Acid Rain and Tropospheric Ozone

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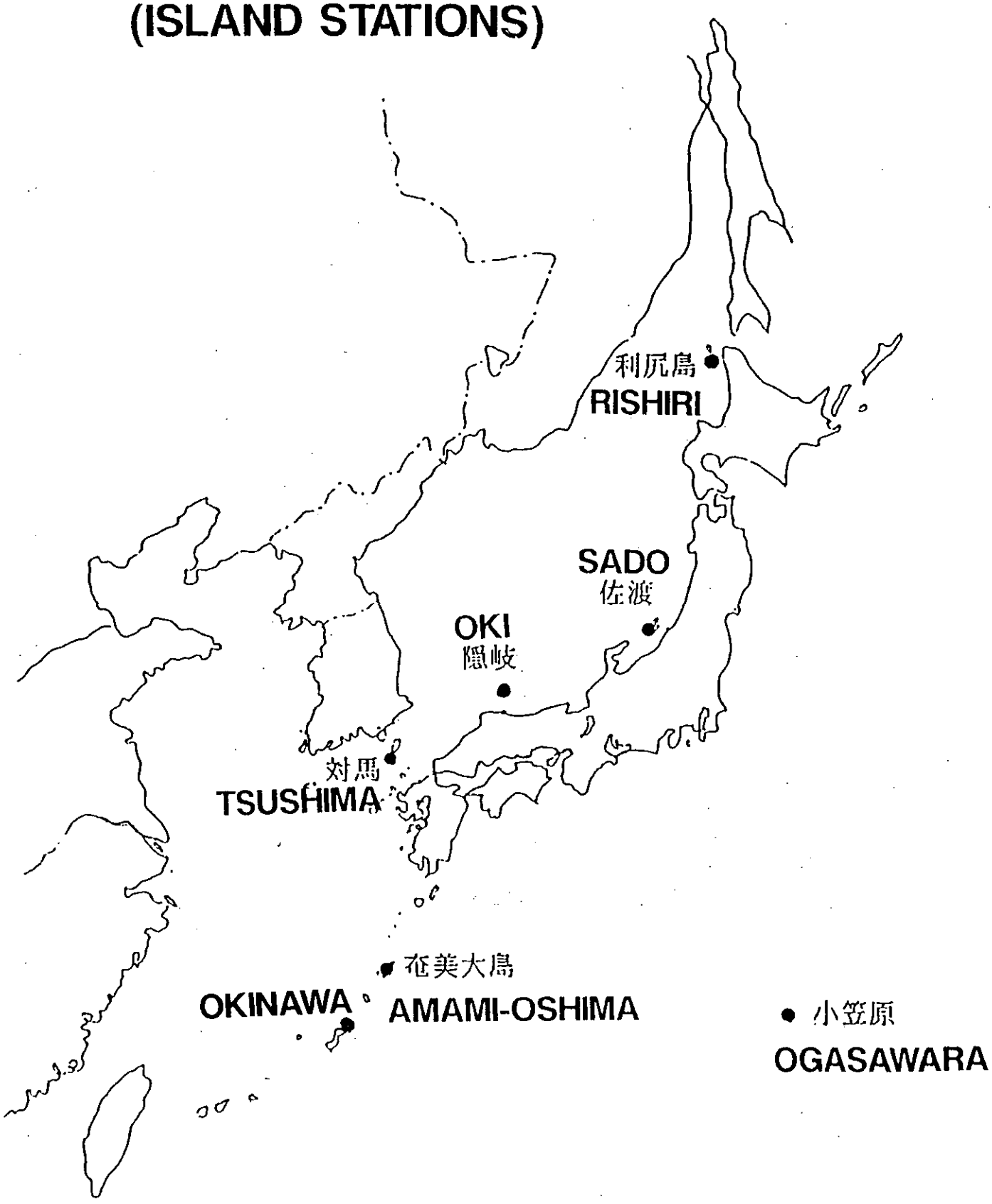
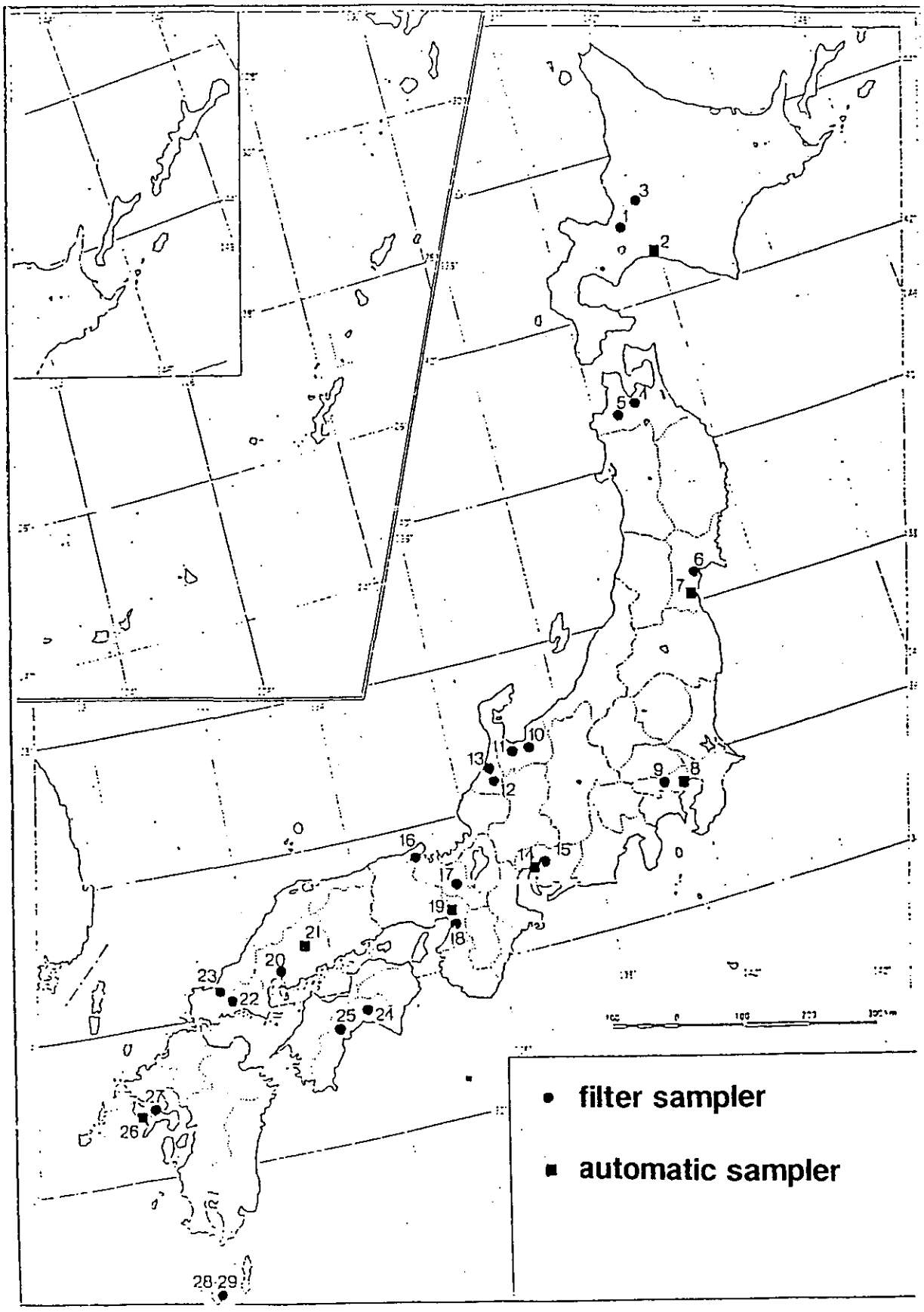
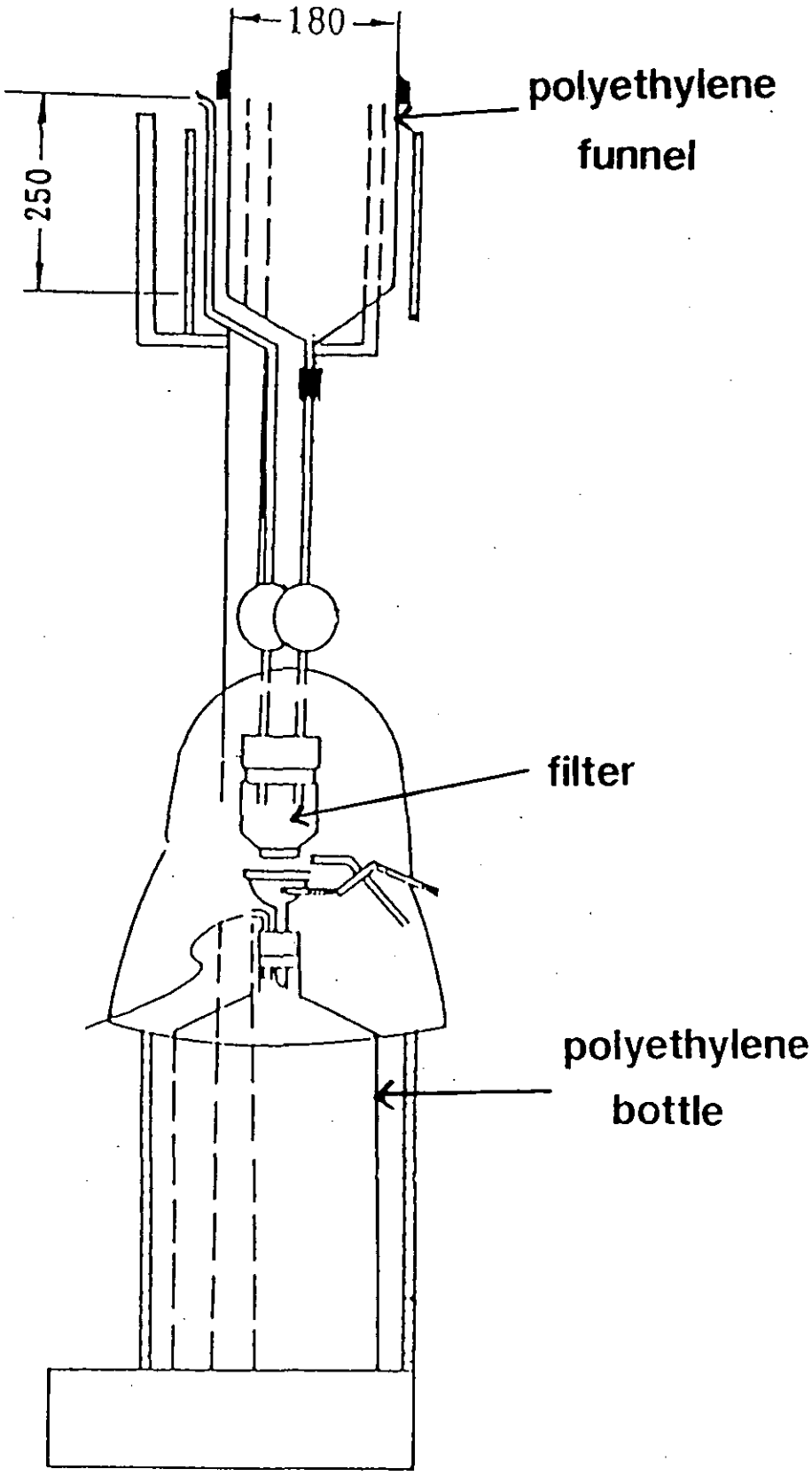
National Institute for Environmental Studies

NATIONAL ACID RAIN SAMPLING STATIONS

(ISLAND STATIONS)

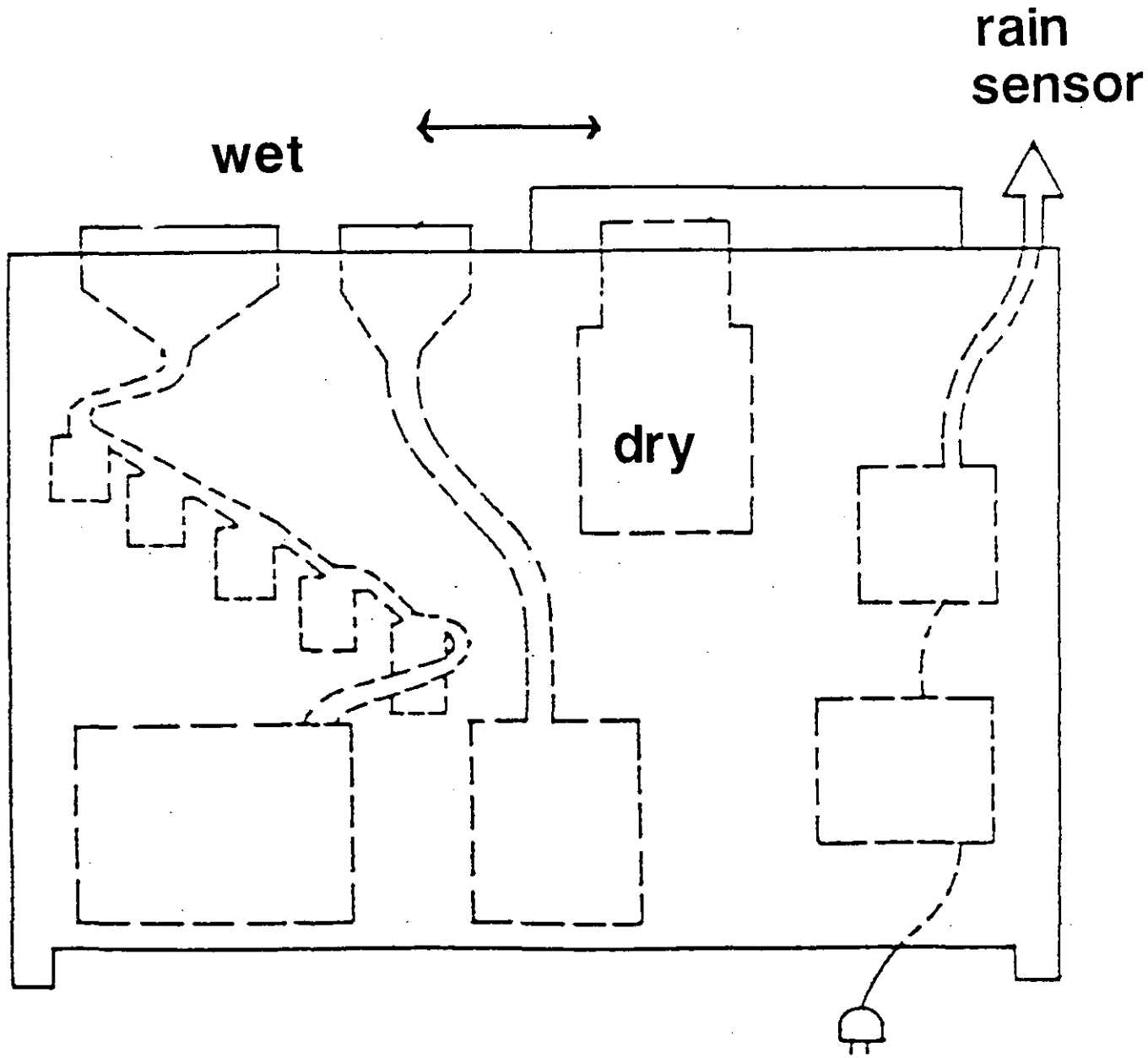


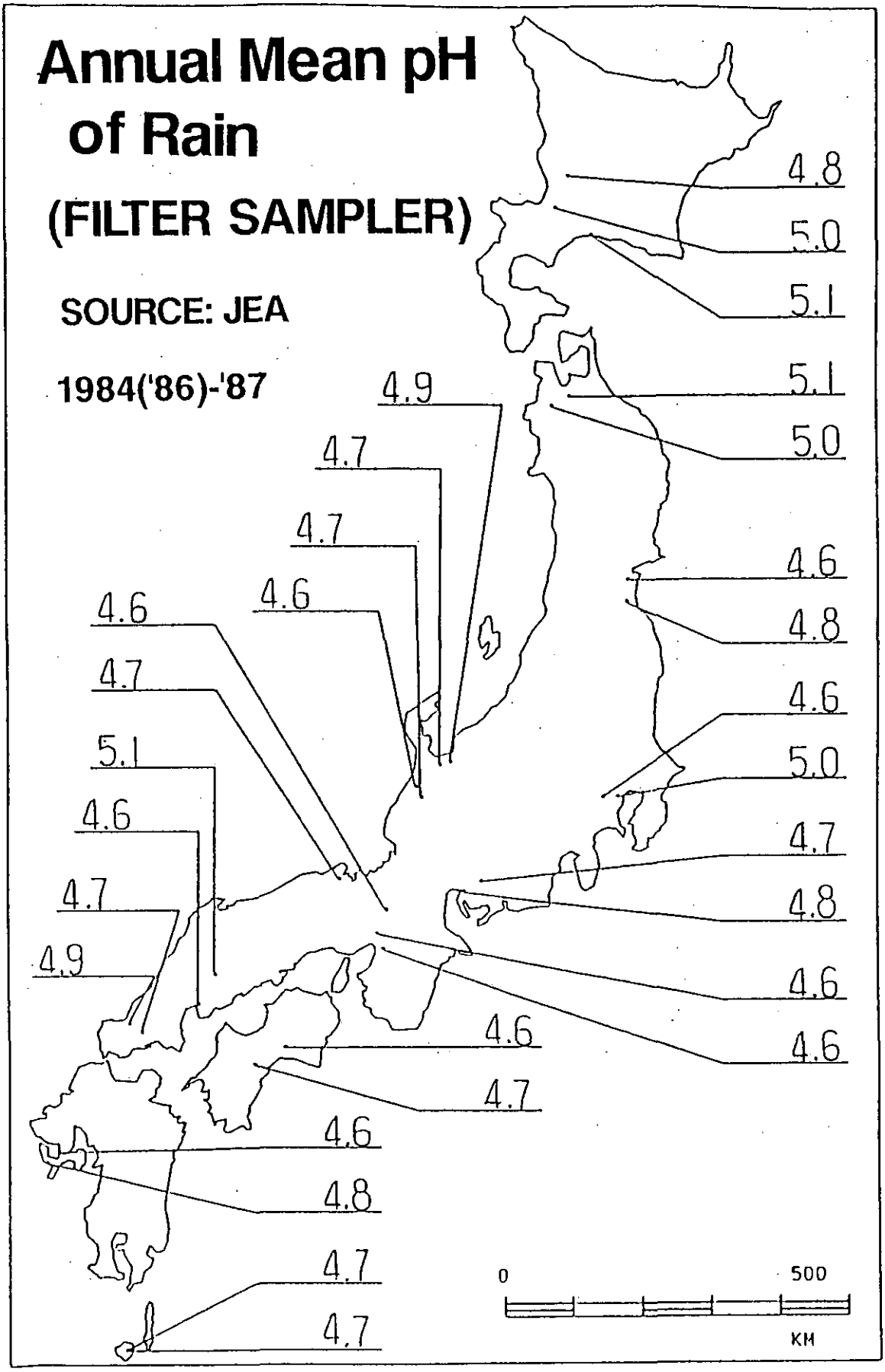

1
2
3
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28-29
filter sampler
automatic sampler

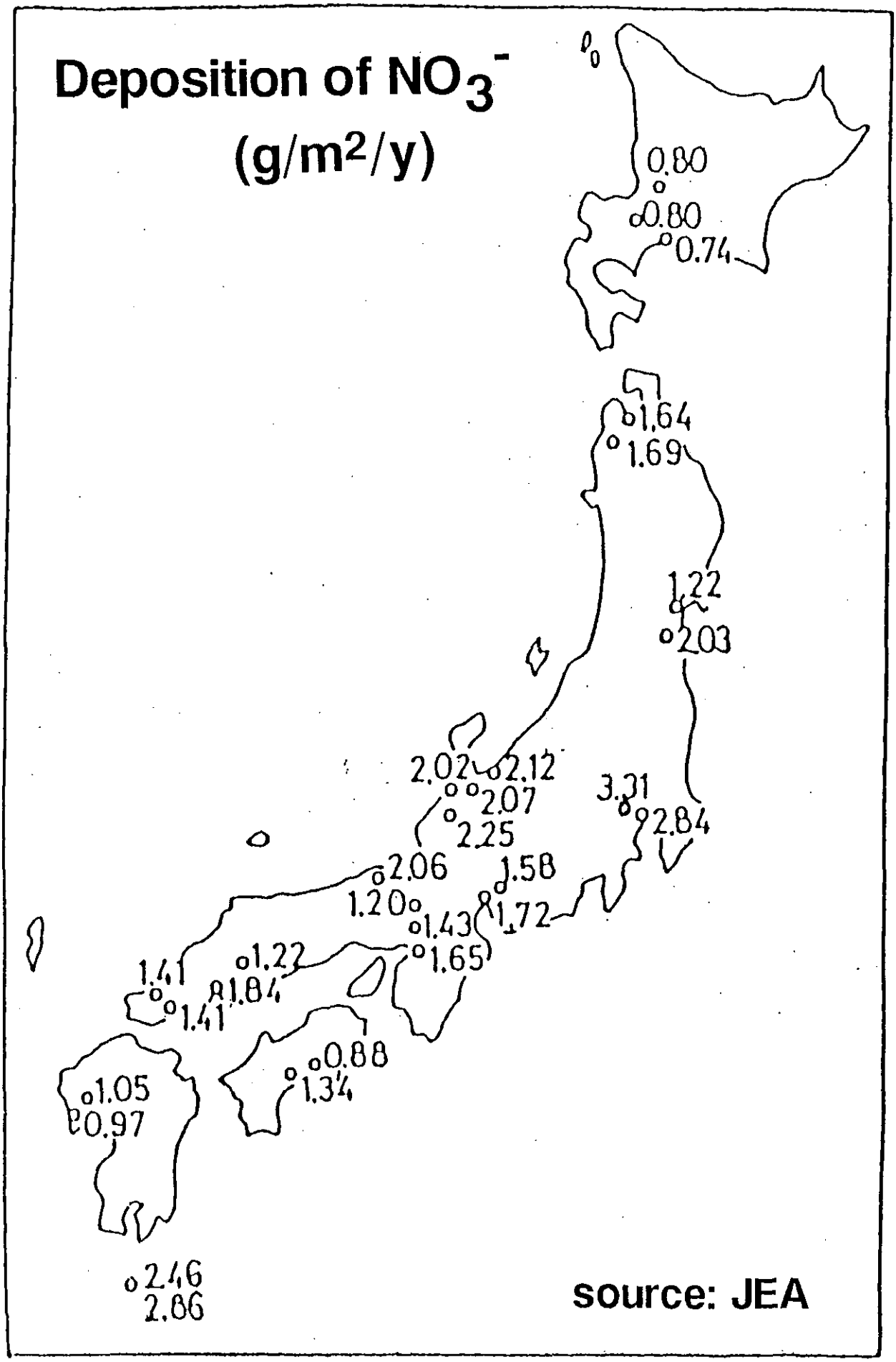


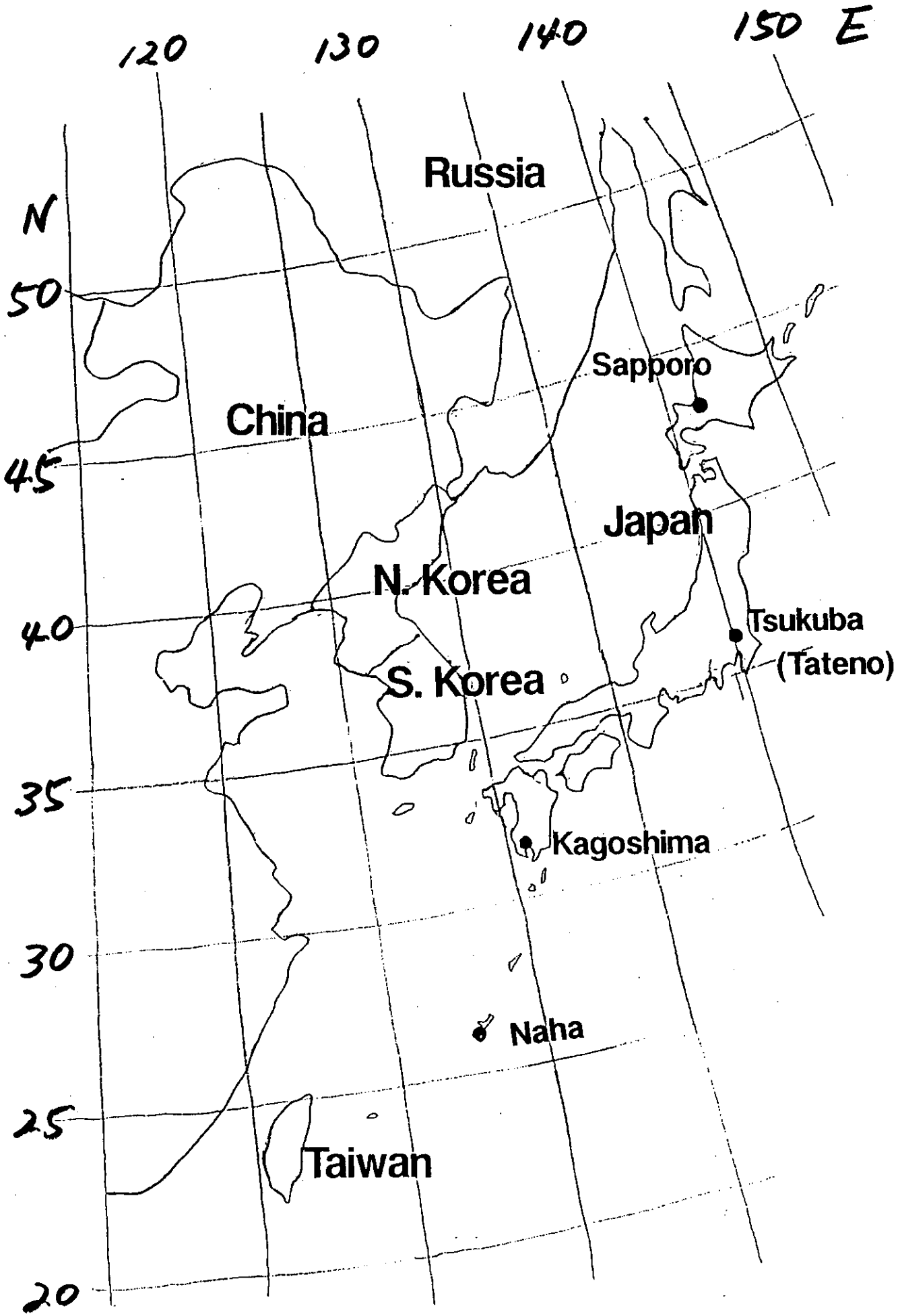
Filtering Sampler

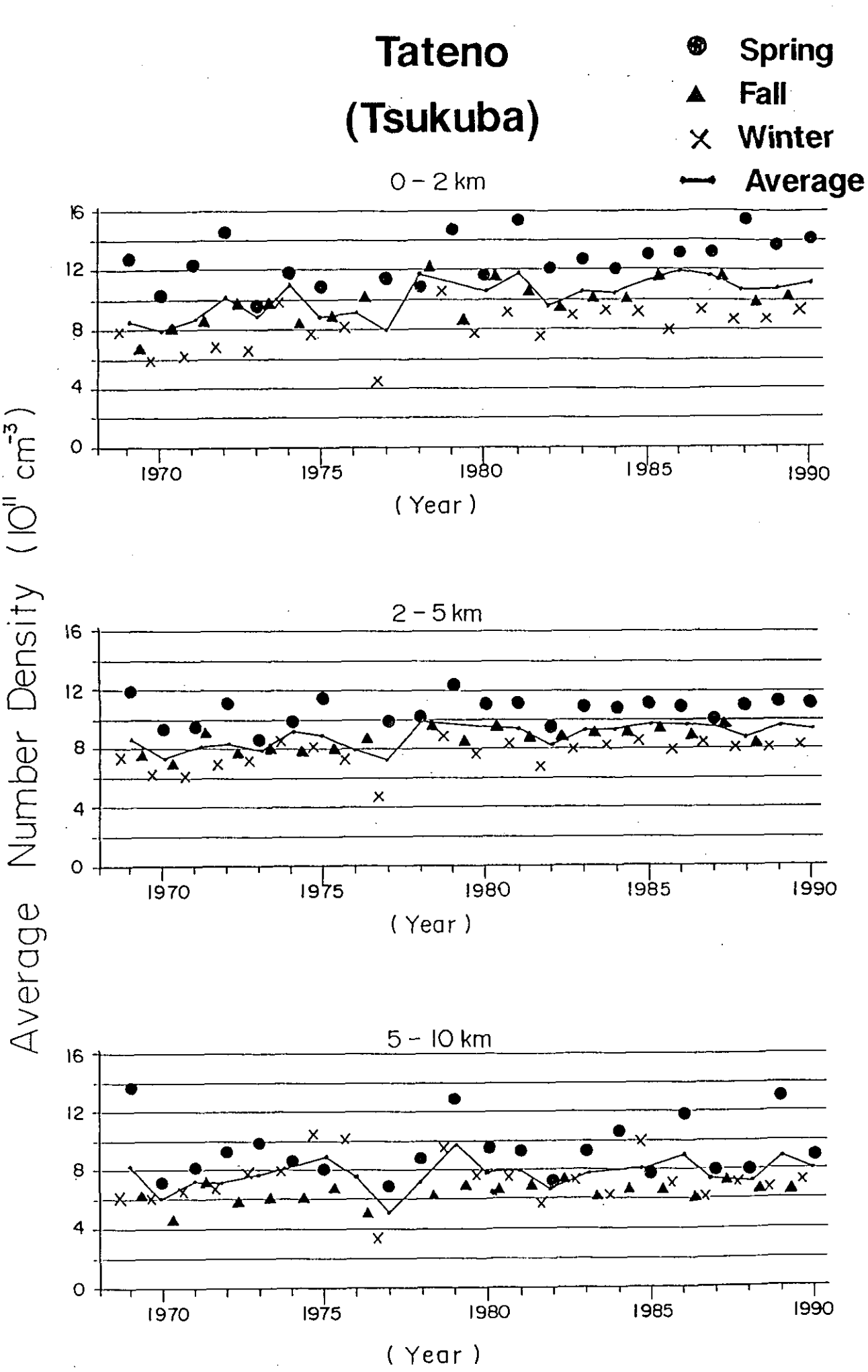
" Automatic " Sampler

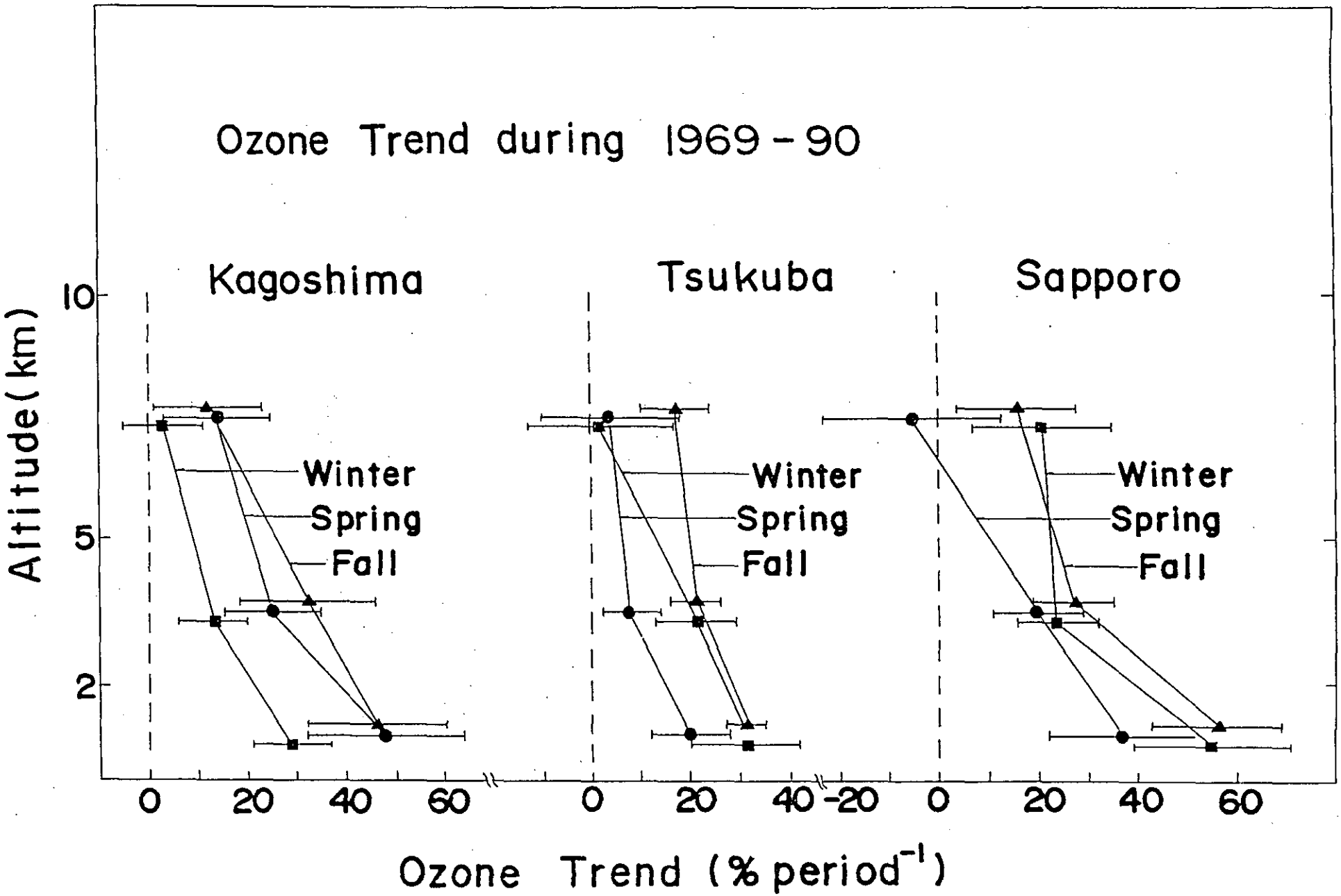



Annual Mean pH of Rain
(FILTER SAMPLER)
SOURCE: JEA
1984('86)-'87
4.8
5.0
5.1
5.1
5.0
4.9
4.7
4.7
4.6
4.6
4.6
4.8
4.7
4.6
5.1
5.0
4.6
4.7
4.7
4.8
4.9
4.6
4.6
4.7
4.6
4.8
4.7
4.7
0
500
KM


Deposition of NO_3^-
(g/m²/y)
0.80
0.80
0.74
1.64
1.69
1.22
2.03
2.02
2.12
2.07
2.25
3.31
2.84
2.06
1.58
1.20
1.43
1.72
1.41
1.22
1.65
1.84
1.41
0.88
1.34
1.05
0.97
2.46
2.86
source: JEA


120
130
140
150 E
N
50
45
40
35
30
25
20
Russia
China
Sapporo
Japan
N. Korea
Tsukuba
(Tateno)
S. Korea
Kagoshima
Naha
Taiwan


Tateno
(Tsukuba)
Spring
Fall
Winter
Average
0 – 2 km
2 – 5 km
5 – 10 km
Average Number Density (10^{11} cm^{-3})
0
4
8
12
16
1970
1975
1980
1985
1990
(Year)


Ozone Trend during 1969-90
Kagoshima
Tsukuba
Sapporo
Winter
Spring
Fall
Altitude(km)
10
5
2
0
20
40
60
-20
Ozone Trend (% period^{-1})

Cape Grim Sulfur Program

Participants

G. Ayers (CSIRO)

J. Ivey (+ others, AGAL)

R. Gillett (CSIRO)

E.Welch (CSIRO)

P. Selleck (CSIRO)

L. Porter (+ others, BoM)

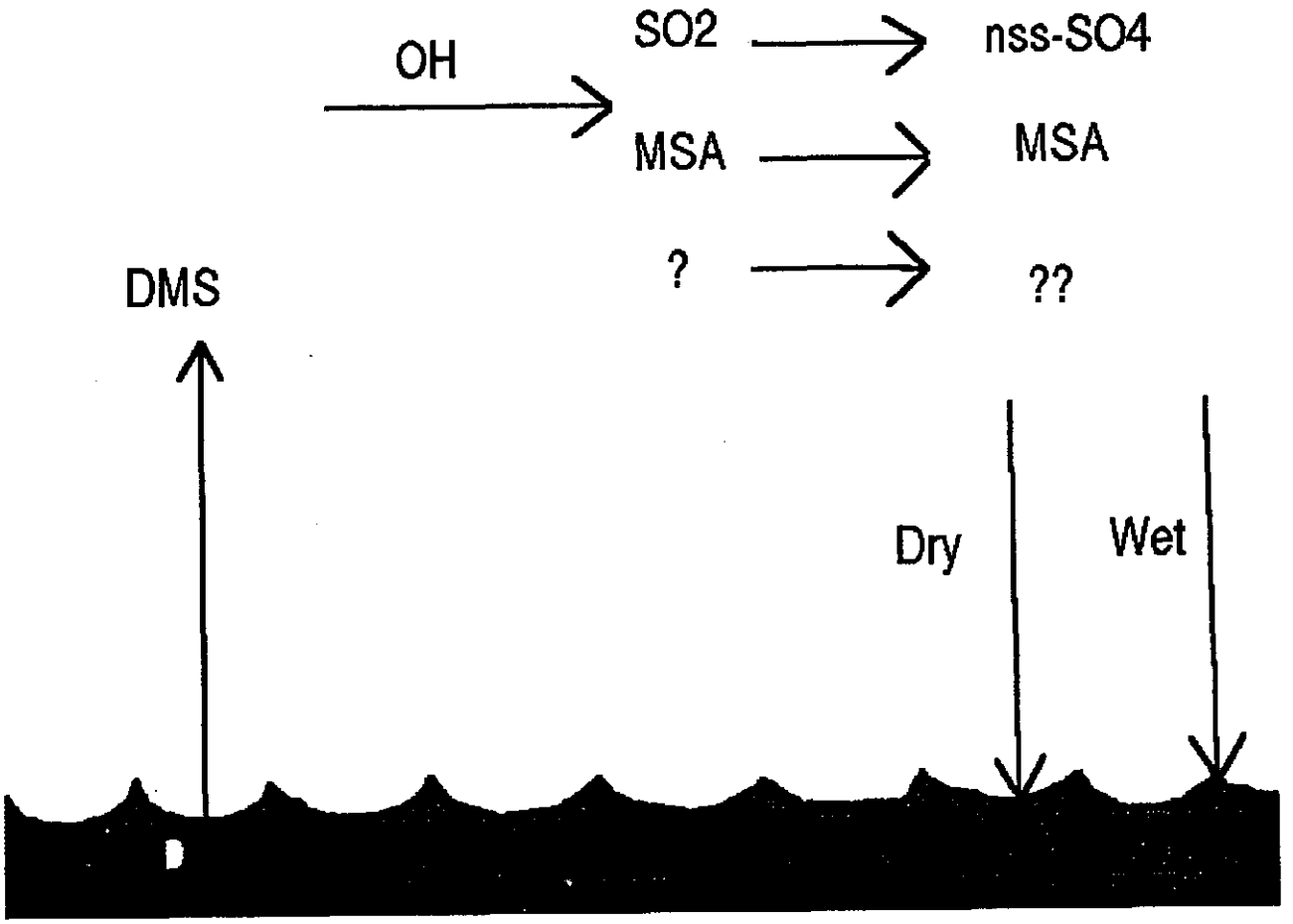
Rationale

Charlson et al. (1987) synthesis of previous work on aerosol effects upon cloud microphysical properties ⇒

dimethyl sulfide-cloud condensation nuclei-cloud ableDo-climate connection .....

Charlson et al. (1991) : model calculation of direct radiative impact of anthropogenic sulfate aerosol on global albedo ⇒

suggests average -1.1 watts m^{-2} over northern hemisphere .....


OH
SO2
nss-SO4
MSA
MSA
?
??
DMS
Dry
Wet

Current Measurement Program at Cape Grim

1. DMS*

2. Hivol aerosol* MSA and nss-SO_4

3. Sub-μm aerosol MSA and nss-SO_4

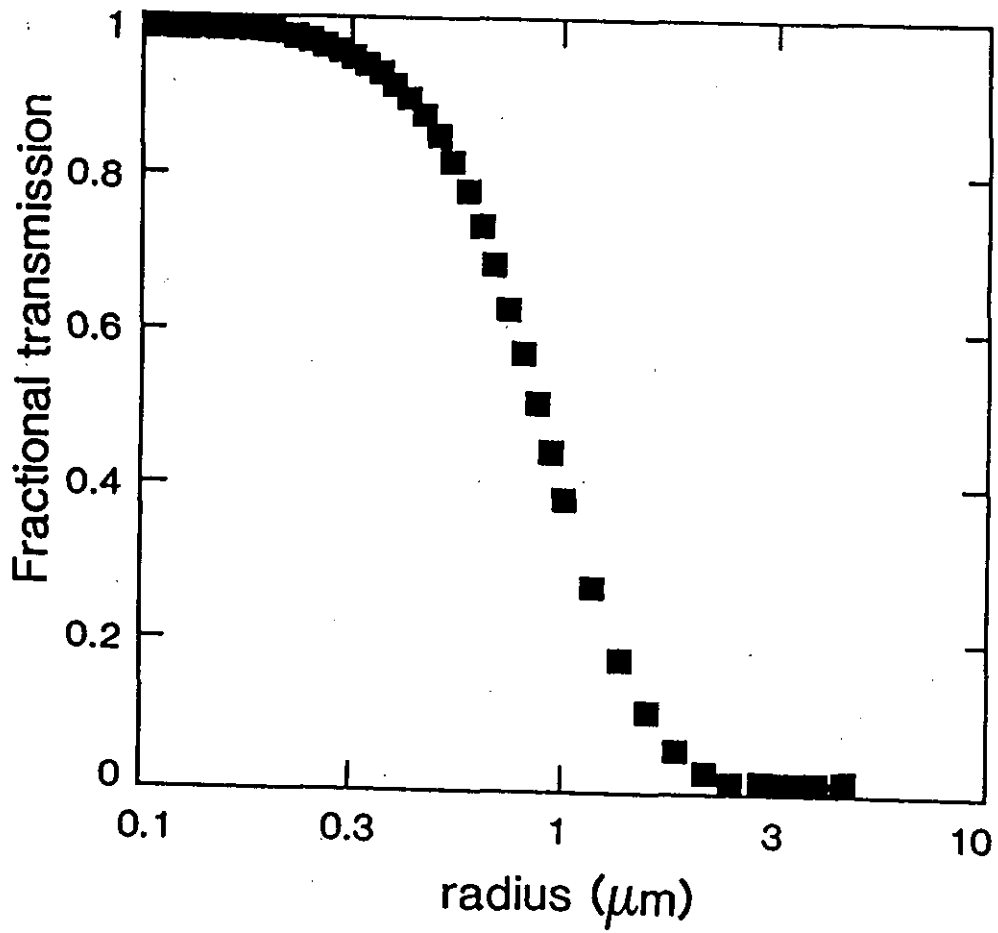
4. Rainwater* MSA (and nss-SO_4)

5. SO_2

6. COS & H_2S ..... under development*

* carried out at AGAL

In addition, aerosol microphysical properties, CN and CCN concentrations, aerosol optical properties are determined in the Cape Grim Aerosol Program (J.Gras).


Fractional transmission
1
0.8
0.6
0.4
0.2
0
0.1
0.3
1
3
10
radius (μm)

Data Records to Date

1. Hivol components 1976 - present

2. Rainwater components 1976 - present

3. DMS Nov. 1988 - present

4. Sub-μm aerosol components Nov. 1988 - present

5. SO_2 Nov. 1990 - present

6. COS and H_2S, under development

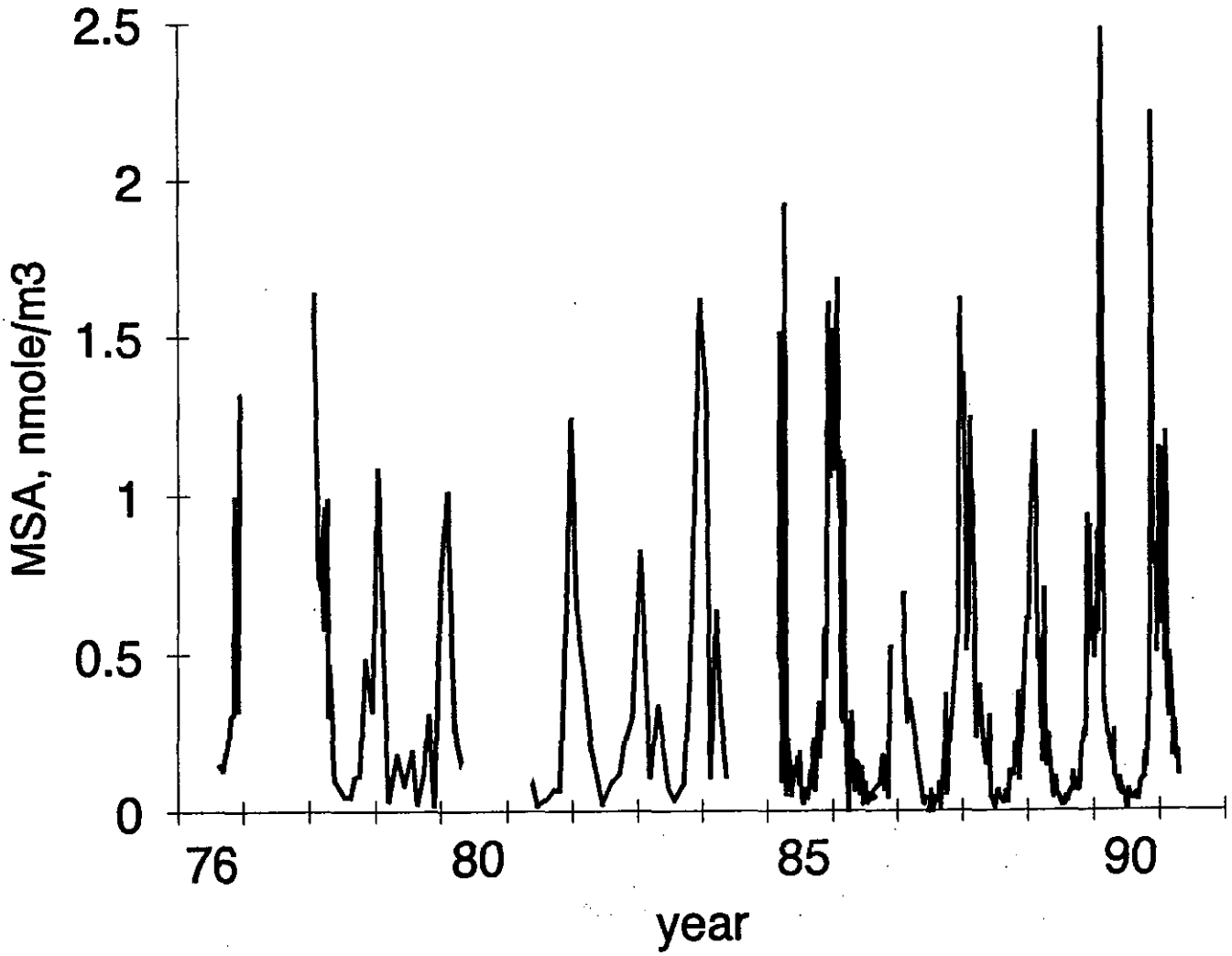
Methods

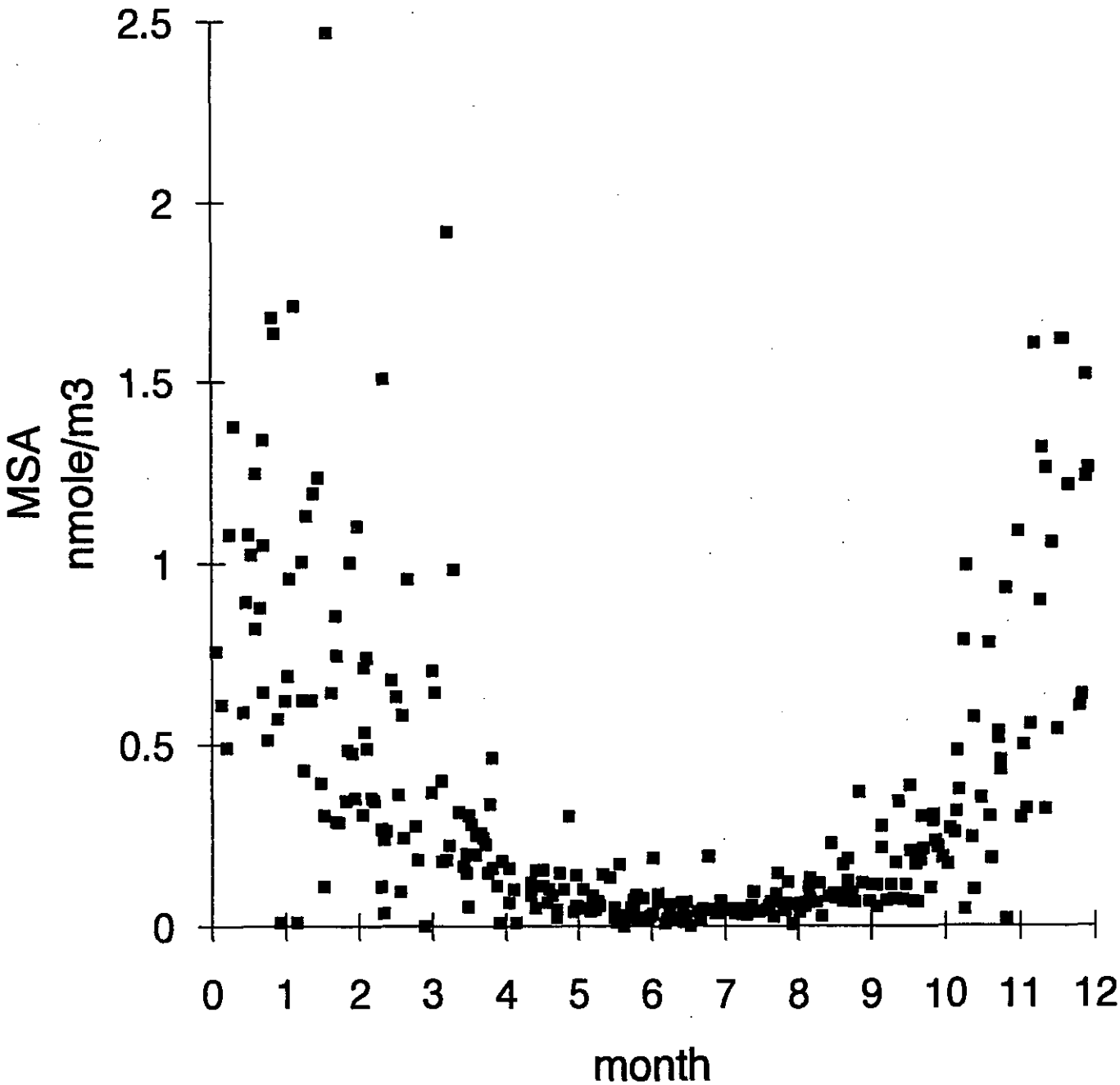
1. Hivol : (baseline switched)
- 10 inch x 8 inch Pallflex teflon-composite filter, at 700-800 L min^{-1}, weekly-average sample, IC and AA analysis.

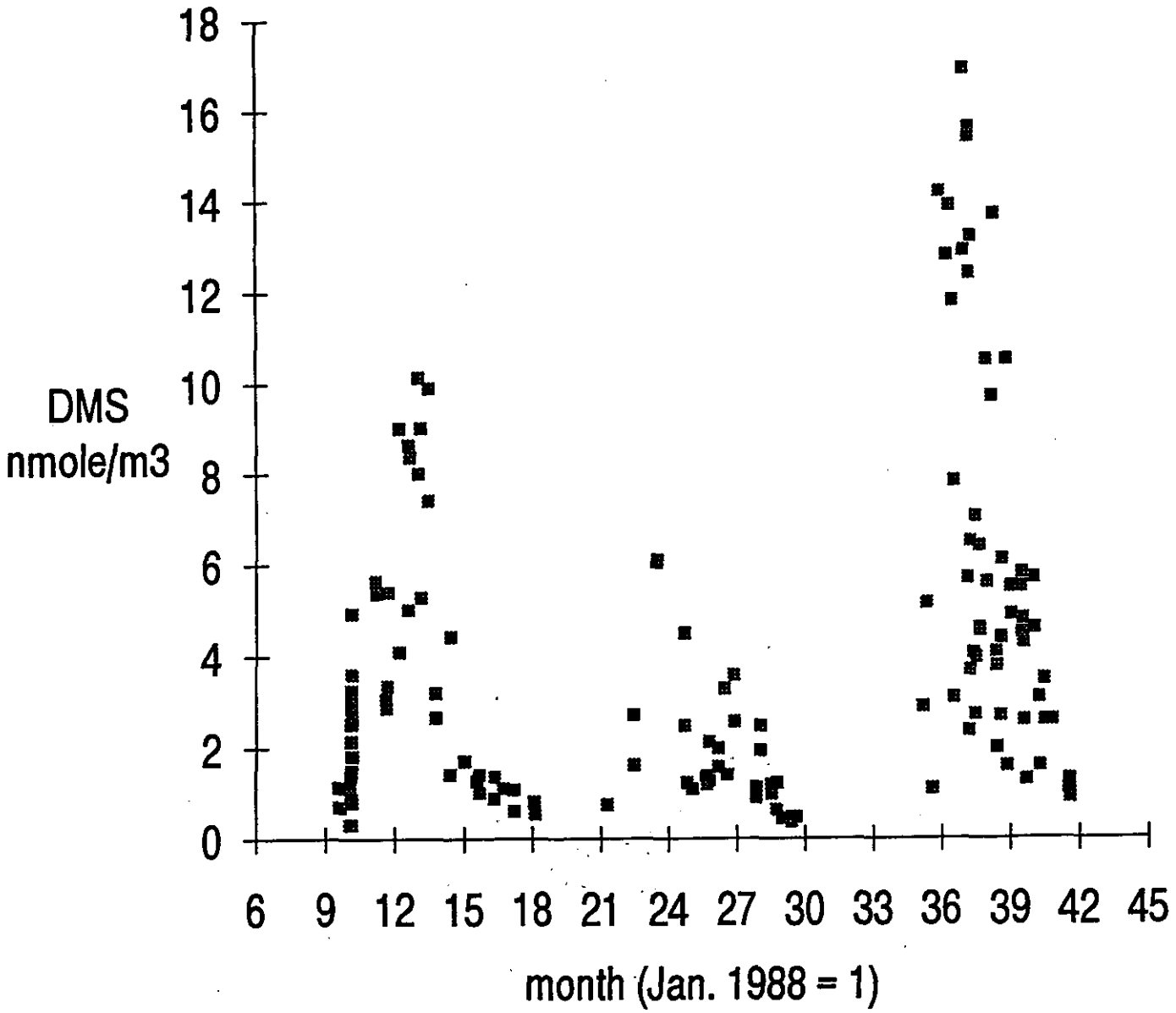
2. Quadrupod (sub-μm) filters : (baseline switched)
- 47 mm 8μm Nuclepore filter followed by 47 mm 1μm Flouropore filter, at 30 L min^{-1}, weekly-average sample, IC analysis

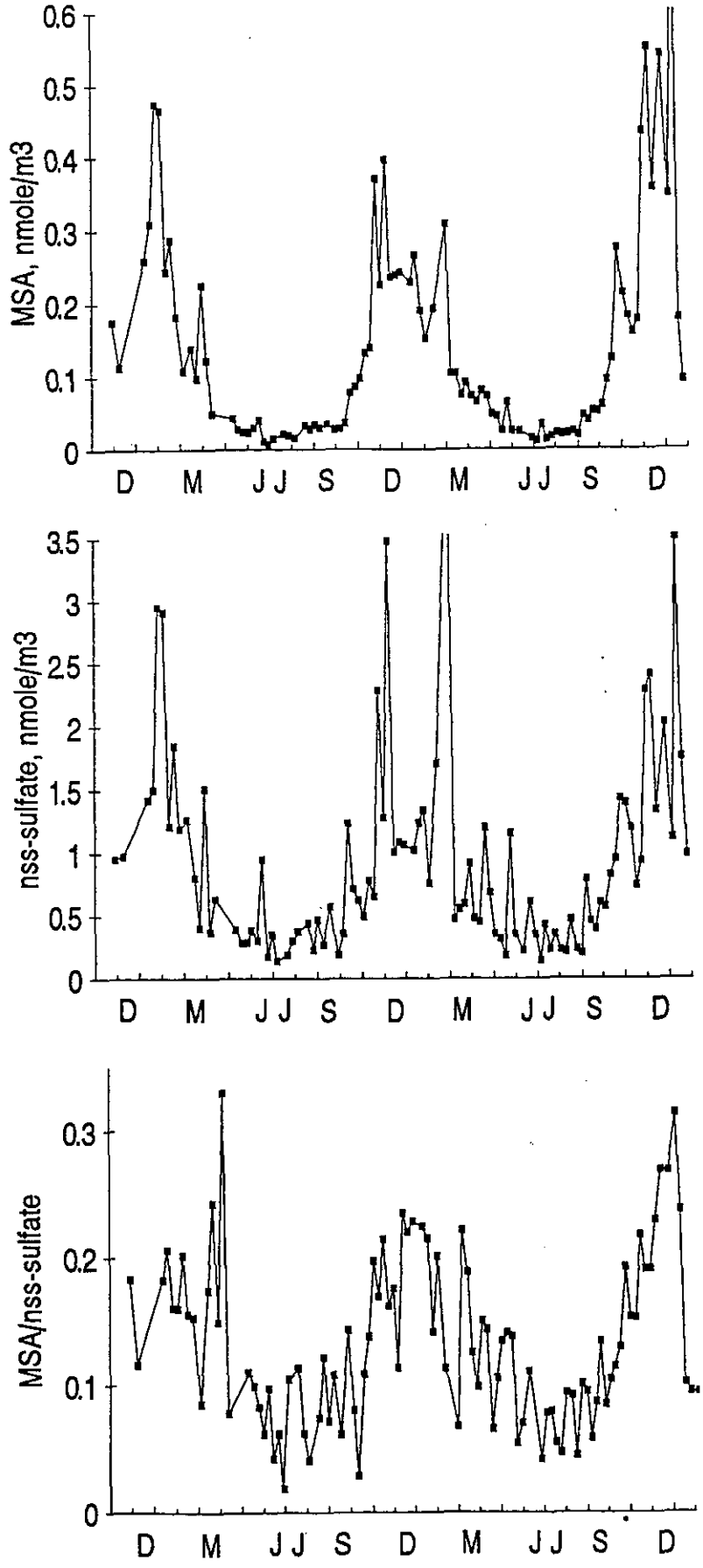
3. DMS : (baseline selected)
- trapping onto a gold surface sputter-coated onto glass wool, at 1 L min^{-1}, weekly-average and 1 hour-average samples, capillary GC analysis

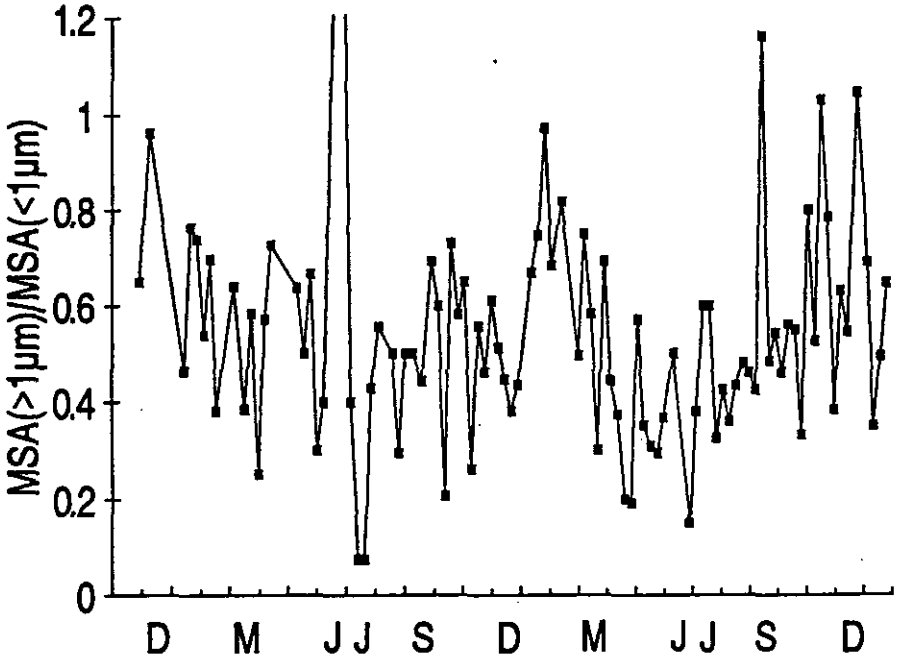
4. SO_2 : (baseline switched) :
- 1μm cut-off impactor, followed by 47 mm 1μm Flouropore filter, then 47 mm glass-fibre filter impregnated with NA_2CO_3, at 30 L min^{-1}, weekly-average, IC analysis

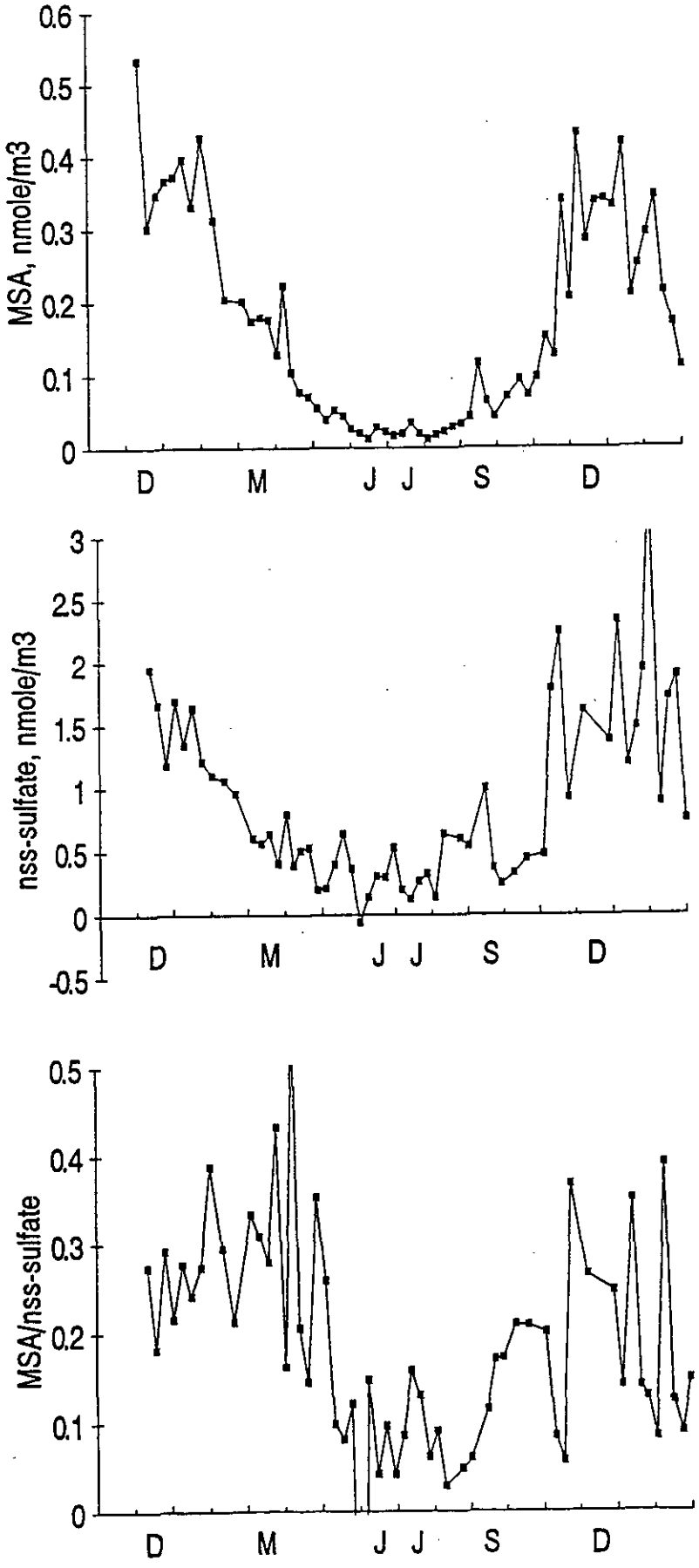

2.5
2
1.5
1
0.5
0
MSA, nmole/m3
76
80
85
90
year

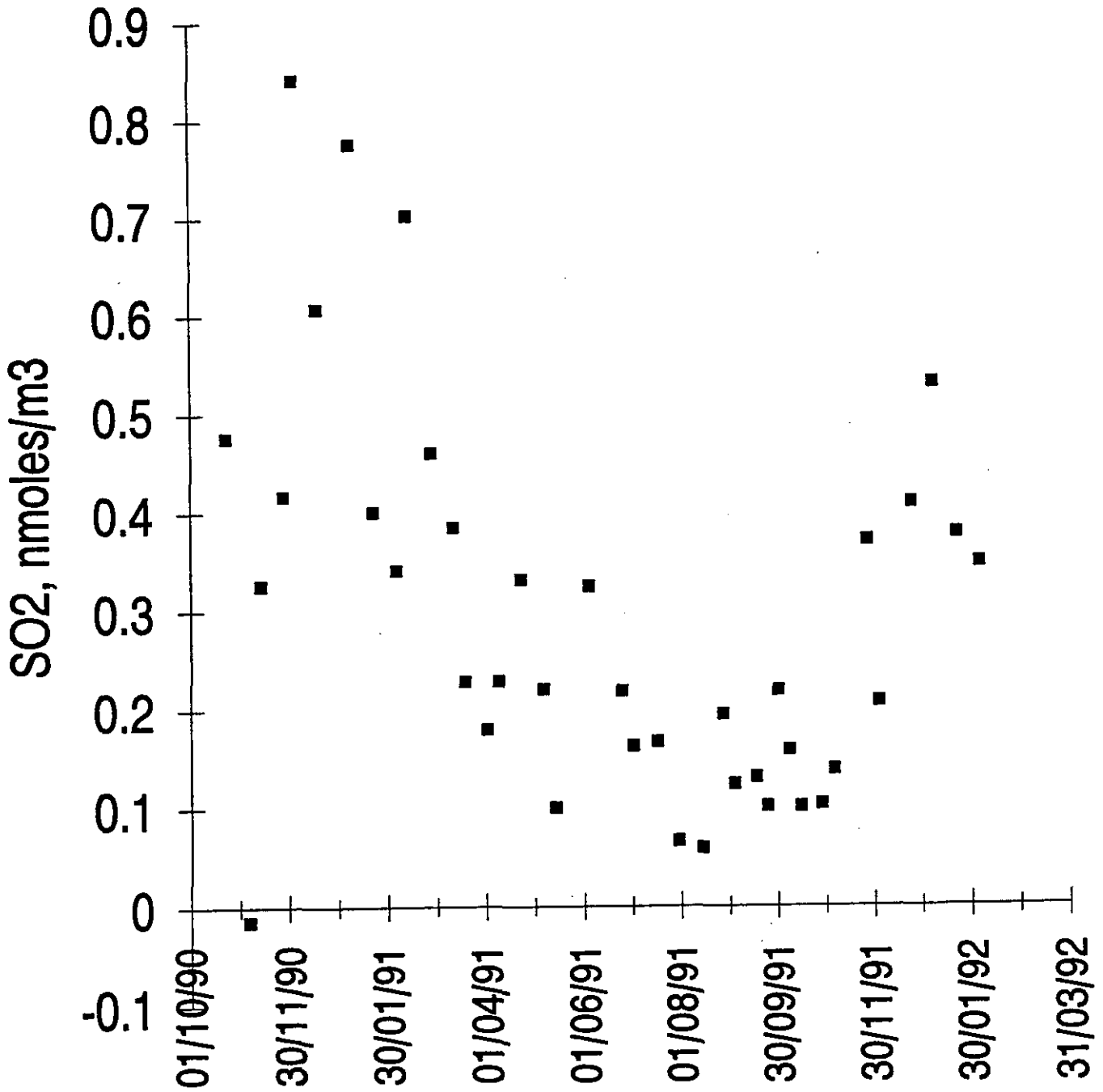

MSA
nmole/m3
2.5
2
1.5
1
0.5
0
0 1 2 3 4 5 6 7 8 9 10 11 12
month


DMS
nmole/m3
18
16
14
12
10
8
6
4
2
0
6
9
12
15
18
21
24
27
30
33
36
39
42
45
month (Jan. 1988 = 1)


MSA, nmole/m3
0.6
0.5
0.4
0.3
0.2
0.1
0
D M J J S D M J J S D
nss-sulfate, nmole/m3
3.5
3
2.5
2
1.5
1
0.5
0
D M J J S D M J J S D
MSA/nss-sulfate
0.3
0.2
0.1
0
D M J J S D M J J S D


MSA(>1μm)/MSA(<1μm)
1.2
1
0.8
0.6
0.4
0.2
0
D
M
J J
S
D
M
J J
S
D


MSA, nmole/m3
0.6
0.5
0.4
0.3
0.2
0.1
0
D
M
J
J
S
D
nss-sulfate, nmole/m3
3
2.5
2
1.5
1
0.5
0
-0.5
D
M
J
J
S
D
MSA/nss-sulfate
0.5
0.4
0.3
0.2
0.1
0
D
M
J
J
S
D


SO2, nmoles/m3
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
01/10/90
30/11/90
30/01/91
01/04/91
01/06/91
01/08/91
30/09/91
30/11/91
30/01/92
31/03/92

M. Raupach (CSIRO)

EDDY CORRELATION

1. *Principle*: $F_c = \overline{w\rho_c} = \bar{w}\bar{\rho}_c + \overline{w'\rho_c'}$

2. *Bandwidth*: $10^{-3} < n < 10$

$n = fz/\bar{u}$

f = frequency
z = height
$\bar{u}$ = mean wind speed

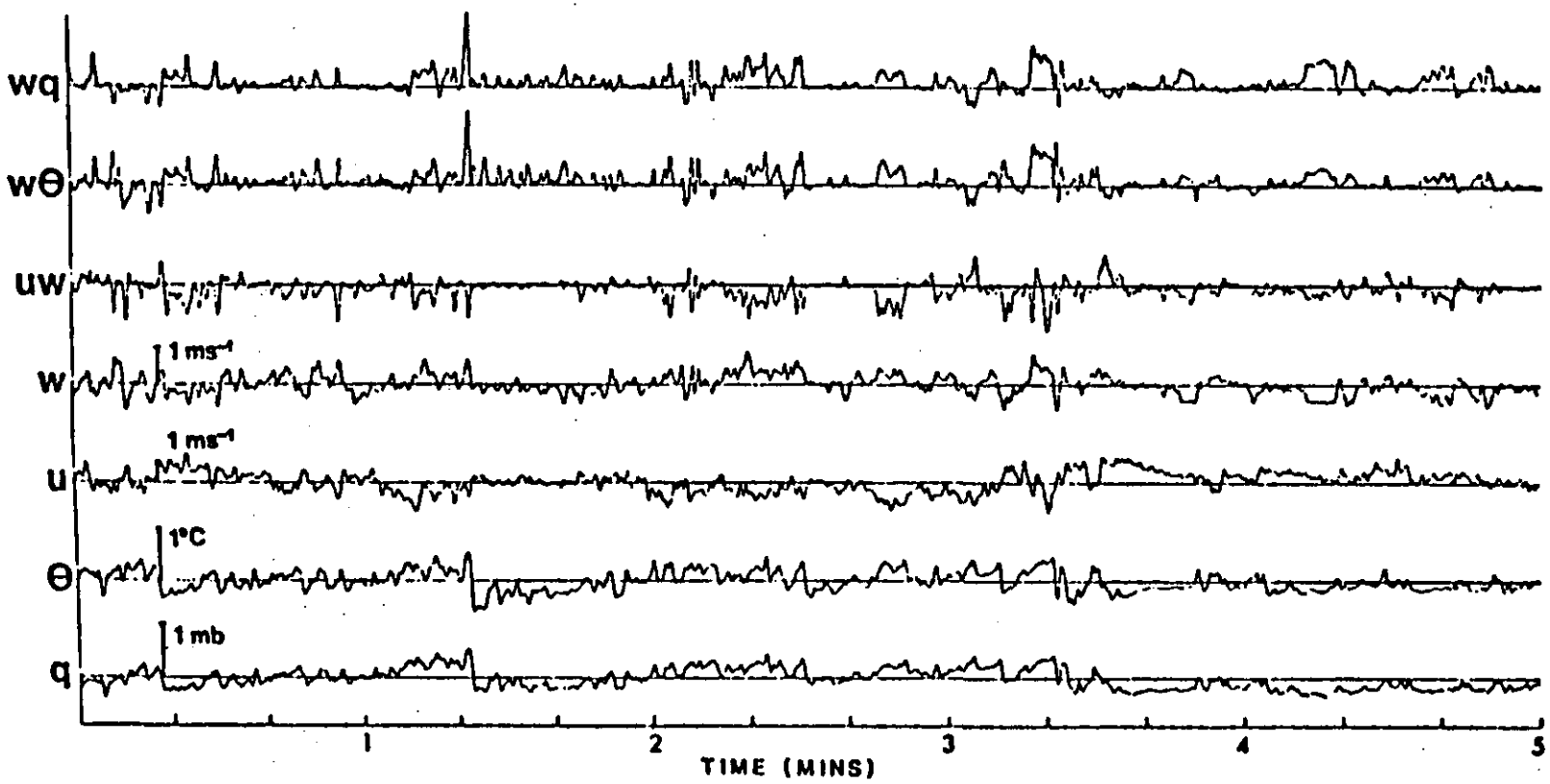
3. *Webb-Pearman-Leuning effect*

4. *Sampling along a tube*

5. *Platform motion*

6. *Avoiding eddy correlation*: inverse methods for inferring F_c from $\bar{\rho}_c$

LAKE ALBERT, SOUTH AUSTRALIA, APRIL 1975



LAKE ALBERT, SOUTH AUSTRALIA, 1975

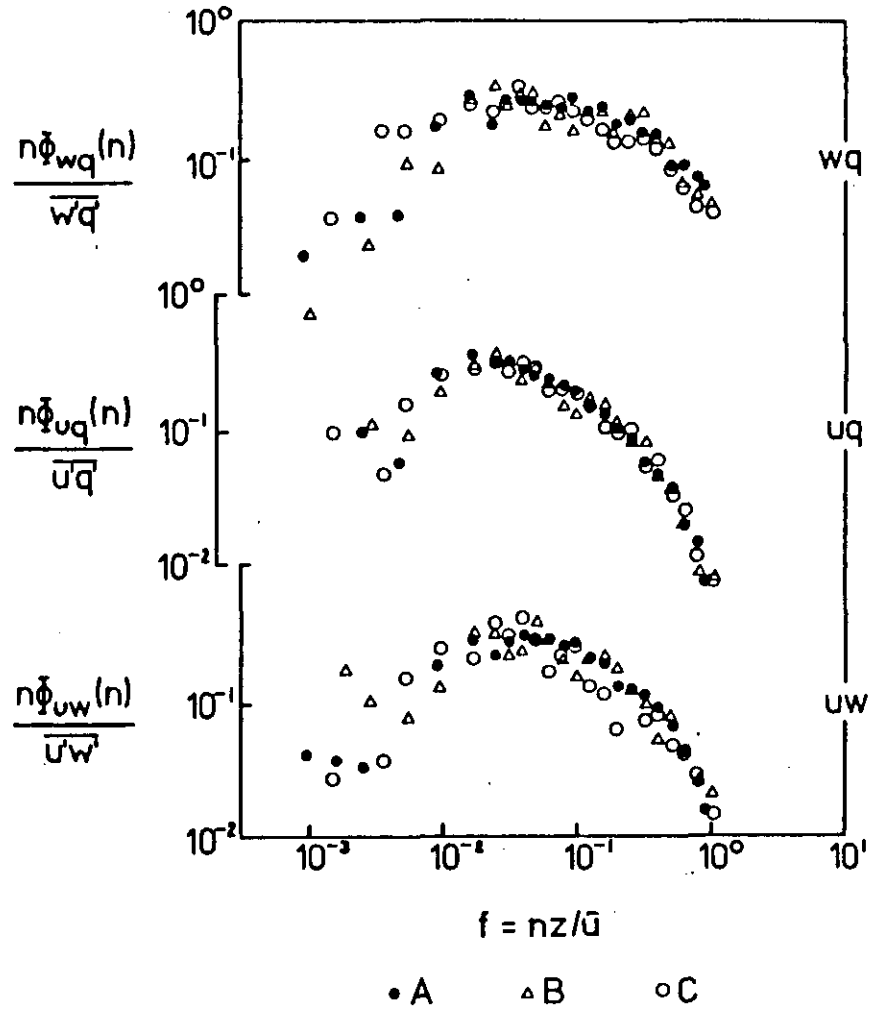
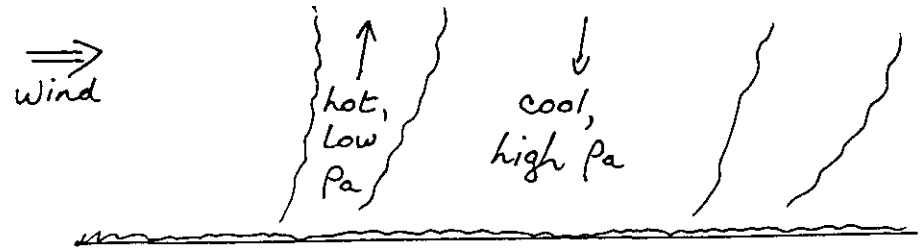


Figure 8. The *wq*, *uq* and *uw* cospectra. The data are grouped in stability bands thus:
band A: $0{\cdot}11 < -z/L < 0{\cdot}18$ (4 runs)
band B: $0{\cdot}18 < -z/L < 0{\cdot}21$ (3 runs)
band C: $0{\cdot}27 < -z/L < 0{\cdot}63$ (5 runs)

WEBB - PEARMAN - LEUNING (WPL) EFFECT



Vertical flux of dry air = $\overline{w\rho_a} = 0$

$$\Rightarrow \bar{w}\bar{\rho}_a + \overline{w'\rho_a'} = 0$$

$$\Rightarrow \bar{w} = -\overline{w'\rho_a'}/\bar{\rho}_a$$

($\bar{w} > 0$ in convection)

For a trace scalar:

$$F_c = \overline{w\rho_c} = \bar{w}\bar{\rho}_c + \overline{w'\rho_c'}$$

(F_c: mass flux; ρ_c: density; WPL correction)

Open path sensor (with temp fluctuations):

$$\bar{w}\bar{\rho}_a = \bar{\rho}_c \left[\overline{w'm'} + (1 + \bar{m}) \frac{\overline{w'\theta'}}{\bar{T}} \right]$$

Closed path sensor (temp fluctuations removed):

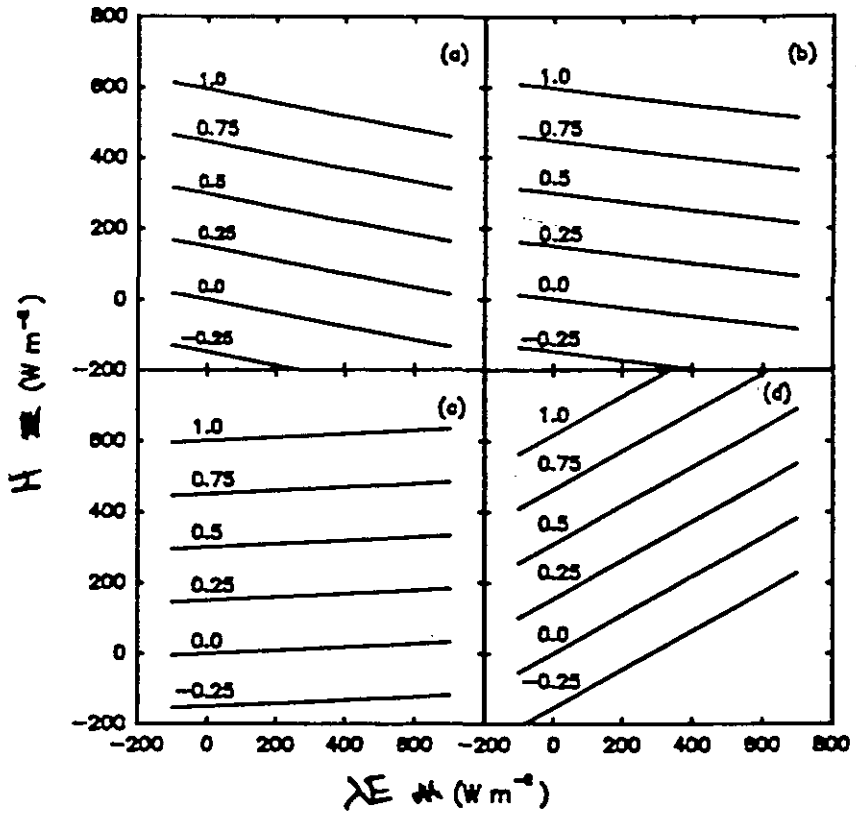
$$\bar{w}\bar{\rho}_c = \bar{\rho}_c \left[\overline{w'm'} + \bar{m} \frac{\overline{w'\theta'}}{\bar{T}} \right]$$

with m = H_2O molar mixing ratio.

$\bar{w}\bar{\rho}_c / F_c$ range:

-0.1 to $\lesssim -1$	(CO_2)
0.25 to 10	(N_2O)
0.04 to 0.6	(CH_4)

LEUNING AND MONCRIEFF (1990)



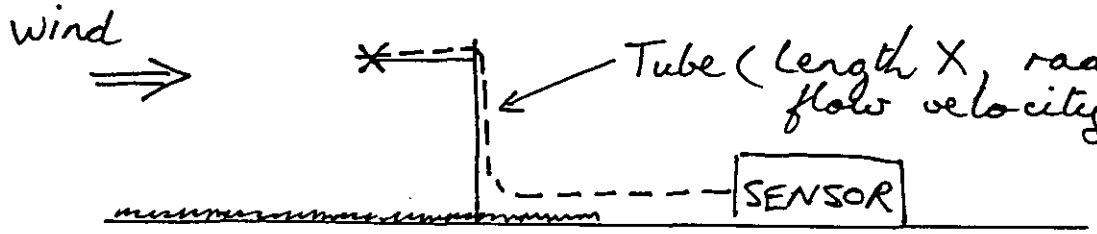
$\overline{w\rho_c}$ for CO_2 ($mg\ m^{-2}\ s^{-1}$)

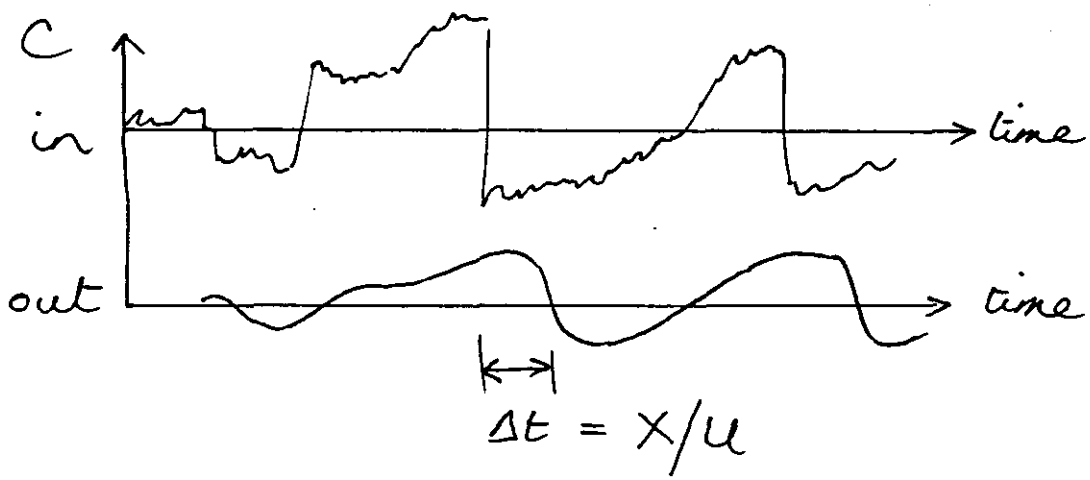
a → b → c → d represents increasing H_2O cross-sensitivity

Fig. 2. Isopleths for the correction to measured CO_2 fluxes as a function of latent and sensible heat fluxes for open-path CO_2 analysers with differing cross-sensitivity to water vapour. (a) $\beta/\alpha = 0$, (b) $\beta/\alpha = 3 \times 10^{-4}$, (c) $\beta/\alpha = 1 \times 10^{-3}$ and (d) $\beta/\alpha = 3 \times 10^{-3}$. Numbers on the lines represent the flux correction to be added to F_{raw} ($mg\ CO_2\ m^{-2}s^{-1}$). Corrections at $H = 0$ also apply to closed-path CO_2 analyser.

SAMPLING THROUGH A TUBE

Lenschow and Raupach, J. Geophys. Res. (1991) 96, 15259-68.





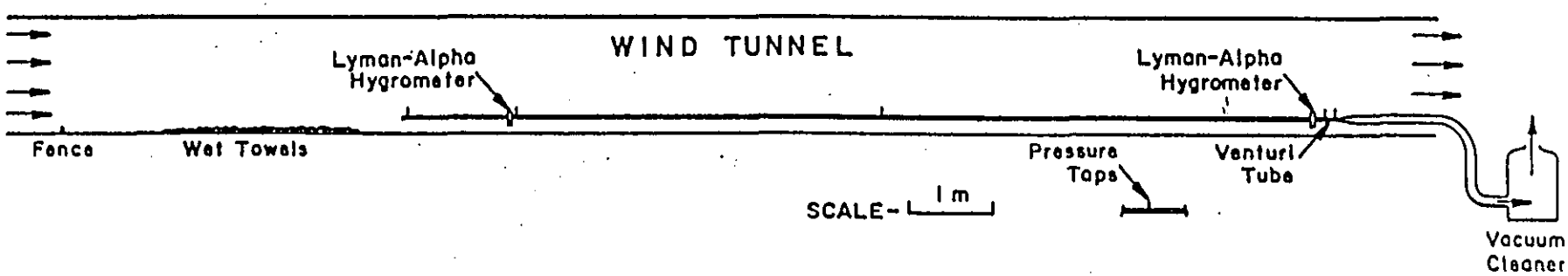
Tube transfer function:

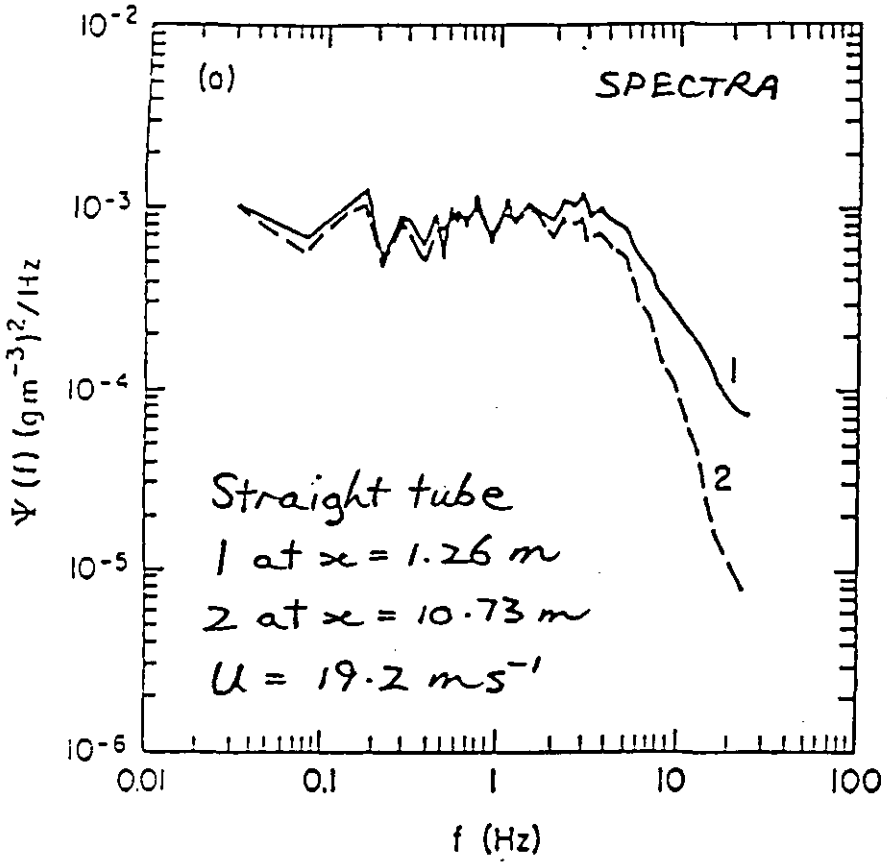
$$\Phi(n) = \frac{\text{amplitude out}}{\text{amplitude in}} = \exp\left(\frac{-n^2 \ln\sqrt{2}}{n_0^2}\right)$$

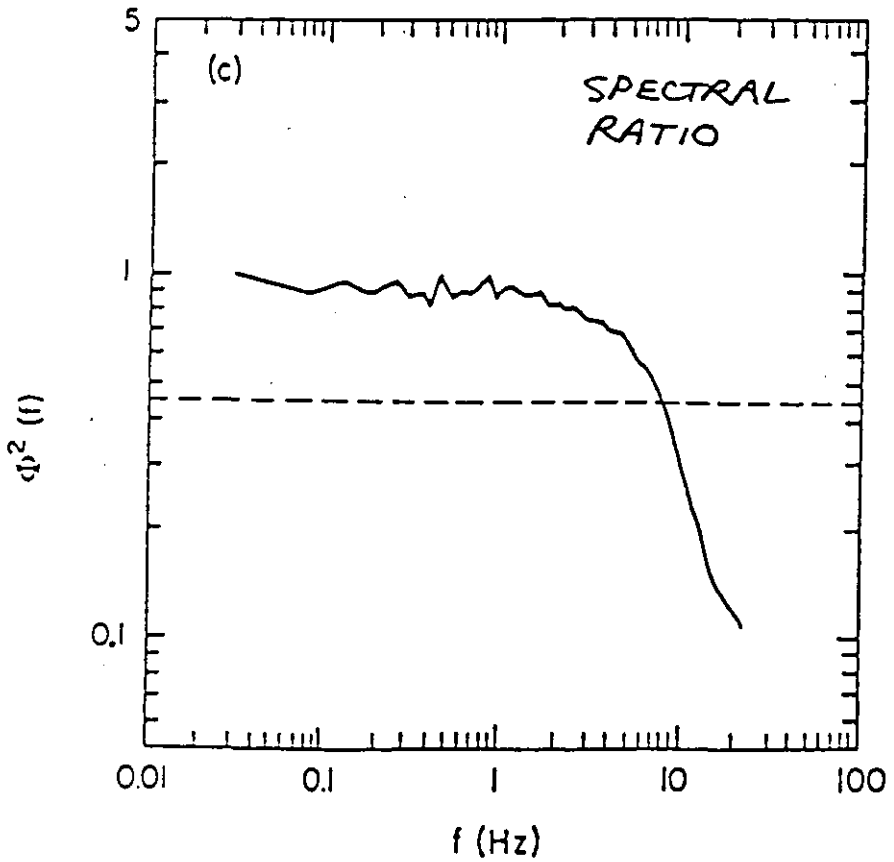
$$n = \frac{b}{U}\sqrt{aX} = \text{dimensionless frequency}$$

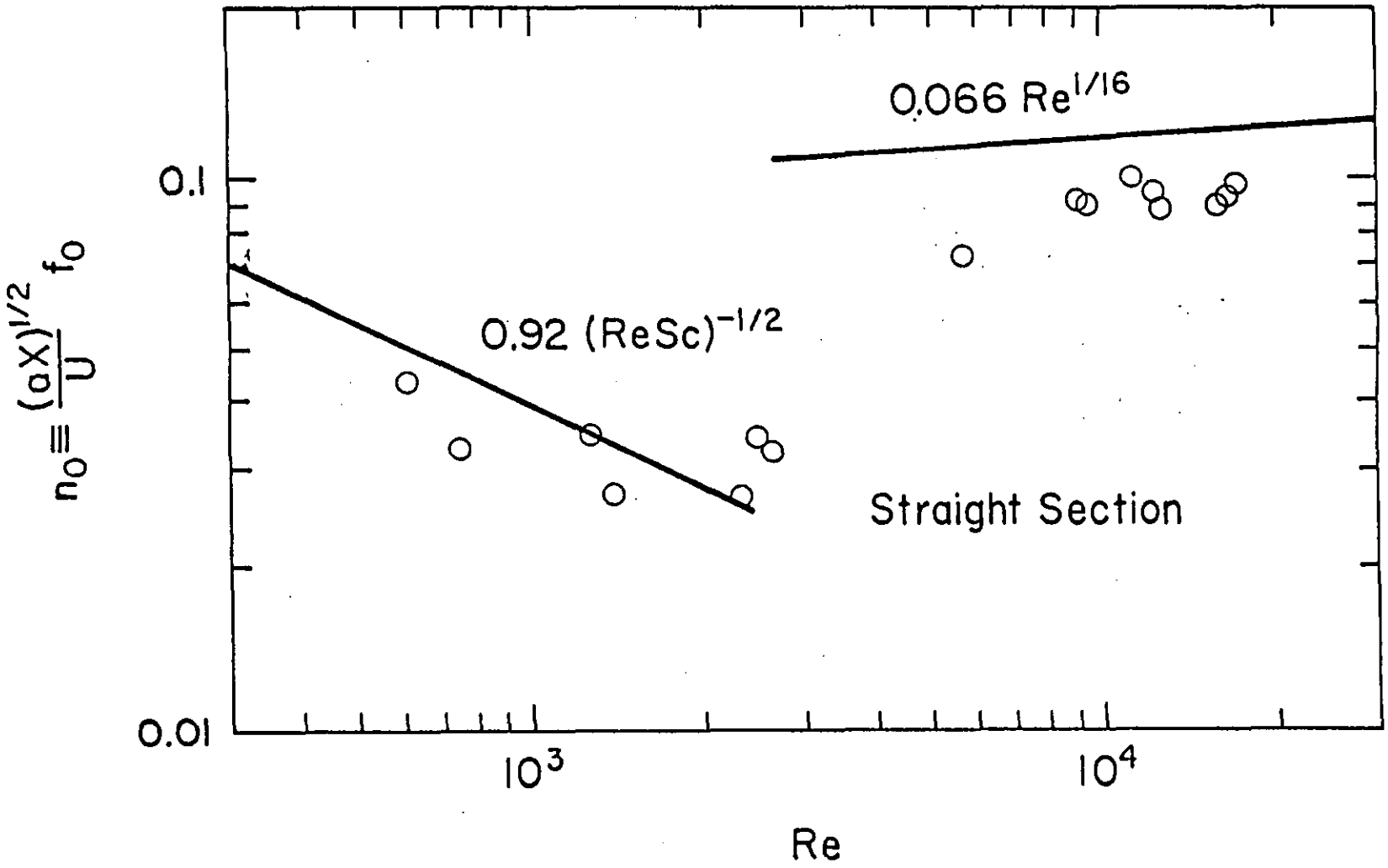
$$n_0 = \begin{cases} 0.92\,(ReSc)^{-1/2} & \text{(laminar)} \\ 0.066\,Re^{1/16} & \text{(turbulent)} \end{cases}$$

Desirable: turbulent flow in tube!
HIGH measurement point!


WIND TUNNEL
Lyman-Alpha Hygrometer
Lyman-Alpha Hygrometer
Fence
Wet Towels
Pressure Taps
Venturi Tube
SCALE- 1 m
Vacuum Cleaner


(a)
SPECTRA
Straight tube
1 at x = 1.26 m
2 at x = 10.73 m
U = 19.2 m s⁻¹
1
2
Ψ (f) (g m⁻³)²/Hz
10⁻²
10⁻³
10⁻⁴
10⁻⁵
10⁻⁶
0.01
0.1
1
10
100
f (Hz)


(c)
SPECTRAL RATIO
Φ² (f)
5
1
0.1
0.01
0.1
1
10
100
f (Hz)


0.066 Re^1/16
0.92 (ReSc)^-1/2
Straight Section
0.1
0.01
10^3
10^4
Re
n_o ≡ (aX)^1/2 / U f_o

LEUNING AND MONCRIEFF (1990)

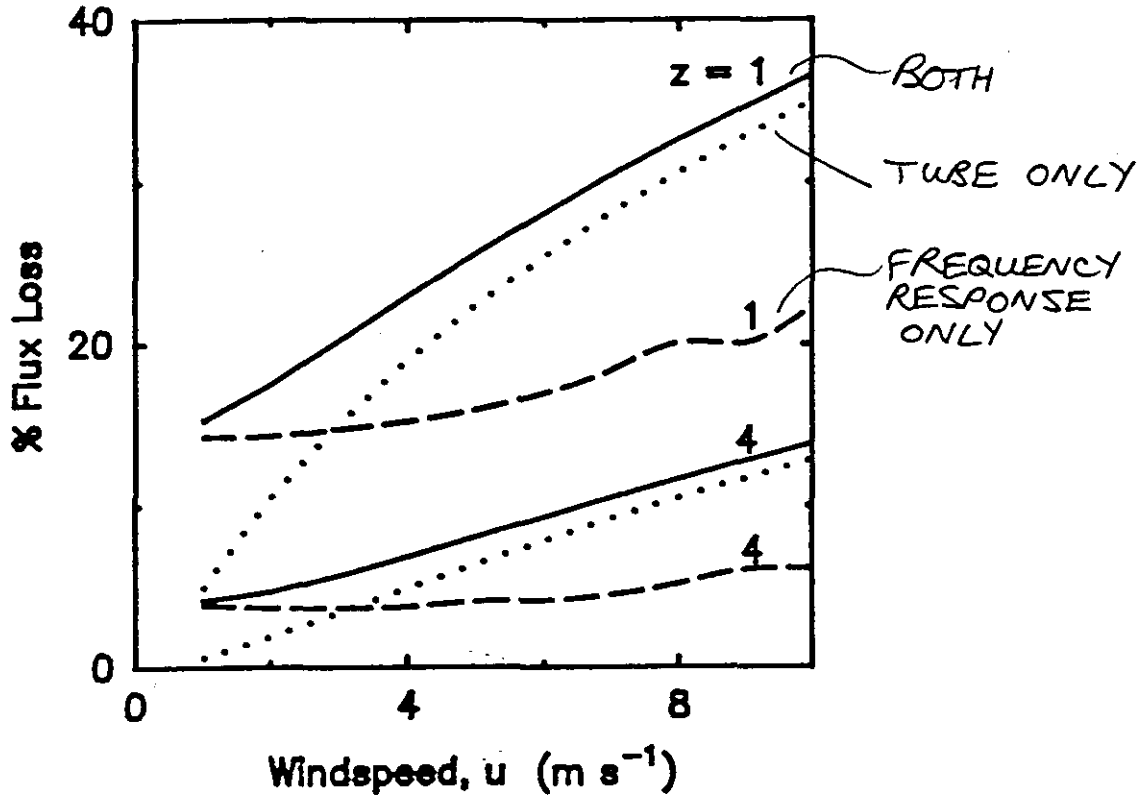
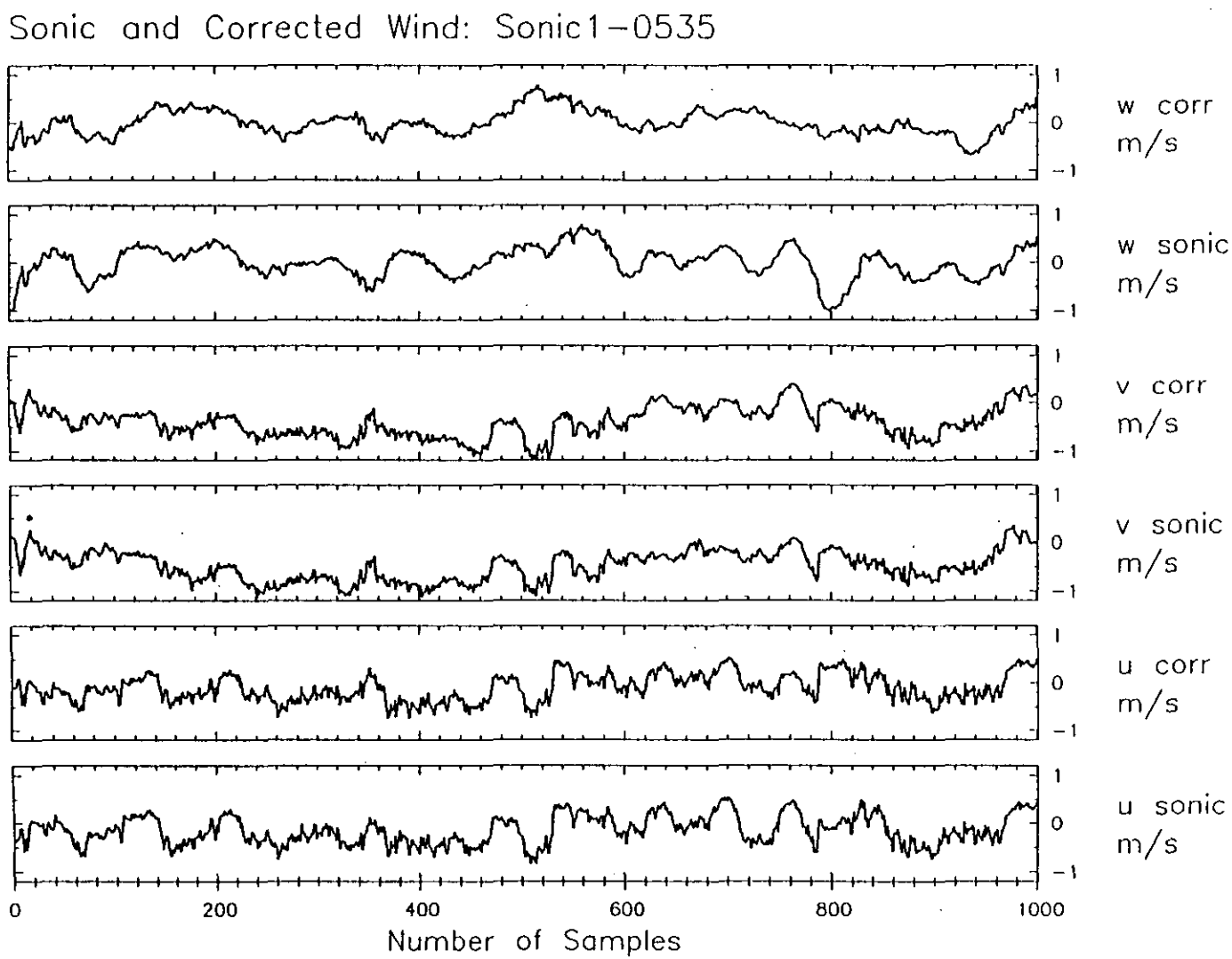
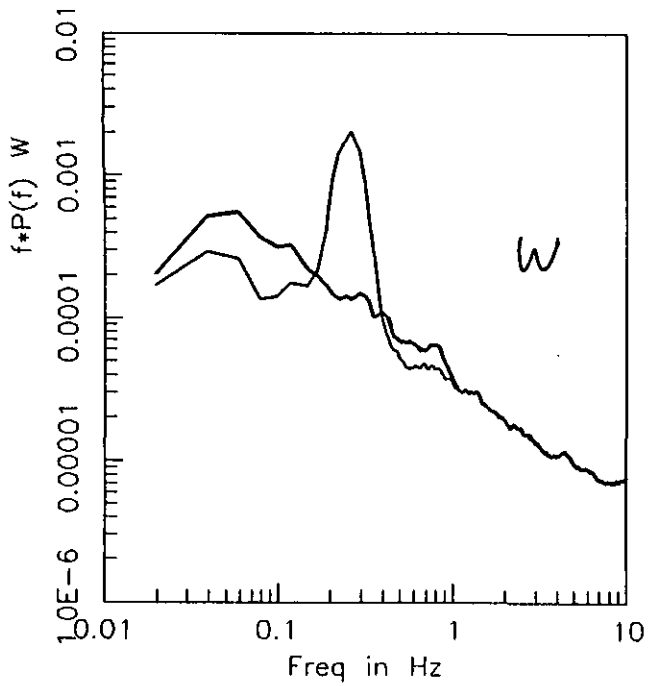


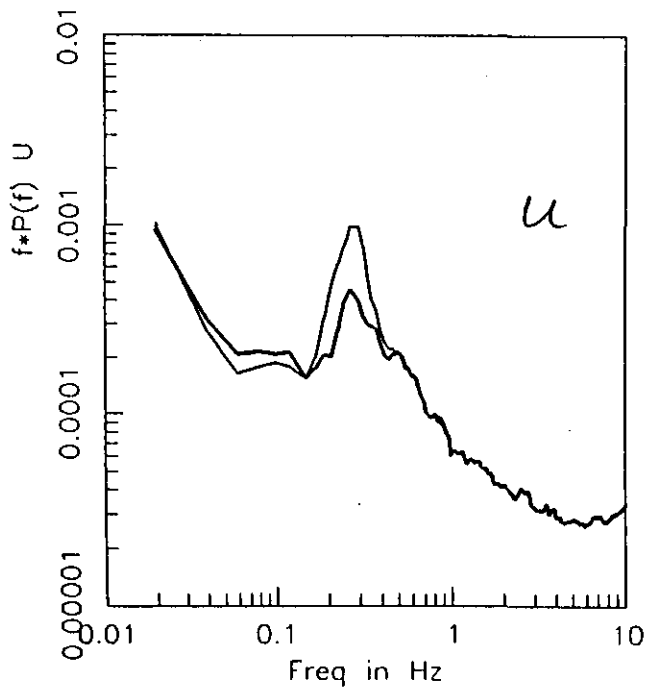
Fig. 3. Estimated percentage loss in measured F_{raw} for a closed-path CO_2 analyser supplied with air sampled through a copper tube $L = 1.5$ m, $r_0 = 3$ mm and $V = 8 \times 10\,m^{-3}\,s^{-1}$. Separation distance between tube inlet and sonic anemometer was 0.18 m. Losses are plotted against windspeed for sensor heights of 1 and 4 m above the zero-plane. Flux losses due to damping of turbulence fluctuations by tube only (.....); flux losses due to limited sensor frequency response but neglecting effect of tube (----) and combined influence of tube and sensor frequency response (——).

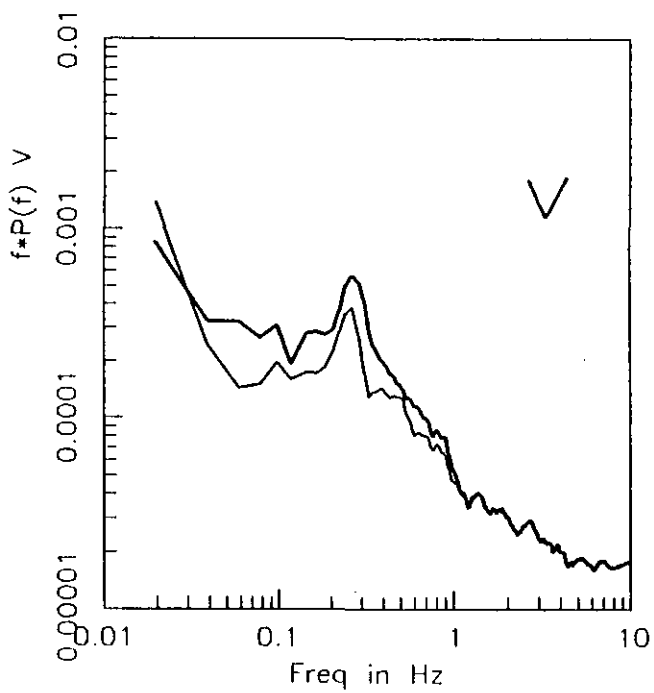
Correction for ship motion:
Shao, Bradley, Coppin (current work)



Sonic 1 - 0535

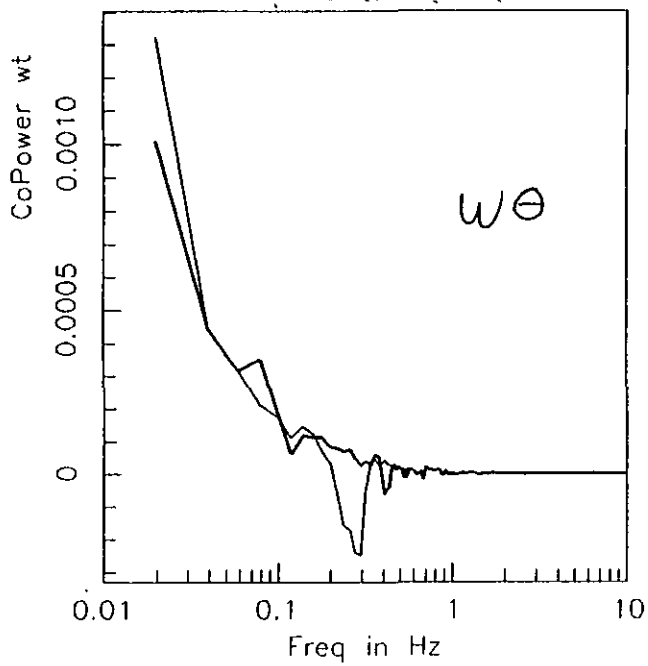


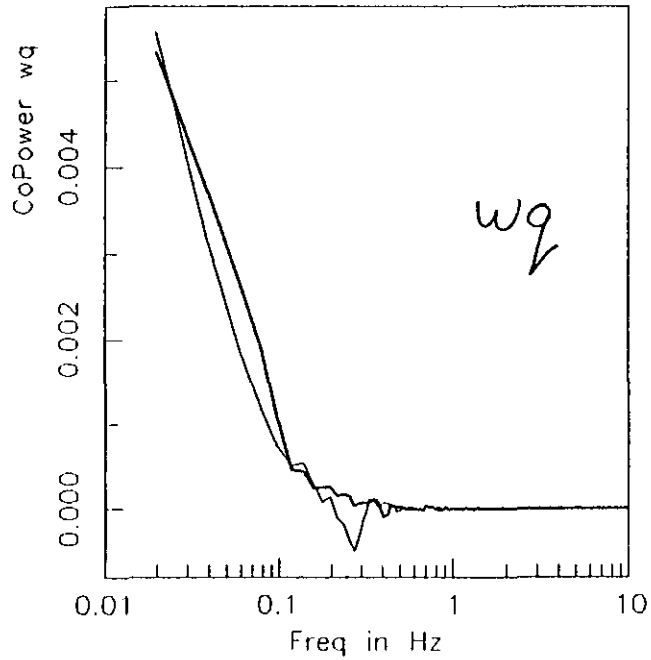


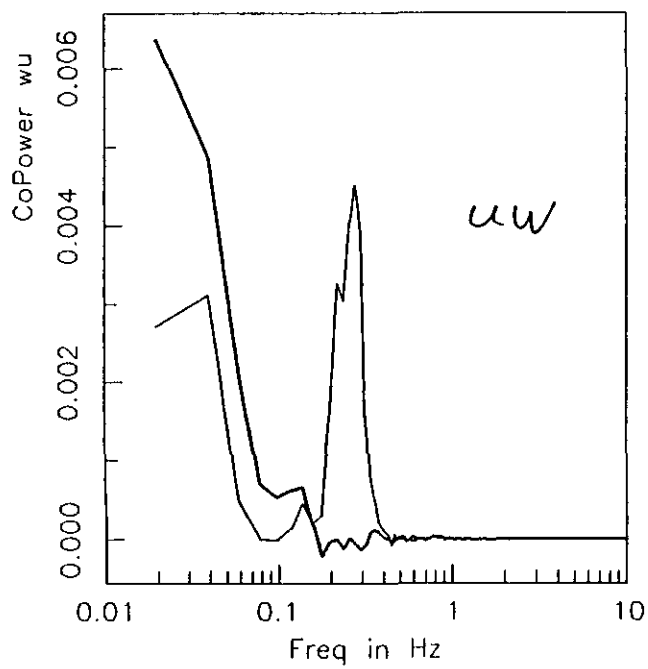


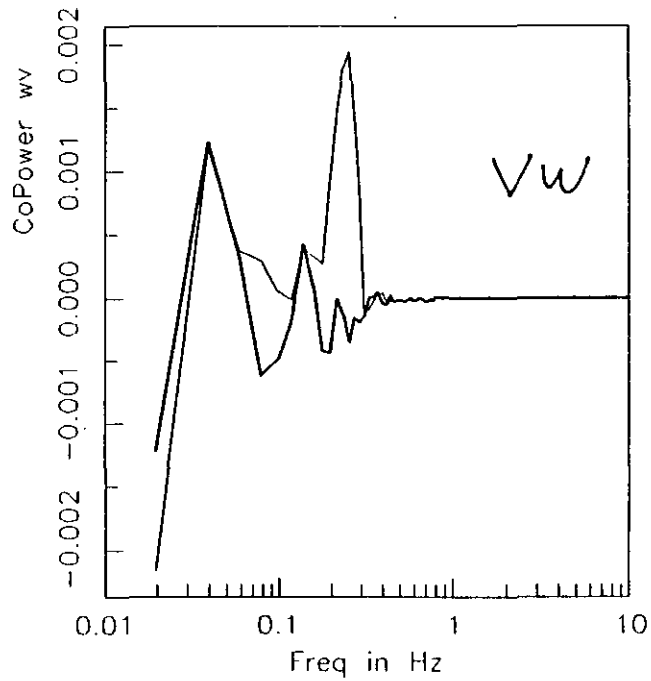
Spe

Sonic 1 - 0535









Co

INVERSE METHODS

- inferring fluxes from near concentrations

1. Canopy scale

$$c_i - c_R = \sum_{j=1}^{n} D_{ij}\, S_j\, \Delta z_j$$

- $c_i - c_R$: concentration at level i
- D_{ij}: dispersion matrix: depends on σ_w, T_L
- $S_j \Delta z_j$: source strength in layer j

2. Scale of planetary convective B.L.

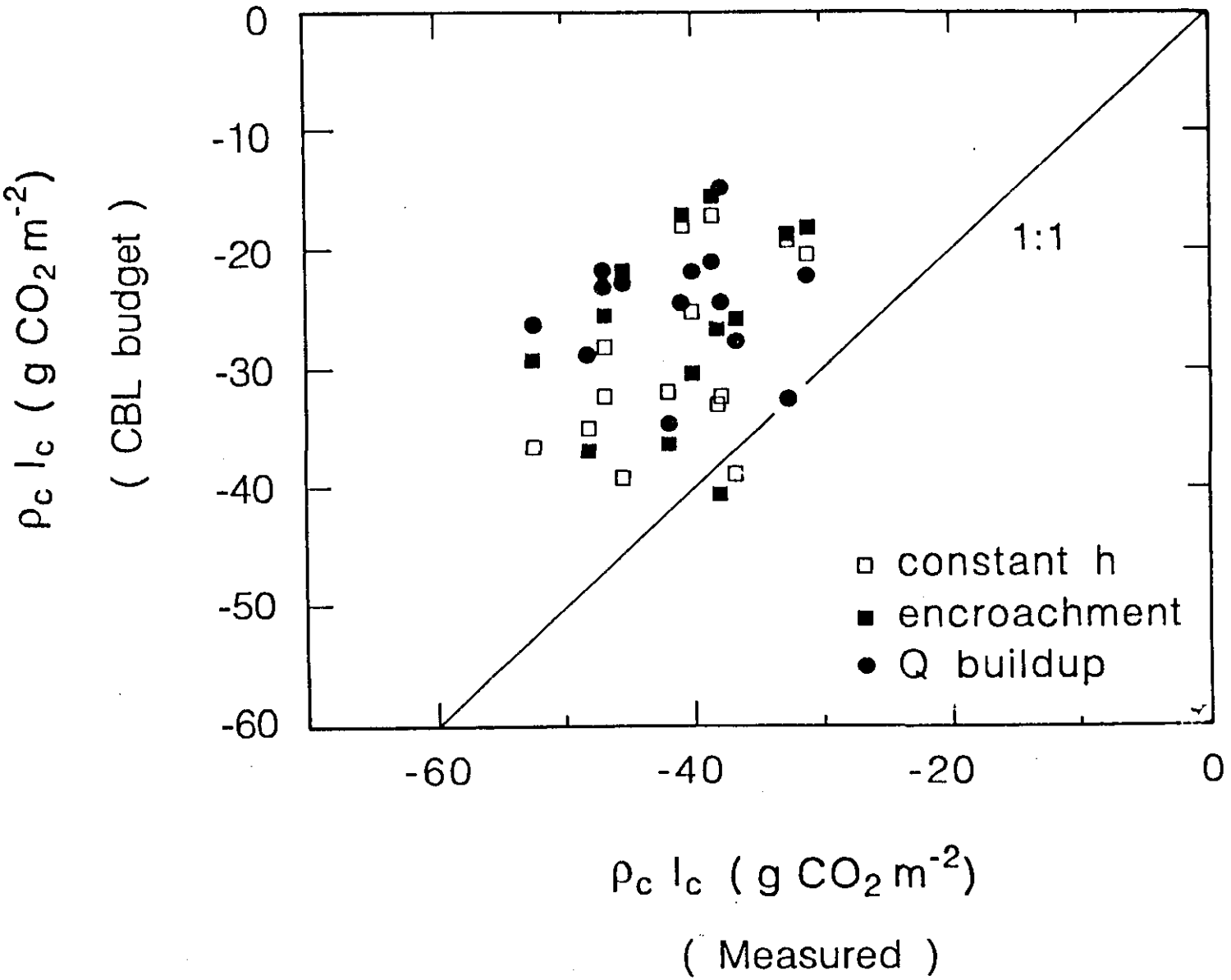
CBL well mixed

$$\frac{dC}{dt} = \frac{F_c}{h} + (C_+ - C)\frac{dh}{dt}$$

$$\Rightarrow \int_0^t F_c\, dt = (C - C_+)\, h(t)$$

(with assumptions)

10 Oct. 1991
0900
1200
1500
Inverse method at z=hc
Energy balance
Eddy correlation
ρc Fc (mg CO2 m-2s-1)
-2
-1
0
b
λE (W m-2)
400
200
0
a
Inverse method
at z=0.25hc
Lysimeters
λE (W m-2)
60
40
20
0


0
-10
-20
-30
-40
-50
-60
-60
-40
-20
0
1:1
constant h
encroachment
Q buildup
ρc Ic (g CO2 m-2)
(CBL budget)
ρc Ic (g CO2 m-2)
(Measured)

DEVELOPMENT OF A GAS CHROMATOGRAPHIC METHOD FOR THE ANALYSIS OF ATMOSPHERIC DIMETHYSULPHIDE

by

J.P.Ivey

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ABSTRACT

This report covers the development of the Dimethylsulphide analysis project of the Sulphur Program at the Australian Baseline Air Pollution Station, Cape Grim. It seeks to document the analytical rational behind the choise of methodology and presents the steps taken to enshore the analytical credibility of the published results. Peculiarities of the gold trapping methodology developed, and the effect of oxidants on trapping efficency are discussed. The chromatography of DMS with respect to potential interference and the quantitation of that gas against reference standards are described. Examples of quantitation of DMS at atmospheric concentrations are presented and the future directions of the analytical program explained

DMS ANALYSIS PROGRAM AT CAPE GRIM

(1) Insitu Day/ Night Grab Samples

60L of air is sampled through a chemisorptive gold sputter coated glass wool containing tube. Oxidants are removed from the sampling line by reaction on a KI/Glycerine coated G/F filter. DMS is then thermally desorbed to a cryogenic loop at the AGAL laboratory and injected into a Dani 6500 gas chromatograph. Column used is a DB1 0.53 IDx 25Mx 5.0um capillary column, a flame photometric detector provides sulphur specific quantitation. Permiation tubes are used for standards.

(2) Integrated DMS Sampling

Air is sampled at 40ml/min. during periods of Baseline conditions through a larger (125cc instead of 20cc) gold trap. The sampling exactly parallels collections of SO_2 and air particulates by high volume filter. The analyses are undertaken in the same manner as the insitu collections.

Table 1

Comparison of the oxidant capacity of several scrubbing systems.

Oxidant Removal Material	Breakthrough Volume (litres)
Untreated glass fibre (G/F) filter	14
Water rinsed G/F filter	12
NaOH (7%) on G/F filter	48
KOH (7%) on G/F filter	75
Na_2CO_3 (7%) on G/F filter	35
Na_2CO_3 on Chromosorb W-AW in Pyrex tube	26
MnO_2 granules in Pyrex tube	25
Vitex (0.5%) on G/F filter	45
Glycerol (5%) on G/F filter	19
KI (5%) on G/F filter	25
Glycerol/Vitex (5%/0.5%) on G/F filter	25
KI/Vitex (5%/0.5%) on G/F filter	64
KI/glycerol (5%/5%) on G/F filter	193
KI/gly/V (5%/5%/0.5%) on G/F filter	263

Table 2

DMS recovery using KI/gly/V and NaOH coated filters.

Air Volume (litres)	Trap 1 KI/gly/V filter (ng DMS m^{-3})	Trap 2 NaOH filter (ng DMS m^{-3})
20	99	96
40	97	98
60	106	103
80	97	94
100	106	106
*200	91	71

* 125cm3 gold traps

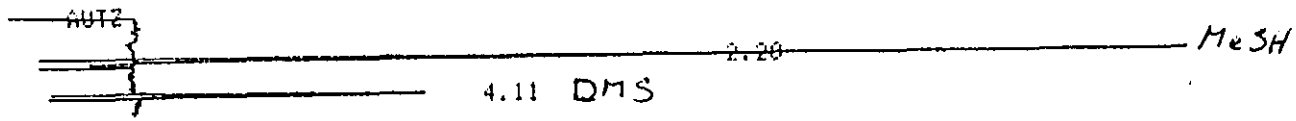
4.03	1572	17757	P	25.2905480
4.28	119	1035		1.4741069
TOTAL		70212		100.0000000

PLOT

NOISE 709 11-9-90 (cont'd)

L-L. 31sec/5ml
5-1ng DMS

IEEE NO	SAMPLE	METHOD	TIME	DATE
00	0159	METHOD1	08:36:57	11:09:90



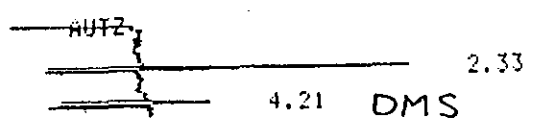
RUN TIME 5.20

DEFAULT 0
NORMALIZATION METHOD USING AREA

TIME	HEIGHT	AREA	%AREA
2.28	30661	179245	76.1768960
4.11	5654	56056	23.8231031
TOTAL		235301	100.0000000

S.L. 31sec/5ml
2-6ng DMS

IEEE NO	SAMPLE	METHOD	TIME	DATE
00	0160	METHOD1	08:43:33	11:09:90



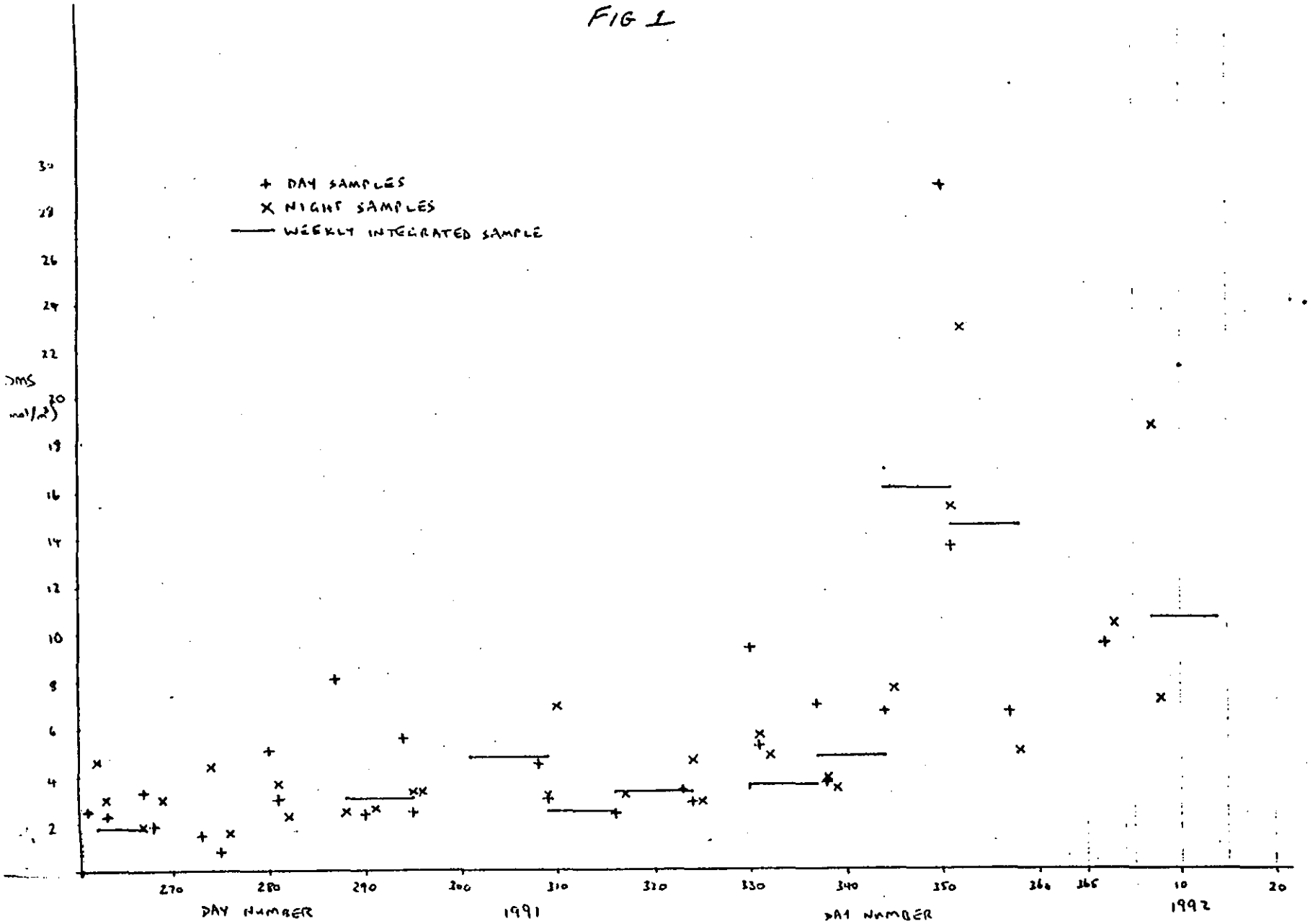
RUN TIME .00

DEFAULT 0
NORMALIZATION METHOD USING AREA

TIME	HEIGHT	AREA	%AREA
2.33	5762	40433	75.1626570
4.21	1339	13361	24.8373420
TOTAL		53794	100.0000000

TRAP A

FIG 1


+ DAY SAMPLES
× NIGHT SAMPLES
—— WEEKLY INTEGRATED SAMPLE
DMS
nmol/m³
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
270
280
290
300
310
320
330
340
350
360
365
10
20
DAY NUMBER
1991
DAY NUMBER
1992

LIMITATIONS OF GOLD TRAPPING

(1) Specific for DMS (other sulphur compounds give variable recoveries and react during hydrogen desorption.

(2) Too dependent on operator. (6 out of 14 weekly samples lost through operator/sampling error.)

(3) Fragility of glass samplers.

(4) Potential for leaks.(Not easily detectable)

CURRENT RESEARCH AND PROGRAM UPGRADE

Unattended GC Analysis at CG

In the current year a GC will be installed at CG to measure DMS and COS continuously. This instrument will be based on oxidant removal by KI filters, 1L air trapping on tenax with GC separation and detection via Hall conductivity in the sulphur mode.

Important elements for success

(1) Calibration by gas standards including SF6 as internal standard.

(2) Cylinder sampling for AED determination at AGAL using identical cylinder standards.

(3) Variable DMS standard introduction (due to large seasonal variation).

(4) Reliability, linearity of calibration and reproducibility.

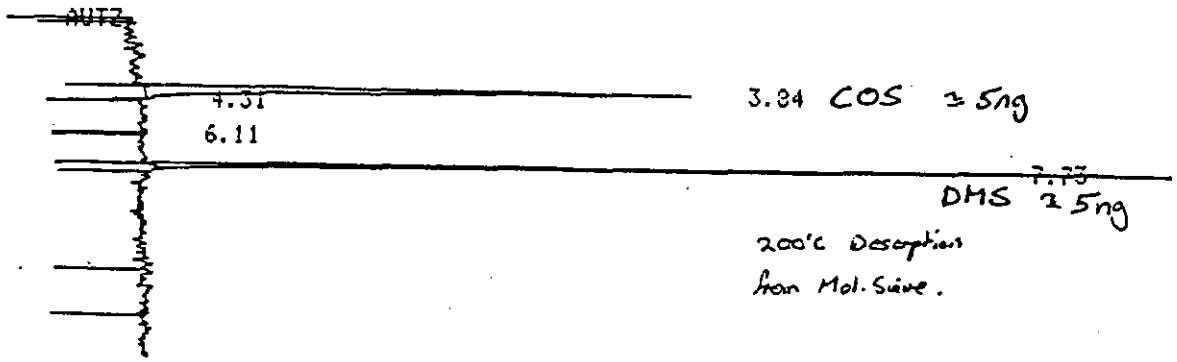
(5) Bracketing standards ie 490& 520ppt for COS (atmospheric conc. ~505ppt).

1.91	1180		
4.36	15609	446353	33.3763792
8.61	8914	67839	5.0727119
8.97	101720	804046	60.1231407
TOTAL		1337332	100.0000000

Fig. 2.

IEEE NO	SAMPLE	METHOD	TIME	DATE
00	0387	METHOD1	14:28:54	10:01:92

55+5L loops.

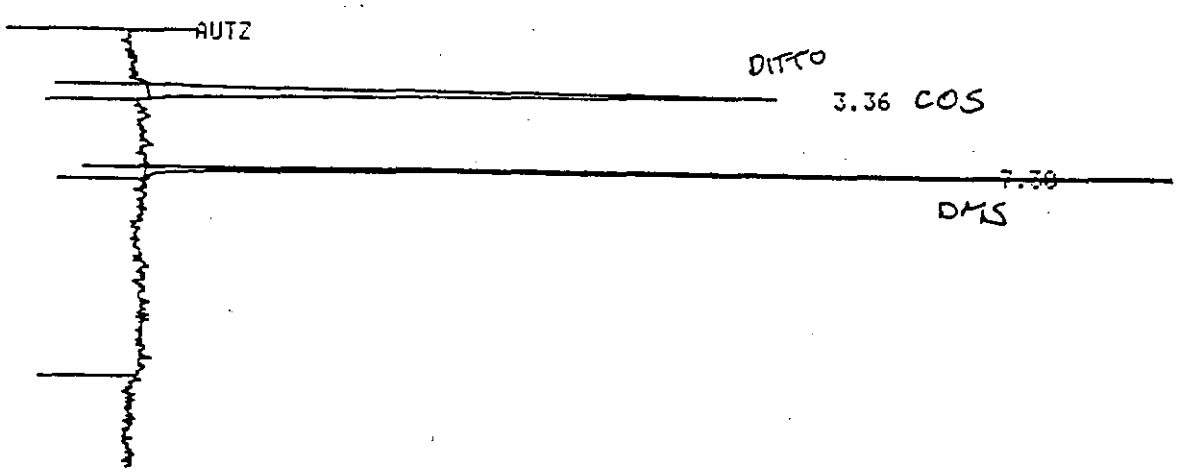


RUN TIME 17.89

DEFAULT 0
NORMALIZATION METHOD USING AREA

TIME	HEIGHT	AREA		%AREA
3.84	9130	226506	P	47.9851020
4.31	222	1326		0.2809119
7.73	27772	244202		51.7339850
TOTAL		472034		100.0000000

IEEE NO	SAMPLE	METHOD	TIME	DATE
00	0388	METHOD1	15:02:33	10:01:92



RUN TIME 22.84

DEFAULT 0
NORMALIZATION METHOD USING AREA

TIME	HEIGHT	AREA	%AREA
3.36	10291	396308	44.0105540
7.38	62278	504176	55.9894450
TOTAL		900484	100.0000000

IEEE NO	SAMPLE	METHOD	TIME	DATE
00	0389	METHOD1	15:36:09	