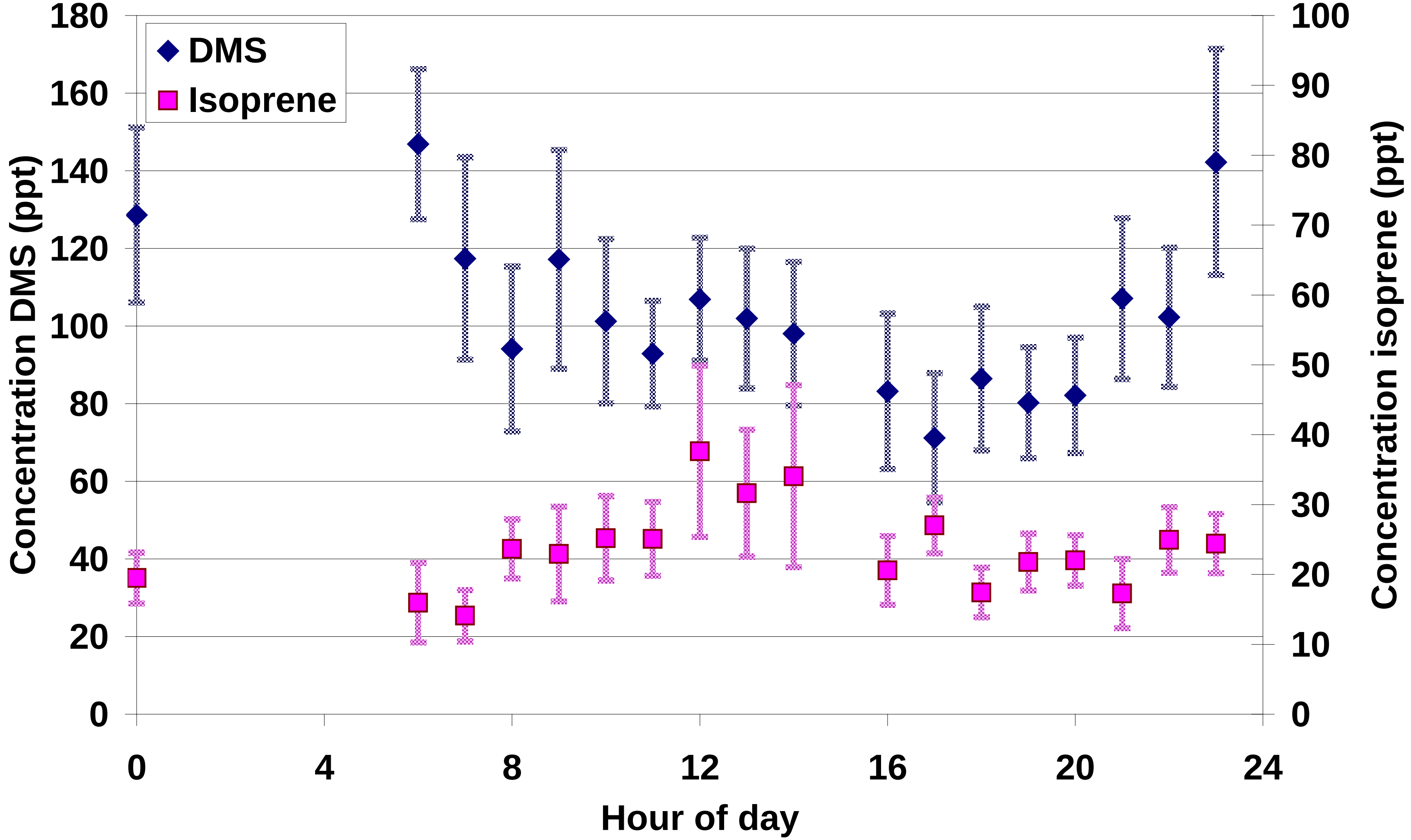
Radon data provided by Wlodek Zahorowski

Results – VOC concentrations (ppt) at Cape Grim and other Oceanic sites

Protonated Mass	Most Probable Compound	Lifetime in marine boundary layer (days)	Cape Grim 2007	Cape Grim 2006 [1]	Cape Grim 1988-1993 [2]	Southern Hemisphere Mid Latitude Oceanic [3] [4]	Tropical Oceanic [5][6][7]
33	Methanol	15	633	476	-	546	575-890
42	Acetonitrile	471	32	25	-	20	111-142
45	Acetaldehyde	0.9	53	nd	-	290	204
59	Acetone	66	61	118	-	127 - 450	466-530
63	DMS	1.5	95	~80	110	77	50-89
69	Isoprene	0.1	21	14	-	40 - 66	-
81	monoterpenes	~0.1	25	nd	-	10	-

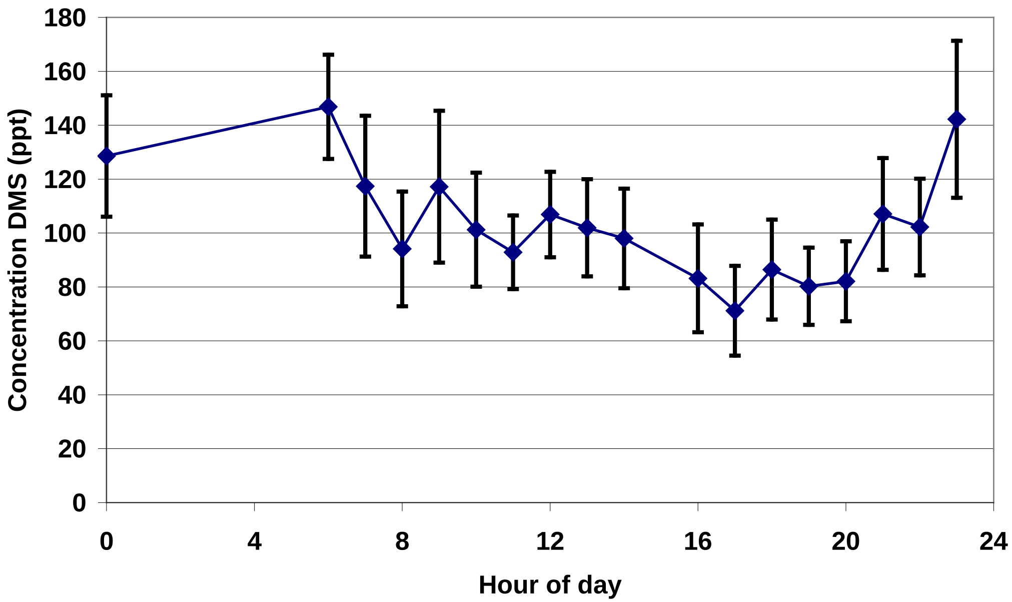
1. Galbally, I.E., et al., Environmental Chemistry, 2007. 4(3): p. 178-182.
2. Ayres, G.P. and R.W. Gillett, Journal of Sea Research, 2000. 43: p. 275-286.
3.Colomb, A., et al., Environmental Chemistry, 2009. 6(1): p. 70-82.
4. Williams, J., et al., Environmental Chemistry, 2010 7(2): p. 171-182.
5. Warneke, C. and J.A. de Gouw, Atmospheric Environment, 2001. 35(34): p. 5923-5933.
6 .Singh, H.B., et al., Journal of Gephysical Research, 2004. 109.
7. Williams, J., et al., Geophysical Research Letters, 2004. 31(23): p. 5.

DMS and Isoprene diurnal cycles in clean air Dec 2007

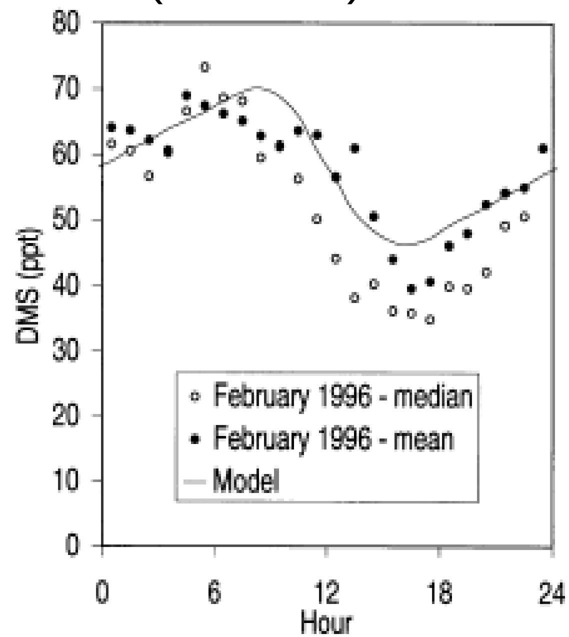


DMS diurnal cycle – past and present

10 days in December 2007 (PTR-MS)



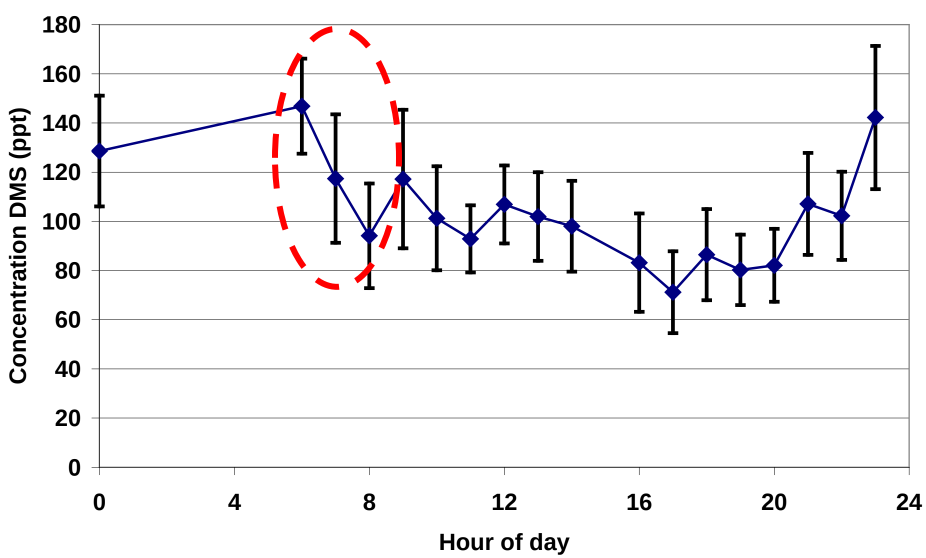
February 1996 (GC-FPD)



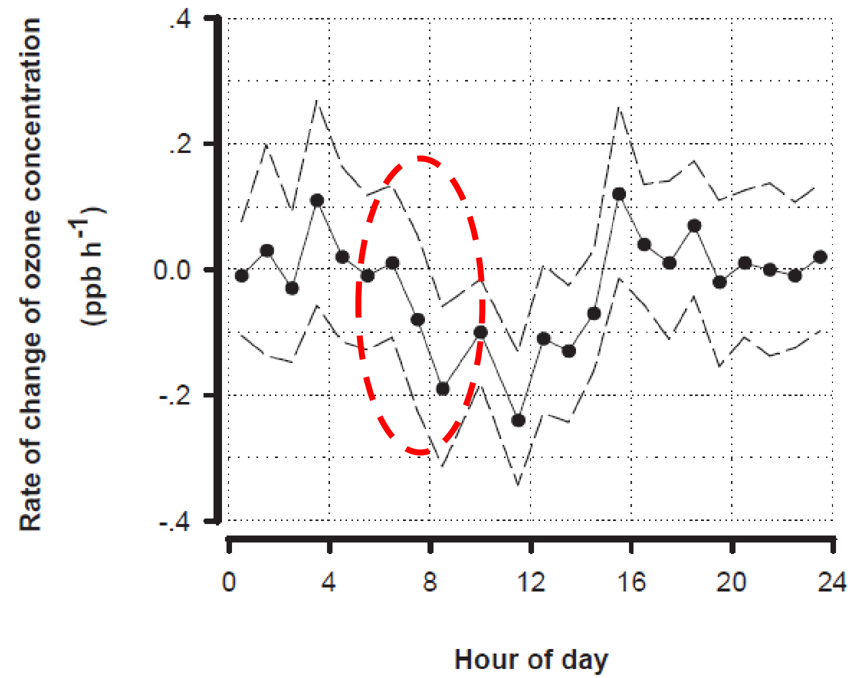
From: Ayers and Gillett, Journal of Sea Research 43 (2000) 275–286

Halogen chemistry?

DMS Dec 2007



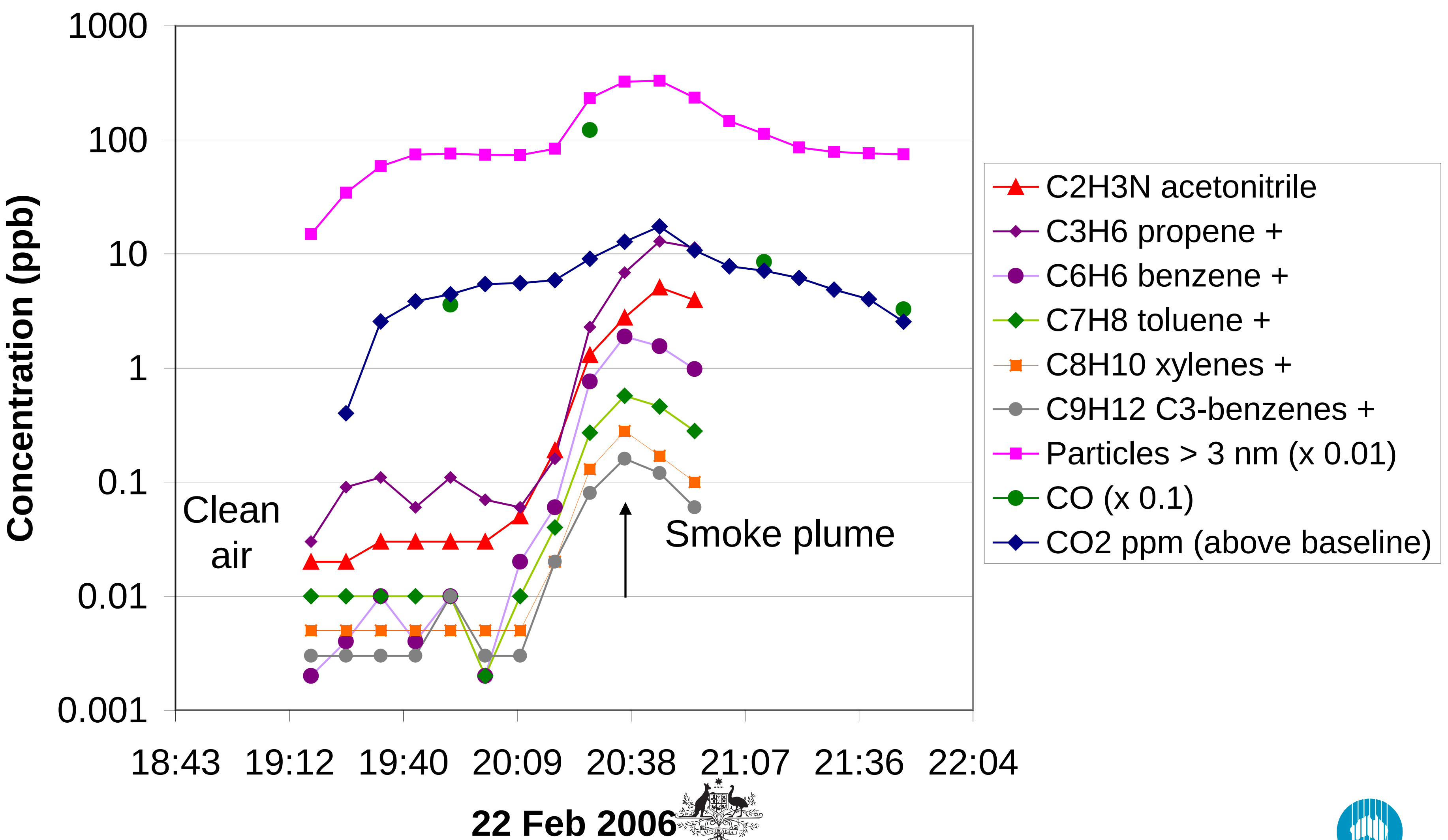
O_3 Dec-Jan 1985-1997



From: Galbally et al, Geophysical Research Letters, 27 (2000), 3841-3844

Local Biomass Burning -Smoke plume from Robbins Island fire 22 Feb 2006

Hydrocarbons and indicators in the smoke plume



Benzene in smoke plume measured by PTR-MS and Medusa GC-MS

PTRMS (1 hour average) and Medusa (20 minute average)

Future Work

- Calibration of AGAGE Medusa GC-MS with VOC standard to extend range
- Future campaigns with
  - particle sizing aerosol, PTR-MS side by side
  - Inlet selective scrubbers on PTR-MS eg acid scrubber (formic & acetic)
  - Switchable Reagent Ion (NO^+, O_2^+, H_3O^+) for better separation of species

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Sarah Lawson

Phone: +61 3 9239 4428

Email: sarah.lawson@csiro.au

Web: www.cawcr.gov.au

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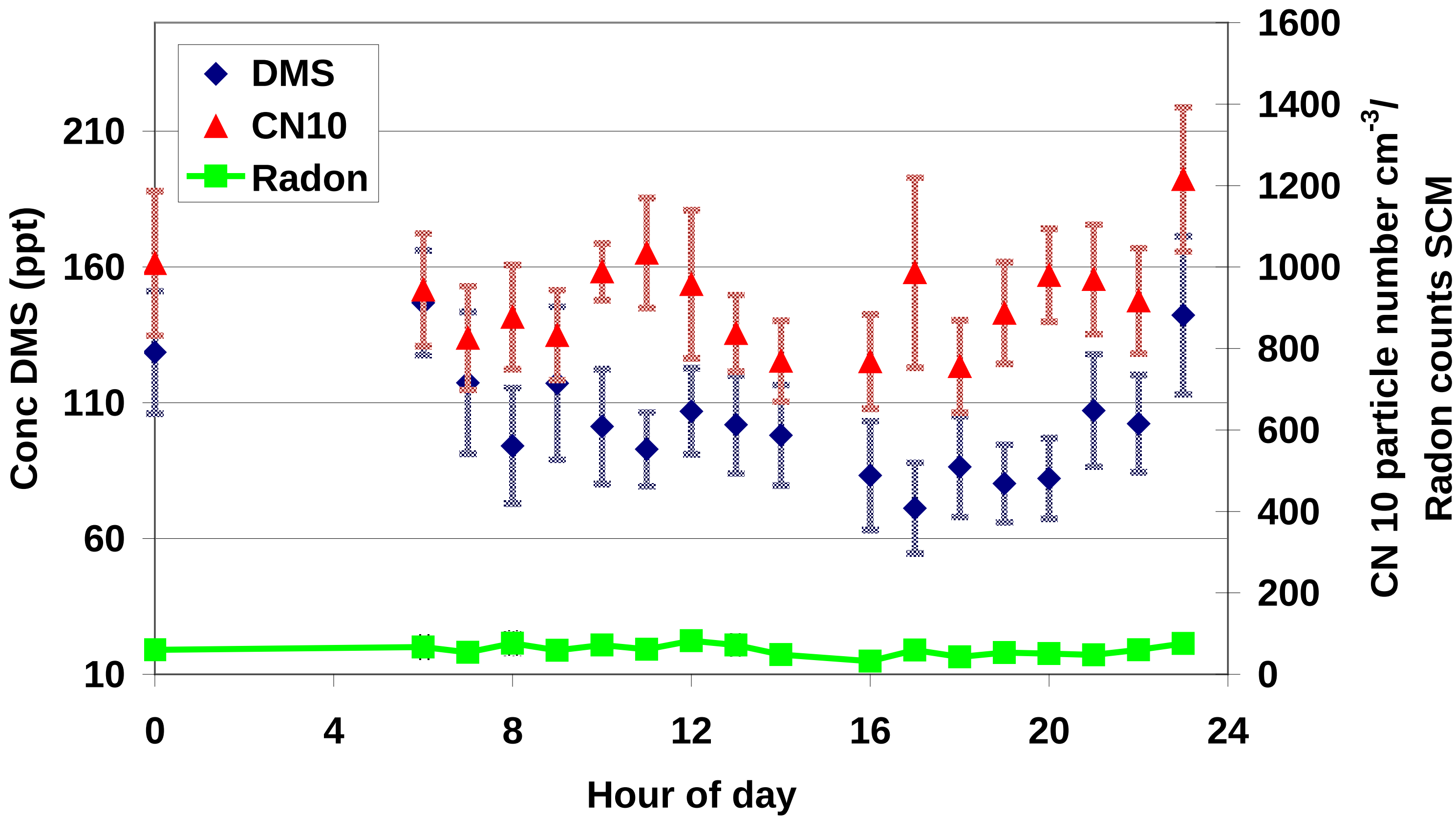
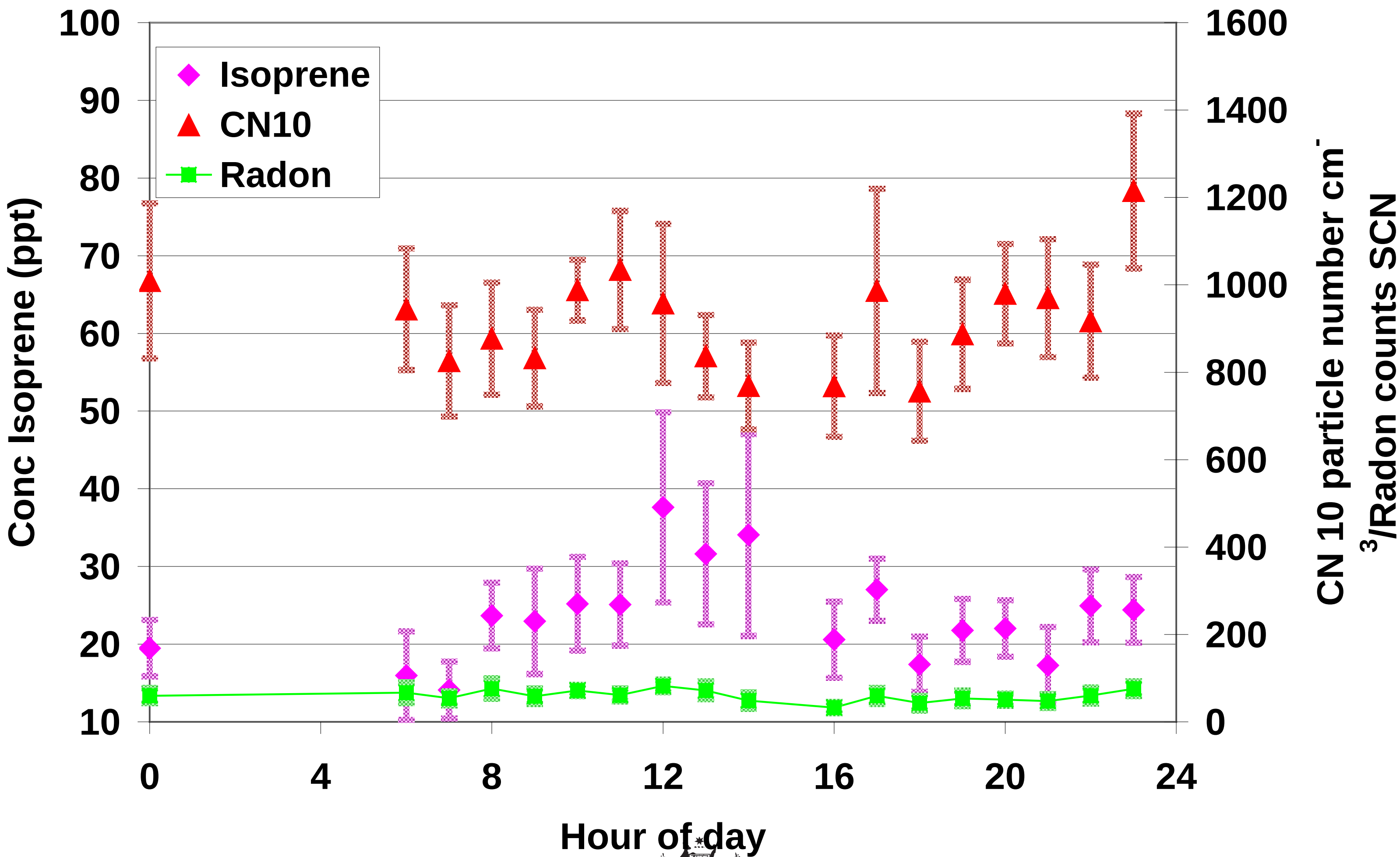
DMS diurnal cycle in clean air



Isoprene diurnal cycle clean air December



VOCs measured at Cape Grim ctd.

- **Medusa (2004 – ongoing)**

benzene	C6H6
toluene	CH3C6H5
acetylene	C2H2
ethylene	C2H4
ethane	C2H6
i-butane	*i*-C4H10
n-butane	*n*-C4H10
1-3, butadiene	C4H6
i-pentane	*i*-C5H12
n-pentane	*n*-C5H12
isoprene	C5H8
ethylbenzene	C8H10
m+p-xylene	*m+p*-C8H10
o-xylene	*o*-C8H10

- **Medusa**

There are preliminary calibration scales for ethane and benzene.

The other compounds are detected via primary and qualifying ions but the calibrations and data quality are not yet assessed

There are 7 background stations with Medusa instrumentation in the world.

VOC Measurement Programs at Cape Grim

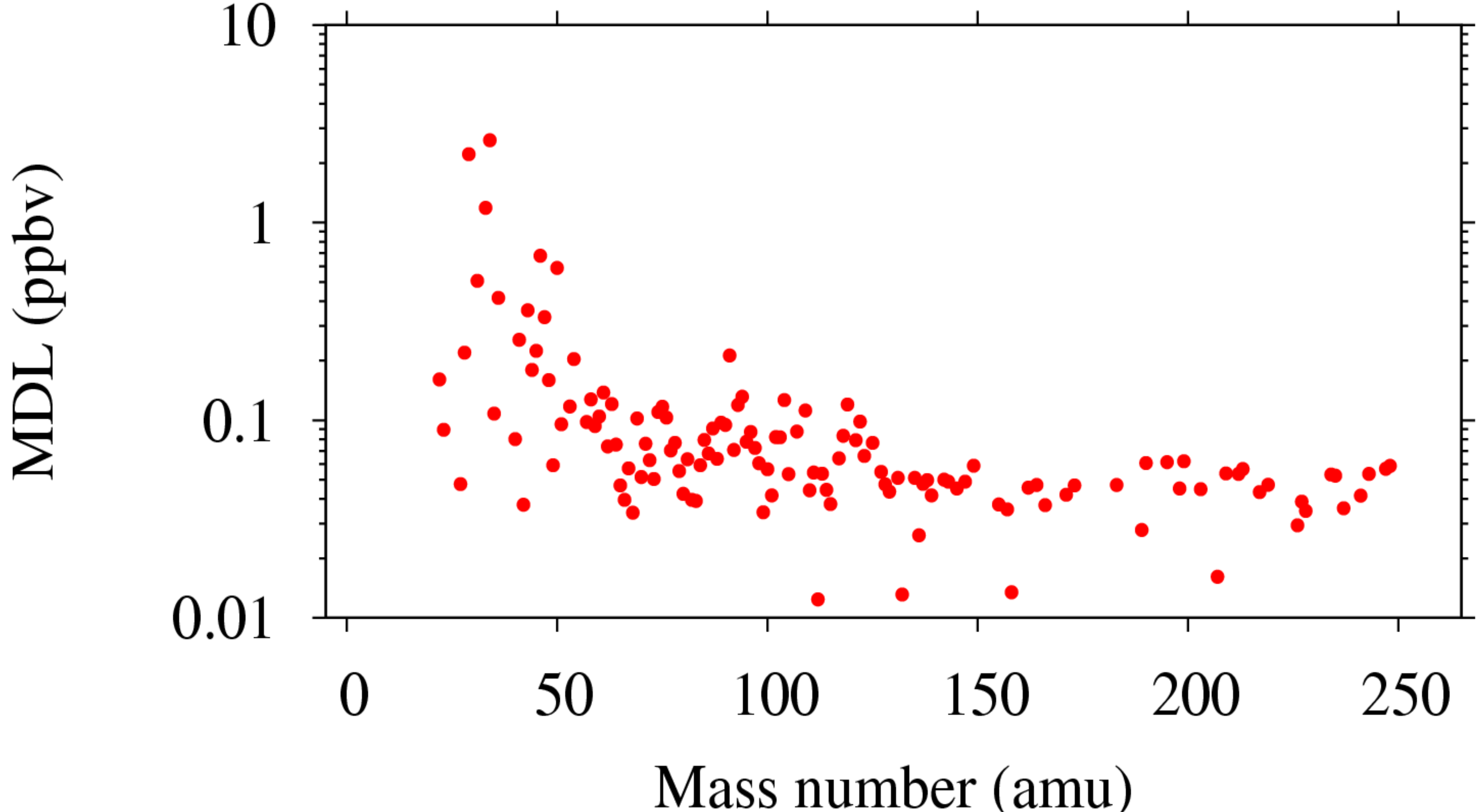
- In-situ flask sampling and GC-MS analyses Nov – Dec 1995 (Ye, Galbally, and Weeks, CSIRO)
- In-situ flask sampling and GC-FID analyses Nov 1998 – Mar 2000 (Kivlighon, Galbally, and Weeks, CSIRO)
- Flask sampling on over-flights and GC-FID analyses Jan 1999 – Mar 2000 (Kivlighon, Galbally, and Weeks, CSIRO)
- In-situ sampling and GC-FID analyses January & February 1999 (Lewis et al., University of Leeds)
- In-situ sampling and GC-MS analyses October 2004 – ongoing (Krummel, Fraser, Steele, Porter, CSIRO, AGAGE)
- Air archive analyses and GC-MS analyses 1978 – present (Krummel, Fraser, Steele, Porter, CSIRO, Miller SIO/NOAA)
- In-situ sampling and PTR-MS analyses 2006 – ongoing on a campaign basis (Galbally, Lawson CSIRO)

MDL

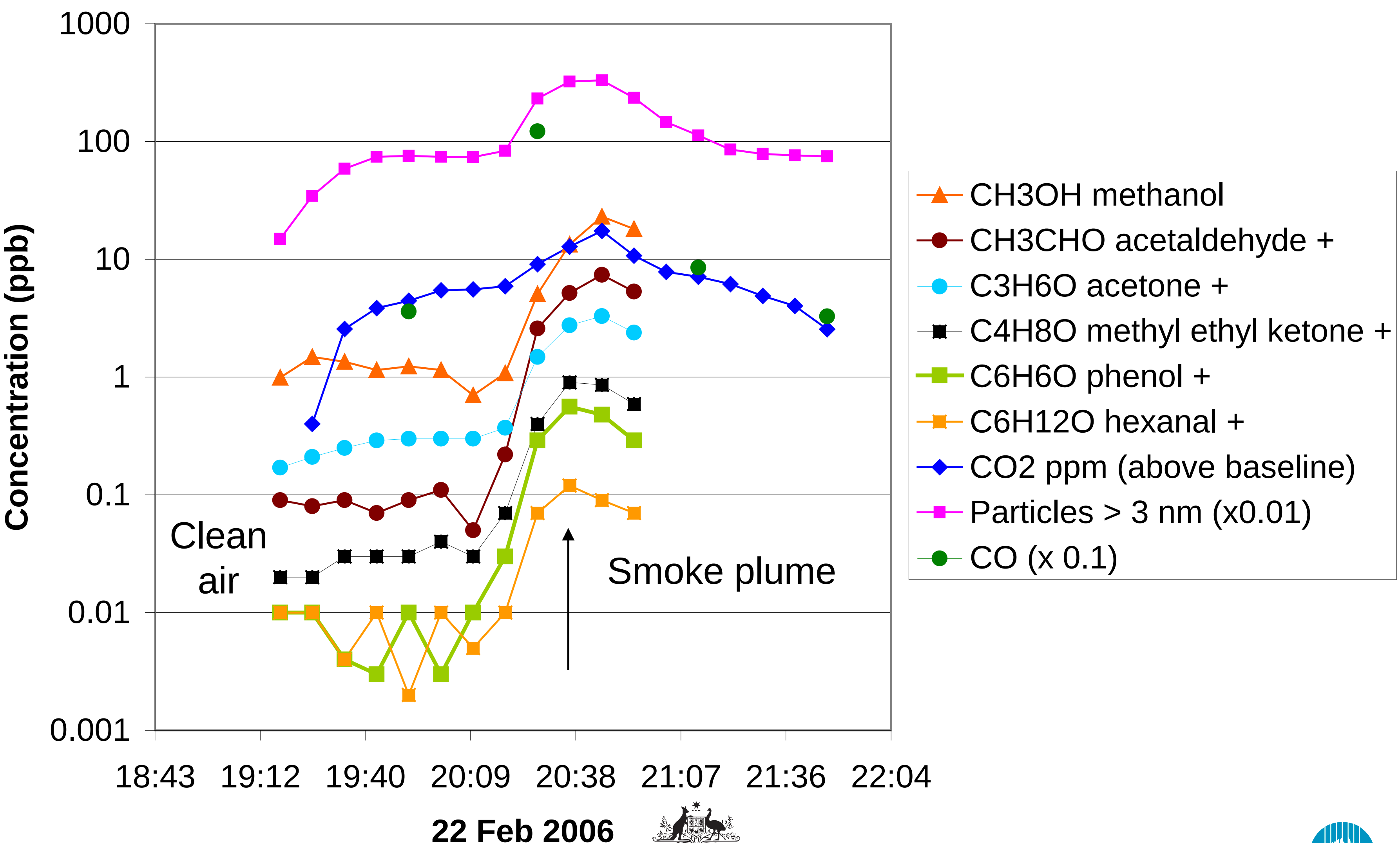
Mass	VOC	MDL for hourly measurement (ppt)	% measurements > MDL (clean air)
33	Methanol	214	85%
42	acetonitrile	34	60%
45	acetaldehyde	27	65%
59	acetone	31	60%
63	DMS	28	90%
69	isoprene	9	85%
81	terpenes	6	90%

MDL calculation determined from scatter in zero measurements based on ISO6879

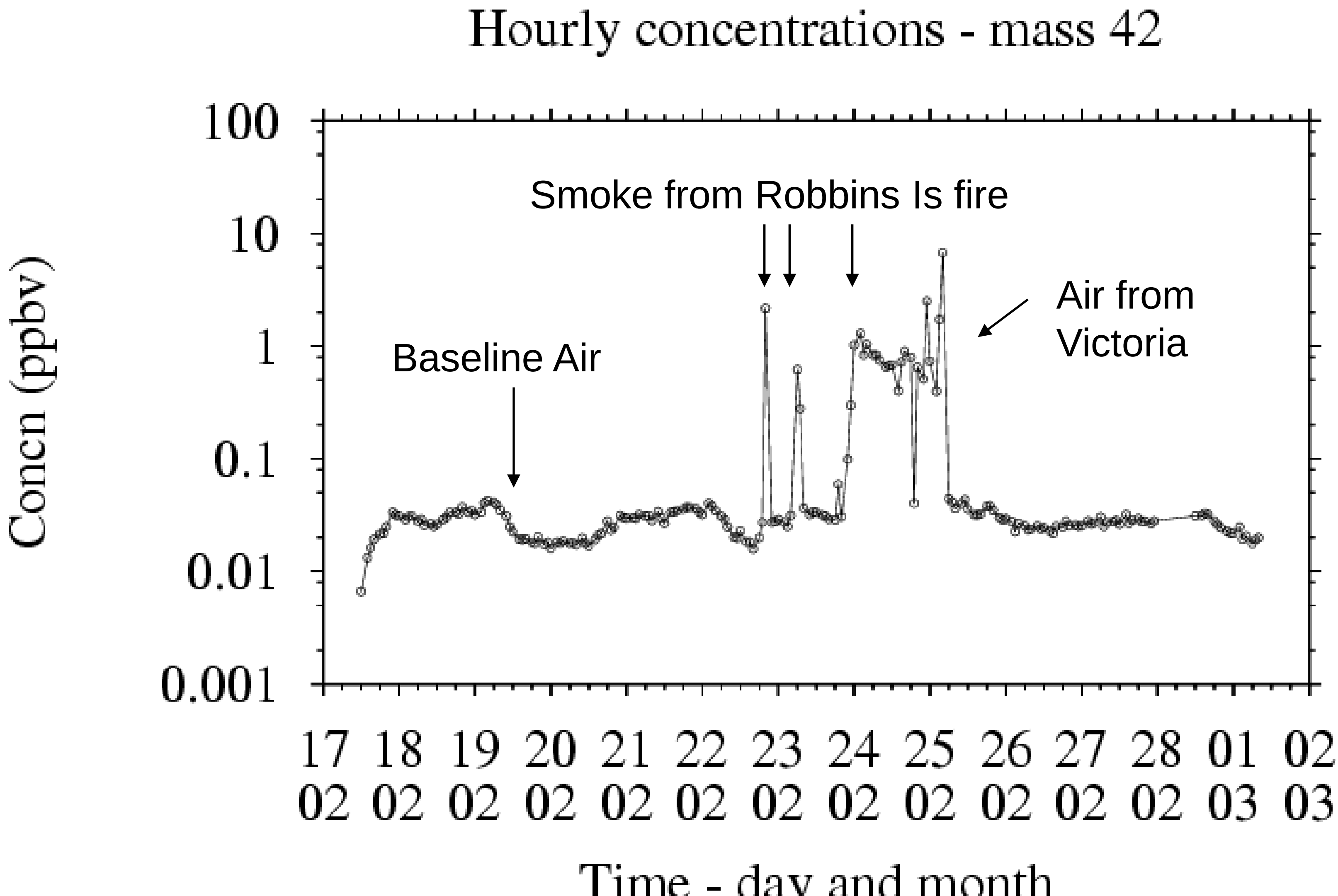
Minimum Detectable Limit (MDL) vs Mass Number, for 1 sec dwell-time



Oxygenated products



Mass 42 Acetonitrile



Baseline wind direction at Cape Grim