METHYL BROMIDE : ITS ATMOSPHERIC SOURCES AND SINKS

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METHYL BROMIDE : OZONE DEPLETING SUBSTANCE

Widely used as a:

- soil fumigant and sterilisation agent before planting
- sterilising agricultural products before export and import

Montreal Protocol timetable:

1991 benchmark year for uses, 42 Gg yr^{-1}

1998 uses to be curtailed

1999 25% reduction on benchmark levels, 31 Gg yr^{-1}

2001 50% reduction, 21 Gg yr^{-1}

2003 only essential uses to remain

METHYL BROMIDE IN THE MONTREAL PROTOCOL

More time has been taken up within the Science Assessments of ozone layer depletion on methyl bromide than on any other ozone-depleting substance.

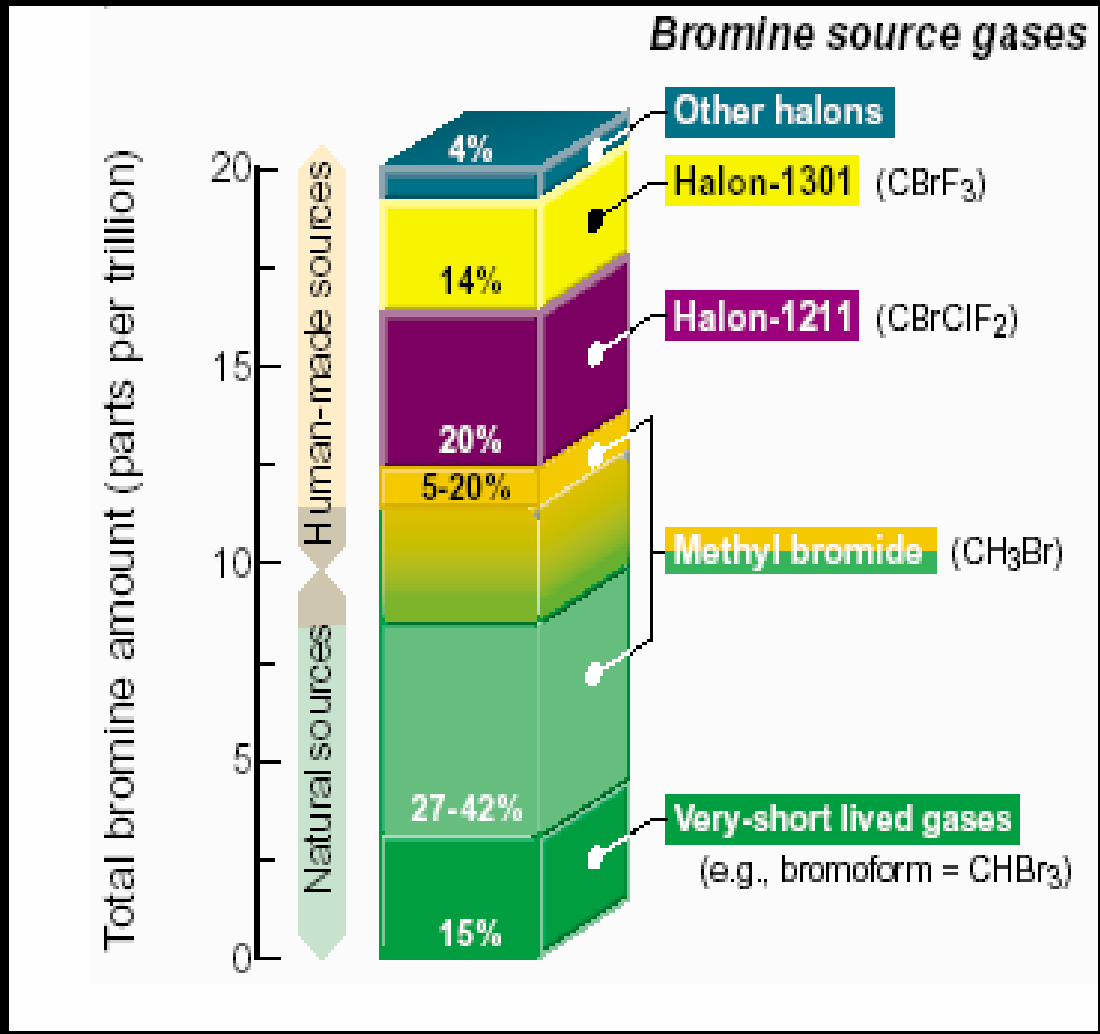
Why is a substance which is so important to policy-makers so embroiled in controversy ?

World Meteorological Organization
Global Ozone Research and Monitoring Project—Report No. 47

SCIENTIFIC ASSESSMENT OF OZONE DEPLETION: 2002

National Oceanic and Atmospheric Administration
National Aeronautics and Space Administration
United Nations Environment Programme
World Meteorological Organization
European Commission

BROMINE CARRIERS TO THE STRATOSPHERE



Source: WMO (2003)

ATMOSPHERIC LIFE CYCLE OF METHYL BROMIDE

Sources

- Human activities
- Biomass burning
- Oceans
- Terrestrial sources

Sinks

- Oxidation by tropospheric OH radicals
- Ocean uptake
- Soil uptake
- Transport to the stratosphere

SOURCES – HUMAN ACTIVITIES

These have been quantified through the Montreal Protocol activities, so for 1992 :

Soil fumigation	26.5 Gg yr^{-1}
Fumigation of durables	6.6 Gg yr^{-1}
Fumigation of perishables	5.7 Gg yr^{-1}
Fumigation of structures	2.0 Gg yr^{-1}
Combustion of leaded petrol	5 Gg yr^{-1}

Source: WMO (2003)

SOURCES – BIOMASS BURNING

Blake et al. (1996)

Mano and Andreae (1994)

Best estimate: 20 Gg yr^{-1} with a range 10 – 40 Gg yr^{-1}

SINKS – OH OXIDATION

Balance between methyl chloroform production and loss gives global mean tropospheric OH concentration

Relative reaction rate coefficients:

OH + methyl chloroform

OH + methyl bromide

Global OH + methyl bromide sink is 80 Gg yr^{-1} with a range of 60 – 100 Gg yr^{-1}

Source: WMO (2003)

SOURCES AND SINKS - OCEAN EXCHANGE

Oceans are both the largest identified source and the second largest sink (after OH oxidation).

Seasonal variations observed in supersaturations and bimodal distribution of emission with temperature.

Net flux is into the ocean and is –21 (-32 to –3) to –14 (-20 to –11) Gg yr^{-1}.

Source: WMO (2003)

SINKS - SOILS

Based on measured soil fluxes to a range of soils including cultivated soils:

Global sink is : 32 Gg yr^{-1} with a range from 32 – 154 Gg yr^{-1}

Source: WMO (2003)

ATMOSPHERIC BUDGET FOR METHYL BROMIDE

All sources:	159	77 – 293	Gg yr^{-1}
All sinks:	204	129 – 387	Gg yr^{-1}
Balance:	-45	-220 – +71	Gg yr^{-1}

Atmospheric lifetime : 0.7 years with range 0.4 – 1.1 years

Source: WMO (2003)

METHYL BROMIDE AND ITS ODP

The current ozone-depletion potential ODP of 0.38 is based on its atmospheric lifetime of 0.7 years.

Its importance as a bromine-carrier to the current stratosphere depends on the fraction of the current mixing ratio which is assumed to be under the influence of human activities.

These are linked because the ocean sinks have been assumed to be efficient, more unknown sources are required, reducing the man-made fraction.

Because the current ODP is relatively low, phase-out had been delayed under the Montreal Protocol until 2003.

METHYL BROMIDE IN SOUTHERN HEMISPHERE AIR RECONSTRUCTED FROM MEASUREMENTS IN FIRN

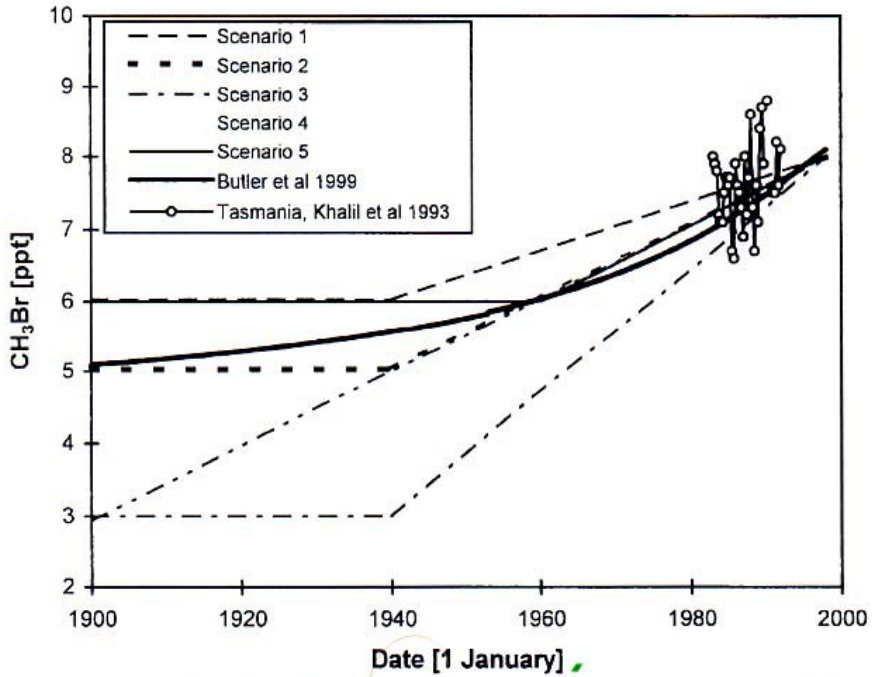


Figure 5. Various Southern Hemispheric (SH) time trend scenarios (lines) assumed for CH_3Br in the firn model (including the previously reported reconstruction of *Butler et al.* [1999]), compared with the SH measurements of *Khalil et al.* [1993] (symbols).

Sturges et al. (2001)

METHYL BROMIDE IN SOUTHERN HEMISPHERE AIR FROM ICE CORES

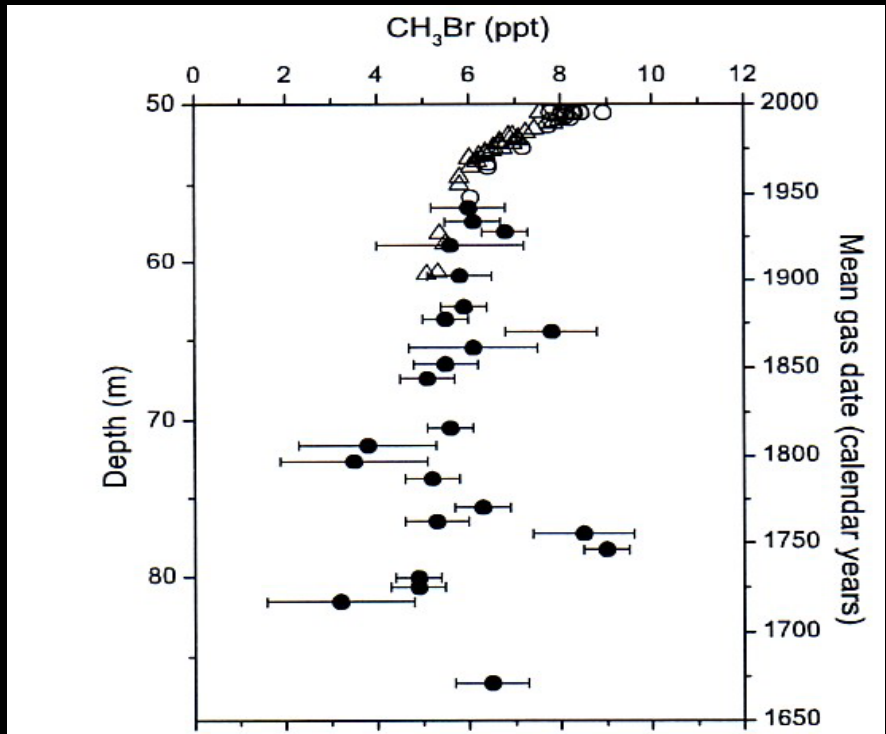


Figure 2. CH_3Br in Siple Dome ice core samples (solid circles) from this study and Siple Dome firn air (open circles) and South Pole firn air (open triangles) results from *Butler et al.* [1999] plotted against mean gas date. The depth scale applies only to the ice core data.

Saltzman et al. (2004)

BASELINE MONITORING OF OZONE-DEPLETING SUBSTANCES AT MACE HEAD, IRELAND

Professor Peter Simmonds, University of Bristol

Baseline monitoring of ozone-depleting substances at Mace Head, Ireland began in 1987 with CFC-11, CFC-12, CCl_4, CH_3CCl_3

Mace Head is part of the ALE/GAGE/AGAGE global baseline monitoring programme.

Originally, baseline measurements were begun by James Lovelock at Adrigole on Bantry Bay, Ireland.

Mace Head,

Ireland

1000s km uninterrupted fetch across North Atlantic Ocean

Long range transport brings polluted air from Europe

OBSERVATIONS OF METHYL BROMIDE

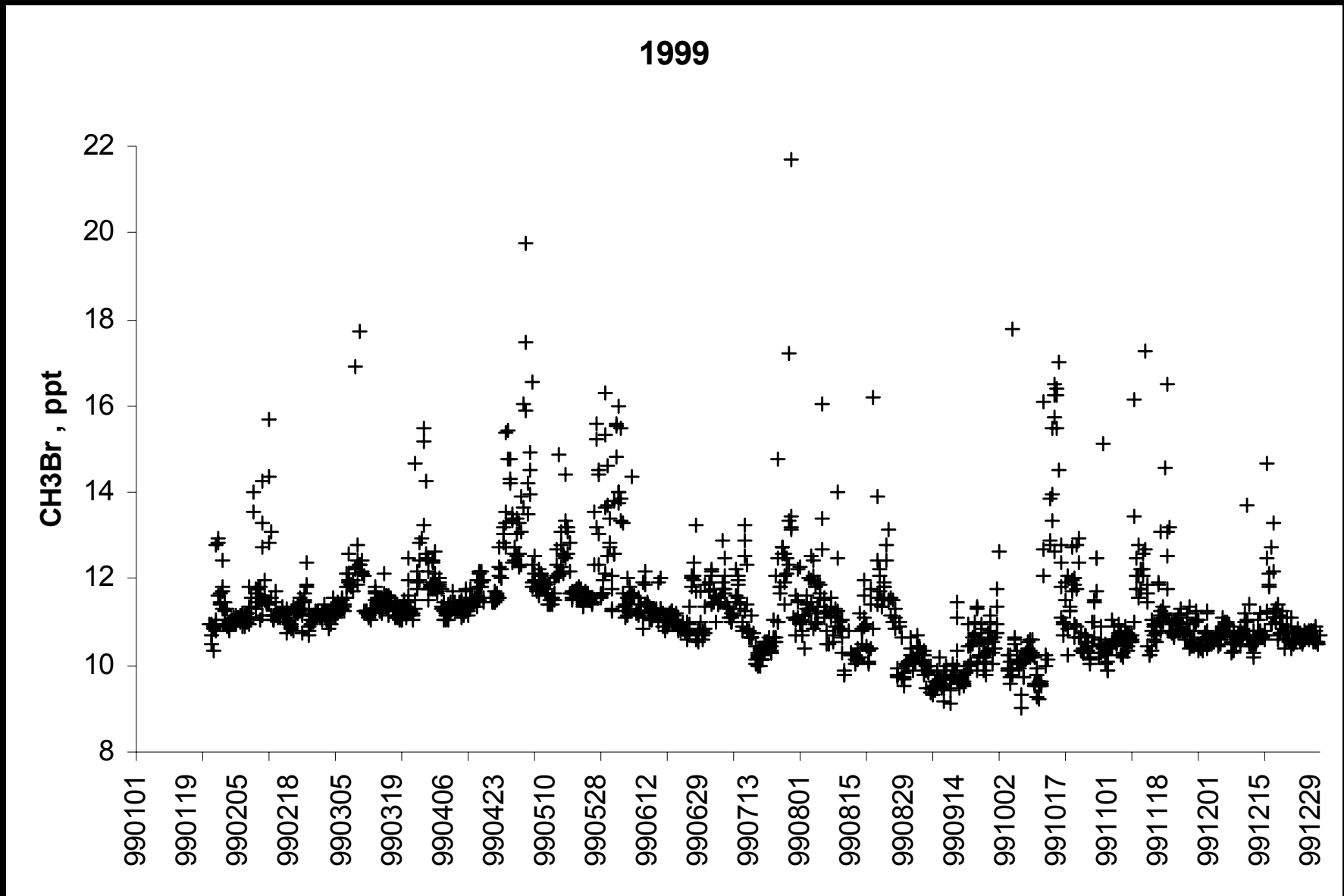
Methyl bromide is monitored using in situ gas chromatography-mass spectrometry

Primary standards have been prepared at Scripps Institute for Oceanography on the SIO-98 scale.

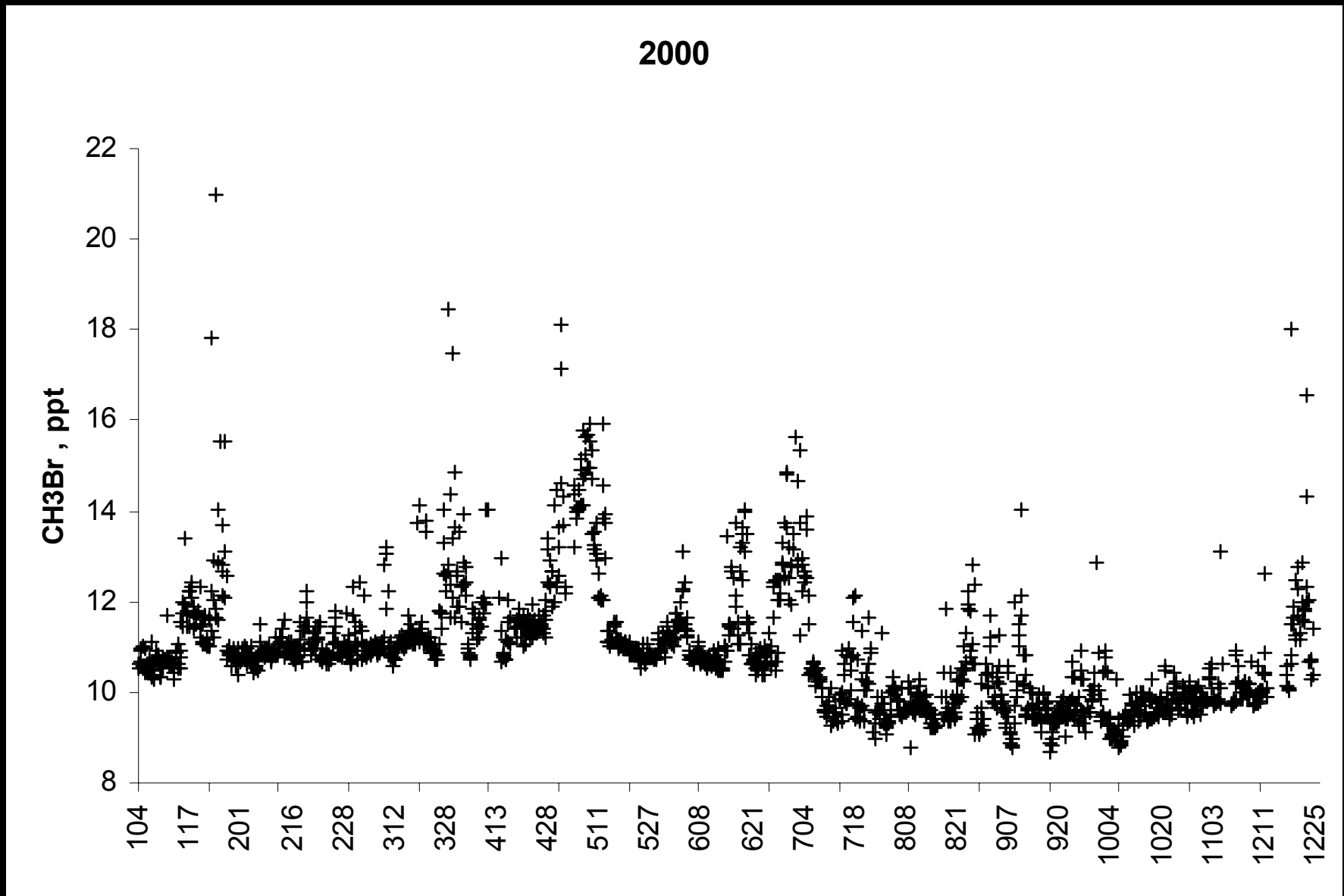
Observations are made every 4 hours.

Precision is $\pm$ 0.52 ppt

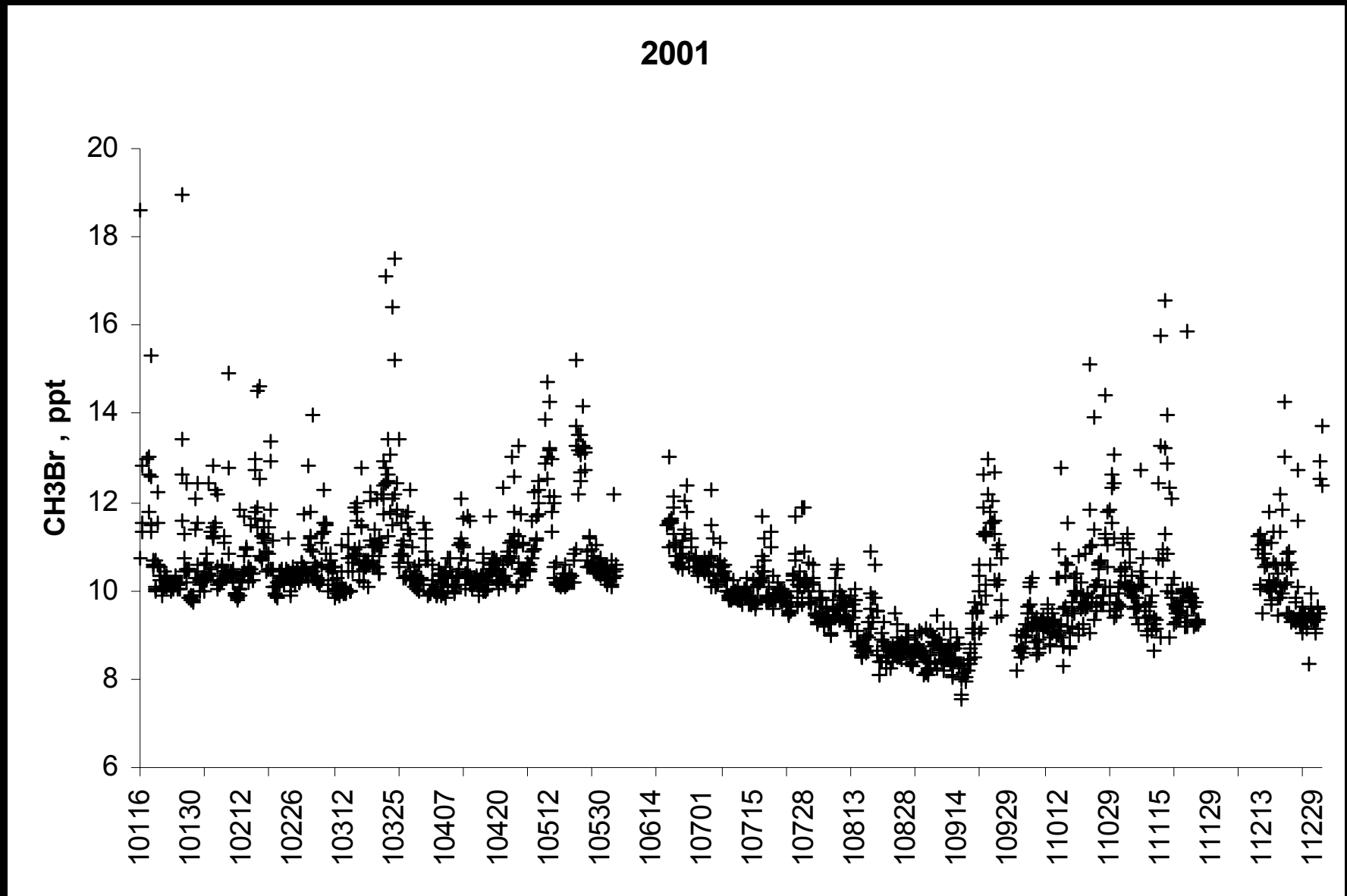
METHYL BROMIDE AT MACE HEAD, IRELAND DURING 1999



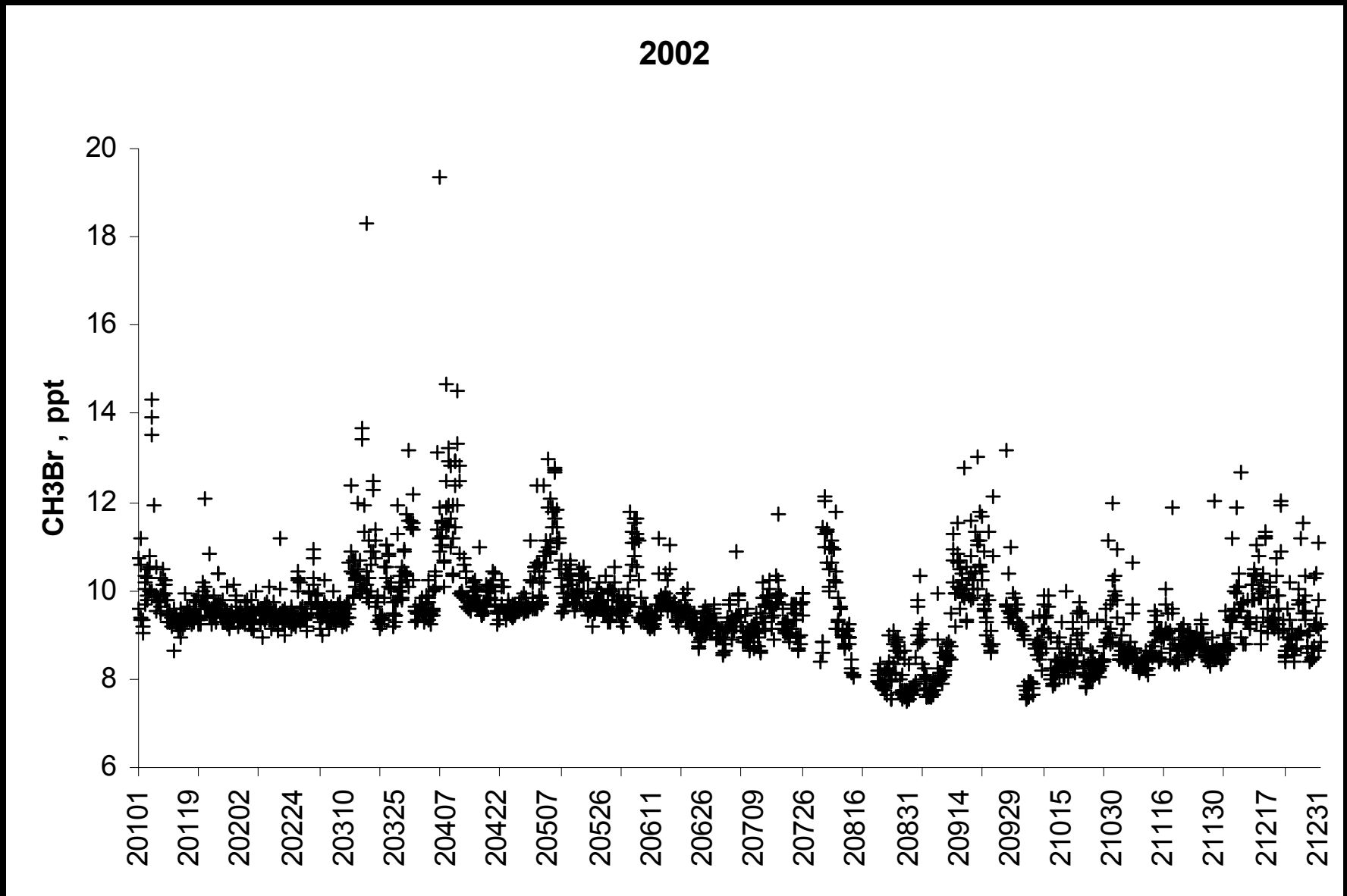
METHYL BROMIDE AT MACE HEAD, IRELAND DURING 2000



METHYL BROMIDE AT MACE HEAD, IRELAND DURING 2001



METHYL BROMIDE AT MACE HEAD, IRELAND DURING 2002



METHYL BROMIDE IN BASELINE AIR MASSES

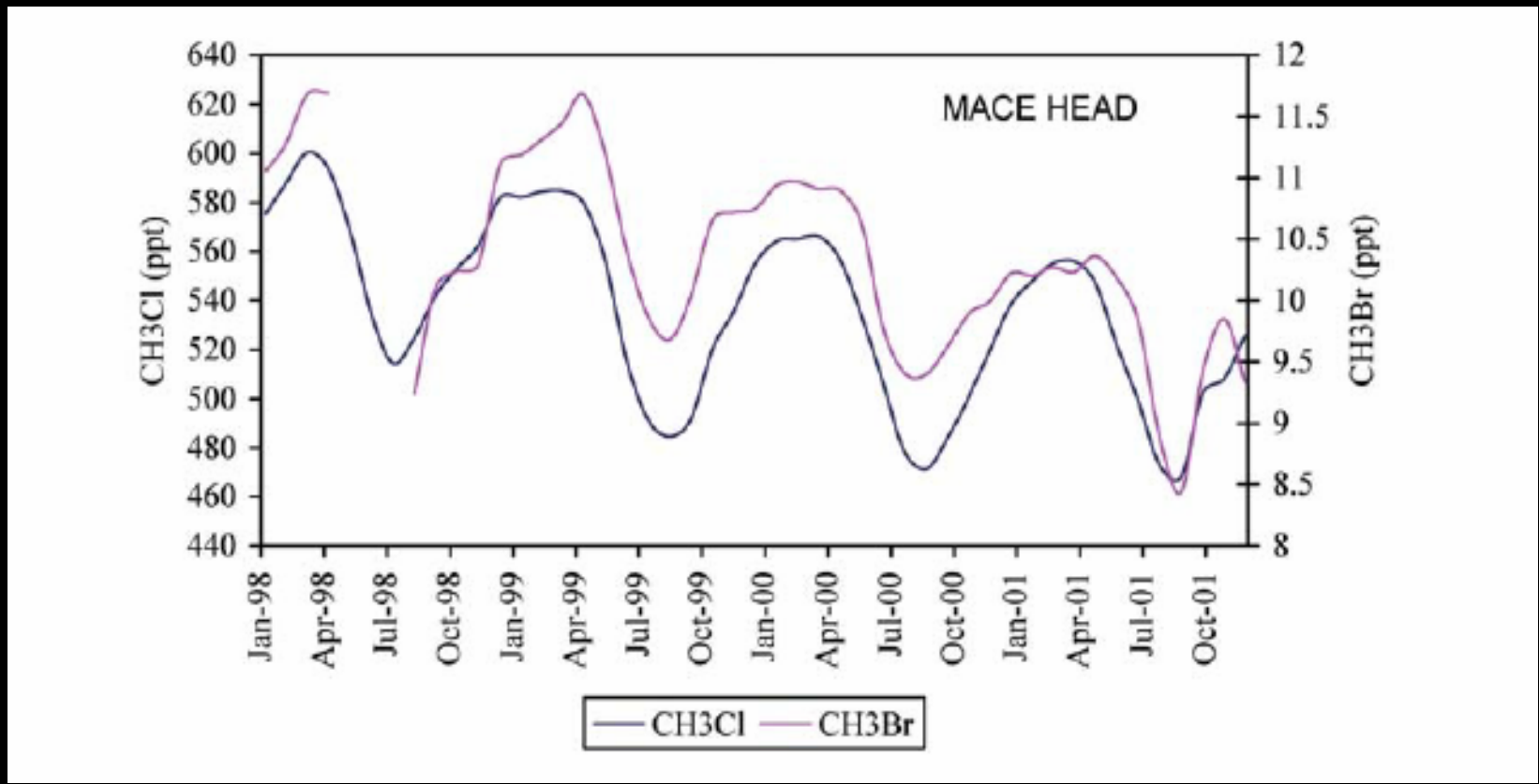
24.6% (7157) of the measurements from 1999-2002 were classified as baseline.

Mean baseline mole fraction was 10.37 $\pm$ 0.05 ppt

Baseline trend 0.31 $\pm$ 0.05 ppt yr^{-1} (or 3.0% yr^{-1})

Seasonal cycle peaks in the spring (May 1999, March 2000, May 2001) with an amplitude (peak-mean) of 0.65 ppt (6.5%)

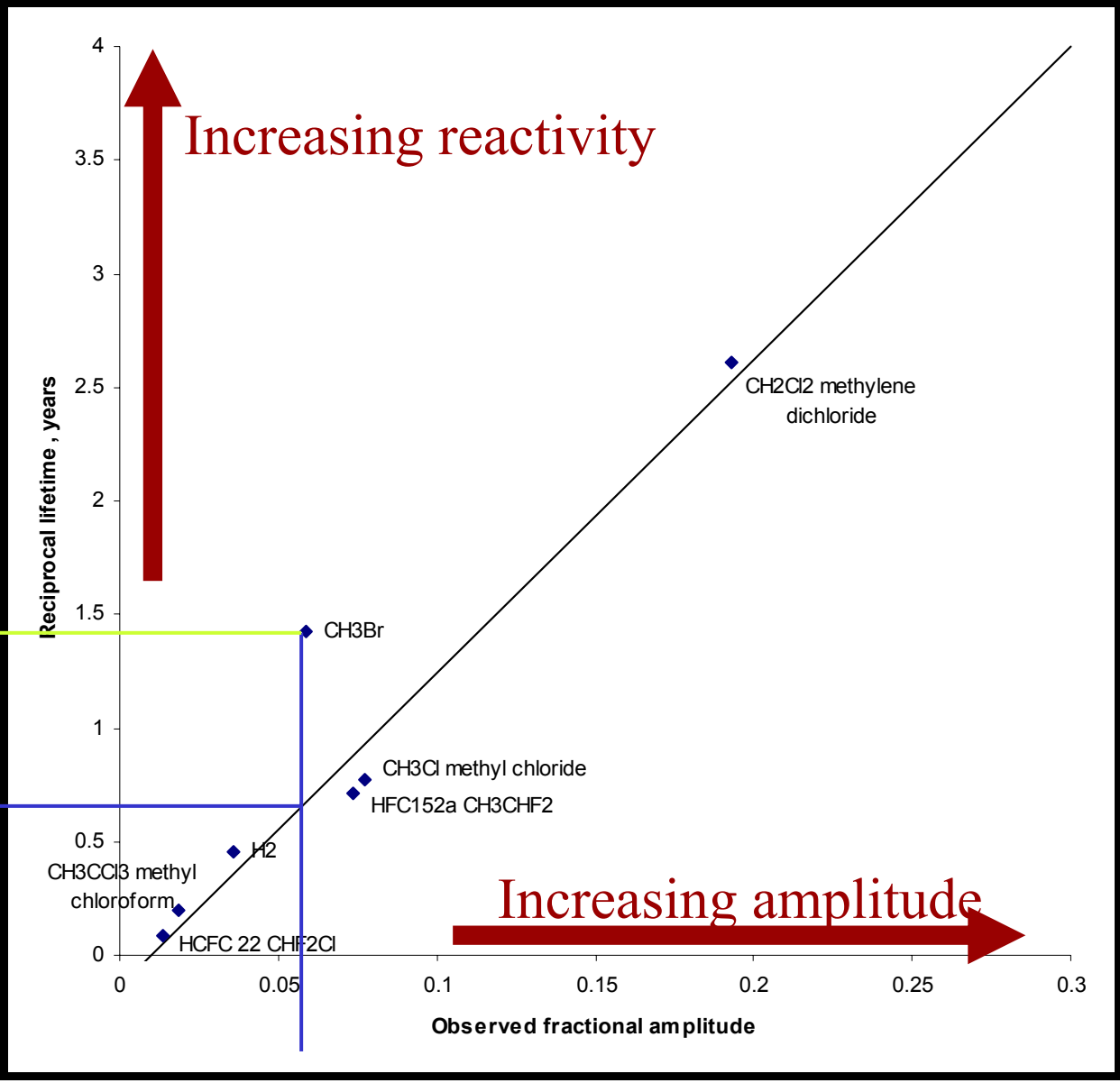
SEASONAL CYCLES IN CH_3Br AND CH_3Cl



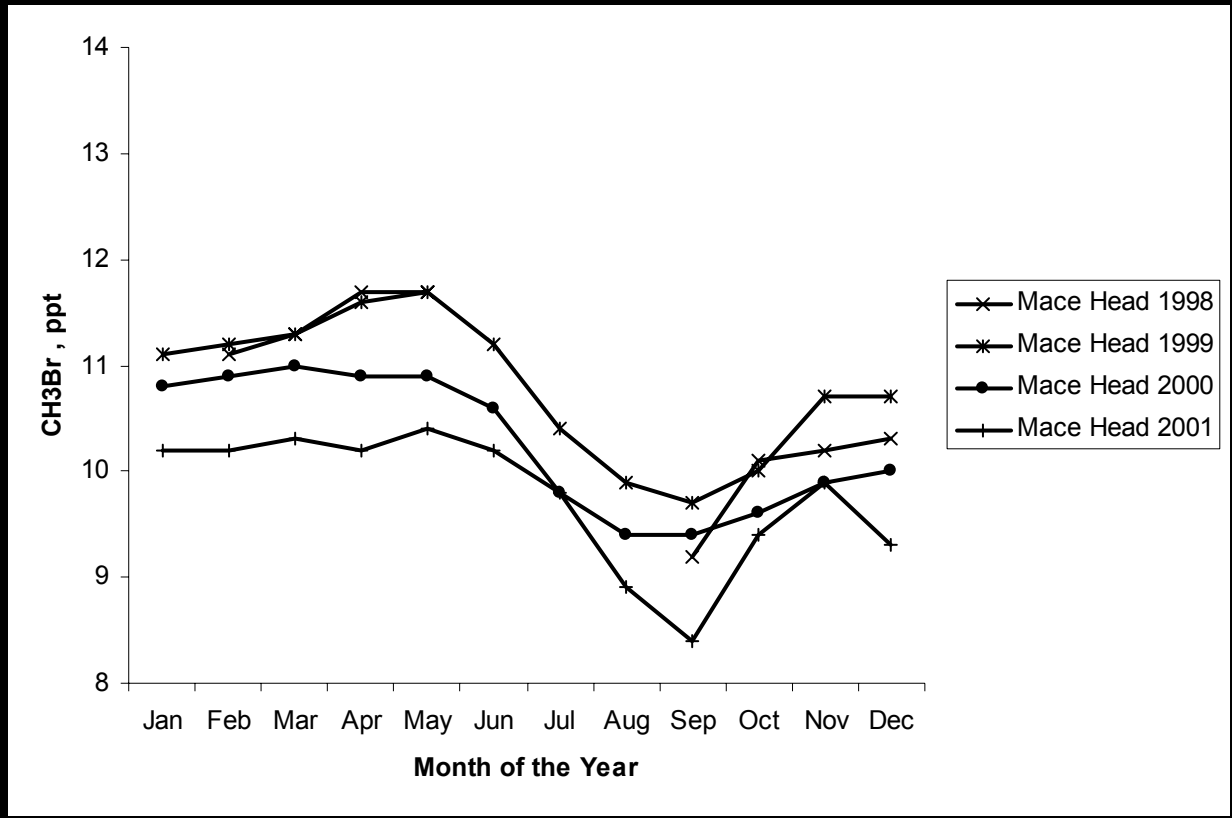
CAN THE STRENGTH OF THE SEASONAL CYCLE OF CH_3Br BE EXPLAINED ?

WMO lifetime of 0.7 years

Lifetime of 1.6 years

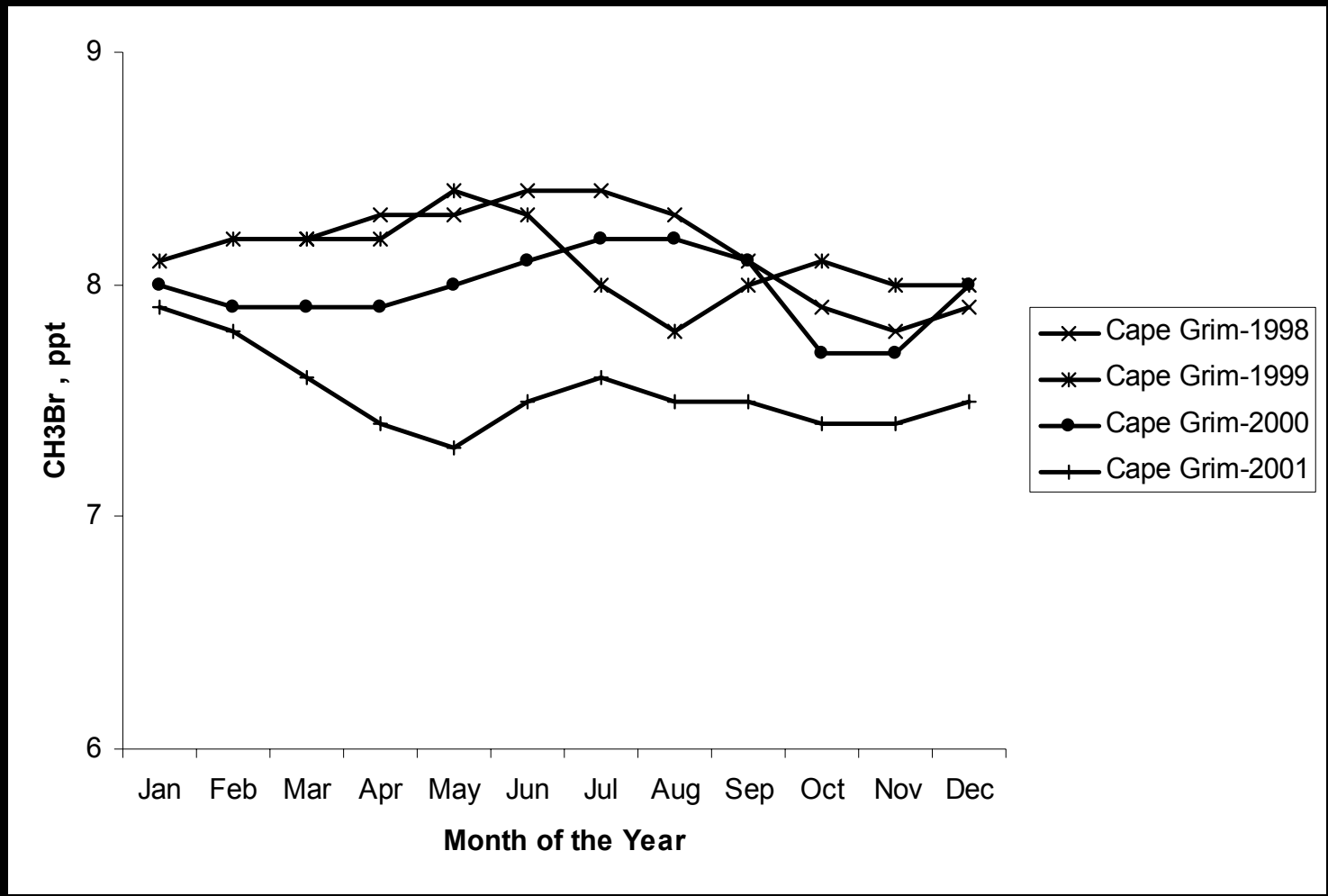


OBSERVED SEASONAL CYCLES AT MACE HEAD, IRELAND



A strong seasonal cycle with a spring-time maximum is observed at Mace Head

OBSERVED SEASONAL CYCLES AT CAPE GRIM, TASMANIA



There is virtually no observed seasonal cycle at Cape Grim

GLOBAL MODELLING OF CH_3Br

- Use of STOCHEM to model seasonal cycles of CH_3Br at Mace Head, Ireland and Cape Grim, Tasmania
- Mace Head station data should constrain terrestrial sources and sinks as well as man-made sources
- Cape Grim station data should constrain ocean sources and sinks

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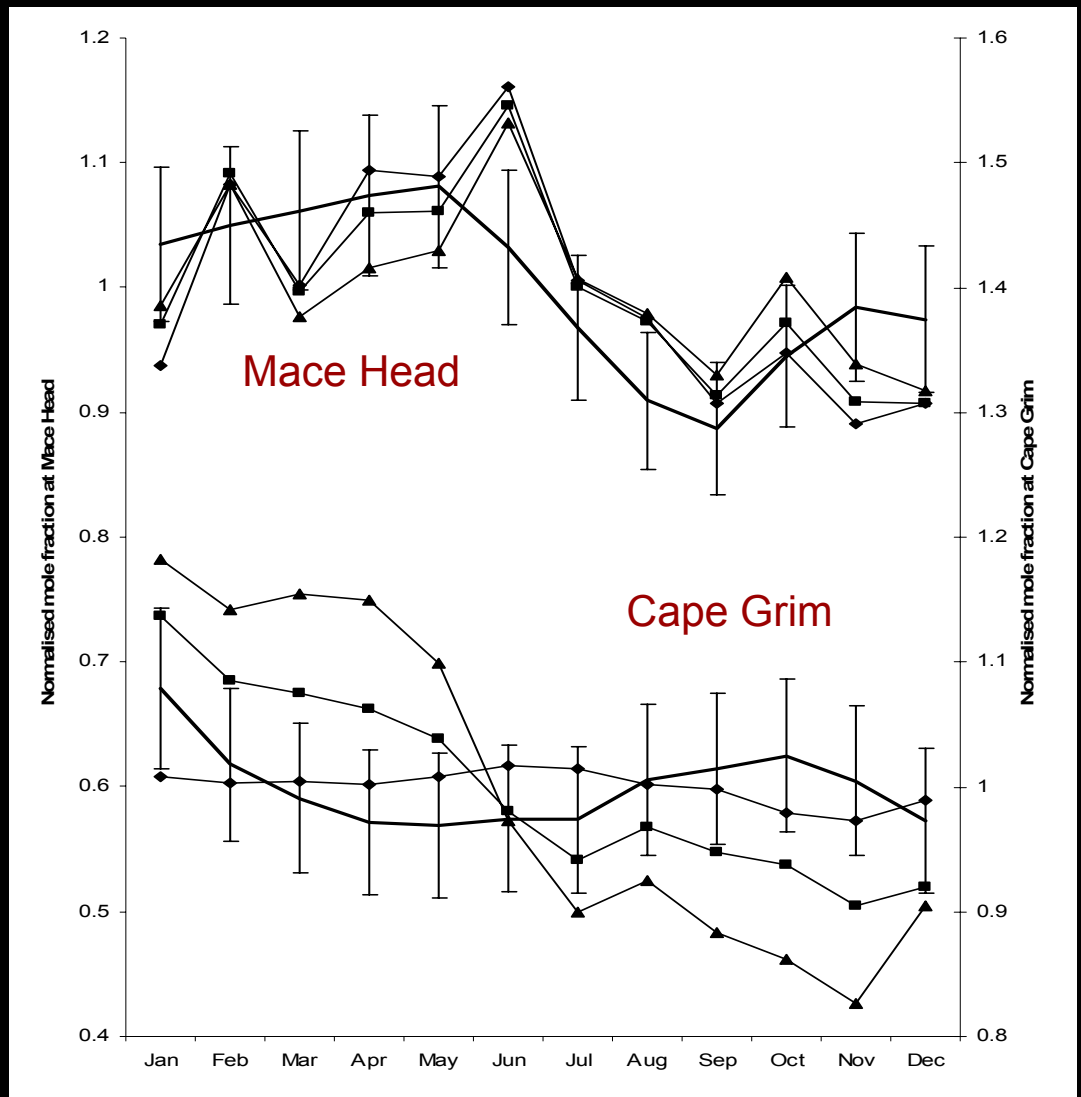
OCEAN SOURCES AND SINKS



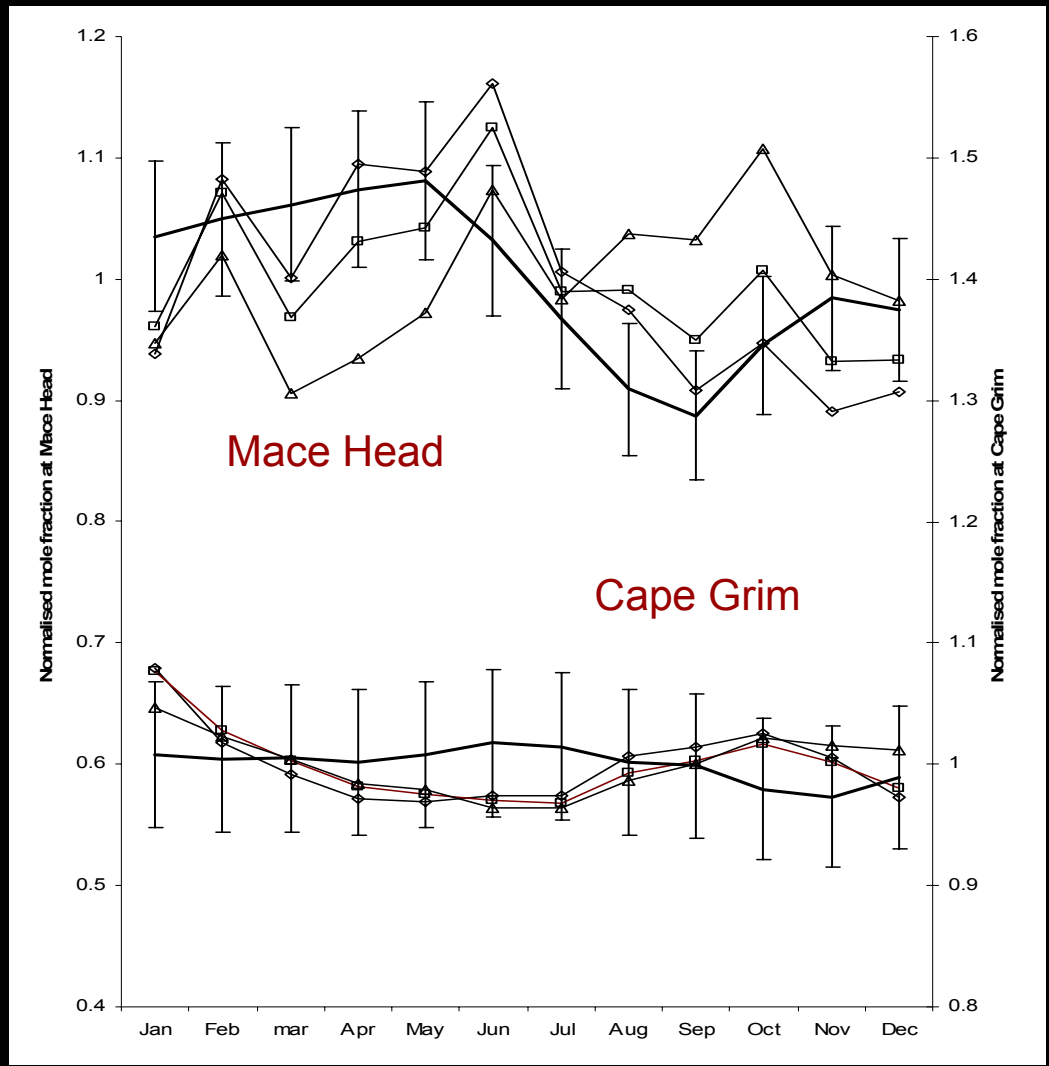
Diamonds – no ocean

Squares – medium ocean

Triangles – high ocean

Weak ocean sources and sinks cannot be ruled out

SOIL SOURCES AND SINKS



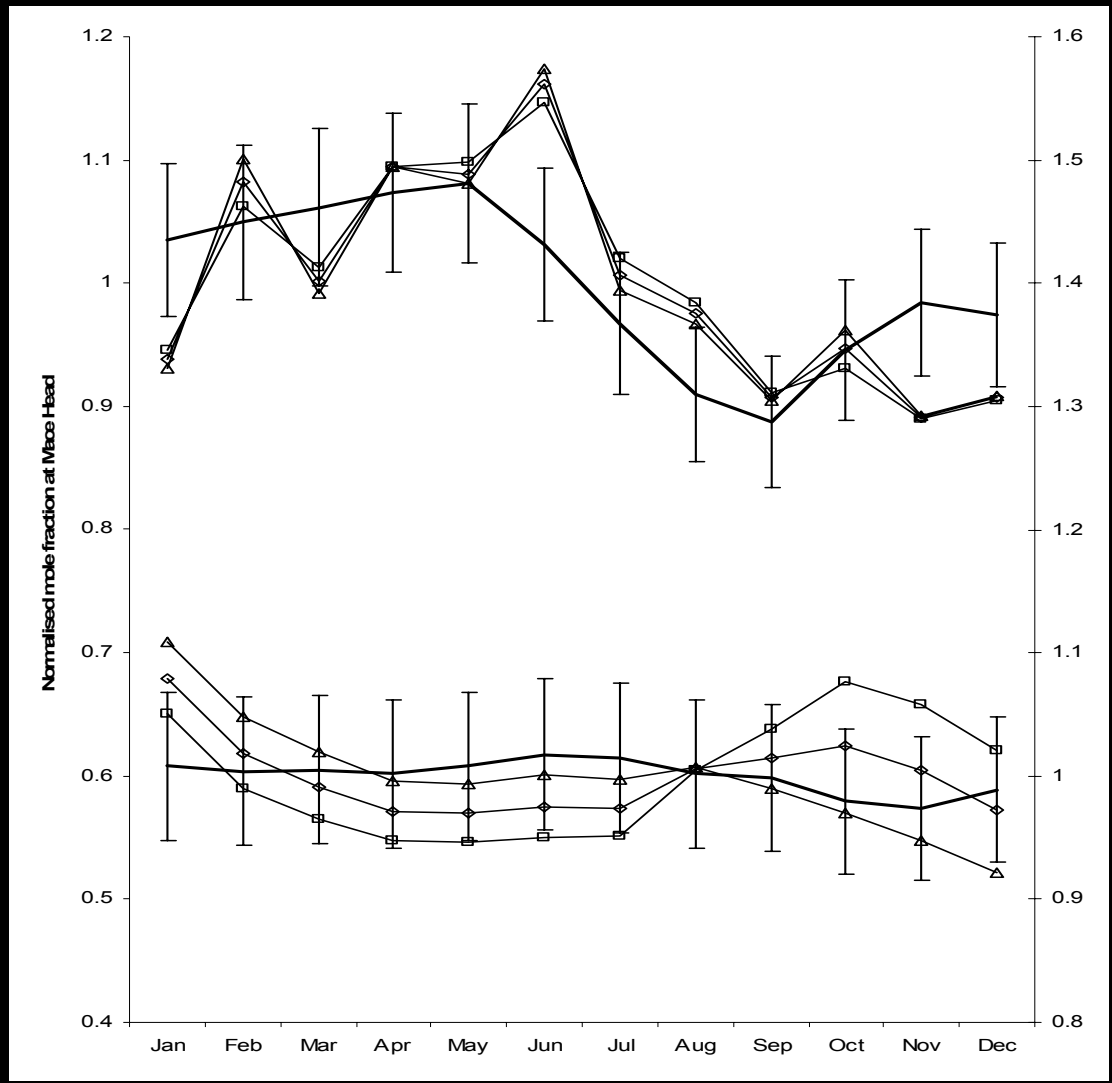
Diamonds – no soils

Squares – medium soils

Triangles – high soils

Weak soils sources and sinks cannot be ruled out

BIOMASS BURNING AND MAN-MADE SOURCES



Diamonds: central burning central man-made

squares: high burning low man-made

Triangles: low burning high man-made

Points to biomass burning towards the higher end of its range

CONCLUSIONS FROM 3-D MODELLING

- No strong evidence from model and observed seasonal cycles at Cape Grim for strong ocean sources and sinks
- No strong evidence from model and observed seasonal cycles at Mace Head for the soil sources and sinks
- Tropical biomass burning appears to be an important source
- Man-made sources are also important
- OH oxidation need be the only important sink

CONCLUSIONS
BASED ON OBSERVATIONS AND MODELLING OF CH_3Br AT MACE HEAD AND CAPE GRIM

- Seasonal cycles can be explained with biomass burning, man-made sources and OH sinks alone
- Cannot entirely rule out small ocean and terrestrial sources or sinks
- Atmospheric lifetime is unlikely to be as short a 0.7 years and may be as long as 1.5 years
- Man-made fraction of CH_3Br sources may be as high as one half but not as low as 0.1 – 0.4
- May be necessary to revisit the life cycle and ODP of CH_3Br

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- To Paul Fraser of the CSIRO, Australia for providing access to the Cape Grim observations.