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The Scientific Application of Baseline Observations of Atmospheric Composition

C.S.I.R.O. ATMOSPHERIC RESEARCH
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Aspendale, Australia
14-17 November, 1988

EXTENDED ABSTRACTS

PREFACE

Dear participant,

Welcome to Melbourne and to our Second Conference on the Scientific Application of Baseline Observations of Atmospheric Composition. During the late seventies members of the Division of Atmospheric Research (CSIRO/DAR) worked with the Federal Departments of Science and other Government agencies towards the establishment of an observatory for the measurement of the composition of background air. A facility was constructed for this purpose at Cape Grim, Tasmania and was opened in 1981. By the time of the first SABOAC meeting it had already provided scientists with important information concerning background concentrations of atmospheric constituents in a region of the world relatively devoid of research institutes and observational programs.

In recent years Cape Grim has been administered by the Australian Bureau of Meteorology and jointly managed by the Bureau and CSIRO/DAR. A working group, comprised mainly of scientists associated with programs at Cape Grim, formulates policies to ensure the continuity of the existing projects as well as the evolution of a program dedicated to providing data which meet the requirements of the global scientific community for the resolution of a wide spectrum of problems. Initially, Cape Grim, and for that matter some of the similar observatories around the world, was founded particularly to document the changes in the atmospheric composition that were potentially significant in climatic stability. This remains an important objective, but the last decade has seen a major advancement in knowledge of atmospheric chemistry. It has become clear that background observations of the composition of the atmosphere are of much wider general importance.

As was noted in the preface to the first SABOAC meeting, there is a need to improve our understanding of the natural processes that result in the circulation of chemical elements through the atmosphere, oceans and biosphere if we are to be able to assess the large-scale environmental consequences of human

activities on the planet. The atmosphere is, for many of these elements, a reservoir whereby global dispersion is achieved, and a reaction vessel wherein chemical transformations occur. Many measurement programs already underway relate to the establishment of a sound understanding of cycles of elements such as carbon, nitrogen and sulphur. Much more remains to be done. Our second SABOAC meeting provides a timely opportunity to present results from programs that were only in early stages at the time of the first meeting.

It is the breadth of this potential application of the Cape Grim facility and other similar observatories which we hope to explore through this Conference. We hope that the meeting will serve to demonstrate the exciting diversity of applications for baseline data and the rapidly evolving nature of the measurement requirements.

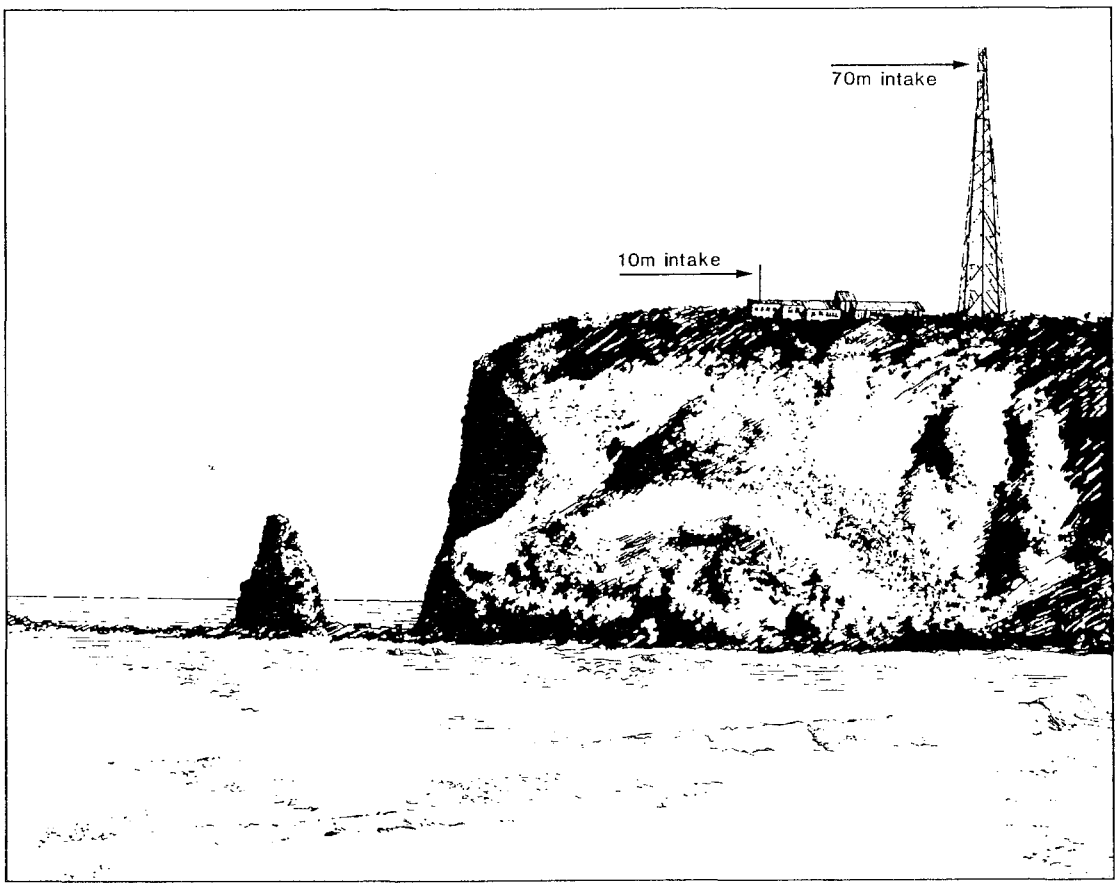
As with the first SABOAC meeting, we have a full program - we have extended the meeting to 4 days and included an excursion break in order to reduce the pressure. As most participants will be aware, during the week preceeding SABOAC II there will be a planning meeting for the International Global Atmospheric Chemistry Program of CACGP. On the weekend between these meetings participants in the ALE-GAGE experiment will meet in Melbourne. A number of the participants from these meetings are staying on for SABOAC II. The interaction between the meetings has been complicated by the forced change of venue that resulted from our accomodation bookings being accepted incorrectly. We apologise to any participants inconvenienced by these changes which were totally outside our control and express our appreciation to the DAR administrative staff who helped to 'pick up the pieces' when disaster struck.

The occasion of the second SABOAC meeting coincides with the end of Bruce Forgan's term as director of the Cape Grim Baseline Air Pollution Station and the arrival of Stephen Wilson as new director. Bruce's period as director began somewhat before our first SABOAC meeting. The quality and extent of the Cape Grim data

to be presented at this meeting reflects admirably on the efforts of Bruce and his staff. We take this opportunity to express our appreciation of Bruce's efforts and to convey out best wishes to Stephen as his successor. A special Cape Grim Working Group meeting has been scheduled for Friday the 18'th to facilitate this changeover. A planning meeting with our New Zealand counterpart will follow aimed at coordinating the two baseline monitoring efforts in our region.

The meeting is being supported financially by funds from the Cape Grim Baseline Air Pollution Station, the CSIRO (Division of Atmospheric Research) and the Bureau of Meteorology. The organisation of the meeting has drawn on staff from each of these organisations and we express our appreciation of their efforts.

The organisers



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* denotes presenter if not first author.
(*) denotes presentation by non-author.
[nn] denotes number of talk.

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21. G Ayers : Numerical study of droplet chemistry in oceanic, wintertime stratus clouds at southern mid-latitudes. [38]
22. L A Barrie & M J Barrie : Lower tropospheric aerosol composition in the high Arctic - 7 years of observations. [43]
23. G Beig and D.K.Chakrabarty : Need for atmospheric composition measurements at equator and low latitude. [22]
25. G Bergametti & P Buat-Ménard * : Temporal variations of aerosol concentrations and fluxes over the Northwestern Mediterranean. [44]
26. B Bonsang, M Kanakidou & G Lambert (P Buat-Ménard *) : Preliminary results of non methane hydrocarbons monitoring at Amsterdam Island. [28]
27. J W Bottenheim & L A Barrie * : Evidence of photochemically induced reactions affecting the trace gas and particle composition of the lower arctic troposphere at polar sunrise. [45]
28. Chen Liqi, Yang Xulin & Huang Jianghuai : Sea-Air exchange of sulfur, phosphorus and nitrogen in marine aerosols over the Antarctic Peninsula waters. [32]
29. T J Conway & K W Thoning : Short term variations of atmospheric carbon dioxide at the South Pole. [11]

30. P Crutzen and K Valentin : Seasonal and latitudinal emission estimates for CH_4 and CO derived with a 2-D model. [8]
31. A L Dick : A simple model for air/snow fractionation of aerosol components over the Antarctic Peninsula. [39]
32. A Downey, D Jasper & J Gras : Lower tropospheric transport over the Southern Ocean. [18]
33. D H Ehhalt : Vertical profiles of NO in the free troposphere based on STRATOZ III. [23]
34. J W Elkins, T M Thompson & J H Butler : Halocarbons F12 and F11 and nitrous oxide measurements from NOAA/GMCC baseline observatories since 1977. [4]
35. I G Enting, J V Mansbridge & G N Newsam : Atmospheric constituent inversion problems : implications for baseline monitoring. [16]
38. I G Enting & F J Robbins : Some applications of Kalman filtering in analysing baseline atmospheric constituent data. [17]
40. R D Evans & W D Komhyr : Total Ozone, Ozone vertical distributions, and stratospheric temperatures at the South Pole, during 1986, 1987 and 1988. [26]
41. B Forgan : Aureole measurements to determine aerosol optical depth at Cape Grim. [46]
42. R J Francey & P P Tans : Oxygen isotopes of CO_2. [13]
43. P J Fraser, I G Enting, R J Francey, F J Robbins & J V Mansbridge : Methane in the southern troposphere. [7]
44. A Gaudry, P Monfray, G Bonsang, G Polian & G Lambert (P Buat-Ménard *) : Long term and seasonal variations of atmospheric CO_2 concentrations at Amsterdam Island (Territoire des Terres Australes et Antarctiques Françaises). [10]
45. J L Gras : Baseline atmospheric condensation nuclei at Cape Grim, 1977-1987. [40]
46. A Henderson-Sellers : Basis for integration of conventional observations of cloud into global nephanalyses. [2]
47. K Higuchi : A time series analysis of CO_2 data from Canadian BAPMoN stations. [9]
48. Takashi Ibusuki & Koji Takeuchi : Chemical composition of rainwater at Tsukuba area, Japan. [37]

49. J Ivey : Rainwater and aerosol methanesulphonate at Cape Grim, Tasmania. [35]
50. K Kawamura and R B Gagosian : Mid-chain ketocarboxylic acids in marine aerosols from the North Pacific. [41]
51. M Manning : Carbon isotopes in New Zealand air. [14]
52. J Miller, G Herbert & J Harris : The interpretation of baseline measurements using back trajectories. [19]
53. B C Nguyen, N Mihalopoulos, S Belviso & J P Putaud : Seasonal variation of atmospheric dimethylsulfide at Amsterdam Island in the southern Indian Ocean. [33]
54. C M R Platt & J Everett : Proposed applications of Lidar at Cape Grim. [47]
55. R Prinn, D Cunnold, R Rasmussen, P Simmonds, F Alyea, A Crawford, P Fraser and R Rosen : Atmospheric trends and emissions of nitrous oxide deduced from nine years of ALE-GAGE data. [3]
56. F S Rowland : Global measurements of total ozone - wintertime loss in the Northern Hemisphere. [25]
57. J Rudolph, A Khedim & D Wagenbach : The seasonal cycle of C_2 and C_3 hydrocarbons in the southern hemisphere. [30]
58. H E Scheel, E-G Brunke & W Seiler : Trace gas measurements at the monitoring station "Cape Point", South Africa. [6]
59. Weihan Su and Wei Li : Study of hydrogen peroxide in the atmosphere. [31]
60. Weihan Su and Ciguang Ma : Study of aerosol on Tibet Plateau and in other clean areas in China. [42]
61. K W Thoning, J T Conway, P P Tans & J T Peterson : Atmospheric CO_2 concentrations during and following the 1987 EL NINO. [12]
62. Ming-Xing Wang and Guo Yu-fu * : Long term trend of trace gases, eg CH_4, CO_2, F-11, F-12 and F-113 measured at a remote site in the NW of China. [5]
63. S Whittlestone : Radon daughter disequilibria in the lower marine boundary layer. [21]
64. S R Wilson & D W T Griffith : Measurements of phosgene ($COCl_2$) and other carbonyl compounds in the atmosphere. [27]
65. Yang Wen-Xiang, Wang Dechun, Wei Rurong and Lai Cong : The identification and characterisation of vapour phase organic pollutants in air in Beijing-Tainjin region. [29]

LATE CHANGES AND ADDITIONS

67 A J Aristarain and R J Delmas : Snow chemistry on southern Patagonia ice field - A preliminary study. [36]

69 R J Atkinson and J R Easson : The Australian ozone monitoring program. [24]

70 J W Silzel and F S Rowland : A simple 20-box atmospheric model: simulations of time evolving atmospheric concentrations and inputs of several halocarbon compounds. [20]

71 N Trivett, K Higuchi and S Symington : Time series analysis of Canadian BAPMoN CO_2 measurements. [9]

72 C Brenninkmeijer, M Manning, E Dlugokencky, P Pohl, D Lowe, R Sparkes and G Wallace : Monitoring the isotopic concentration of atmospheric carbon monoxide at Baring Head New Zealand. [15]

A LIST OF PARTICIPANTS FOLLOWS THE ABSTRACTS

MEETING GUIDE

CONFERENCE DETAILS

Venue : The talks will be held in the Lecture Theatre of the CSIRO Division of Atmospheric Research (DAR, see map). The Division is at the corner of Station St and Robinson Pde, Aspendale, with telephone number 586 7666, Telex number AA34463 and Fax number 586 7600.

Registration : This is to be paid to the Conference Secretary on arrival. The fee, which has been reduced to A$100 or A$40 per day, includes lunch, morning and afternoon tea, ice-breaker, Wednesday afternoon Excursion and Conference Dinner.

Talks : 30 minutes has been allowed for each participant. We appreciate that this is too short for adequate presentation of a complete paper. However, it is absolutely essential to keep to this time so that everyone has equal time. Chairmen are advised to insist on 20 minutes for the presentation of the paper and 10 minutes for discussion.

Slides should be handed to the projectionist at least 10 minutes before the start of the session in which your talk is scheduled. All other aids are available, but please ensure that your requirements are known by contacting either Mr. David Whillas or Mr. Geoff Richards well ahead of time.

Publications :

1. Extended Abstracts will be distributed before the Conference.
2. The editors of the Journal of Atmospheric Chemistry have once again agreed in principle to the publication of papers from SABOAC. The plan is for 2 special editions of the journal. Papers submitted at the time of the conference, as originally requested, will begin assessment almost immediately (possibly involving other participants). An absolute, final deadline for submission of late papers is 28 February 1989.

On acceptance of their paper authors will be advised on the preferred method of providing a final manuscript (eg camera-ready or diskette). Papers will undergo a rigorous reviewing process and the 2 SABOAC editions of JAC will be limited to about 20 papers (authors of papers not included in the special issues can of course submit their papers through the normal channels). For the information of authors the scope of JAC is reproduced here:

> "The journal is devoted to the study of the chemistry of the Earth's atmosphere with emphasis on the region below about 100 km. The strong interdisciplinary nature of atmospheric chemistry leads it to embrace many varied sciences, but the journal concentrates on the following topics:
> (1) Observational, interpretative and modelling studies of composition and physico-chemical processes in the Earth's atmosphere, excluding air pollution problems of only local importance. (2) The role of the atmosphere in biogeochemical cycles; the chemical interaction of ocean, land surface, biosphere with the atmosphere. (3) Laboratory studies of the mechanics in homogeneous and heterogeneous transformation processes in the atmosphere. (4) Description of major advances in instrumentation developed for the measurement of atmosphere composition and chemical properties."

Morning/afternoon Coffee and Lunches : Refreshments and lunches will be taken in building 20 (see map). The cost of these is included in the registration fee. Some snack foods can be purchased from the canteen.

ADDITIONAL ACTIVITIES

Visit to Cape Grim : This will be on Sunday the 13'th and will leave from Moorabbin airport (approximately 6 km from Aspendale).

Ice-breaker : This will be in the canteen at Aspendale at 5.30 on Monday the 14'th.

Excursion : We will visit the Mornington Peninsula on the afternoon of Wednesday November 16; a cut lunch will be provided en route. The excursion will be followed by the Conference dinner.

Cape Grim Working Group Meeting : This meeting is for lead scientists and will be on Friday November 18.

NZ-Australian Co-ordination Meeting : This will involve selected scientists discussing the co-ordination of respective national baseline monitoring activities in the Australasian/Antarctic region. It will take place on Friday November 18.

GENERAL

Telephone Calls : Local calls may be made from the Division by dialling '0' followed by the local number. Overseas calls need to be placed through the Receptionist by dialling '9'. The area code for Melbourne is '03' and applies to all telephone numbers given below if dialling from outside Melbourne or Frankston.

Accomodation : This will be mainly at the Colonial Motor Inn, Frankston and will include a continental breakfast. The cost is A$49 for a single room or $60 ($30 each) for a twin room. The address is 406 Nepean Highway, Frankston, with telephone number 781 5544. Transport to and from Aspendale will be arranged each day and will include the return from the Conference dinner.

Organisation : The Conference organisers are

Convenors: Roger Francey (in lieu of Graeme Pearman).
Secretaries: Helen Goodman (in lieu of Val Jemmeson).
Organising Committee: Ian Enting, David Jasper, John Gras.
Editorial Board: Roger Francey, Ian Enting, Graeme Pearman, John Gras.

After Hours contact numbers are

H. Goodman 580 4968
R. Francey 707 4179
D. Jasper 467 1994
I. Enting 583 8822
J. Gras 561 7072
G. Pearman 580 5960

Banking : Banks in Australia are open from 9.30 a.m. until 4 p.m. Monday to Thursday and 9.30 a.m. until 5 p.m. Friday. Please

ensure that you have your passport and identification papers with you when changing money. (The Aspendale branch of the State Bank of Victoria is located 150 metres south of the Division.)

Photocopying : Please contact the Conference Secretaries.

General Travel : Ms. Mouy Kaing in the General Office will be pleased to assist you.

Suburban travel : Aspendale is on the railway line from Frankston to Melbourne; Frankston station is about 600 metres south of the Colonial Motor Inn. A number of schemes exist for travelling on the suburban rail line, e.g. 'off-peak'. The cost of a daily 'anywhere travelcard' is $5.00. This alllows travel on any suburban trains, trams and buses for the whole day. Trains run between Frankston and the City at least every 30 minutes. The journey from Frankston to Aspendale takes approximately 20 minutes and from Aspendale to Melbourne another 45 minutes.

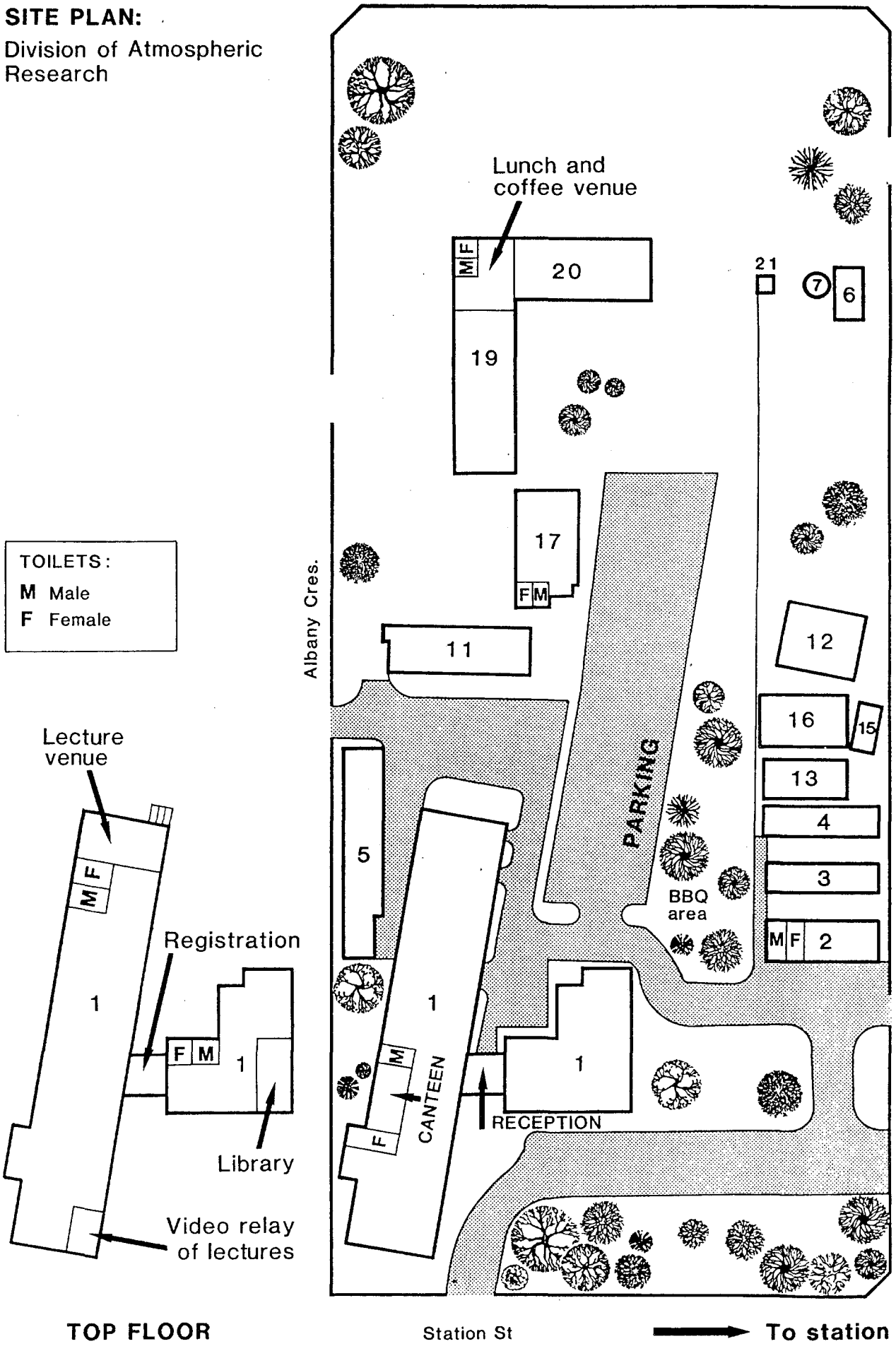
Local Eating Houses :

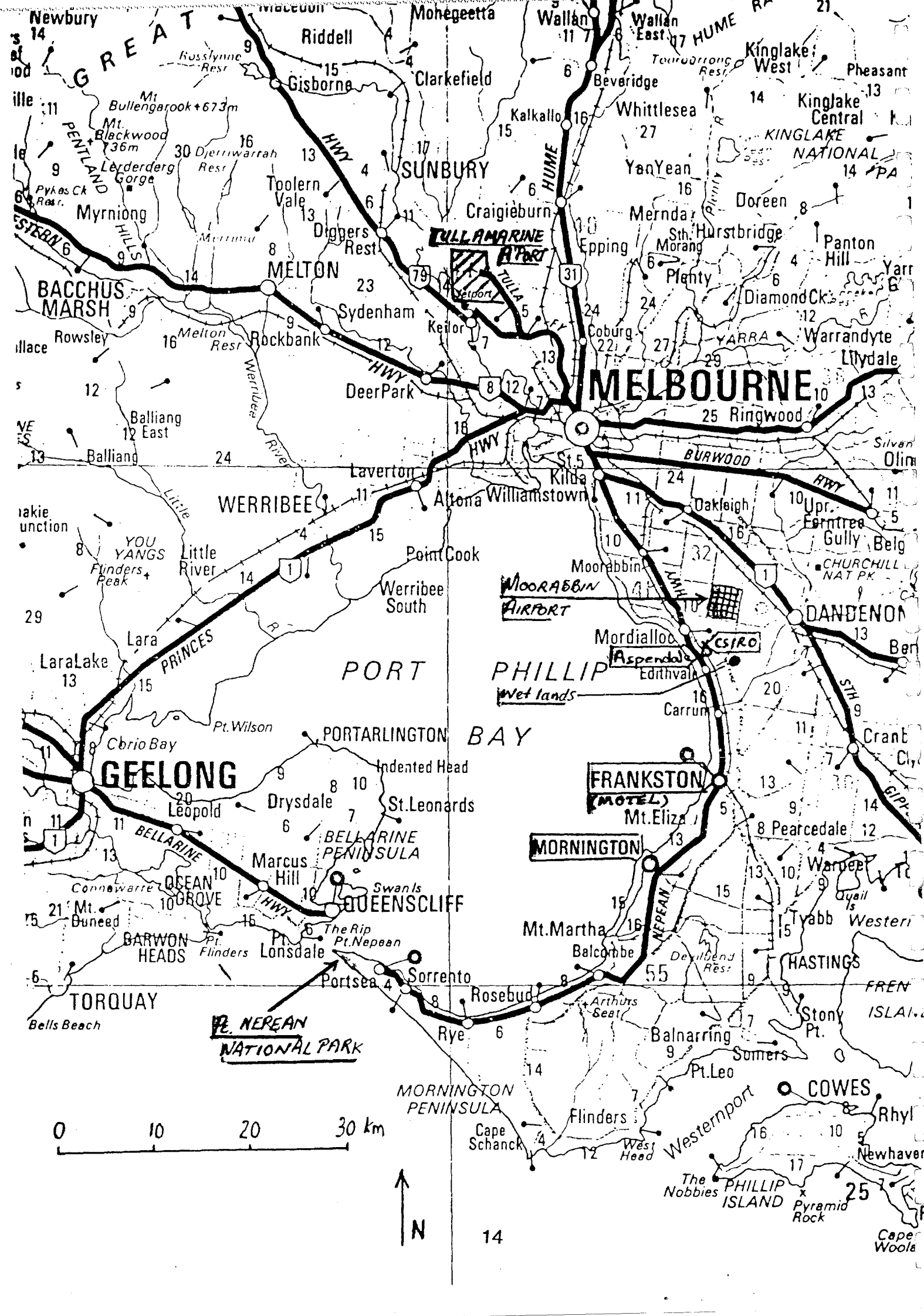
1. All suburbs have a variety of inexpensive 'take-away' food shops.
2. Hotel opening hours have been extended since SABOAC I with many hotels open until 3 a.m.
3. General stores or 'milk bars' are often open until 9 p.m. Most other shops close at 5 or 5.30 p.m. on Mondays to Thursdays and 9p.m. on Fridays.
4. Medium Priced Restaurants

Many of these are BYO (Bring Your Own), i.e., they do not sell liquor but allow patrons to consume their own. Liquor can be purchased at specific retail outlets during normal trading hours and at hotel bottle shops at later times. Frankston has numerous restaurants within walking distance of the Colonial Motor Inn. Chinese, Japanese, Italian, French, Greek, Indian and Mongolian meals are all available. The only restaurant within walking distance of the Division is the "Fook Hing" (BYO, Chinese). It is on the Nepean Highway opposite the Railway Station.

SITE PLAN:

Division of Atmospheric Research





Newbury
GREAT
Riddell
Monegeetta
Wallan
Wallan East
HUME
Kinglake West
Pheasant
Gisborne
Clarkefield
Beveridge
Whittlesea
Kinglake Central
Mt Bullengarook 673m
Mt. Blackwood 736m
PENTLAND
Lerderderg Gorge
Djerriwarrah Resr
Kalkallo
KINGLAKE NATIONAL PA
SUNBURY
YanYean
Toolern Vale
Myrniong
Craigieburn
Mernda
Doreen
Diggers Rest
TULLAMARINE A'PORT
Epping
Sth. Morang
Hurstbridge
Panton Hill
MELTON
Plenty
BACCHUS MARSH
Sydenham
Keilor
Diamond Ck
Rowsley
Melton Resr
Rockbank
Coburg
YARRA
Warrandyte
Lilydale
DeerPark
MELBOURNE
Ringwood
Balliang East
Balliang
Werribee River
Laverton
St. Kilda
BURWOOD HWY
Altona
Williamstown
WERRIBEE
Oakleigh
Upr. Ferntree Gully
YOU YANGS
Little River
Point Cook
Moorabbin
CHURCHILL NAT PK
Flinders Peak
Werribee South
MOORABBIN AIRPORT
DANDENON
Lara
Mordialloc
CSIRO
Aspendale
LaraLake
PRINCES
PORT PHILLIP BAY
Edithvale
Wet lands
Carrum
Pt. Wilson
PORTARLINGTON
Cranb
Corio Bay
GEELONG
Indented Head
FRANKSTON (MOTEL)
Leopold
Drysdale
St. Leonards
Mt. Eliza
Pearcedale
BELLARINE
BELLARINE PENINSULA
MORNINGTON
Marcus Hill
Warneet
Connewarre
OCEAN GROVE
Swan Is
QUEENSCLIFF
Quail Is
Mt. Duneed
Tyabb
Western
BARWON HEADS
Pt. Flinders
Pt. Lonsdale
The Rip
Pt. Nepean
Mt. Martha
NEPEAN
Balcombe
Devilbend Resr
HASTINGS
Portsea
Sorrento
TORQUAY
Rosebud
Arthurs Seat
Stony Pt.
Bells Beach
Pt. NEPEAN NATIONAL PARK
Rye
Balnarring
Somers
Pt. Leo
MORNINGTON PENINSULA
COWES
Flinders
Westernport
Rhyl
Cape Schanck
West Head
Newhaven
The Nobbies
PHILLIP ISLAND
Pyramid Rock
Cape Woola
0 10 20 30 km
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SABOAC II (1988) - PROGRAM

(Attending or first author only)

MONDAY 14 NOVEMBER

0830 - 0930	REGISTRATION (Cape Grim film in theatre)
0930 - 1030	WELCOME: Chair: Dr G B Tucker 1. D Gauntlett: Introduction 2. A Henderson-Sellers : Basis for integration of conventional observations of cloud into global nephanalyses
1030 - 1100	Morning tea
1100 - 1230	NON-REACTIVE GASES(1) - Chair: Dr J Peterson 3. R Prinn : Atmospheric trends and emissions of nitrous oxide deduced from nine years of ALE-GAGE data 4. J Elkins : Halocarbons F12 and F11, and nitrous oxide measurements from NOAA/GMCC baseline observatories since 1977 5. Guo Yu-fu : Long term trend of trace gases, eg CH_4, CO_2, F-11, F-12 and F-113 measured at a remote site in the NW of China
1230 - 1315	Lunch
1315 - 1515	NON-REACTIVE GASES(2) - Chair: Dr J Peterson 6. H E Scheel : Trace gas measurements at the monitoring station "Cape Point", South Africa 7 P Fraser : Methane in the southern troposphere 8. P Crutzen : Seasonal and latitudinal emission estimates for CH_4 and CO derived with a 2-D model 9. K Higuchi : A time series analysis of CO_2 data from Canadian BAPMoN stations
1515 - 1545	Afternoon Tea
1545 - 1715	NON-REACTIVE GASES(3) - Chair: Dr P Crutzen 10. A Gaudry : Long term and seasonal variations of atmospheric CO_2 concentrations at Amsterdam Is (presenter P Buat-Menard) 11. T Conway : Short term variations of atmospheric carbon dioxide at the South Pole 12. J Peterson : Atmospheric CO_2 concentrations during and following the 1987 EL NINO
1715 - 1830	ICEBREAKER (then bus to Motel)

TUESDAY 15 NOVEMBER

0830 - 1030 NON-REACTIVE GASES(4) - Chair: Dr P Crutzen

13. R Francey : Oxygen isotopes of CO_2
14. M Manning : Carbon isotopes in New Zealand air
15. C Brenninkmeijer : Carbon-14 in carbon monoxide
16. I Enting : Atmospheric constituent inversion problems : implications for baseline monitoring

1030 - 1100 Morning tea

1100 - 1300 GENERAL(1)/TRANSPORT(1) - Chair: Dr M Manton

17. I Enting : Some applications of Kalman filtering in analysing baseline atmospheric constituent data
18. A Downey : Lower tropospheric transport over the Southern Ocean
19. J Miller : The interpretation of baseline measurements using back trajectories
20. F S Rowland : A simple 20-box atmospheric model: simulation of time evolving atmospheric concentrations and inputs of several halocarbons compounds

1300 - 1400 Lunch

1400 - 1530 REACTIVE GASES(1)- Chair: Dr M Manton

21. S Whittlestone : Radon daughter disequilibria in the lower marine boundary layer
22. G Beig : Need for atmospheric composition measurements at equator and low latitude
23. D Ehhalt : Vertical profiles of NO in the free troposphere based on STRATOZ III

1530 - 1600 Afternoon Tea

1600 - 1730 REACTIVE GASES(2)- Chair: Dr M Andreae

24. R Atkinson : The Australian ozone monitoring program
25. F S Rowland : Wintertime losses of ozone in the northern high latitudes - new statistical analyses of Dobson data since 1965
26. R Evans : Total ozone, ozone vertical distributions, and stratospheric temperatures at the South Pole, Antarctica in 1986, 1987 and 1988

1800 Bus to motel

WEDNESDAY 16 NOVEMBER

0830 - 1030	REACTIVE GASES(3)- Chair: Dr M Andreae 27. S Wilson : Measurements of phosgene ($COCl_2$) and other carbonyl compounds in the atmosphere 28. B Bonsang : Preliminary results of non methane hydrocarbons monitoring at Amsterdam Island (presenter P Buat-Menard) 29. Yang Wen-Xiang : The identification and characterization of vapour phase organic pollutants in air in Beijing-Langfun-Taijin region 30. J Rudolph : The seasonal cycle of C_2 and C_3 hydrocarbons in the southern hemisphere
1030 - 1100	Morning tea
1100 - 1300	REACTIVE GASES/PARTICLES(1) - Chair: Dr D Ehhalt 31. Su Weihan : Study of hydrogen peroxide in the atmosphere 32. Chen Liqi : Sea-Air exchange of sulfur,nitrogen and phosphorous in marine aerosols over the Antarctic Peninsula waters 33. B Nguyen : Seasonal variation of atmospheric dimethyl sulfide at Amsterdam Island in the southern Indian Ocean 34. M Andreae : Atmospheric sulfur species over the southern ocean off Tasmania
1305-	Bus to Mornington Peninsula SCHEDULING HERE IS A LITTLE TIGHT !! The master plan is: 1310: arr. EDITHVALE WETLANDS (with a choice of activities: view birds from hide, eat lunch in car park, QUICK walk to kangaroos) 1340: dep. WETLANDS for motel (5 minute stop) 1500: arrive POINT NEPEAN NATIONAL PARK (cut lunch en route) NOTE: IF TALKS RUN OVER SCHEDULE THE WETLANDS VISIT WILL BE CANCELLED !
1500 - 1700	Conducted tour of POINT NEPEAN NATIONAL PARK
1800 (approx.)	Royal Hotel, Mornington Esplanade, for drinks and DINNER at 1830.
2030	Bus return

THURSDAY 17 NOVEMBER

0830 - 1030 REACTIVE GASES/PARTICLES(2) - Chair: Dr D Ehhalt

35. J Ivey : Rainwater and aerosol methanesulphonate at Cape Grim, Tasmania
36. A Aristarain : Snow chemistry on southern Patagonia ice field - a preliminary study (presenter P Buat-Menard)
37. T Ibusuki : Chemical composition of rainwater at Tsukuba area, Japan
38. G Ayers : Numerical study of droplet chemistry in oceanic, wintertime stratus cloud at southern mid-latitudes

1030 - 1100 Morning tea

1100 - 1300 REACTIVE GASES/PARTICLES(3) - Chair: Dr L Barrie

39. A Dick : A simple model for air/snow fractionation of aerosol components over the Antarctic Peninsula
40. J Gras : Baseline atmospheric condensation nuclei at Cape Grim, 1977-1987
41. K Kawamura : Mid-chain ketocarboxylic acids in marine aerosols from the North Pacific
42. Weihan Su : Study of aerosol on Tibet Plateau and in other clean areas in China.

1300 - 1400 Lunch

1400 - 1530 REACTIVE GASES/PARTICLES(4) - Chair: Dr G Pearman

43. L Barrie : Lower tropospheric aerosol composition in the high Arctic - seven years of observations
44. P Buat-Menard : Temporal variations of aerosol concentrations and fluxes over the Northwestern Mediterranean
45. L Barrie : Evidence of photochemically-induced reactions affecting the trace gas and particle composition of the lower arctic troposphere at polar sunrise

1530 - 1600 Afternoon Tea

1600 - 1700 PARTICLES/SCATTERING - Chair: Dr G Pearman

46. B Forgan : Aureole measurements to determine aerosol optical depth at Cape Grim
47. M Platt : Proposed applications of Lidar at Cape Grim

1700 - 1710 CONCLUDING COMMENTS : Dr G Pearman

ABSTRACTS

In order of first author

ATMOSPHERIC SULFUR SPECIES OVER THE SOUTHERN OCEAN OFF TASMANIA

M.O. Andreae[1,4], G.P. Ayers[2], H. Berresheim[1,5], R.W. Gillett[2], and J.T. Merrill[3]

[1]Department of Oceanography, Florida State University
Tallahassee, Fl 32306, USA
[2]Division of Atmospheric Research, CSIRO, Mordialloc, Australia
[3]Graduate School of Oceanography, University of Rhode Island,
Kingston, RI, USA
[4]Present address: Max Planck Institute for Chemistry
PO Box 3060 Mainz, Fed. Rep. Germany
[5]Present address: Georgia Institute of Technology,
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We determined the vertical distributions of dimethylsulfide (DMS), sulfur dioxide (SO_2), aerosol methanesulfonate (MSA), non-seasalt sulfate (nss-SO_4^{2-}), and other aerosol ionic species in the marine atmosphere off Tasmania (Australia) during December 1986. DMS concentrations in the mixed layer (ML) were typically between 15-60 pptv, similar to ground-level values (44+/-11 pptv) measured at Cape Grim in the same time period. DMS decreased in the free troposphere (FT) to values near 1-2 ppt at 3 km. DMS lifetime over the Southern Ocean is estimated to be at least 1-2 days. Typical MSA concentrations were 14 pptv in the ML and around 4 pptv in the FT. SO_2 concentrations showed little vertical structure and varied within a range of 4-22 pptv between different flight days. A strong increase in SO_2 concentration was observed in the upper FT. NSS-SO_4^{2-} profiles tended to parallel those of MSA, except when airmasses showed evidence of advection from Africa or Australia. In contrast to SO_2, nss-SO_4^{2-} values decreased significantly in the upper FT. The MSA/nss-SO_4^{2-} mole ratio over the Southern Ocean was substantially higher (0.3-0.5 in the ML, 0.1-0.2 in the lower FT, 0.45 at 5.3 km) compared to values previously reported for other ocean areas. Rainwater samples collected in Tasmania during the same period showed similar MSA/nss-SO_4^{2-} ratios. Box model calculations suggest that the oxidation of DMS to MSA and nss-SO_4^{2-} can explain most of the observed amount of these sulfur species in the aerosol. These particles may also form the major reservoir for cloud condensation nuclei in the atmosphere over the Southern Ocean.

Numerical Study of Droplet Chemistry in Oceanic, Wintertime Stratus Cloud at Southern Mid-Latitudes

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Abstract

Cloud droplet chemistry is modelled for the first 150 metres of rise in a wintertime, mid-latitude, marine stratus cloud using observations made at and near the Cape Grim Baseline Station as a source of input parameters. The emphasis in this work was to study the variation in droplet chemistry as a function of both droplet size and nucleus composition, with a particular focus on the way in which oxidation of dissolved sulfur dioxide varied.

At 150 m above the condensation level solute concentration as a function of droplet size was found to increase by as much as 2 to 3 orders of magnitude for only a factor of 2 increase in droplet radius, primarily as a consequence of the 1/r dependence in the droplet growth equation. This size dependence exists at all levels in the model cloud, and has a significant influence on oxidation rate of sulfur dioxide in droplets growing on "sulfate" nuclei, oxidation by ozone being favoured in the smallest droplets, but oxidation by hydrogen peroxide being favoured in the larger droplets. Oxidation by ozone is favoured at all sizes in droplets formed on sea-salt nuclei as a result of the initially high alkalinity of these droplets, and overall is the more important oxidation pathway.

Volume-weighted mean pH values in the range 5 to 6 were predicted from sensitivity studies in which input variables were varied over reasonable ranges, in agreement with two sets of measured, bulk cloudwater pH data obtained near Cape Grim.

LOWER TROPOSPHERIC AEROSOL COMPOSITION IN THE HIGH ARCTIC: SEVEN YEARS OF OBSERVATIONS

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Currently from the baseline air chemistry observatory at Alert (82.5°N) in the Canadian high Arctic, there exists seven years (1980 to 1987) of weekly aerosol data for 24 constituents. Composition was analyzed by a combination of liquid ion chromatography, inductively-coupled plasma emission spectroscopy and instrumental neutron activation analysis. In addition to routine observations, several springtime intensive studies have yielded information on aerosol constituents and associated gas phase precursors. A principal component analysis of 143 weekly samples from the polluted winter months December to May reveals four principal factors associated with soil (Al, Ca, Mg, Fe, Mn, V, Cr, Ba, Ni, Sr, P), sea salt (Na, Cl, K^+, Mg, Sr), anthropogenic ($SO_4^=$, H^+, NH_4^+, K^+, Mn, V, Cr, Ba, Ni, Pb, P), and a photochemical source (H^+, $SO_4^=$, Br). NO_3^- and Cu did not behave well. The seasonal variation of representative elements from each of these factors is discussed. The photochemical factor is apparently related to common photochemical sources of the particulate constituents at polar sunrise. This is manifested by an increase in the ratio of $SO_4^=/SO_2$ as the sun rises in March and April and in a peak in filterable Br in April. Filterable iodine shows a peak a polar sunrise but is uncorrelated on a daily basis with filterable Br. The possibility of explaining $SO_4^=$, a major constituent of Arctic haze, in terms of contributions from various sources - including a photochemical one - is examined.

(Paper to be presented at the Second International Conference on the Scientific Application of Baseline Observations of Atmospheric Composition, Australia, November 14-18 1988)

NEED FOR ATMOSPHERIC COMPOSITION MEASUREMENTS AT EQUATOR AND LOW LATITUDE

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It is known now that the man-made activities are significantly influencing the natural biogeochemical cycles of nitrogen, carbon, hydrogen and phosphorus on earth. The present study mainly concentrate on the nitrogen cycle of the tropical region. The atmosphere of tropics is always a subject of special attention due to its peculiarities such as the presence of strong upwelling motion, low tropopause temperature and high tropopause height, and the high rate of bio-mass burning compared to the other latitudes. In the nitrogen cycle the NO_x gas is catalytically destroying ozone. Data for the last 30 years collected at 6 different stations in India which covers the latitude range from 10°N to 34°N show that the trends of variation of ozone with years are not identical for all the stations. This is definitely due to the effect of local meteorological parameters. As for example the ozone variations at two stations, Kodaikanal(a hill top) and New Delhi(which is inside the city) are apparently in opposite phase. To study the coupling between NO_x and ozone, the ground based measurements of NO_2 by absorption spectroscopy were started at Ahmedabad(23°N) in 1984. The results show that the 1988 values of column density of NO_2 has increased by about 20% from the 1984 values. In-situ measurements of vertical distribution of N_2O and CH_4 using cryogenic sampling technique made from Hyderabad (17°N), India in 1985 and 1987 show a higher values of the mixing ratios and less fall off with increase of height compared to the mid-latitudes indicating thereby the effect of upwelling motion. Another species of importance is water vapour . The column density of H_2O have been measured from 1976 to 1982 using IR-detector with two filters near Ahmedabad(Kulkarni et al, private communication). Besides the seasonal variation, it does not appear to show any systematic trend with years. Around 1979-80, however, a marked decrease (by about 15%) was noticed compared to the other years which recovered in 1982.

Realizing the importance of transport process, balloon measurements of eddy diffusion coefficient using chemical release technique have been made in 1985 and 1988. Results show that eddy-diffusion coefficient varies from 5×10^3 to 5×10^4 cm^2 s^{-1} for

the altitude region of 10 to 30 km. These values are about an order of magnitude higher than the predicted theoretical values.

From the above data, no clear picture emerges. We will, therefore, continue the above measurement for some more time. Besides, the measurement of NO_3 and water vapour have now been initiated using the ground based spectrometer. Also the monitoring of species N_2O_5, ClO, and OH are being planned using the FT - spectrometer.

TEMPORAL VARIATIONS OF AEROSOL CONCENTRATIONS AND FLUXES OVER THE NORTHWESTERN MEDITERRANEAN

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Beginning in 1985 a continuous aerosol sampling program has been undertaken at a coastal station in northwestern Corsica Island. This site is 300 m above sea-level and at least 20 km from local pollution sources. It is exposed during 80% or more of the time to maritime air masses which have travelled over the western Mediterranean from southern, western and northern directions. 24-hour air filtration samples were collected on 0.4 µm pore size Nuclepore filters from a tower 10 m high. Total (wet + dry) atmospheric deposition was sampled 2 m above ground level in an hemispheric plastic collector with a sampling duration of about 15 days. Elemental tracers of various continental aerosol sources and source regions were analyzed by X-ray fluorescence and atomic absorption.

Backward 3-dimensional air-mass trajectories were computed every day for various barometric levels. The results allowed to determine the various source regions contributing to the atmospheric concentrations observed for each element: western and northern Europe for pollutant elements (Pb, Zn, S); Africa for elements of crustal origin (Al, Si, Fe). The atmospheric concentrations of all these elements exhibit a seasonal pattern which is inversely related to the frequency and amount of rainfall such that the highest concentrations are observed between May and October. Elements of crustal origin exhibit sporadic but intense concentration peaks that are superimposed on this general pattern. Air mass trajectories and satellite imagery show that these events are associated with the advection of Saharan air masses which is of a frontal type.

Precipitations occuring along the trajectories were also estimated by the trajectory model and reported when greater than 0.1 mm/h. They were shown to be a major factor controlling short term changes in atmospheric concentrations which are generally 5 times lower during periods when precipitation occurred the day before sampling.

Results from total deposition measurements indicate that during periods of no precipitation the deposition is generally lower and that the temporal variability of the atmospheric deposition fluxes is related to the occurence of precipitation. However, the observed variations are not linearly related with the amount of rainfall. Precipitation frequency and, to a lesser extent, changes in precipitation type are the major factors controlling the seasonal and interannual patterns which we observe.

PRELIMINARY RESULTS OF NON METHANE HYDROCARBONS MONITORING AT AMSTERDAM ISLAND

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Since 1985, C_2-C_6 non methane hydrocarbons (NMHC) have been measured at Amsterdam Island. Generally, we can observe a seasonal cycle for long lived species such as ethane and acetylene, with a maximum of their mixing ratios from June to August. According to the general trends of the air masses circulation over the Indian Ocean, this maximum can be partly attributed to advection of continental air.

Short lived species such as ethene and propene show a large variability of their mixing ratio. According to the supersaturation of seawater in NMHC, this variability can be due to the variation of the strength of the marine source.

The composition of the air can be compared to the composition of the dissolved gases in seawater, by using the relative abundance of the NMHC with respect to propene locally produced. For the short lived NMHC the composition of the air is very close to that of seawater and presents a low seasonal variability which could be attributed to possible local sources and sinks seasonal variations. For the long lived species such as C_2-C_3 alkanes and acetylene, a well defined seasonal cycle of their relative abundances confirms the presence of a continental component over the island during late fall and winter.

Scientific application of baseline observations of atmospheric composition

Melbourne, Australia, November 14-18, 1988

EVIDENCE OF PHOTOCHEMICALLY-INDUCED REACTIONS AFFECTING THE TRACE GAS AND PARTICLE COMPOSITION OF THE LOWER ARCTIC TROPOSPHERE AT POLAR SUNRISE

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ABSTRACT

The Arctic atmosphere offers a unique laboratory in which to study atmospheric chemical reactions under cold, relatively dry conditions. At the Earth's poles, there is essentially one day and one night per year separated by polar sunrise and sunset. The rapid change from total absence of sunlight to complete light is not immediately accompanied by a change in the meteorological characteristics of the atmosphere that have a strong influence on thermal reactions(i.e. temperature) or the vertical dispersion of atmospheric trace constituents(i.e. thermal stability). Thus, by studying the change in atmospheric composition of the Arctic atmosphere around polar sunrise and sunset, photochemical effects can be isolated from meteorological ones. Thus, something can be learned about photochemically-induced chemical reactions. The Arctic troposphere differs from that of the Antarctic in that it is much more polluted(especially at polar sunrise) by anthropogenic emissions from the surrounding continents and it is influenced by the underlying Arctic ocean rather than a solid ice sheet.

For almost a decade, air chemistry studies have been undertaken in the Canadian Arctic. Many of these have been at the baseline observatory at Alert(82.5 ^{o}N, 62.3 ^{o}W). These complemented by observations made in other areas provide a rich source of information that points to several photochemically-induced changes at polar sunrise. This paper reviews the experimental evidence for such changes. This includes results from the first Polar Sunrise Experiment conducted from February to April 1988. Reactions in the lower troposphere influencing the oxidation of sulphur and nitrogen oxides, the destruction of lower tropospheric ozone and the production of particulate bromine originating from marine organobromides are indicated.

(paper to be presented at the Second International Conference on the Scientific Application of Baseline Observations of Atmospheric Composition, Australia, Nov. 14-18 1988)

SEA AIR EXCHANGE OF SULFUR, PHOSPHORUS AND NITROGEN IN MARINE AEROSOLS OVER THE ANTARCTIC PENINSULA WATERS

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This paper studied the marine aerosols collected from the Pacific and the Antarctic Peninsula atmosphere. The result shows that the mean Na^{+}/Mg^{++} ratio of the marine aerosols is 8.5 close to the seawater figure of 8.6, suggesting the sodium and magnesium would derive from seawater. Contents of sulfur, phosphorus, and nitrogen in marine aerosols over the Antarctic Peninsula waters would be mainly controlled by natural cycling, such as sea-air exchange, biosphere-atmosphere exchange, weathering-atmosphere transport, or photochemical reactions. Non sea salt sulfate (nss SO_4) in the Antarctic Peninsula atmosphere can be traced to dimethylsulfide (DMS) produced from marine organism activities, which can be oxided into SO_2, and sulfate in the atmosphere. Its recycling flux is 2.6 μg S/cm² yr. Most of nitrate found in the south ocean aerosol have uniform concentrations, which can be explained as due to HNO_3 from lightning, through gas-particle transformation on the aerosol surface. Flux of nitrogen from air to the Antarctic Peninsula waters is 0.57 μg N/cm² yr, providing a stable input of nitrate to seawater for marine living. Water soluble phosphorus was found much higher concentrations in the Antarctic Peninsula aerosol, a flux of 0.12 μg P/cm² yr to seawater. Their sources can be majorly attributed to a long distance transport of dust from desert in the southern hemisphere. The organic phosphorus shows a significant correlation with Na, indicating the major organic P in the marine aerosol may be from seawater.

Short Term Variations of Atmospheric Carbon Dioxide at the South Pole

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Atmospheric carbon dioxide (CO_2) concentration at the South Pole has been measured by an in situ non-dispersive infrared analyzer since 1975. A previous analysis of the data from 1975-1982 had concluded that CO_2 variations occuring over periods shorter than 5 days were not significant. Recent improvements in the measurement precision have prompted an analysis of the short term variations in the CO_2 concentrations measured during 1986. This analysis revealed seven periods, lasting from 2.8 to 7.5 days, of significant CO_2 anomalies (0.2-0.3 ppm) with respect to a curve obtained by digitally filtering the data.

The CO_2 concentrations during these periods are often highly correlated with variations in O3, aerosol light scattering, condensation nuclei, and temperature. In addition, the CO_2 variations at the surface are associated with the occurrence of warmer air at the 650-600 mbar level and, especially during winter, with a weakening or complete breakdown of the surface temperature inversion. These results, combined with a previously established connection between aerosol light scattering and transport of marine aerosols to the South Pole, suggest that anomalies in CO_2 concentration at the South Pole are associated with transport, from lower latitudes, of air that has had a recent marine influence.

These results provide the first evidence linking small but significant variations in atmospheric CO_2 concentration at the South Pole to synoptic scale air mass changes. Further, the occurrence of negative CO_2 anomalies in austral summer and positive anomalies in winter, associated wtih transport of marine air, is consistent with recent results from a 2-D model showing the southern oceans to be a CO_2 sink during summer and a CO_2 source during winter.

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SEASONAL AND LATITUDINAL EMISSION ESTIMATES FOR CH_4 AND CO DERIVED WITH A 2-D MODEL

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Abstract: Observed CH_4 (Steele et al.) and CO distributions (Dianov-Klokov et al.) have been introduced in a two-dimensional photochemical model of the troposphere to make estimates of their seasonal and latitudinal distributions. Additionally, an attempt was made to derive information on the source terms of these trace gases, such as from the tropical and high latitude wetlands and rice fields for CH_4, and natural hydrocarbon oxidation for CO.

A SIMPLE MODEL FOR AIR/SNOW FRACTIONATION OF AEROSOL COMPONENTS OVER THE ANTARCTIC PENINSULA

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Aerosols collected at three remote sites on the Antarctic Peninsula have been investigated using bulk chemical analysis and scanning electron microscopy. Accurate trace element concentrations have been determined and the general physical characteristics of marine, crustal and sulphate aerosol components have been identified. Analyses of fresh snow from the same site has shown that air/snow fractionation of these components occurs, with marine aerosols being removed most efficiently, followed by crustal material, then sulphate. These results contrast with measurements made at the South Pole, where crustal aerosols are removed more efficiently than the marine component.

Understanding this fractionation is of great importance to snow chemists trying to compare the composition of snow from different sites, or to interpret changes along an ice core in terms of changes in atmospheric aerosol composition. However, few attempts have been made to model the aerosol removal processes which are important in clean polar air. Those models which do exist cannot predict fractionation as they do not distinguish between the different physical characteristics of the various aerosol components.

A simple model for removal processes is set up here, using observed aerosol characteristics and measured air and snow concentrations. The model indicates that wet removal is more important than dry deposition for all aerosols of significant mass. However, whilst crustal aerosol may be removed by nucleation of snow and ice crystals and below cloud scavenging, sea-salt and sulphate components are principally removed by riming. Differences in the relative importance of these processes may account for the different aerosol removal efficiencies found over the Peninsula and at the South Pole.

LOWER TROPOSPHERIC TRANSPORT OVER THE SOUTHERN OCEAN

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Radon and particle concentrations during 1987 at Macquarie Island, half-way between Australia and Antarctica, and at Cape Grim in Tasmania's north-west coast, are examined.

Ninety-six hour back trajectories based on twelve hourly analyses over the Australian region are used to explore transport of continental material across the Southern Ocean. This study suggests that at least twenty-five percent of the variance of radon at Macquarie Island can be accounted for by meridional transport from the Australian continent.

Back trajectories at intervals of one hour are used to demonstrate the agreement between episodes of trajectories passing over the Australian continent and episodes of elevated radon concentration. Trajectory errors are discussed.

Wind roses are compared with back trajectories in their efficiency at depicting episodes of continental air incursion.

A simple synoptic model associated with significant transport across the Southern Ocean is suggested.

VERTICAL PROFILES OF NO IN THE FREE TROPOSPHERE BASED ON STRATOZ III

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Using a chemiluminescent detector, vertical profiles of NO were measured during the STRATOZ III mission from June 4 to June 26, 1984. They cover the latitudes between 60°N and 60°S and the altitudes between 0 km and 12 km. The continental profiles in the northern hemisphere and in the tropics exhibit a C-shaped profile with high NO concentrations in the planetary boundary and in the upper troposphere.

Comparison of the latitudinally averaged vertical NO profile with those of C_2H_4 and C_3H_6 from STRATOZ III indicates that fast vertical transport - presumably by convective clouds - must be responsible for the high NO concentrations in the upper troposphere. Downward transport of NO_y from the stratosphere is a minor contribution. A 1D-model with a simple stochastic cloud transport reproduces the observed profiles of NO and allows one to deduce further details of the transport.

Halocarbons F12 and F11, and nitrous oxide measurements from NOAA/GMCC baseline observatories since 1977.

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This talk will describe atmospheric measurements of halocarbons F12 (CCl_2F_2) and F11 (CCl_3F), and nitrous oxide (N_2O) from NOAA/GMCC baseline stations at Point Barrow, Alaska, Mauna Loa, Hawaii, American Samoa, and South Pole, Antarctica and Niwot Ridge, Colorado from 1977 to the present. The NOAA/GMCC program began modestly in 1977 by collecting a pair of flasks each week at every station and shipping the flasks back to the Boulder lab for analysis by electron capture-gas chromatography (EC-GC). In situ gas chromatographs were installed between 1986 and 1987 at all NOAA/GMCC baseline stations under the Radiatively Important Trace Species (RITS) program. The goal was to provide higher time resolution (once every three hours) for measurements of these RITS gases, because of their importance in maintaining both the equilibrium concentration of stratospheric ozone and the radiative budget of the earth's atmosphere.

A precise method (±0.1-±0.2% 1sd) for atmospheric N_2O analysis which involves backflushing a pre-column and EC-GC, will be presented. High precision is required for the analysis of atmospheric N_2O since the average growth rate is about 0.2% per year and the interhemispheric difference is less 0.3%. The method also has been shown to improve the precision of F12 and F11 measurements, and may be useful for other electrophillic gases.

A comparsion of our station data to measurements by other researchers will be discussed. Measurements of these RITS gases from the Soviet-American Gas and Aerosol (SAGA-II) experiment aboard the Soviet research ship, Akademik Korolev, during the El Niño-Southern Oscillation event of 1987 will be presented. During this cruise, a pollution event with elevated levels of N_2O, F12 and F11 from an air mass originating over the populated southeastern region of Australia was observed over 500 km away from the source.

Calculations of the atmospheric lifetimes for F12 and F11 will be presented using data collected by NOAA/GMCC. A global budget for N_2O and the role of the ocean as a source for atmospheric N_2O will be highlighted.

ATMOSPHERIC CONSTITUENT INVERSION PROBLEMS: IMPLICATIONS FOR BASELINE MONITORING

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Poorly-conditioned inverse problems are extremely common in atmospheric constituent studies because observations of concentration data yield only indirect information about the source and sink processes that are of most interest. Because of the relatively recent growth in the field of atmospheric chemistry, there has been relatively little systematic investigation of these inverse problems. In the CSIRO program of studying long-lived atmospheric constituents we have taken two approaches in the investigation of relevant inverse problems. The first approach is that in our use of numerical models we aim to take into account the poorly-conditioned aspects of the various problems. We explicitly consider the sensitivity to data errors and attempt to estimate the inherent limitations on resolution that may arise in such inversion problems. Examples of such work using numerical models are given by Enting and Pearman (1987) and Enting and Mansbridge (1989).

The second approach is to consider simplified models for which analytic or semi-analytic solutions can be obtained so that we can specifically analyse the properties of the inverse problems. A simple example involving deconvolution problems is given by Enting and Mansbridge (1987). We have recently been engaged in a series of studies concerning determination of the spatial distribution of sources and sinks of atmospheric constituents. (Newsam and Enting, 1988,1989; Enting and Newsam, 1989).

In these studies we have used a purely diffusive model of atmospheric transport. Our first studies concerned the determination of surface sources from surface concentration data. We found that this inverse

problem exhibited a degree of noise amplification linear in n, the meridional wave-number. (This result is in agreement with the studies using a two-dimensional numerical model, thus giving some confirmation that relevant results can be obtained using a purely diffusive model of transport). If we were attempting to invert vertically-averaged data to determine surface sources then the noise amplification would grow as n^2 as is found in vertically-averaged models (Bolin and Keeling, 1963). Thus it seems that the main source of errors and instabilities in the use of vertically-averaged models is not so much the poor representation of atmospheric transport involved in a one-dimensional diffusive model but rather the errors involved in equating surface concentrations to vertically-averaged concentrations. We have proposed a simple correction procedure for one-dimensional models in order to reduce such errors.

Another important aspect of the determination of surface sources from surface concentration data is the extent to which the results are sensitive to vertical transport process, vertical resolution and the treatment of the lower boundary. Again this result arises from both our analytic and numerical studies (see also Tans et al., 1989). This sensitivity has serious implications for the interpretation of baseline concentration data because a correct interpretation of such data will require a detailed description of the vertical transport in the region of the observing site so that the surface concentration data can be correctly related to concentrations in the free troposphere.

Our most recent studies have considered the determination of sources and sinks in the free troposphere, with particular emphasis on sinks involving oxidation by OH. Our analytic studies confirm that, as might be expected, given only two-dimensional surface data we can only determine two-dimensional projections of the OH sink. These projections take the form of weighted vertical averages over components expressed in terms of their horizontal or temporal variation. The greater the variability the more the weighted average is biased towards the surface.

In spite of the fact that we cannot determine the full vertical dependence of the OH sink from a knowledge of both surface concentrations and surface sources (as we have, with low resolution, for CH_3CCl_3), the information is still sufficient for use as a 'correction term' when calculating the influence of the OH sink on compounds such as CH_4. While CH_3CCl_3 data give only a set of weighted averages of components, these weighted averages

are essentially the same ones that are needed to calculate the effect of the OH sink on surface concentrations of CH_4. Thus we can determine the surface sources of CH_4 by inverting surface CH_4 concentrations after applying a correction based on CH_3CCl_3 data. In practice the main limitation will be the low resolution with which the CH_3CCl_3 data are known. Some preliminary results of such a calculation are presented by Fraser et al. at this meeting.

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SOME APPLICATIONS OF KALMAN FILTERING IN ANALYSING BASELINE ATMOSPHERIC CONSTITUENT DATA

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The use of Kalman filtering in atmospheric constituent studies is relatively recent. The main applications have been the studies of monthly mean CO_2 data by Surendran and Mulholland (1986,1987). The formalism is potentially very powerful. One of the most important characteristics is the ease with which non-stationary processes can be treated. The method also automatically calculates the variances of its various estimates. The formalism is built round the concept of a state-space model which describes the statistics of the time series in terms of a state that evolves auto-regressively in time. The observed time series is regarded as a combination of various components of the state. An important example of this is when two components (x_1 and x_2) represent the secular trend and seasonal cycle. The observed time series is regarded as a sum of these two components (plus noise). The Kalman filtering formalism produces estimates of the state vector and so in this case it would produce (simultaneous) estimates of the seasonal cycle and secular component. The estimates can be obtained in real-time, i.e. the secular component and cycle at time t can be estimated using observations for times $t' \leq t$. However better estimates can be obtained by taking lagged estimates that used data for times $t' \leq t + L$. For the problem of separating secular terms from seasonal cycles using monthly data, lags of $L = 6$ months are appropriate as in non-recursive filtering (Enting and Robbins, 1989).

When analysing monthly mean data, one of the main types of non-stationarity that can occur is through missing data. The recursive filtering formalism can adapt to such non-stationarity and the variance of the estimates increases when data are missing, reflecting the loss of information on which to base the estimates.

We present examples of such applications of Kalman filtering in the analysis of methane from the CSIRO flask sampling program. (Further details of the methane data and our analyses are presented at this meeting by Fraser et al.).

One problem in time series analysis for which Kalman filtering may be particularly appropriate is in the selection of baseline data. Examination of data such as hourly mean CO_2 concentrations from Cape Grim shows that the data record is episodic and cannot reasonably be treated as statistically stationary. We present some preliminary attempts at modelling the Cape Grim hourly mean CO_2 data in terms of a baseline level plus episodic perturbations associated with particular meteorological conditions, and show the estimated baseline concentrations.

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TOTAL OZONE, OZONE VERTICAL DISTRIBUTIONS, AND STRATOSPHERIC TEMPERATURES AT THE SOUTH POLE, DURING 1986, 1987 AND 1988

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Total ozone decreased over the South Pole to a record low of 127 Dobson Units (DU) in early October 1987 compared with 160 DU in October 1986. ECC ozonesonde soundings made during both years showed the ozone depletion at 11-23 km in 1987 to be greater in vertical extent and magnitude, and to proceed more rapidly. By early October 1987, virtually all ozone was depleted from a 4 km thick atmospheric layer centered at 17 km. Because of a three-week delay in the time of the polar vortex breakdown in 1987 compared with 1986, stratospheric temperatures in the heart of the ozone deletion region were 10-40° colder in the mid-to-late November 1987. Preliminary results from the 1988 ozone hole season also will be presented.

AUREOLE MEASUREMENTS TO DETERMINE AEROSOL OPTICAL DEPTH AT CAPE GRIM

Bruce Forgan
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The measurement of optical depth by sunphotometers has attempted to give the research community an indication of aerosol transmission through the atmosphere. To a large extent it has failed in the Southern Hemisphere where the error of measurement is larger than the typical aerosol optical depth. Furthermore, these simple, but inaccurate measurements do not indicate important properties, for example, size distribution and single scattering albedo. Aureole measurements have been used in the past to determine aerosol size distributions but have required sophisticated instruments, models and mathematical techniques as determine physical properties of aerosols.

Simple instruments and techniques based on sunphotometry and developed at Cape Grim BAPS, have significantly improved the accuracy of low level aerosol optical depth determination. In addition, the obtained data are capable of monitoring single scattering albedo and with additional computation, aerosol size distribution. These simple methods will be described briefly, and the implications of using then will be investigated by examining the data record from Cape Grim. The annual variation in aerosol optical depth, single scattering and size distribution at Cape Grim BAPS, as derived from a year's data, will be described.

Oxygen Isotopes of CO_2

R J Francey[1] and P P Tans[2]

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ABSTRACT

The study of oxygen-18/oxygen-16 ratio in atmospheric CO_2 has been largely neglected. Three CSIRO programs have been accumulating information on this ratio:

(1) in situ CO_2 collection at Cape Grim since 1982;

(2) air collection in 5 litre flasks from the surface BAPMoN stations of South Pole (90°S), Cape Grim (41°S), Samoa (14°S), Mauna Loa (20°N) and Pt. Barrow (71°N) since early 1984. Supplementary collections have started from Mawson (68°S), Macquarie Is (54°S), Niwot Ridge (40°N) and Alert (81°N); and,

(3) air collections in 5 litre flasks from aicraft over SE Australia since 1985.

The data are a by-product of measurement of the carbon-13/carbon-12 ratio in atmospheric CO_2, a primary objective of the programs. The CSIRO programs are unusual in that water vapour is removed at the point of collection.

The $\delta^{18}O$ data exhibit a strong pole to pole gradient, with marked seasonality which varies in both amplitude and phase (with respect to season) between the hemispheres. Marked secular variation on a timescale of several years is also already evident.

Attempts to explain the data have centered on mechanisms involving hydration of CO_2, permitting oxygen exchange between the CO_2 and H_2O. The slow exchange rate appears to exclude the most obvious sources of water (oceanic or atmospheric) as sources of the temporal and spatial variations. One mechanism, involving catalysed CO_2 exchange with leaf water, is identified as a prime canditate which can contribute to the gross spatial features of the observations.

However, one-dimensional box modelling and two-dimensional source deductions both reveal the inadequacy of this mechanism as a sole explanation for the surface observations. In addition, the vertical $\delta^{18}O$ profiles in CO_2 over SE Australia, clearly suggest another exchange mechanism. We hope to have some suggestions by the time of the talk!

METHANE IN THE SOUTHERN TROPOSPHERE

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We describe the CSIRO methane flask sampling program and present the results through to June 1988. Flask samples have been obtained from Cape Grim, Tasmania, since April 1978, from Mawson, Antarctica since March 1980 and from our aircraft program since October 1980. This sampling network has been augmented by measuring CH_4 in flasks collected for the DAR stable isotope program since late 1983 or early 1984. These flasks are obtained from the South Pole, Samoa, Mauna Loa and Barrow. We are able to compare our results for these sites to results from the NOAA/GMCC program. For Cape Grim we can compare our results to both the NOAA/GMCC and OGC data. In each case the differences are small but some appear to be statistically significant. Our sampling network has been extended to include Macquarie Island (since February 1986), Jabiru (inland Northern Territory) since January 1987, and intermittent sampling on the Great Barrier Reef since May 1985.

The time series have been analysed by a variety of techniques. Regression analyses in terms of a polynomial secular term, and a Fourier expansion of the seasonal cycle have been performed for all data sets. The trends and cycles have also been analysed using digital filtering. These techniques provide estimates that include the interannual variability in the trends and cycles. Two types of filtering have been applied to the methane data. Firstly fixed-length filters (chosen to be asymmetric to reduce data loss from the ends of the records) were used. Secondly a recursive (Kalman filtering) approach was used. This approach is relatively new in atmospheric constituent studies and some of the motivation and technical details are described in a companion paper at this conference.

In each case the analysis indicates a general decrease in the growth rate of methane. The interannual variation in the seasonal cycles do not seem to show any globally coherent behaviour.

Some preliminary modelling studies are presented.

Scientific Application of Baseline Observations of Atmospheric Composition, Melbourne, Australia, Nov. 14-18, 1988.

Long term and seasonal variations of atmospheric CO_2 concentrations at Amsterdam Island (Territoire des Terres Australes et Antarctiques Françaises).

by A. Gaudry, P. Monfray, G. Bonsang, G. Polian and G. Lambert.

Summary:

Atmospheric carbon dioxide has been monitored at Amsterdam Island since October 1980. Variations due to local sources are small at this isolated location and can easily be discarded, according to meteorological criteria.

Remaining variations are particularly smooth, compared to most of the other baseline stations. However, two main non-random variations can be observed. First, in 1982/1983, an exceptional El Nino/Southern Oscillation (ENSO) occurred. It was preceded, during the period January 1981 to October 1982, by a short but clear decrease in the CO2 increase rate. This was followed by a rapid and significant increase of the increase rate from November 1982 to October 1983,and then a return to usual values, from November 1983 to the present.

Such an infrequent event is able to modify the seasonal variations. At Amsterdam Island, in addition to the normal late winter maximum in August of 0.4 ppm, a secondary maximum is usually observed in austral summer (December to February). Because we have a simultaneous record of the continental tracer ^{222}Rn, it is possible to show that, for a low recent continental influence ($Rn < 1 pCi/m^3$), this secondary maximum was enhanced.

If the record corresponding to the ENSO event period (November 1982 to October 1983) is discarded, the global feature is practically unchanged, if only data from times of low recent continental influence are considered. The ENSO event did not notably change the magnitude of the secondary maximum, when the recent continental influence was low. By contrast, for a time of strong recent continental influence, the ENSO resulted in a decrease of the secondary maximum, i.e. an effect which could be compared to smaller CO_2 emissions from the continental vegetation.

These results will be compared to a 3D GCM model of seasonal variations developed by M. Heimann.

Baseline atmospheric condensation nuclei at Cape Grim 1977-1987.

J.L.Gras

CSIRO Division of Atmospheric Research

Abstract

The meaning of "baseline" in relation to measurements of CN at sites such as Cape Grim is discussed and the idea that a "baseline" applies only in a statistical sense advocated. Use of the concentration frequency-distribution geometric-mean is proposed as the best measure of CN concentrations. Variations in CN concentrations at Cape Grim for periods greater than twelve months are derived by Kalman filtering the monthly estimates of geometric mean concentration obtained from 1977 to 1987. Significant variations are shown to be present on this time scale with quasi-periodic oscillations in concentration. Linking of major fluctuations to El-Nino Southern Oscillation perturbations in the regional circulation is suggested.

BASIS FOR INTEGRATION OF CONVENTIONAL OBSERVATIONS OF CLOUD INTO GLOBAL NEPHANALYSES

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Paper proposed for Scientific Application of Baseline Observations of Atmospheric Composition (SABOAC) meeting, November 14–18, 1988, Melbourne

Abstract

Water vapour is the largest and, radiatively, the most important trace gas in the Earth's atmosphere. Cloud amount and cloud optical depth feedbacks are, as yet, poorly understood and improvements in model parameterization schemes await an adequate observational data base. Satellite retrievals do not, and will not for some time, provide more than "snapshot" (a few months to a few years) records. Conventional surface-based observations of cloudiness could complement the global coverage offered by satellite retrievals if a sound relationship between the two observational measurements could be found. Observations underline the importance of the vertical dimension of clouds which affects the observational geometries from satellites and the surface. A new basis for the relationship between the (vertical) earthview of cloud amount and the (whole dome) skycover of cloud amount has been sought. Over six thousand eight hundred all-sky camera photographs, representing a considerable range of seasonal and climatological conditions, have been analyzed to give rise to a database from which predictive relationships for earthview, E, and skycover, S, have been established.

Cubic functions are the most soundly based both physically and empirically. We find:

$$S = 0.574 + 2.406\ E - 0.523\ E^2 + 0.042\ E^3$$

and

$$E = 0.004 - 0.014\ S + 0.299\ S^2 - 0.021\ S^3$$

for the prediction of skycover from earthview and earthview from skycover, respectively. If earthview is required from skycover observations then $E \simeq S$ could be used with little additional error. Hence conventional surface observations of skycover could be compared directly with satellite-derived earthview values. More importantly, these results do not support the widespread assumption that conventional (surface) observations of cloud amount always exceed the earthview cloud retrieval. Furthermore, climate model predictions of total cloud amount may also be interpreted *via* these relationships. GCM-predicted layer cloud amounts can be synthesized into "modelled E" values using the random overlap formula and hence it is possible to construct "modelled S" values which are directly comparable with conventionally observed cloud climatologies. The "baseline" observation of skycover by clouds therefore provides a valuable validation tool for both satellite programmes and climate models.

A TIME SERIES ANALYSIS OF CO_2 DATA FROM CANADIAN BAPMON STATIONS

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Abstract not received, check late Abstracts section.

CHEMICAL COMPOSITION OF RAINWATER AT TSUKUBA AREA, JAPAN

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In order to know the scavenging and chemical processes by/in atmospheric water droplets which are important informations for understanding the phenomenon of acid precipitation, chemical analyses were performed on 408 sequential precipitation samples, collected at Tsukuba (80 km northeast of Tokyo, a relatively unpolluted area), during the period from September 1984 to March 1986. The collection was done with an automated rainwater sampler equipped with pH and conductivity meters. The chemical species analyzed and the volume-weighted average concentrations (μM) were: H^+ (41.7), SO_4^{2-} (19.4), NO_3^- (22.0), Cl^- (28.6), NH_4^+ (40.1), Na^+ (13.2), Ca^{2+} (5.4), Mg^{2+} (4.2) and reactive species of H_2O_2(1.4) and SO_2 aq. (0.32). The concentrations of trace metal elements (Fe, Mn, Ni, Zn, Ba, Sr, Si, V, Cu and Pb) were also determined. From principal factor analysis of the data, both natural and anthropogenic components were identified (the contribution of soil dust was larger than the others). The seasonal change in the concentrations of the chemical species was discussed in terms of the change in meteorological conditions (air flow direction, solar and rainfall intensities etc.). H_2O_2 concentration showed a strong diurnal variation with a maximum in the afternoon. The maximum H_2O_2 concentration and the minimum SO_2.aq one were observed in sunny seasons. These observations suggest that the production of H_2O_2 may be controlled by photochemical activity and H_2O_2 may play a significant role in oxidation of SO_2 in raindrops. By seeing relationships between the trace metal elements and SO_4^{2-} concentrations, the importance of Fe and Mn catalyzed oxidation of SO_2 is also suggested.

RAINWATER AND AEROSOL METHANESULPHONATE AT CAPE GRIM

J. Ivey

AGAL, Kingston, Tasmania

Abstract not received, check late Abstracts section.

ABSTRACT for SABOAC II meeting, November 14-17, 1988, Melbourne

MID-CHAIN KETOCARBOXYLIC ACIDS IN MARINE AEROSOLS FROM THE NORTH PACIFIC

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During a gas chromatographic and mass spectrometric study of organic compounds in marine aerosols obtained from SEAREX North Pacific cruises, we discovered a series of previously unreported mid-chain ketocarboxylic acids in a range of C6-C15 with a maximum generally at C11. These ketoacids showed the isomeric distributions with a keto group at different positions. The most abundant species was 5-oxoundecanoic acid. These ketoacids were sometimes dominant organic compound class identified in the marine aerosols, being more abundant than fatty acids and n-alkanes: ketoacid concentrations ranged from 0.04 to 19 ng/m3.

The characteristic distribution pattern of ketoacids has not been detected in conceivable source materials of aerosols, including terrestrial higher plants, soil particles and marine organisms. We consider that isomeric mid-chain ketocarboxylic acids are produced in the atmosphere by photochemical oxidations of certain precursors including semi-volatile saturated monocarboxylic acids which can be derived from the atmospheric oxidation of biogenic unsaturated fatty acids.

CARBON ISOTOPES IN NEW ZEALAND AIR

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Some uses of carbon isotope measurements in trace gases are discussed briefly. Excess C-14 in CO_2 from nuclear weapons testing shows a seasonal cycle at the surface that is due to seasonal variation in transport from the stratosphere to troposphere. The phase and amplitude of this cycle places constraints on upper atmosphere transport used in global circulation models. C-14 measured in methane allows a determination of the amount of methane generated by fossil carbon sources. Recent data show this fraction to be around 30%, however the interpretation is complicated by C-14 methane produced by nuclear power plants.

THE INTERPRETATION OF BASELINE MEASUREMENTS USING BACK TRAJECTORIES

J. Miller, G. Herbert and J. Harris

Air Resources Laboratory, NOAA

The use of single back trajectory calculations to interpret atmospheric chemistry has become widespread. Particularly, this technique has been employed at baseline sites such as Mauna Loa, HI; Barrow, AK; American Samoa; Amsterdam Island and others. In this presentation, we will discuss the following:

1. Examples of more recent back trajectory results using both manual and statistical methods.

2. The use of trajectory analysis during the AGASP program at Barrow, Alaska.

3. A new approach to trajectory calculations which employs fields generated by a numerical forecast model.

SABOAC II

"Scientific Application of Baseline Application of Atmospheric Composition"
Melbourne (Australia), November 14-18, 1988

SEASONAL VARIATION OF ATMOSPHERIC DIMETHYLSULFIDE AT AMSTERDAM ISLAND IN THE SOUTHERN INDIAN OCEAN

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ABSTRACT

Daily mesurements of atmospheric dimethylsulfide (DMS) were made for two years in a marine site at remote area: the Amsterdam island located in the southern Indian Ocean (37°47'S -77°31'E). DMS concentrations were also measured in sea water. A seasonal variation is observed for both DMS in the atmosphere and in the sea-surface. The monthly average of DMS concentrations in the surface coastal seawater and in the atmosphere varied respectively from 0.3 to 2.0 $nmol.l^{-1}$ and from 1.4 to 11.3 $nmol.m^{-3}$ (34 to 274 pptv), with the higest values in summer. The monthly variation of sea-to-air flux of DMS from the southern Indian Ocean ranges from 0.7 to 4.4 $\mu mol.m^{-2}.d^{-1}$.

PROPOSED APPLICATIONS OF LIDAR AT CAPE GRIM

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2. Tasmanian Development Authority, Hobart, Tas, 7000, Australia.

A low-energy large-aperture lidar will be deployed shortly at Cape Grim to measure profiles of aerosols and clouds. The height distribution of aerosol backscatter in the atmospheric boundary layer and the inversion height, will be used to compare with the total measured aerosol optical depth, making allowances for stratospheric aerosol.

An international experiment, the Experimental Cloud Lidar Pilot Study (ECLIPS) will take place over designated periods in 1989/1990, and the Cape Grim lidar will also be deployed in this study. The lidar can detect high cirrus clouds because of its large aperture. The ECLIPS will be described briefly.

The lidar is a prototype which is being developed by Tasmanian Companies in collaboration with CSIRO, DAR, with support from the Tasmanian Development Authority, CSIRO and the Cape Grim Baseline Station.

ATMOSPHERIC TRENDS AND EMISSIONS OF NITROUS OXIDE DEDUCED FROM NINE YEARS OF ALE-GAGE DATA

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We present and interpret long-term measurements of the chemically and radiatively important trace gas nitrous oxide obtained during the Atmosphere Lifetime Experiment (ALE), and its successor the Global Atmospheric Gases Experiment (GAGE). The ALE/GAGE data for nitrous oxide comprising over 90,000 individual calibrated real-time air analyses carried out over a nine-year (July 1978 - June 1987) time period indicate a global average linear trend in N_2O of $0.30 \pm 0.09\%$ year^{-1} (2σ) with the increase accelerating at a rate of about 0.03% year^{-2} in this period.

Interpretation of the data using inverse theory and a 9-box (grid) model of the global atmosphere indicates that the measured trends and latitudinal distributions are consistent with the hypotheses that stratospheric photodissociation is the major atmospheric sink for N_2O and that the temporal N_2O increase in caused about equally by increases in anthropogenic N_2O emissions associated with fossil fuel combustion, and agriculturally-related biomass burning and resultant soil disturbance. Our data suggest comparable contributions by biomass burning and fossil fuel combustion contrary to some previous ideas. Accepting the theoretically-calculated N_2O lifetime of 166 ± 16 years due to stratospheric destruction only, we deduce from the ALE/GAGE data a 9-year average global N_2O emission rate of 20×10^{12} gm N_2O year^{-1} but with anomalously large (25-35% larger) emissions in the 1981-82 and 1984-85 time periods associated perhaps with enhanced tropical wildfires.

GLOBAL MEASUREMENTS OF TOTAL OZONE - WINTERTIME LOSS IN THE NORTHERN HEMISPHERE

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Total column ozone data over the past 22-30 years from ground-based Dobson stations between 30°N and 64°N have been analysed for residual trends after allowance for ozone cycles with the seasons, the QBO and the 11-year sunspot cycle. Multiple regressions have been calculated from about 30 individual Dobson stations, and for latitudinal band averages covering three latitude ranges from 30°N to 64°N. The residual linear trends show a measurable decrease in the annual average total column ozone of 1.7% to 3.0% from 1969 to 1986 in all latitude bands from 30°N to 64°N. The decreases are largest in the winter months (2.3% to 6.2%) of December through March, and contrast with smaller losses (-0.2% to -1.9%) in the summer (May through August).

The winter/summer differences are especially large in the two most northerly bands. An obvious possibility is that the wintertime losses are enhanced through heterogeneous chemical processes analogous to those found in the Antarctic ozone hole. In contrast to the tight polar vortex in the south, the Arctic air masses tend to pass through the polar night and back into sunlight again. Any chemical effects causing ozone depletion in the Arctic winter would therefore be distributed over a much larger total volume of air than in the Antarctic.

Previous statistical analyses have been conducted as tests of one-dimensional model calculations and have not considered possible winter/summer differences. Our statistical analyses have treated each set of monthly values (i.e. all values for January) as a separate data group for trend determination.

THE SEASONAL CYCLE OF C_2 AND C_3 HYDROCARBONS IN THE SOUTHERN HEMISPHERE

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During a four year period, measurements of light nonmethane hydrocarbons were made at the German Antartic station at 70°36'S and 8°22'W. The average mixing ratios were 370 ppt for ethane, 360 ppt for ethene, 11 ppt for acetylene, 70 ppt for propane, and 210 ppt for propene. Acetylene and ethane showed a clear seasonal cycle with highest mixing ratios in late austral summer and minimum values during late southern hemispheric winter. These seasonal variations can be explained by the change of the atmospheric removal rates with season. But the seasonal variation of one of the major sources for ethane and acetylene, namely biomass burning, could also qualitatively explain the observed seasonal variations.

The more reactive alkenes also exhibit a seasonal cycle but their maximum mixing ratios are observed in early fall. In addition they show a rather large variability. Most probably the observed ethene and propene mixing ratios are the result of oceanic emissions in the vicinity of the Antarctic station. The seasonal cycle of propane shows no clear maximum. Tentatively this can be explained by the combined effects of the seasonal cycles of atmospheric removal and source strength.

Trace Gas Measurements at the Monitoring Station "Cape Point", South Africa

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Abstract:

Beginning in 1978, a measuring station has been built up at Cape Point (34°21'S, 18°29'E). It now permits monitoring of the concentrations of CO, CH_4, N_2O, O_3, $CFCl_3$, CH_3CCl_3, and CCl_4. Most recently the program has been expanded to measurements of NO and NO_y. Location and instrumentation of the station are described as well as the procedure of data processing. The results obtained are presented in form of monthly means. Data are discussed with respect to long-term trends and seasonal variations of the trace gases. For CO and CH_4 very similar seasonal variations have been observed, indicating interrelations between these two gases. For CO and O_3 no significant changes of the mean annual concentrations can be established for the observation periods of 10 and 5 years, respectively. The concentrations observed for $CFCl_3$ and N_2O yield a time-constant rate of increase. The increase rates obtained for CH_4 and CCl_4 are analyzed for temporal changes during the last years.

STUDY OF HYDROGEN PEROXIDE IN ATMOSPHERE

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Hydrogen peroxide (H_2O_2) concentrations were measured at two sites. One was in Lushan Mountain in May 1987. The other was in Beijing in August 1987 and in December 1986. The Automated Fluorometric Method was used for analyzing hydrogen peroxide. The concentrations of hydrogen peroxide ranged from approximately 0.50 to 4.32 ppb on Lushan Mountain. The concentrations of hydrogen peroxide ranged from approximately 0.05 to 1.49 ppb in August in Beijing. There was only 0.01 ppb H_2O_2 in December in Beijing.

STUDY OF AEROSOL ON TIBET PLATEAU AND IN OTHER CLEAN AREAS IN CHINA

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On Peak Southern Jiabava (Tibet Plateau), Lushan Mountain (province Jiangsi), Changjiajie (Province Hunan), Flower Mountain and Shangdianzi (Beijing, Near Great Wall), aerosol samples have been collected by using cascade samplers. For comparison aerosol samples from Beijing City, Pacific Ocean and Southern Pole also have been collected. Samples were analyzed with PIXE or XFA instruments. For further utilizing observation data factor analysis and enrichment factor calculation were performed to process the data.

It has been found that on Tibet Plateau the aerosol is not polluted too much, its sulfur and silica contents are relatively lower than that at other clean areas, although a little higher than that in Southern Pole and on Pacific Ocean, Lushan Mountain and Changjiajie are relatively clean too. As a tracer element for pollution sulfur exits mainly in coarse particles and has a high enrichment factor (EF) of about 190, but for fine particles EF of sulfur is low. This shows that particles in Tibet and some clean areas do not contain much new product of atmospheric reaction but mostly aged particles. The results of factor analysis shows that the main source of particles at clean area is from earth crust since in the first factor Si, Ca, Ti, Fe have high loadings. The other source of particles is the primary and secondary air pollutants of human activities since the loadings of S and Pb have their maxima in the second factor.

ATMOSPHERIC CO_2 CONCENTRATIONS DURING AND FOLLOWING THE 1987 EL NINO.

K.W. Thoning , T.J. Conway , P.P Tans , and J.T. Peterson

ABSTRACT. Measurements of atmospheric CO_2 concentrations from weekly flask samples taken at several NOAA/GMCC flask sampling sites from north polar to south polar latitudes and from three continuous in-situ infrared CO_2 analyzers (located at American Samoa; Barrow, Alaska; and Mauna Loa Observatory, Hawaii) showed a larger than expected increase in concentrations during the end of 1987 and the first part of 1988. The growth rates of CO_2 during that time were computed by removing the seasonal cycle at each station with a series of yearly harmonic terms and a low pass Fourier Transform filter, then computing the derivative of the remaining trend. These rates were found to be near 3 ppm per year, significantly larger than the global average of about 1.4 ppm per year in recent years. These rates also were found to correlate with sea surface temperatures during the El Nino/Southern Oscillation (ENSO) event of 1987, with the largest CO_2 growth rates occurring as the ENSO event was waning. Curiously, although the 1982-83 ENSO event was more significant than the 1987 event in terms of large-scale meteorological effects, the latter event had a greater effect on CO_2 growth rates.

LONG-TERM TRENDS OF TRACE GASES, EG CH_4, CO_2, F-11, F-12 AND F-113 MEASURED AT A REMOTE SITE IN THE NW OF CHINA

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Abstract not received, check late Abstracts section.

RADON DAUGHTER DISEQUILIBRIA IN THE LOWER MARINE BOUNDARY LAYER

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Radon daughters are produced as free ions, but they become attached to aerosol particles at a rate depending on the particle concentration. In the lower marine boundary layer, most of those which do not become attached plate out on the ocean surface. In this paper a simple model is used to examine the influence of several parameters on radon/radon daughter disequilibria in maritime air. The model is compared with experimental data from Cape Grim.

The radon daughter to radon ratio, "f", decreases from 1 to 0.4 as the particle concentration falls from 1000 to 100 cm^{-3}. At 100 cm^{-3}, the standard deviation of the distribution of measured "f" values is about 30%, indicating that the particle concentration is not the only factor influencing the loss of radon daughters. The implication is that radon daughters can be used to measure radon concentrations at sea level with an accuracy of about 30%, provided the particle concentration is known.

The measurements show that there is a very low proportion of unattached daughters in the air between 70 and 165 m above sea level. According to the model, this implies that mixing of air up to about 200 m is usually rapid enough to result in plate-out of radon daughters on the ocean on a time scale of less than 100 s.

MEASUREMENTS OF PHOSGENE ($COCl_2$) AND OTHER CARBONYL COMPOUNDS IN THE ATMOSPHERE

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From an aircraft-based sampling program, we have made a series of measurements of phosgene, $COCl_2$, at high latitudes in the upper troposphere and lower stratosphere using the Matrix Isolation - FTIR spectroscopy technique. The measurements show a mixing ratio of 17 pptv in the upper troposphere, increasing to an average 22 pptv in the lower stratosphere. These values indicate the contribution not only of CCl_4, but also of the more reactive chlorocarbons such as $CHCl_3$, CH_3CCl_3, C_2HCl_3 and C_2Cl_4 to the chlorine chemistry of the lower stratosphere.

The FTIR spectra of these samples also allow the detection and measurement of a number of other species, including the carbonyl compounds COFCl, COF_2, CH_2O and CH_3CHO. Preliminary analyses of these measurements will be briefly presented.

THE IDENTIFICATION AND CHARACTERIZATION OF VAPOUR PHASE ORGANIC POLLUTANTS IN AIR IN BEIJING-TAINJIN REGION

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The organic compounds in air include two kinds of compounds-vapour phase organic compounds and particulate organic materials.It was reported that man made organic vapour phase compounds in all of the world estimated about 7.5*10(13)g per year.It is about 10 to 15 times more than that of particulate organic materials.Recently the research work of VPO has attracted more attention.They pay more attention on trace organic compounds in atmophere.A lot of reports were published about POM.but very few reports about VPO.

In order to understand the components and distribution of vapour phase organic in air in Beijing -Tainjin,we collected the VPO samples in winter of 1983 and in summer of 1984.The analyses of the VPO samples were performed by HP 5880 GC equipped with fused Silica capillary column and Finnigan 4020 GC/MS. and data system.

Late abstracts

(and last minute talks)

SNOW CHEMISTRY ON SOUTHERN PATAGONIA ICE FIELD - A PRELIMINARY STUDY

by Alberto J. Aristarain, Instituto Antártico Argentino and CONICET, Mendoza, Argentina, and Robert J. Delmas, Laboratoire de Glaciologie et Geophysique de l'Environnement, Grenoble, France

Paleoenvironmental data covering the last centuries are scarce in the Southern Hemisphere. For southern high latitudes, various ice cores have been analyzed. For mid latitudes, potential sites for glaciochemical investigations are nearly unexplored. We present the first chemical measurements performed on a shallow ice core drilled on the Southern Patagonia Ice Field (SPIF). SPIF is located at the extreme southern part of South America between 48°20' and 51°30' S. With an area of 13500 Km2, SPIF is the 3rd largest ice cap in the world.

The study site (50°38'S, 73°15'W) is located in the accumulation area of the huge Perito Moreno glacier at an elevation of 2680 m, just at the ice divide between the Atlantic and the Pacific. The drilling operation was achieved in the frame of the French-Argentinian scientific cooperation with the logistical support of the Instituto Antártico Argentino.

A 13.17 m deep firn core was obtained on September 1st 1986. It was stored in a freezer and then subsampled with great precautions in a mountainer hut by operators wearing clean clothes and masks. 45 distinct samples, placed in sealed plastic bags, were transported in a solid state to Grenoble (France), via Buenos Aires and Paris. Aliquots were taken for stable isotope analysis. Chemical measurements were performed at the Laboratoire de Glaciologie et Géophysique de l'Environnement, in clean air conditions by ion chromatography (Dionex 2010) NA^+, Cl^-, $SO_4^=$, NO_3^-, K^+ and NH_4^+ were obtained.

The results indicate that the time period covered by the profile is 5.5 yr (local mean accumulations 1.2 m of water equiv.). The temperature measured on the glacier at 13 m depth is 0°C, which indicates that this glacier is temperate. This conclusion is confirmed by the chemical concentrations which exhibit a decrease as a function of depth, particularly for the acid anions SO_4 and NO_3. For the other elements this effect is less marked.

The mean chemical composition of the upper 5 samples -which represent about 1 yr of precipitation and which suffered little wash out by melting, is the following (in $\mu Eq\,l^{-1}$): Na: 4.86; Cl: 5.48; NO_3: 0.33; SO_4: 1.27, excess SO_4: 0.7

The low nitrate and excess sulphate values seem to be typical of South Pacific areas.

...

The conclusion of this study is that this glacier, even-though located at a relatively high elevation, is not appropiate for glaciochemical measurements of polar type. Nevertheless, the marked seasonal variations which can be observed in the isotope profile encourage further paleoclimatic studies. Profiles of unsoluble particles could also be well preserved at this site, where the thickness of the ice is entirely unknown (may be several hundred meters).

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THE AUSTRALIAN OZONE MONITORING PROGRAM

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The Australian ozone monitoring network was established during the 1950s. It currently comprises five stations, each equipped with a Dobson spectrophotometer and at one of which an ozone sonde program is also conducted. The data from each station are regularly submitted to WODC, Toronto, for publication.

Examination of the Dobson calibration and maintenance records has revealed discrepancies which suggest that the published data do not comprise a reliable record for scientific study.

Since 1983 the network has been progressively upgraded and the Dobson instruments recalibrated by standardised, fully-traceable procedures. More recently, a detailed re-examination of the calibration and maintenance records has commenced, enabling reassessment and correction of some of the earlier data. In the light of this work, the degree of confidence which may currently be attached to each station's data set is discussed.

Corrected data from two of the stations have been analysed and recent ozone decreases are reported and compared with those detected by the NASA Ozone Trends Panel. Also, data from each station are presented which provide the first evidence that during December 1987 southern Australia was subjected to an ozone decrease directly resulting from the break up of the Antarctic 'ozone hole'!

In conclusion current plans for a future expansion of the Australian ozone monitoring program are presented.

A SIMPLE 20-BOX ATMOSPHERIC MODEL: SIMULATION OF TIME-EVOLVING ATMOSPHERIC CONCENTRATIONS AND INPUTS OF SEVERAL HALOCARBON COMPOUNDS

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A simple global atmospheric model consisting of twenty equal-volume boxes has been developed for use in the estimation of atmospheric trace gases. Sixteen of the boxes represent latitude bands encompassing the lower troposphere, while four overlying boxes permit an alternate path for North-South transport. The model's parameter set empirically determines the rates of transport among the boxes; published measurements of the atmospheric concentrations of the chloro-fluorocarbons CFC-11 (CCl_3F) and and CFC-12 (CCl_2F_2) have been employed to establish values for these empirical transport parameters. The model has been used to evaluate yearly source strengths for CFC-11 and CFC-12, and to study the relationship between various atmospheric lifetimes and the corresponding requisite source strengths for these compounds. Source strengths are calculated by means of a fully-automated optimization procedure. With the addition of a sink scheme corresponding to the reaction with HO radical, and varying both with latitude and season, the model simulates atmospheric concentrations of methylchloroform (CH_3CCl_3) and other atmospheric trace gases whose primary sink mechanism is reaction with hydroxyl radical. In addition to a conventional Eulerian algorithm, a stochastic (Monte-Carlo) formulation of inter-box transport yields estimates of the variability of trace gas concentrations at various latitudes.

TIME SERIES ANALYSIS OF CANADIAN BAPMON CO_2 MEASUREMENTS

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Many analysis schemes which are applied to "continuous" atmospheric CO_2 data are not easily applied to the discrete CO_2 flask sample data such as those obtained at 3 Canadian stations: Alert, Sable Island, and Cape St. James. Interpolation or curve fitting scheme applied to irregularly spaced flask data from each network could have a significant effect on the global interpretation of CO_2 trends and cycles. In this paper, we evaluate the long term trend and seasonal cycle of the concentration of atmospheric CO_2 at 3 Canadian BAPMoN stations using 3 different interpolation schemes: step-wise multiple regression, median and climatologically weighted average. We have found that quantitative interpretation of the CO_2 measurements in terms of trend and seasonal cycle is dependent on the curve fitting method used. Bi-modal distribution (two "humps") during the winter season seems to be, however, independent of analysis technique, and appears to be quite real. This feature is also evident at Pt. Barrow.

MONITORING THE ISOTOPIC COMPOSITION OF ATMOSPHERIC CARBON MONOXIDE AT BARING HEAD, NEW ZEALAND

Carl Brenninkmeijer, Martin Manning, Ed Dlugokencky,
Peter Pohl, Dave Lowe, Roger Sparks and Gavin Wallace

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Over the past year several methods for determining the $^{13}C/^{12}C$, $^{18}O/^{16}O$ and $^{14}C/^{12}C$ ratio of atmospheric carbon monoxide have been tried out. The stable isotopic composition of CO, in particular for oxygen, is expected to provide information on the contribution from various CO sources. The amount of ^{14}CO in the atmosphere can be used to estimate average OH levels as has been shown by Andreas Volz. For the stable isotopes the method developed by Charlie Stevens works very well but processing times are long. Carbon 14 is measured with our tandem accelerator, after diluting the sample with dead carbon. The dilution increases the amount of carbon sufficiently for preparing a target, and brings the specific activity in the range of the carbon-14 standards.

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